Cl-SO_4 Mass Ratio as an Indicator of Contamination of Freshwater Resources in Kuwait by Seawater and Oilfield Brine

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***Abstract*-The mass ratio of chloride to sulfate in different samples of groundwater from the Raudhatain - Umm AL-Aish area of Kuwait was investigated to assess the extent of contamination of the groundwater by the seawater used for extinguishing the oil fire ignited by the Iraqi Army during the 1991 Gulf War and by the brine that gushed out with oil from the damaged wells. Previous investigations indicated that the seawater from the Arabian Gulf, which was used for fire fighting, had the total dissolved solids (TDS) contents of 45,000 mg/l and a Cl/SO_4 mass ratio of 7.19. The brines produced with oil from the Sabriya and the Raudhatain oil fields adjacent to the freshwater fields of Umm Al-Aish and Raudhatan were characterized by TDS in the range of 172,000 to 256,000 mg/l and Cl/SO_4 mass ratio in the range of 118 to 267. In contrast, unpolluted (with no petroleum hydrocarbon) groundwater in the water fields had TDS in the range of 320 to 5,500 mg/l and Cl/SO_4 mass ratio below 1.3. It was, therefore, surmised that wherever groundwater in the study area had Cl/SO_4 mass ratio values higher than about 1.5, contamination by seawater and/or oilfield brine could be suspected; and when this value exceeded 7.5, contamination by oilfield brine could be inferred. The current investigation observed Cl/SO_4 mass ratio as high as 23.5 in areas where groundwater had high (>0.05 soil oil equivalent [SOE] units) hydrocarbon content. Positive correlations between TDS, hydrocarbon content and Cl/SO_4 mass ratio in such areas suggested that hydrocarbons and salts from seawater and oilfield brine moved together and did contaminate the groundwater in some parts of the study area.**

Key Words-Groundwater; Pollution; Raudhatain; Umm Al-Aish; Petroleum Hydrocarbon

I. INTRODUCTION

Monitoring of the water quality in the freshwater fields of Raudhatain and Umm Al-Aish in Kuwait (Fig. 1) since 1993had established that the contamination of the freshwater resources in these areas was a result of hydrocarbon spilled over the surface from the oil wells damaged by the Iraqi Army in 1991[1][5]. It had also been surmised that the seawater used subsequently for extinguishing the oil-well fires was another source of contamination, leading to the increase in the salinity of groundwater in the area. Brine, which was often produced with oil and had possibly flowed from at least some of the damaged wells, was an additional source of salt pollution. The freshwater in the areas under reference, however, occurred as lenses floating on the brackish to saline water. The encroachment of brackish to saline water from the surrounding areas and from below due to the production from these fields was, therefore, also a possibility. To prove conclusively the contamination by seawater and oilfield brine from surface, it was postulated that the higher values of the mass ratio of chloride to sulfate for seawater and brine might act as an indicator of the contamination of freshwater from these sources. The investigation reported here explored this possibility.

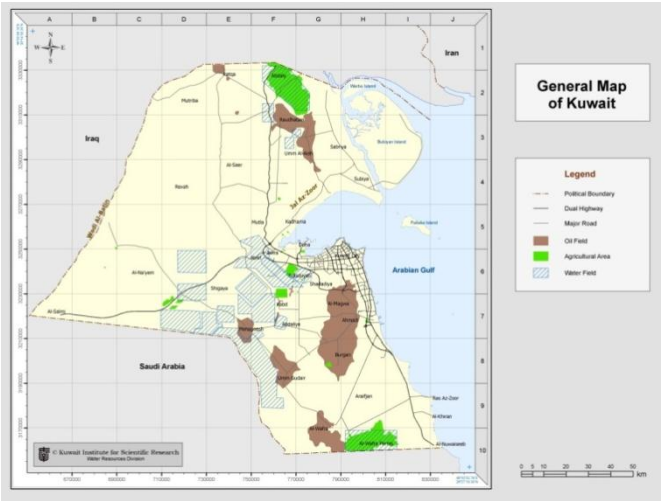

Fig. 1Location map of water and oil fields of Kuwait

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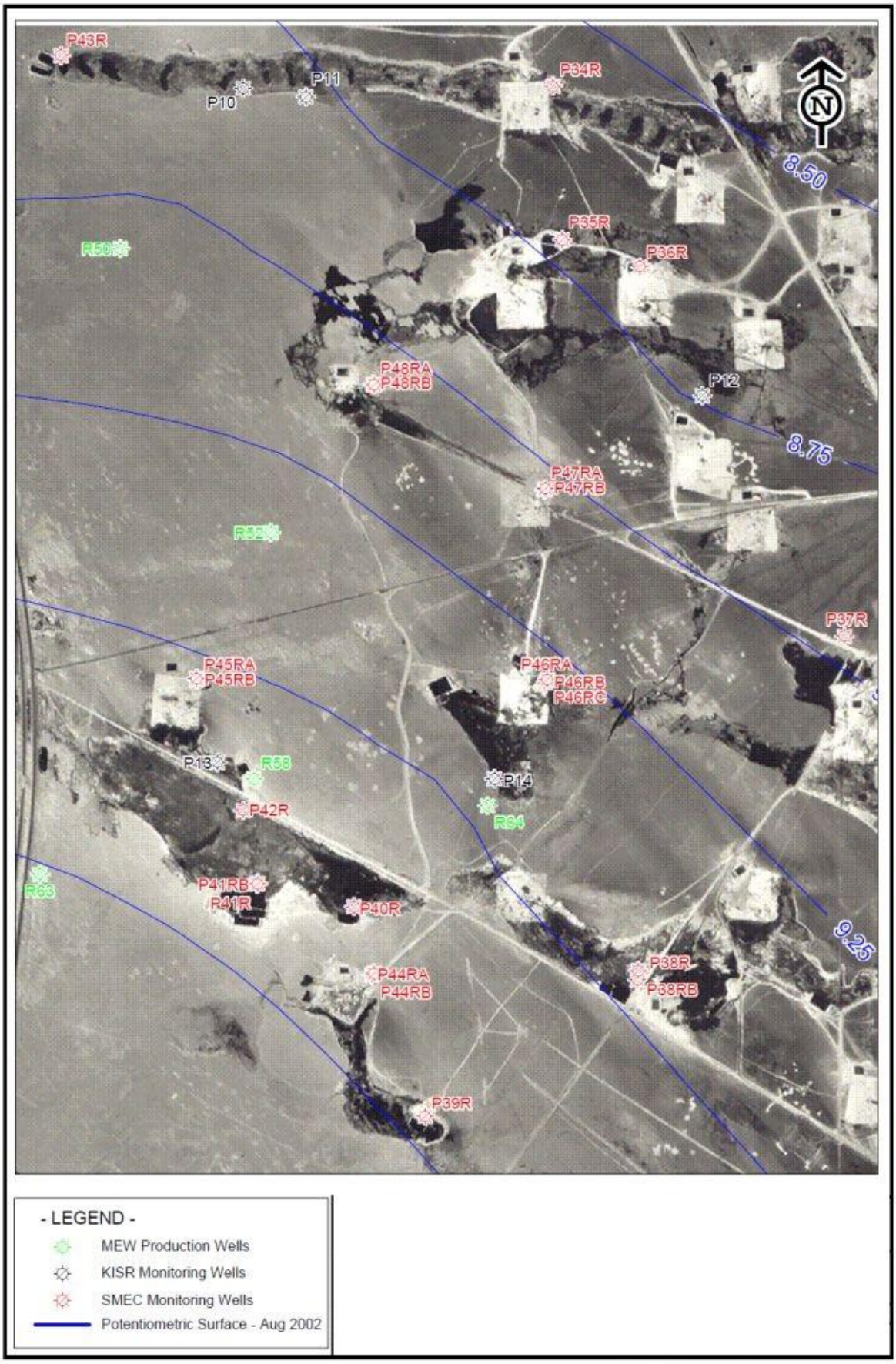

Fig. 2 Polluted southeastern part of the Raudhatain Water Field showing oil lakes, oil pits and courses of oil flows

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II. METHODOLOGY

Main methodology used in the study was the comparison of the Cl/SO_4 mass ratio in seawater, oilfield brine and uncontaminated groundwater with that of groundwater suspected to be contaminated by one or both of the first two groups. The association of increasing hydrocarbon contamination with higher total dissolved solids content had been considered to be an indication of the pollution by dissolved solids sourcing from the ground surface where seawater and/or oilfield brine remained intermingled with oil accumulated in surface depressions (oil lakes or oil collection pits; Figs. 2 and 3). Additionally, the salts left in the soil after the evaporation of these waters could also be the sources of pollution. It was hypnotized that the infiltrating rainwater has carried these salts, along with the dissolved hydrocarbons, to the groundwater during the winter rainy season. Cross-plots and linear regression, generated using GRAPHER software (Version 10) [4], andcluster and discriminant analysis, carried out with SYSAT software system (Version 13.00.05) [6], were the main tools for exploring the association of polluted groundwater withsources of salts and hydrocarbons. It may be noted here that the presence of hydrocarbon has been taken as an indicator of pollution of groundwater, though it is theoretically possible that, at least in a few cases, groundwater may be contaminated by salts derived from seawater or oilfield brine or both without affected by hydrocarbon.

Cl/SO_4 Ratio in Seawater, Oilfield Brine and Uncontaminated Groundwater of Kuwait

A. Seawater

Dr. J. Floor Anthoni (2006) has presented the average seawater composition as shown in Table 1 (available at www.seafriends.org.nz/oceano/seawater.htm, accessed on 28th April, 2014). As per these data, the Cl/SO_4 mass ratio for average seawater is: 19345/2701 = 7.16. The composition of seawater of the Arabian Gulf in Kuwait, as presented at http://www.quia.com/files/quia/users/marshall55/Major_ion_composition_of_seawater.pdf and accessed on 28th April, 2014, is shown in Table 2. The Cl/SO_4 mass ratio for Arabian Gulf derived from these data is: 23000/3200 = 7.19.

B. Oilfield Brine in Kuwait

The composition of brine produced with oil in North Kuwait is presented in Table 3 (personal communication from Dr. EssamSayed, Senior Research Scientist at the Water Research Center of Kuwait Institute for Scientific Research). The total dissolved solids content of the brine samples (14 in number) ranges between 172,312 mg/l and 217,432 mg/l with an average value of 199,436 mg/l.The Cl/SO_4 mass ratio for the same samples ranges in value from 118 to 267 over a period of 20 months with average at 198.

TABLE 1 MAJOR ION COMPOSITION OF AVERAGE SEAWATER

Chemical Ion	Valence	Concentration ppm, mg/kg	Part of Salinity %	Molecular Weight	mmol/ kg
Chloride (Cl)	-1	19345	55.03	35.453	546
Sodium (Na)	+1	10752	30.59	22.990	468
Sulfate (SO_4)	-2	2701	7.68	96.062	28.1
Magnesium (Mg)	+2	1295	3.68	24.305	53.3
Calcium (Ca)	+2	416	1.18	40.078	10.4
Potassium (K)	+1	390	1.11	39.098	9.97
Bicarbonate (HCO_3)	-1	145	0.41	61.016	2.34
Bromide (Br)	-1	66	0.19	79.904	0.83
Borate (BO_3)	-3	27	0.08	58.808	0.46
Strontium (Sr)	+2	13	0.04	87.620	0.091
Fluoride (F)	-1	1	0.003	18.998	0.068

TABLE 2 MAJOR ION COMPOSITION OF SEAWATER IN THE MIDDLE EAST REGION (MG/L)

Chemical Ion	Typical Seawater	Eastern Mediterranean	Arabian Gulf at Kuwait	Red Sea at Jeddah
Chloride (Cl^-)	18980	21200	23000	22219
Sodium (Na^+)	10556	11800	15850	14255
Sulfate (SO_4^{2-})	2649	2950	3200	3078
Magnesium (Mg^{2+})	1262	1403	1765	742
Calcium (Ca^{2+})	400	423	500	225
Potassium (K^+)	380	463	460	210
Bicarbonate(HCO_3)	140	-	142	146
Strontium (Sr^{2+})	13	-	-	-
Bromide (Br^-)	65	155	80	72
Borate (BO_3^{3-})	26	72	-	-
Fluoride (F^-)	1	-	-	-
Silicate (SiO_3^{2-})	1	-	1.5	-
Iodide (I-)	<1	2	-	-
Others	-	-	-	-
Total dissolved solids	34483	38600	45000	41000

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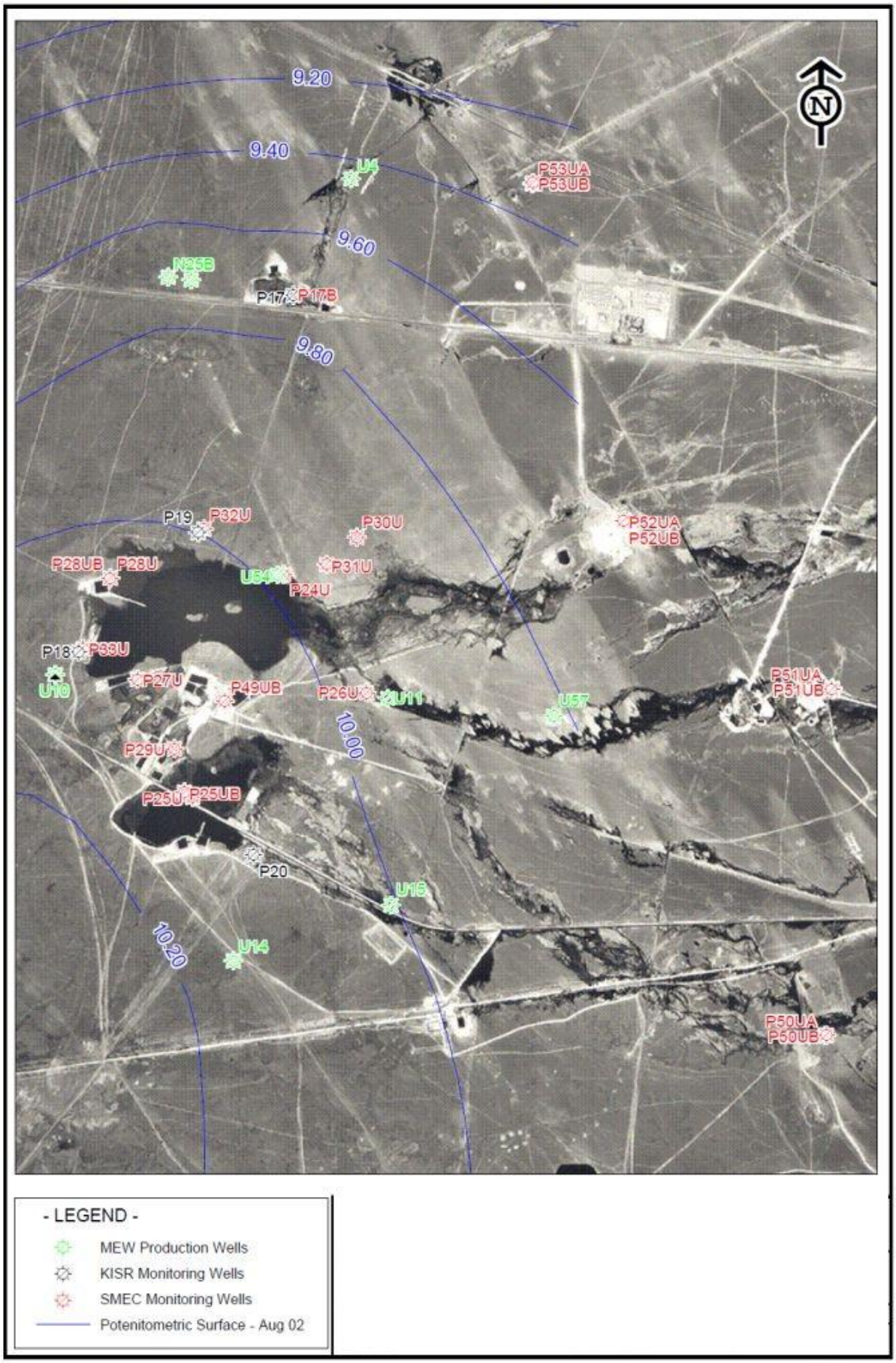

Fig. 3 Oil lake at the center of the Umm Al-Aish Water Field with courses of oil flows and near-by oil pits

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TABLE 3 RESULTS OF CHEMICAL ANALYSIS OF SALINE WATER SAMPLES COLLECTED FROM GC 15

Parameter	Date and Sample Reference						
	1-5-06 KISR	8-5-06 KISR	16-5-06 KISR	23-5-06 KISR	20-6-06 KISR	11-7-06 KISR	16-8-06 KISR
pH	5.76	5.85	5.18	5.15	5.08	4.79	5.19
EC (mS)	200	201	202	211	211	216	210
Ca^{2+}	14400	13120	1289	13160	13440	12160	15040
Mg^{2+}	2624	2770	2750	2770	2916	2595	3280
TSS	153	199	309	200	426	429	253
NH_3	82	50	80	70	80	100	90
DO	1.80	1.30	2.90	2.50	1.90	2.20	2.20
NO_3	3.80	24.00	4.00	3.80	21.00	9.00	14.00
SO_4^{2}-	510	700	620	650	610	840	690
HCO_3^{-*}	78	70	26	22	20	26	28
Cl^-	136000	128800	120400	121818	128400	120000	126000
Na^+	88229	83559	78109	79029	83299	77850	81742
Ba	89	89.1	117	91	70		60.2
Sr+	595	615	510	435	228		314
K	2180	2100	3725	2610	1945		1565
SiO_2	0.81	0.64	0.77	8	12.1		13.4
Al	<0.1	<0.1	1.000	<0.1	<0.1		<0.1
Oil content	1.800	1.500		0.74	1.400		1.210
TDS	199004	196993	202252	203504	214892	194152	213728
Cl/SO_4	266.67	184.00	194.19	187.41	210.49	142.86	182.61

* mg/l as $CaCO_3$

TABLE 3 (CONT'D.)

Parameter	Date and Sample Reference						
	19-9-06 KISR	7-11-06 KISR	28-11-06 KISR	26-12-06 KISR	9-5-07 KISR	2-7-07 KISR	22-1-08 KISR
pH	6.06	5.24	6.20	6.01	5.92	5.77	5.94
EC (mS)	194	209	202	217	203	212	208
Ca^{2+}	11080	13040	13401	14080	13840	13320	13120
Mg^{2+}	2380	2867	2570	1302	1409	1798	1823
TSS	139	4068	510	236	199	225	250
NH_3	60	90	100	70	90	80	70
DO				<1	2.10	1.64	1.25
NO_3	6.00	6.00	32.00	28.00	4.00	16.00	3.00
SO_4^{2}-	820	780	740	580	680	560	500
HCO_3^{-*}	93	49	80	13	41	47	64
Cl^-	96800	114000	124000	139600	144500	140500	133500
Na^+	62799	73957	80445	90565	93744	91149	86608
Ba	62		60.2	62	2.2	3.57	
Sr+	413		314	413	375	444	
K	4510		1565	4510	2855	4095	
SiO_2	3.6		13.4	3.6	1.3	83	
Al	<0.1		<0.1	<0.1	<0.1	<0.05	
Oil content	0.024		1.210	0.024	0.67		
TDS	172312	196260	196104	217432	198534	195834	191108
Cl/SO_4	118.05	146.15	167.57	240.69	212.50	250.89	267.00

* mg/l as $CaCO_3$

Statistics of the Main Parameters of Interest:

DOI: 10.5963/JWRHE0401003

Parameter	Maximum	Minimum	Average	Standard Deviation	Coefficient of Variation
Sulfate	840 mg/l	500 mg/l	663 mg/l	108 mg/l	0.16
Chloride	144,500 mg/l	96,800 mg/l	126,737 mg/l	12,357.5 mg/l	0.098
TDS	217,432 mg/l	172,312 mg/l	199,436 mg/l	11,319 mg/l	0.057
Cl/SO_4	267	118	198	46.5	0.23

III. RESULTS AND DISCUSSIONS

A. Graphical Analysis of Data

Tables 4 and 5 indicate that uncontaminated groundwater (samples with non-detectable hydrocarbon) in that area is characterized by TDS varying between 400 – 5,500 mg/l and Cl/SO_4 between 0.1 and 1.3. Though a general trend of the rise in Cl/SO_4 mass ratio with the total dissolved solids content can be seen, the correlation between the two is not that significant (Fig. 4). The correlation is, however, strong (coefficient of determination, R^2, ≥ 0.95) where the groundwater contamination is confirmed by the high concentration of hydrocarbon derived pollutants (Fig. 5), as in the Umm Al-Aish field. The distinctive chemical characteristics of seawater, oilfield brine, unpolluted and polluted groundwater with respect to the Cl/SO_4 mass ratio and TDS contents can be visualized in Figs. 6a & 6b. As the spectrometric measurement data for hydrocarbon contents are not available for seawater and oilfield brine, hydrocarbon contents have not been used as a distinguishing parameter for these four water types. As shown in Figs. 6a and 6b, it is apparent that seawater and oilfield brine can be easily distinguished from groundwater with the help of Cl/SO_4 mass ratio and TDS contents. Some overlap of the polluted and unpolluted groundwater can, however, be observed in these plots. It is discerned from Fig. 7 that the overlap occurs when the degree of contamination is low (Cl/SO_4 ratio less than 2 and hydrocarbon content is below 0.02 SOE units).It may further be noted from these figures that while some of the samples have been polluted by both hydrocarbon and sea or brine water, others have mainly been affected by sea or brine water (high Cl/SO_4 ratio and/or higher than 5000 mg/l TDS, but low hydrocarbon contents). This is more apparent in Fig. 8 where variation of all three parameters has been taken in to account. This suggests contamination by seawater and/or oilfield brine independent of hydrocarbon contamination.

TABLE 4 CHLORIDE, SULFATE, CL/SO4 MASS RATIO AND TOTAL DISSOLVED SOLIDS CONTENTS OF GROUNDWATER FROM NORTH KUWAIT

Well ID	Sulfate						Chloride						Cl/SO_4	Total Dissolved Solids					
	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV		No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV
P-01	3	151	164	134	15.28	0.10	3	50	54	46	4.25	0.08	0.3	3	413	499	367	74.27	0.18
P-02	3	109	112	106	3.00	0.03	3	19	21	18	1.54	0.08	0.2	3	329	360	300	30.02	0.09
P-03	3	186	188	183	2.52	0.01	3	41	46	38	4.39	0.11	0.2	3	416	469	345	63.93	0.15
P-04	2	234	246	221	17.68	0.08	2	86	94	77	12.02	0.14	0.4	2	515	533	496	26.16	0.05
P-05	2	1314	1315	1312	2.12	0.00	2	491	617	364	178.90	0.36	0.4	2	2265	2429	2100	232.64	0.10
P-06	2	1135	1193	1076	82.73	0.07	2	481	508	453	38.89	0.08	0.4	2	2342	2424	2260	115.97	0.05
P-07	2	1437	1454	1419	24.75	0.02	2	157	157	157	0.00	0.00	0.1	2	2030	2355	1705	459.62	0.23
P-08	2	639	661	616	31.82	0.05	2	130	147	112	24.75	0.19	0.2	2	1056	1124	987	96.87	0.09
P-09	3	67	94	39	27.51	0.41	3	85	116	58	28.95	0.34	1.3	3	583	937	392	306.89	0.53
P-10	3	435	463	397	34.27	0.08	3	140	251	84	96.07	0.69	0.3	3	876	983	733	128.83	0.15
P-11	2	419	433	405	19.80	0.05	2	202	207	197	7.07	0.04	0.5	2	949	1006	891	81.32	0.09
P-12	3	1662	2157	1270	452.38	0.27	3	917	1086	723	182.75	0.20	0.6	3	3027	3314	2720	297.54	0.10
P-13	3	215	217	210	4.04	0.02	3	502	554	462	47.23	0.09	2.3	3	1510	1782	1112	352.15	0.23
P-14	3	258	269	240	15.95	0.06	3	86	124	56	34.82	0.41	0.3	3	1555	3145	737	1377.45	0.89
P-15	3	4733	5717	3953	899.63	0.19	3	2055	2380	1873	281.88	0.14	0.4	3	8394	9701	6560	1635.47	0.19
P-16	3	2590	3040	2172	434.92	0.17	3	929	1074	727	180.31	0.19	0.4	3	4313	4879	3590	658.69	0.15
P-17	3	175	178	170	4.16	0.02	3	63	67	54	7.44	0.12	0.4	3	620	727	513	107.00	0.17
P-	3	205	262	176	49.0	0.2	3	174	402	53	197.	1.1	0.8	3	810	979	583	204.4	0.2

DOI: 10.5963/JWRHE0401003

17B					8	4					25	3						1	5
P-18	3	126	146	114	17.21	0.14	3	2407	2605	2026	329.70	0.14	19.0	3	5580	5740	5356	199.84	0.04
P-19	2	145	148	142	4.24	0.03	2	593	606	580	18.38	0.03	4.1	2	1836	1943	1728	152.03	0.08
P-20	3	602	633	584	26.96	0.04	3	303	352	267	43.69	0.14	0.5	3	1299	1460	1175	146.19	0.11
P-21	2	361	364	358	4.24	0.01	2	269	270	267	2.12	0.01	0.7	2	1038	1136	940	138.59	0.13
P-22	3	323	362	297	34.21	0.11	3	41	43	39	2.14	0.05	0.1	3	602	664	558	55.08	0.09
P-23	2	1884	2053	1714	239.71	0.13	2	1821	1869	1773	67.88	0.04	1.0	2	5385	6259	4510	1236.73	0.23
P-24U	3	144	194	117	43.62	0.30	3	1026	1138	889	126.36	0.12	7.1	2	2558	3105	2010	774.28	0.30

TABLE 4 (CONTD.)

Well ID	Sulfate						Chloride						Cl/SO$_4$	Total Dissolved Solids					
	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV		No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV
P-25UA	3	557	650	508	80.85	0.15	3	567	617	541	43.64	0.08	1.0	3	1725	1983	1551	228.11	0.13
P-25UB	3	600	613	574	22.23	0.04	3	5002	5847	4570	731.51	0.15	8.3	3	8631	9715	7160	1320.88	0.15
P-26U	3	168	247	88	79.50	0.47	3	355	953	52	517.95	1.46	2.1	3	433	547	315	116.04	0.27
P-27U-1	3	175	218	132	43.00	0.25	3	2080	2371	1735	321.27	0.15	11.9	3	4255	5912	3364	1436.10	0.34
P-28UA	3	203	233	167	33.32	0.16	3	348	424	294	68.07	0.20	1.7	3	1032	1144	968	97.32	0.09
P-28UB	3	298	320	264	29.87	0.10	3	1522	1800	1341	244.19	0.16	5.1	3	3723	4328	2970	690.88	0.19
P-28UC	3	793	863	752	60.68	0.08	3	1002	1205	857	180.83	0.18	1.3	3	2998	3670	2642	582.58	0.19
P-29U	3	637	710	598	63.27	0.10	3	515	516	513	1.50	0.00	0.8	3	1730	1920	1571	176.55	0.10
P-30U	3	125	132	114	9.87	0.08	3	113	117	110	3.75	0.03	0.9	3	526	618	427	95.73	0.18
P-30UB	3	131	135	123	6.93	0.05	3	51	62	41	10.60	0.21	0.4	3	406	449	380	37.29	0.09
P-31U	3	101	106	98	4.36	0.04	3	287	313	238	42.16	0.15	2.8	3	843	1020	728	155.56	0.18
P-31UB	3	111	114	109	2.52	0.02	3	63	98	40	30.55	0.48	0.6	3	414	434	397	18.68	0.05
P-32U	3	54	65	42	11.53	0.21	3	1272	1442	1132	157.04	0.12	23.5	3	3912	3997	3852	75.83	0.02
P-32UB	3	260	275	241	17.24	0.07	3	758	782	715	37.53	0.05	2.9	3	2225	2540	1769	404.38	0.18
P-33U	3	430	442	418	12.01	0.03	3	1369	1552	1127	218.46	0.16	3.2	3	2797	3060	2342	395.88	0.14
P-33UA	3	106	144	70	37.04	0.35	3	2011	2704	1058	853.02	0.42	19.0	2	5254	5525	4983	383.25	0.07
P-33UB	3	147	239	86	80.88	0.55	3	3246	3283	3207	37.92	0.01	22.0	3	6452	7692	5318	1190.50	0.18
P-34R	3	1957	2326	1551	388.78	0.20	3	584	678	534	81.14	0.14	0.3	3	3712	3775	3625	77.83	0.02
P-34RB	3	1674	1846	1546	154.62	0.09	3	661	672	645	14.36	0.02	0.4	2	3852	3890	3813	54.45	0.01
P-35R	2	3318	3326	3309	12.02	0.00	2	1749	1801	1696	74.25	0.04	0.5	2	6057	7263	4850	1706.25	0.28
P-	2	161	173	148	173.9	0.	2	914	968	860	76.37	0.08	0.6	2	397	397	397	0.00	0.00

DOI: 10.5963/JWRHE0401003

35RB		0	3	7	5	11									7	7	7		
P-36R	3	2086	2325	1901	216.97	0.10	3	3963	4324	3595	364.40	0.09	1.9	3	7932	9339	6910	1259.59	0.16
P-37R	3	450	760	281	268.83	0.60	3	314	426	226	102.08	0.33	0.7	3	1123	1542	912	362.58	0.32
P-38RA	3	2636	3054	2283	389.59	0.15	3	691	840	563	139.82	0.20	0.3	3	4477	4494	4443	29.44	0.01
P-38RB	3	2459	2789	2282	286.31	0.12	3	1588	1838	1448	217.11	0.14	0.6	3	5298	5910	4460	751.10	0.14
P-39R	3	1863	2142	1660	249.83	0.13	3	374	465	327	78.26	0.21	0.2	3	2597	3161	1569	891.42	0.34

TABLE 4 (CONTD.)

Well ID	Sulfate						Chloride						Cl/ SO_4	Total Dissolved Solids					
	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV		No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV
P-40R	2	217	224	210	9.90	0.05	2	291	303	279	16.97	0.06	1.3	2	1271	1342	1200	100.41	0.08
P-40RB	2	143	145	140	3.54	0.02	2	289	292	286	4.24	0.01	2.0	2	1018	1103	933	120.21	0.12
P-41RA	3	324	366	292	38.14	0.12	3	2495	2942	2074	434.33	0.17	7.7	3	4638	5923	3840	1123.87	0.24
P-41RB	3	56	67	46	10.60	0.19	3	513	606	451	81.68	0.16	9.2	3	980	1005	950	27.84	0.03
P-41RC	3	555	732	453	154.12	0.28	3	223	228	216	6.20	0.03	0.4	3	1179	1224	1092	75.36	0.06
P-42R	3	350	390	321	35.64	0.10	3	897	1224	691	286.08	0.32	2.6	2	1896	2630	1162	1038.03	0.55
P-43R	3	265	498	147	202.08	0.76	3	312	458	85	199.32	0.64	1.2	3	1054	1217	806	218.09	0.21
P-43RB	3	147	155	139	8.02	0.05	3	1039	1146	940	102.94	0.10	7.1	3	2007	2387	1812	329.41	0.16
P-44RA	3	715	724	708	8.33	0.01	3	507	884	268	330.33	0.65	0.7	3	1608	1659	1573	45.18	0.03
P-44RB	3	420	553	330	117.37	0.28	3	266	469	115	182.47	0.68	0.6	3	1148	1703	809	484.34	0.42
P-45RA	3	850	977	771	110.86	0.13	3	324	372	292	42.15	0.13	0.4	3	1879	1977	1809	87.43	0.05
P-45RB	3	204	222	190	16.26	0.08	3	93	111	76	17.81	0.19	0.5	3	675	721	621	50.40	0.07
P-46 RA-1	2	270	335	205	91.92	0.34	2	918	1553	283	898.03	0.98	3.4	2	1562	2088	1036	743.88	0.48
P-46 RB	2	425	435	414	14.85	0.03	2	246	293	198	67.18	0.27	0.6	2	1118	1120	1116	2.83	0.00
P-46 RC	2	319	384	254	91.92	0.29	2	1977	3880	74	2691.25	1.36	6.2	2	668	668	667	0.71	0.00
P-47RA-1	3	1040	1233	844	194.52	0.19	3	284	319	239	40.72	0.14	0.3	3	1888	2148	1745	225.80	0.12
P-47-RB	3	1068	1242	937	157.12	0.15	3	300	331	282	27.08	0.09	0.3	3	1864	2146	1711	244.51	0.13
P-48RA	2	915	935	895	28.28	0.03	2	282	286	277	6.36	0.02	0.3	2	1828	2050	1605	314.66	0.17
P-48RB	2	1019	1034	1004	21.21	0.02	2	315	318	311	4.95	0.02	0.3	2	1759	1870	1648	156.98	0.09
P-49UA-1	3	474	498	455	22.05	0.05	3	944	1436	689	426.03	0.45	2.0	3	2218	3104	1734	768.39	0.35
P-49UB	3	561	581	542	19.52	0.03	3	4437	5073	4033	557.26	0.13	7.9	3	8189	9810	6390	1716.88	0.21
P-	3	180	226	129	486.	0.	3	1903	2076	1682	2014	0.11	10.6	1	41200	412	412		

DOI: 10.5963/JWRHE0401003

50UA-1		2	2	3	35	27		1	4	1	.20					00	00		
P-50UB	3	1730	2234	1084	588.00	0.34	3	23728	24388	22955	723.15	0.03	13.7	1	46231	46231	46231		
P-51-UA	3	3264	3763	2463	700.64	0.21	3	1061	1148	916	126.71	0.12	0.3	1	3614	3614	3614		
P-51UB	3	1941	2944	210	1505.38	0.78	3	1112	1400	678	382.54	0.34	0.6	3	4946	5631	4080	791.07	0.16

TABLE 4 (CONTD.)

Well ID	Sulfate						Chloride						Cl/SO$_4$	Total Dissolved Solids					
	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV		No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV
P-52UA	3	751	781	729	27.06	0.04	3	380	437	328	54.49	0.14	0.5	3	1609	1728	1405	177.73	0.11
P-52UB	3	768	1055	257	443.41	0.58	3	910	1492	318	587.01	0.65	1.2	3	2751	3668	935	1572.44	0.57
P-53UA	3	322	334	314	10.41	0.03	3	204	222	190	16.38	0.08	0.6	3	846	968	717	125.62	0.15
P-53UB	3	436	456	410	23.71	0.05	3	232	258	197	31.47	0.14	0.5	3	981	1041	895	76.39	0.08
P-54RA	3	1517	1564	1461	52.00	0.03	3	1572	1728	1467	137.77	0.09	1.0	3	3928	4194	3630	283.36	0.07
P-54RB	3	414	664	289	216.22	0.52	3	275	327	226	50.68	0.18	0.7	3	955	1079	890	107.43	0.11
P-54RC	3	941	1515	629	497.46	0.53	3	511	566	429	72.19	0.14	0.5	3	1727	1850	1605	122.50	0.07
P-55RA	3	579	599	557	21.03	0.04	3	147	158	141	9.17	0.06	0.3	3	1168	1252	1075	88.84	0.08
P-55RB	3	835	937	767	89.77	0.11	3	546	622	476	73.12	0.13	0.7	3	2018	2060	1962	50.62	0.03
P-56R	3	202	236	142	52.37	0.26	3	408	650	122	266.55	0.65	2.0	3	1924	2299	1642	338.09	0.18
P-57R	3	2135	2382	1972	217.72	0.10	3	1012	1123	947	96.98	0.10	0.5	3	3152	4522	725	2107.91	0.67
P-58UA	3	152	166	142	12.49	0.08	3	676	851	576	152.09	0.23	4.4	3	1812	2049	1559	245.39	0.14
P-58UB	3	91	98	83	7.51	0.08	3	654	761	548	106.66	0.16	7.2	3	1866	1976	1718	133.28	0.07
P-59UA	3	174	189	162	13.75	0.08	3	490	560	442	62.07	0.13	2.8	2	1420	1550	1289	184.55	0.13
P-59UB	3	143	152	136	8.33	0.06	3	317	340	290	25.04	0.08	2.2	3	1090	1248	933	157.51	0.14
P-60UA	3	134	140	125	7.77	0.06	3	425	508	372	72.82	0.17	3.2	3	1473	1616	1300	160.03	0.11
P-60UB	3	42	50	33	8.62	0.20	3	788	911	704	109.24	0.14	18.6	3	2128	2533	1369	657.81	0.31
P-61UA	3	70	76	67	4.93	0.07	3	513	579	448	65.44	0.13	7.3	3	1336	1499	1028	266.89	0.20
P-61UB	3	35	40	31	4.73	0.14	3	613	757	531	124.57	0.20	17.7	3	1760	2229	1076	605.82	0.34
P-62U	3	219	332	35	160.73	0.73	3	257	314	219	49.80	0.19	1.2	3	905	969	852	59.18	0.07
P-63U	3	695	774	639	70.54	0.10	3	3392	5645	528	2612.68	0.77	4.9	3	8933	10092	6650	1977.21	0.22
P-64RA	2	1609	1769	1448	226.98	0.14	3	1613	1878	1406	241.07	0.15	1.0	3	4408	4705	3920	426.16	0.10
P-64RB	3	1565	1758	1401	180.34	0.12	3	1389	1637	1196	225.76	0.16	0.9	3	4062	4330	3590	410.26	0.10
P-65RA	3	225	241	214	14.36	0.06	3	288	412	96	169.07	0.59	1.3	3	1258	1624	737	463.54	0.37

DOI: 10.5963/JWRHE0401003

P-65RB	3	57	66	53	7.51	0.13	3	35	42	24	9.72	0.28	0.6	3	366	422	319	52.18	0.14

TABLE 4 (CONTD.)

Well ID	Sulfate						Chloride						Cl/SO_4	Total Dissolved Solids					
	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV	No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV		No. of Mea.	Avg. (mg/l)	Max. (mg/l)	Min. (mg/l)	STDV (mg/l)	CV
P-66RA	3	374	439	325	58.53	0.16	3	677	775	515	141.42	0.21	1.8	3	1935	2053	1734	174.95	0.09
P-66RB	3	96	119	79	20.53	0.21	3	369	627	216	224.90	0.61	3.8	3	1055	1192	841	187.54	0.18
P-67RA	2	1455	1478	1432	32.53	0.02	2	905	919	890	20.51	0.02	0.6	2	3132	3603	2660	666.80	0.21
P-67RB	2	1542	1582	1501	57.28	0.04	2	1752	1839	1664	123.74	0.07	1.1	2	4481	5261	3700	1103.79	0.25
P-68RA	3	665	1918	38	1084.84	1.63	3	28	33	25	4.33	0.15	0.0	2	320	384	255	91.22	0.29
P-68RC	3	322	340	310	15.70	0.05	3	192	211	179	16.75	0.09	0.6	2	764	809	719	63.64	0.08
U-04	3	457	940	210	418.04	0.91	3	61	65	56	4.97	0.08	0.1	3	589	696	445	129.67	0.22
U-10	3	588	660	526	67.49	0.11	3	308	341	290	28.44	0.09	0.5	3	1353	1497	1188	155.50	0.11
U-11	3	452	519	360	82.25	0.18	3	170	187	155	16.15	0.09	0.4	3	1021	1180	832	175.84	0.17
U-54	3	144	220	101	65.76	0.46	3	1704	1997	1524	256.40	0.15	11.8	3	4295	5298	3369	966.84	0.23
R-52	2	321	324	317	4.95	0.02	2	99	104	94	7.07	0.07	0.3	2	813	853	773	56.57	0.07
R-63A-PW	3	1075	1180	970	105.00	0.10	3	1725	3962	533	1938.53	1.12	1.6	2	2145	2409	1881	373.35	0.17
R-64	2	197	199	194	3.54	0.02	2	77	78	75	2.12	0.03	0.4	2	513	518	507	7.78	0.02

Notes:
STDV: Standard Deviation; CV: Coefficient of Variation (Standard Deviation/Average)

TABLE 5 HYDROCARBON CONTENTS OF GROUNDWATER SAMPLES FROM NORTH KUWAIT

Well ID	**Field**	**Hydrocarbon**						**Hydrocarbon Pollution Status**
		No. of Mea.	**Avg. (SOE)**	**Max. (SOE)**	**Min. (SOE)**	**STDV (SOE)**	**CV**	
P-01	Raudhatain	3	Not Detected					Unpolluted
P-02	Raudhatain	3	Not Detected					Unpolluted
P-03	Raudhatain	3	Not Detected					Unpolluted
P-04	Raudhatain	3	Not Detected					Unpolluted
P-05	Raudhatain	3	Not Detected					Unpolluted
P-06	Raudhatain	3	Not Detected					Unpolluted
P-07	Raudhatain	3	Not Detected					Unpolluted
P-08	Raudhatain	3	Not Detected					Unpolluted
P-09	Raudhatain	3	Not Detected					Unpolluted
P-10	Raudhatain	2	0.0013	0.0013	0.0013	Not Determined	Not Determined	Polluted
P-11	Raudhatain	2	0.0011	0.0011	0.0010	0.0001	0.0673	Polluted
P-12	Raudhatain	3	0.0110	0.0130	0.0100	0.0017	0.1575	Polluted
P-13	Raudhatain	3	0.0077	0.0090	0.0070	0.0012	0.1506	Polluted
P-14	Raudhatain	3	Not Detected					Unpolluted
P-15	Raudhatain	3	0.0040	0.0050	0.0030	0.0010	0.2500	Polluted
P-16	Raudhatain	2	0.0050	0.0090	0.0010	0.0057	1.1314	Polluted
P-17	Umm Al-Aish	3	0.0593	0.0700	0.0500	0.0101	0.1697	Polluted

DOI: 10.5963/JWRHE0401003

P-17B	Umm Al-Aish	3	0.0090	0.0120	0.0070	0.0026	0.2940	Polluted
P-18	Umm Al-Aish	3	0.3550	0.4000	0.2650	0.0779	0.2196	Polluted
P-19	Umm Al-Aish	3	0.1887	0.2000	0.1800	0.0103	0.0544	Polluted
P-20	Umm Al-Aish	3	0.0049	0.0060	0.0040	0.0010	0.2071	Polluted
P-21	Umm Al-Aish	3	Not Detected					Unpolluted
P-22	Umm Al-Aish	3	Not Detected					Unpolluted
P-23	Umm Al-Aish	2	0.0014	0.0019	0.0009	0.0007	0.5051	Polluted

TABLE 5 (CONTD.)

Well ID	**Field**	**Hydrocarbon**						**Hydrocarbon Pollution Status**
		No. of Mea.	**Avg. (SOE)**	**Max. (SOE)**	**Min. (SOE)**	**STDV (SOE)**	**CV**	
P-24U	Umm Al-Aish	3	0.0327	0.0420	0.0270	0.0081	0.2493	Polluted
P-25UA	Umm Al-Aish	3	0.0050	0.0075	0.0024	0.0026	0.5135	Polluted
P-25UB	Umm Al-Aish	1	0.0014	0.0014	0.0014			Polluted
P-26U	Umm Al-Aish	3	0.0017	0.0020	0.0012	0.0005	0.2665	Polluted
P-27U-1	Umm Al-Aish	3	0.2300	0.3300	0.1500	0.0917	0.3985	Polluted
P-28UA	Umm Al-Aish	3	0.0787	0.0990	0.0670	0.0177	0.2247	Polluted
P-28UB	Umm Al-Aish	2	0.0095	0.0110	0.0080	0.0021	0.2233	Polluted
P-28UC	Umm Al-Aish	3	Not Detected					Unpolluted
P-29U	Umm Al-Aish	3	0.0100	0.0160	0.0040	0.0060	0.6000	Polluted
P-30U	Umm Al-Aish	3	Not Detected					Unpolluted
P-30UB	Umm Al-Aish	3	Not Detected					Unpolluted
P-31U	Umm Al-Aish	1	0.0010					Polluted
P-31UB	Umm Al-Aish	3	Not Detected					Unpolluted
P-32U	Umm Al-Aish	3	0.0387	0.0420	0.0340	0.0042	0.1077	Polluted
P-32UB	Umm Al-Aish	3	0.0117	0.0140	0.0100	0.0021	0.1784	Polluted
P-33U	Umm Al-Aish	3	0.1080	0.1300	0.0940	0.0193	0.1786	Polluted
P-33UA	Umm Al-Aish	3	0.5367	0.8800	0.3200	0.3007	0.5604	Polluted
P-33UB	Umm Al-Aish	3	0.4733	0.8100	0.1700	0.3213	0.6788	Polluted
P-34R	Raudhatain	3	0.0033	0.0040	0.0030	0.0006	0.1732	Polluted
P-34RB	Raudhatain	3	0.0033	0.0040	0.0030	0.0006	0.1732	Polluted
P-35R	Raudhatain	3	0.0150	0.0180	0.0100	0.0044	0.2906	Polluted
P-35RB	Raudhatain	2	0.0015	0.0015	0.0014	0.0001	0.0488	Polluted
P-36R	Raudhatain	3	0.0170	0.0180	0.0160	0.0010	0.0588	Polluted
P-37R	Raudhatain	3	0.0016	0.0019	0.0014	0.0003	0.1541	Polluted

TABLE 5 (CONTD.)

Well ID	Field	Hydrocarbon						Hydrocarbon Pollution Status
		No. of Mea.	Avg. (SOE)	Max. (SOE)	Min. (SOE)	STDV (SOE)	CV	
P-38RA	Raudhatain	3	0.0110	0.0140	0.0080	0.0030	0.2727	Polluted
P-38RB	Raudhatain	3	Not Detected					Unpolluted
P-39R	Raudhatain	3	0.0092	0.0100	0.0076	0.0014	0.1506	Polluted
P-40R	Raudhatain	2	0.0015	0.0015	0.0014	0.0001	0.0488	Polluted
P-40RB	Raudhatain	1	0.0009	0.0009	0.0009			Polluted
P-41RA	Raudhatain	3	0.0090	0.0100	0.0080	0.0010	0.1111	Polluted
P-41RB	Raudhatain	2	0.0010	0.0010	0.0010	Not Determined	Not Determined	Polluted
P-41RC	Raudhatain	0						Unpolluted
P-42R	Raudhatain	3	0.0047	0.0047	0.0046	0.0001	0.0124	Polluted

DOI: 10.5963/JWRHE0401003

P-43R	Raudhatain	3	0.0477	0.0490	0.0450	0.0023	0.0484	Polluted
P-43RB	Raudhatain	1	0.0010	0.0010	0.0010			Polluted
P-44RA	Raudhatain	3	Not Detected					Unpolluted
P-44RB	Raudhatain	3	Not Detected					Unpolluted
P-45RA	Raudhatain	3	Not Detected					Unpolluted
P-45RB	Raudhatain	3	Not Detected					Unpolluted
P-46 RA-1	Raudhatain	2	0.0085	0.0100	0.0070	0.0021	0.2496	Polluted
P-46 RB	Raudhatain	1	0.0010	0.0010	0.0010			Polluted
P-46 RC	Raudhatain	3	Not Detected					Unpolluted
P-47RA-1	Raudhatain	1	0.0015	0.0015	0.0015			Polluted
P-47-RB	Raudhatain	3	Not Detected					Polluted
P-48RA	Raudhatain	3	0.0020	0.0022	0.0017	0.0003	0.1280	Polluted
P-48RB	Raudhatain	3	Not Detected					Unpolluted
P-49UA-1	Umm Al-Aish	3	0.0120	0.0160	0.0070	0.0046	0.3819	Polluted
P-49UB	Umm Al-Aish	3	0.0133	0.0180	0.0100	0.0042	0.3122	Polluted

TABLE 5 (CONTD.)

Well ID	Field	Hydrocarbon						Hydrocarbon Pollution Status
		No. of Mea.	Avg. (SOE)	Max. (SOE)	Min. (SOE)	STDV (SOE)	CV	
P-50UA-1	Umm Al-Aish	2	0.0049	0.0050	0.0048	0.0001	0.0289	Polluted
P-50UB	Umm Al-Aish	3	0.0061	0.0075	0.0054	0.0012	0.1931	Polluted
P-51-UA	Umm Al-Aish	3	0.0087	0.0120	0.0040	0.0042	0.4804	Polluted
P-51UB	Umm Al-Aish	2	0.0040	0.0040	0.0040	Not Determined	Not Determined	Polluted
P-52UA	Umm Al-Aish	1	0.0050	0.0050	0.0050			Polluted
P-52UB	Umm Al-Aish	3	0.0046	0.0050	0.0040	0.0005	0.1124	Polluted
P-53UA	Umm Al-Aish	3	Not Detected					Unpolluted
P-53UB	Umm Al-Aish	3	0.0015	0.0016	0.0014	0.0001	0.0667	Polluted
P-54RA	Raudhatain	2	0.0017	0.0020	0.0013	0.0005	0.3000	Polluted
P-54RB	Raudhatain	3	Not Detected					Unpolluted
P-54RC	Raudhatain	1	0.0010	0.0010	0.0010			Polluted
P-55RA	Raudhatain	3	Not Detected					Unpolluted
P-55RB	Raudhatain	1	0.0013	0.0013	0.0013			Polluted
P-56R	Raudhatain	3	0.0033	0.0040	0.0030	0.0006	0.1732	Polluted
P-57R	Raudhatain	3	0.0024	0.0030	0.0020	0.0005	0.2205	Polluted
P-58UA	Umm Al-Aish	3	0.1767	0.2200	0.1500	0.0379	0.2143	Polluted
P-58UB	Umm Al-Aish	3	0.0097	0.0110	0.0080	0.0015	0.1580	Polluted
P-59UA	Umm Al-Aish	3	0.1700	0.2200	0.1100	0.0557	0.3275	Polluted
P-59UB	Umm Al-Aish	3	0.0026	0.0030	0.0020	0.0005	0.2035	Polluted
P-60UA	Umm Al-Aish	3	0.1487	0.1660	0.1300	0.0180	0.1213	Polluted
P-60UB	Umm Al-Aish	3	0.0110	0.0130	0.0100	0.0017	0.1575	Polluted
P-61UA	Umm Al-Aish	3	0.0307	0.0360	0.0260	0.0050	0.1641	Polluted
P-61UB	Umm Al-Aish	3	0.0024	0.0030	0.0020	0.0005	0.2109	Polluted
P-62U	Umm Al-Aish	3	Not Detected					Unpolluted

TABLE 5 (CONTD.)

Well ID	Field	Hydrocarbon						Hydrocarbon Pollution Status
		No. of Mea.	Avg. (SOE)	Max. (SOE)	Min. (SOE)	STDV (SOE)	CV	
P-63U	Umm Al-Aish	3	0.0033	0.0037	0.0030	0.0004	0.1093	Polluted

DOI: 10.5963/JWRHE0401003

P-64RA	Raudhatain	3	Not Detected					Unpolluted
P-64RB	Raudhatain	3	Not Detected					Unpolluted
P-65RA	Raudhatain	2	0.0025	0.0030	0.0020	0.0007	0.2828	Polluted
P-65RB	Raudhatain	1	0.0340	0.0340	0.0340			Polluted
P-66RA	Raudhatain	3	0.0100	0.0240	0.0020	0.0122	1.2166	Polluted
P-66RB	Raudhatain	2	0.0015	0.0020	0.0009	0.0008	0.5364	Polluted
P-67RA	Raudhatain	3	0.0049	0.0060	0.0040	0.0010	0.2040	Polluted
P-67RB	Raudhatain	3	0.0120	0.0150	0.0100	0.0026	0.2205	Polluted
P-68RA	Raudhatain	3	Not Detected					Unpolluted
P-68RC	Raudhatain	3	Not Detected					Unpolluted
U-04	Umm Al-Aish	3	Not Detected					Unpolluted
U-10	Umm Al-Aish	3	Not Detected					Unpolluted
U-11	Umm Al-Aish	1	0.0056	0.0056	0.0056			Polluted
U-54	Umm Al-Aish	3	0.0903	0.1200	0.0710	0.0261	0.2887	Polluted
R-52	Raudhatain	3	Not Detected					Unpolluted
R-63A-PW	Raudhatain	3	Not Detected					Unpolluted
R-64	Raudhatain	3	Not Detected					Unpolluted

Notes:
STDV: Standard Deviation; CV: Coefficient of Variation (Standard Deviation/Average)

SOE: Standard Oil-Contaminated Soil Equivalents. In this study, the water extract of the polluted soil from the Well P-19 site in the Umm Al-Aish water field has been taken as the standard for the measurement of hydrocarbon content. The groundwater sample to be analyzed has been excited by ultraviolet (UV) radiation with a wavelength of 240 nm. The hydrocarbon content has been expressed as the ratio of the area under the emitted fluorescence band (365 to 395 nm) for the analyzed groundwater sample, to that of the standard.

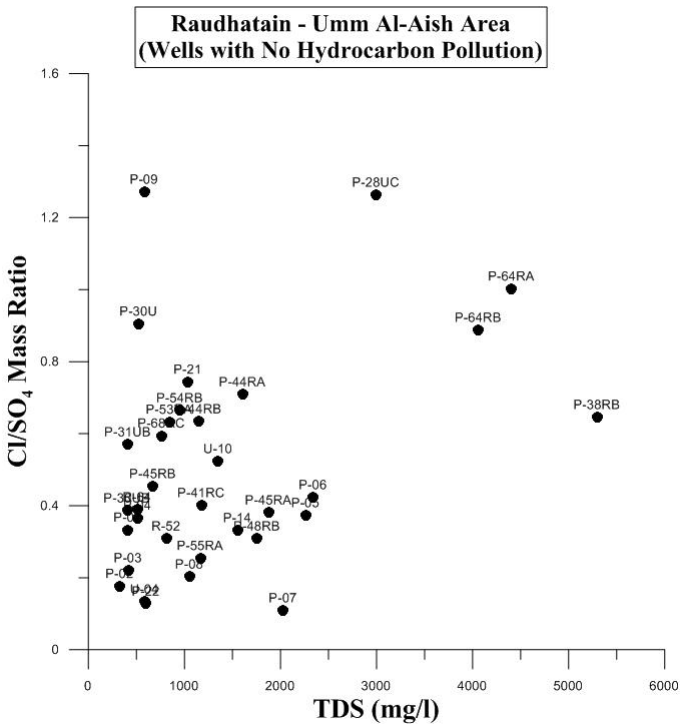

Fig. 4 Cross-plot of CL/SO_4 mass ratio against total dissolved solids (TDS) in unpolluted groundwater

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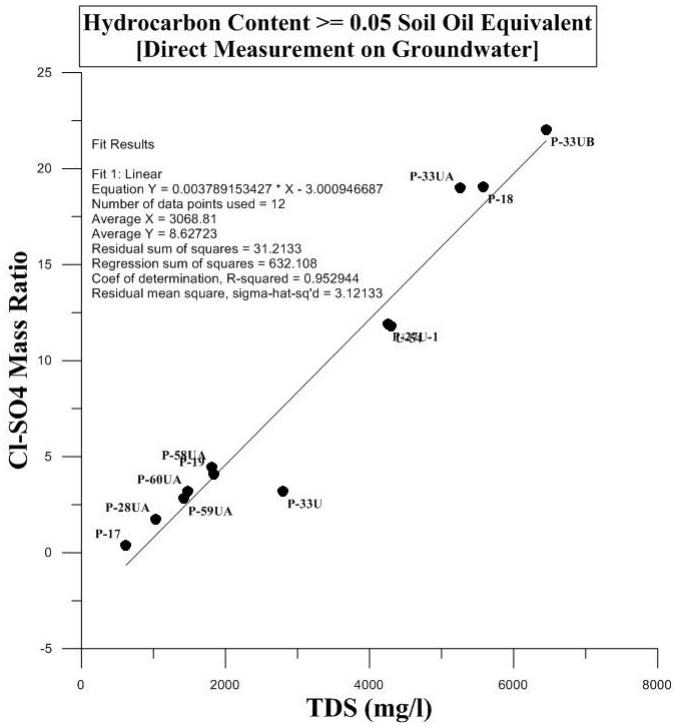
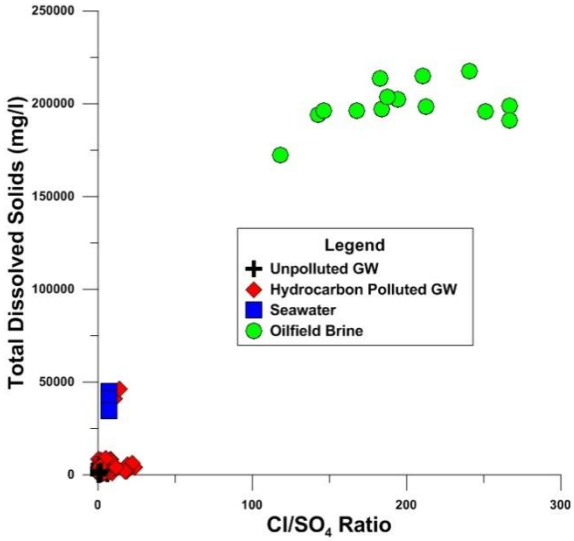


Fig. 5Cl/SO_4versus total dissolved solids (TDS) plot in contaminated aquifer



(a)

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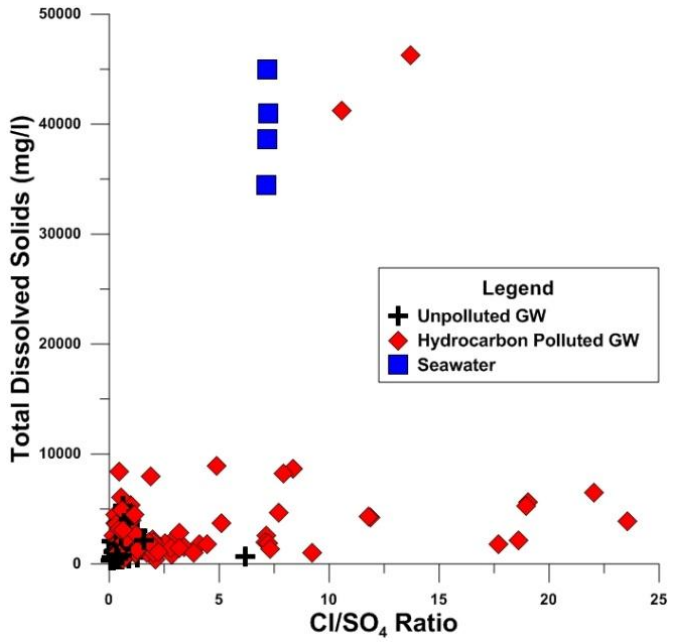

(b)

Fig. 6 Cross-plot of total dissolved solids (TDS) versus CL/SO_4 mass ratio for (a) seawater, oilfield brine and groundwater; and (b) seawater and groundwater from North Kuwait

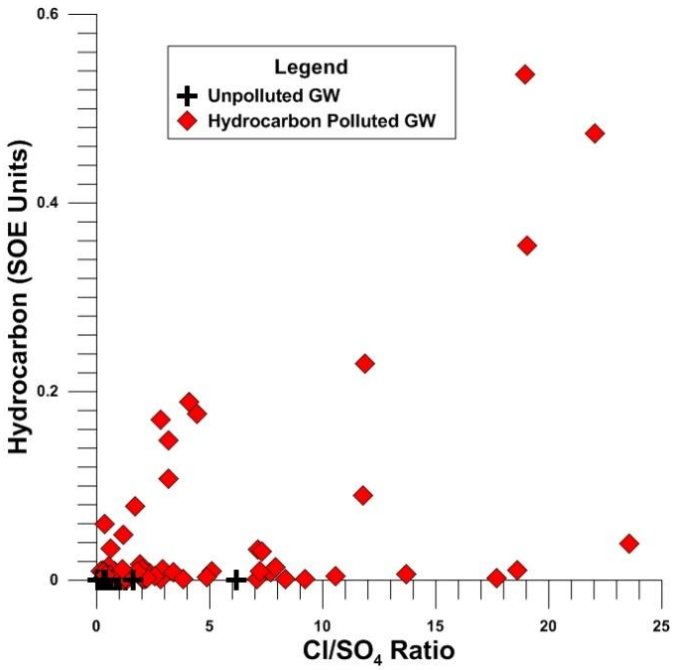

Fig. 7Cross-plot of hydrocarbon versusCl/SO_4 mass ratio for polluted and unpolluted groundwater from North Kuwait

DOI: 10.5963/JWRHE0401003

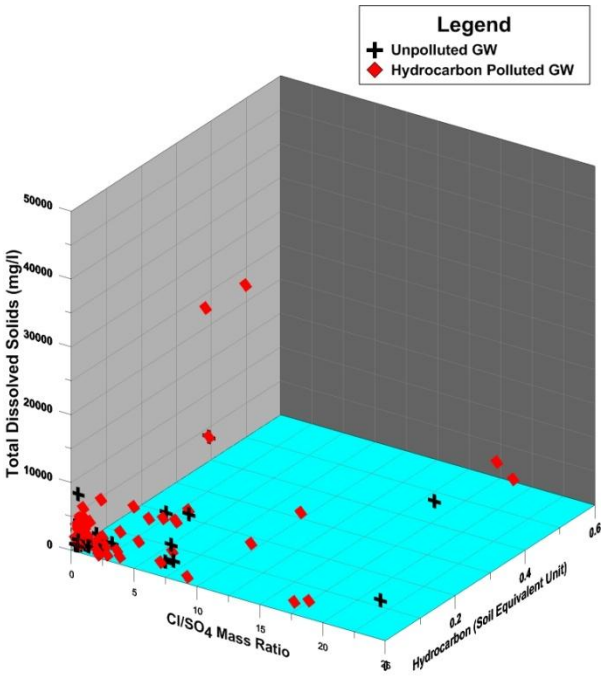

Fig. 8 3-D plot of total dissolved solids (TDS), Cl/SO_4 and hydrocarbon contents for groundwater samples from North Kuwait

B. *Statistical Analysis of Data*

Cluster analysis of different combinations of Cl/SO_4 mass ratio, hydrocarbon content and TDS values for groundwater (both polluted and unpolluted), seawater and oil field brine samples has been carried out to find out whether these parameters can group the water samples according to their source. In the first attempt, the available data were attempted to be classified into four clusters using TDS and CL/SO_4 mass ratio. In the absence of compatible measurement of hydrocarbon across the groups, this parameter was not used for clustering. The results indicate that though oilfield brine and seawater can be easily grouped into separate clusters with the help of these two parameters (Fig. 9 and Table 6), it is not possible to separate the polluted and unpolluted groundwater samples on the basis of these two parameters. Very low values of both the parameters for groundwater samples (both polluted and unpolluted) with respect to those of seawater and brine are probably the cause of this failure. It may be noted here that the groundwater samples from wells P-50-UA-1 and P-50-UB are grouped in the 'seawater' cluster (Table 6) because of high TDS contents (> 40,000 mg/l) and Cl/SO_4 ratios (>10) and suggest very high level of contamination of groundwater by seawater in the vicinity of these two wells which are in close proximity of each other. Another point of interest is that the two brine samples with the lowest (118) and the highest (267) Cl/SO_4ratio has been included inthe fourth cluster (Table 6). Results of the hierarchial cluster analysis of the data confirm the same result and are presented in Fig. 10.

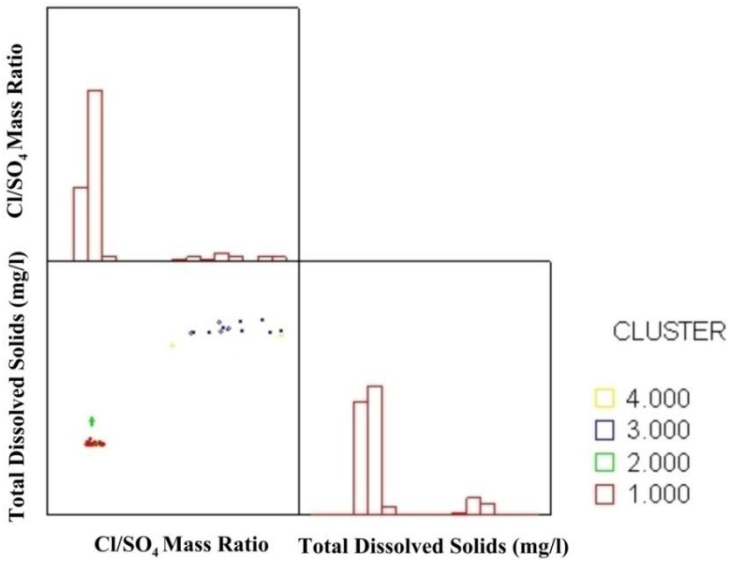

Fig. 9 Cluster analysis results of groundwater, seawater and oilfield brine samples based on Cl/SO_4 mass ratio and total dissolved solids contents

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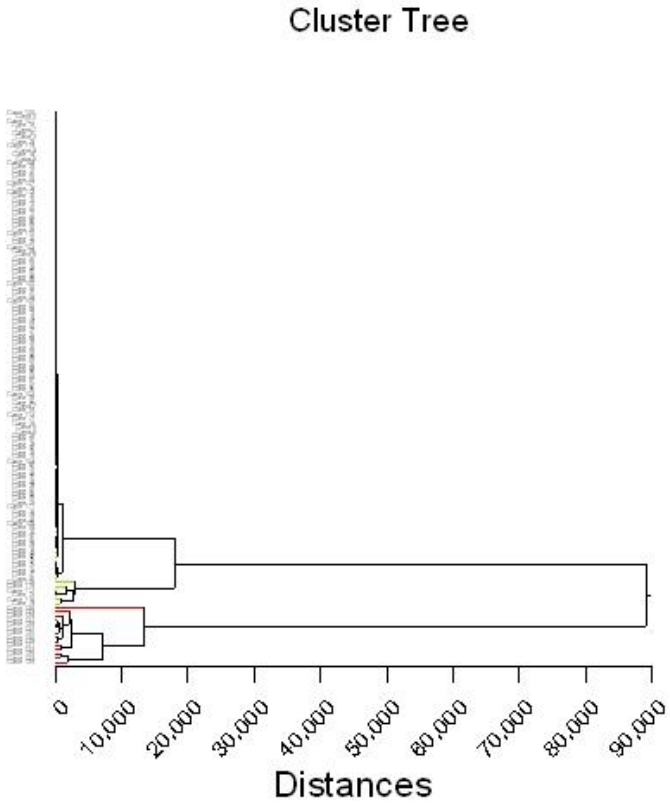

Fig. 10.Hierarchial analysis results of groundwater, seawater and oilfield brine samples based on Cl/SO4 mass ratio and total dissolved solids contents

The results of the linear discriminant analysis of the same data based on the same two parameters are also presented in Table 6. Table 7 presents the classification matrix derived from the analysis. The results again point out the inability of Cl/SO_4 and TDS values to correctly identify the groundwater samples that have been polluted by hydrocarbon when these values are low. The overlap of the polluted and unpolluted groundwater samples in such cases are indicated in the score plot presented in Fig. 11. The categorization of samples P-50-UA-1 and P-50-UB as seawater and the location of the two brine samples with the minimum and maximum Cl/SO_4 ratio (samples Brine190906 and Brine220108, respectively) outside the general envelop of brine data are also illustrated in this figure. As can be seen from Table 6, the discriminant analysis using quadratic relation did not improve the situation in any substantive way.

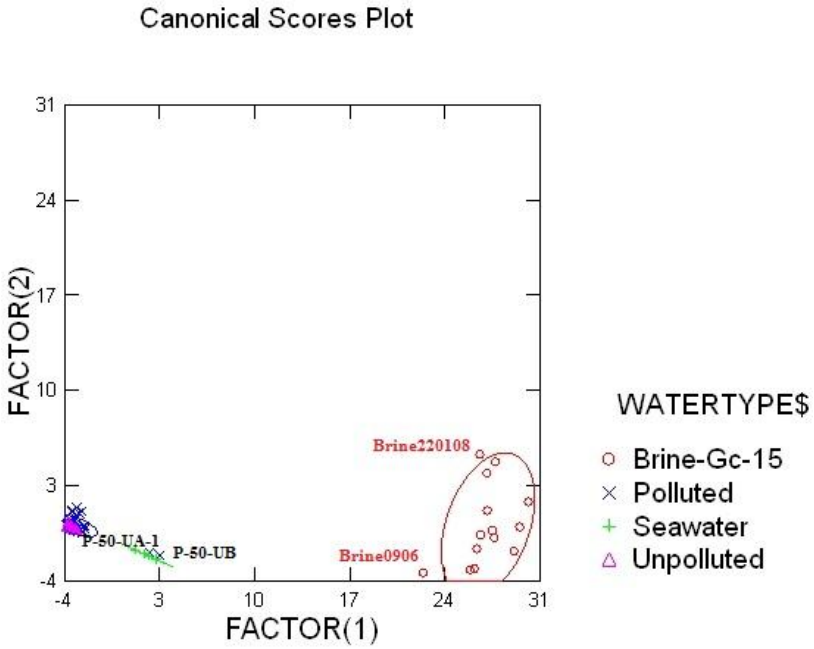

Fig. 11 Canonical score of discriminant analysis of full data using total dissolved solids (TDS) and Cl/SO4 mass ratio as predictors

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TABLE 6 RESULTS OF CLUSTER AND DISCRIMINANT ANALYSES FOR GROUNDWATER AND OIL FIELD BRINE SAMPLES FROM NORTH KUWAIT AND TYPICAL SEAWATER FROM MIDDLE EAST

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.MatchB
P-01	151	50	0.33	413	Not Detected	Unpolluted	1	0	0
P-02	109	19	0.18	329	Not Detected	Unpolluted	1	0	0
P-03	186	41	0.22	416	Not Detected	Unpolluted	1	0	0
P-04	234	86	0.37	515	Not Detected	Unpolluted	1	0	0
P-05	1314	491	0.37	2265	Not Detected	Unpolluted	1	0	0
P-06	1135	481	0.42	2342	Not Detected	Unpolluted	1	0	0
P-07	1437	157	0.11	2030	Not Detected	Unpolluted	1	0	0
P-08	639	130	0.20	1056	Not Detected	Unpolluted	1	0	0
P-09	67	85	1.27	583	Not Detected	Unpolluted	1	0	0
P-10	435	140	0.32	876	0.0013	Polluted	1	1	1
P-11	419	202	0.48	949	0.0011	Polluted	1	1	1
P-12	1662	917	0.55	3027	0.0110	Polluted	1	0	1
P-13	215	502	2.34	1510	0.0077	Polluted	1	1	1
P-14	258	86	0.33	1555	Not Detected	Unpolluted	1	0	0
P-15	4733	2055	0.43	8394	0.0040	Polluted	1	0	0
P-16	2590	929	0.36	4313	0.0050	Polluted	1	0	1

TABLE 6 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.Match B
P-17	175	63	0.36	620	0.0593	Polluted	1	1	1
P-17B	205	174	0.85	810	0.0090	Polluted	1	1	1
P-18	126	2407	19.05	5580	0.3550	Polluted	1	0	0
P-19	145	593	4.09	1836	0.1887	Polluted	1	1	0
P-20	602	303	0.50	1299	0.0049	Polluted	1	1	1
P-21	361	269	0.74	1038	Not Detected	Unpolluted	1	0	0
P-22	323	41	0.13	602	Not Detected	Unpolluted	1	0	0
P-23	1884	1821	0.97	5385	0.0014	Polluted	1	0	0
P-24U	144	1026	7.14	2558	0.0327	Polluted	1	0	0
P-25UA	557	567	1.02	1725	0.0050	Polluted	1	1	1
P-25UB	600	5002	8.34	8631	0.0014	Polluted	1	0	0
P-26U	168	355	2.12	433	0.0017	Polluted	1	1	1
P-27U-1	175	2080	11.88	4255	0.2300	Polluted	1	0	0
P-28UA	203	348	1.72	1032	0.0787	Polluted	1	1	1
P-28UB	298	1522	5.11	3723	0.0095	Polluted	1	0	0
P-28UC	793	1002	1.26	2998	Not Detected	Unpolluted	1	1	0
P-29U	637	515	0.81	1730	0.0100	Polluted	1	1	1

TABLE 6 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.Match B
P-30U	125	113	0.91	526	Not Detected	Unpolluted	1	0	0
P-30UB	131	51	0.39	406	Not Detected	Unpolluted	1	0	0
P-31U	101	287	2.84	843	0.0010	Polluted	1	1	1
P-31UB	111	63	0.57	414	Not Detected	Unpolluted	1	0	0
P-32U	54	1272	23.55	3912	0.0387	Polluted	1	0	0
P-32UB	260	758	2.92	2225	0.0117	Polluted	1	1	1

DOI: 10.5963/JWRHE0401003

P-33U	430	1369	3.18	2797	0.1080	Polluted	1	0	0
P-33UA	106	2011	18.97	5254	0.5367	Polluted	1	0	0
P-33UB	147	3246	22.03	6452	0.4733	Polluted	1	0	0
P-34R	1957	584	0.30	3712	0.0033	Polluted	1	0	1
P-34RB	1674	661	0.39	3852	0.0033	Polluted	1	0	1
P-35R	3318	1749	0.53	6057	0.0150	Polluted	1	0	0
P-35RB	1610	914	0.57	3977	0.0015	Polluted	1	0	1
P-36R	2086	3963	1.90	7932	0.0170	Polluted	1	0	0
P-37R	450	314	0.70	1123	0.0016	Polluted	1	1	1

TABLE 6 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.Match B
P-38RA	2636	691	0.26	4477	0.0110	Polluted	1	0	1
P-38RB	2459	1588	0.65	5298	Not Detected	Unpolluted	1	1	1
P-39R	1863	374	0.20	2597	0.0092	Polluted	1	1	1
P-40R	217	291	1.34	1271	0.0015	Polluted	1	1	1
P-40RB	143	289	2.03	1018	0.0009	Polluted	1	1	1
P-41RA	324	2495	7.71	4638	0.0090	Polluted	1	0	0
P-41RB	56	513	9.22	980	0.0010	Polluted	1	1	0
P-41RC	555	223	0.40	1179	Not Detected	Unpolluted	1	0	0
P-42R	350	897	2.56	1896	0.0047	Polluted	1	1	1
P-43R	265	312	1.18	1054	0.0477	Polluted	1	1	1
P-43RB	147	1039	7.09	2007	0.0010	Polluted	1	0	0
P-44RA	715	507	0.71	1608	Not Detected	Unpolluted	1	0	0
P-44RB	420	266	0.63	1148	Not Detected	Unpolluted	1	0	0
P-45RA	850	324	0.38	1879	Not Detected	Unpolluted	1	0	0
P-45RB	204	93	0.45	675	Not Detected	Unpolluted	1	0	0

TABLE 6 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.Match B
P-46 RA-1	270	918	3.40	1562	0.0085	Polluted	1	1	0
P-46 RB	425	246	0.58	1118	0.0010	Polluted	1	1	1
P-46 RC	319	1977	6.20	668	Not Detected	Unpolluted	1	0	1
P-47RA-1	1040	284	0.27	1888	0.0015	Polluted	1	1	1
P-47-RB	1068	300	0.28	1864	Not Detected	Polluted	1	1	1
P-48RA	915	282	0.31	1828	0.0020	Polluted	1	1	1
P-48RB	1019	315	0.31	1759	Not Detected	Unpolluted	1	0	0
P-49UA-1	474	944	1.99	2218	0.0120	Polluted	1	1	1
P-49UB	561	4437	7.91	8189	0.0133	Polluted	1	0	0
P-50UA-1	1802	19031	10.56	41200	0.0049	Polluted	3	1	0
P-50UB	1730	23728	13.72	46231	0.0061	Polluted	3	1	0
P-51-UA	3264	1061	0.33	3614	0.0087	Polluted	1	0	1
P-51UB	1941	1112	0.57	4946	0.0040	Polluted	1	0	0
P-52UA	751	380	0.51	1609	0.0050	Polluted	1	1	1
P-52UB	768	910	1.19	2751	0.0046	Polluted	1	1	1
P-53UA	322	204	0.63	846	Not Detected	Unpolluted	1	0	0
P-53UB	436	232	0.53	981	0.0015	Polluted	1	1	1

DOI: 10.5963/JWRHE0401003

TABLE 6 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.Match B
P-54RA	1517	1572	1.04	3928	0.0017	Polluted	1	0	1
P-54RB	414	275	0.66	955	Not Detected	Unpolluted	1	0	0
P-54RC	941	511	0.54	1727	0.0010	Polluted	1	1	1
P-55RA	579	147	0.25	1168	Not Detected	Unpolluted	1	0	0
P-55RB	835	546	0.65	2018	0.0013	Polluted	1	1	1
P-56R	202	408	2.02	1924	0.0033	Polluted	1	1	1
P-57R	2135	1012	0.47	3152	0.0024	Polluted	1	0	1
P-58UA	152	676	4.44	1812	0.1767	Polluted	1	1	0
P-58UB	91	654	7.21	1866	0.0097	Polluted	1	1	0
P-59UA	174	490	2.81	1420	0.1700	Polluted	1	1	1
P-59UB	143	317	2.22	1090	0.0026	Polluted	1	1	1
P-60UA	134	425	3.18	1473	0.1487	Polluted	1	1	1
P-60UB	42	788	18.61	2128	0.0110	Polluted	1	0	0
P-61UA	70	513	7.30	1336	0.0307	Polluted	1	1	0
P-61UB	35	613	17.69	1760	0.0024	Polluted	1	0	0
P-62U	219	257	1.17	905	Not Detected	Unpolluted	1	1	1
P-63U	695	3392	4.88	8933	0.0033	Polluted	1	0	0

TABLE 6 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.Match B
P-64RA	1609	1613	1.00	4408	Not Detected	Unpolluted	1	1	0
P-64RB	1565	1389	0.89	4062	Not Detected	Unpolluted	1	1	0
P-65RA	225	288	1.28	1258	0.0025	Polluted	1	1	1
P-65RB	57	35	0.61	366	0.0340	Polluted	1	1	1
P-66RA	374	677	1.81	1935	0.0100	Polluted	1	1	1
P-66RB	96	369	3.83	1055	0.0015	Polluted	1	1	0
P-67RA	1455	905	0.62	3132	0.0049	Polluted	1	0	1
P-67RB	1542	1752	1.14	4481	0.0120	Polluted	1	0	1
P-68RA	665	28	0.04	320	Not Detected	Unpolluted	1	0	0
P-68RC	322	192	0.59	764	Not Detected	Unpolluted	1	0	0
U-04	457	61	0.13	589	Not Detected	Unpolluted	1	0	0
U-10	588	308	0.52	1353	Not Detected	Unpolluted	1	0	0
U-11	452	170	0.38	1021	0.0056	Polluted	1	1	1
U-54	144	1704	11.80	4295	0.0903	Polluted	1	0	0
R-52	321	99	0.31	813	Not Detected	Unpolluted	1	0	0
R-63A-PW	1075	1725	1.60	2145	Not Detected	Unpolluted	1	0	0
R-64	197	77	0.39	513	Not Detected	Unpolluted	1	0	0

TABLE 6 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO_4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster Group	Disc.Match A	Disc.Match B
Mediterranean	2950	21200	7.19	38600	NA	Seawater	3	0	0
Arabian Gulf	3200	23000	7.19	45000	NA	Seawater	3	0	0
Red Sea	3078	22219	7.22	41000	NA	Seawater	3	0	0
Typ.Seawater	2649	18980	7.16	34483	NA	Seawater	3	0	0
Brine-010506	510	136000	266.67	199004	NA	Brine	2	0	0
Brine-080506	700	128800	184.00	196993	NA	Brine	2	0	0

DOI: 10.5963/JWRHE0401003

Brine160506	620	120400	194.19	202252	NA	Brine	2	0	0
Brine230506	650	121818	187.41	203504	NA	Brine	2	0	0
Brine200606	610	128400	210.49	214892	NA	Brine	2	0	0
Brine110706	840	120000	142.86	194152	NA	Brine	2	0	0
Brine160806	690	126000	182.61	213728	NA	Brine	2	0	0
Brine190906	820	96800	118.05	172312	NA	Brine	4	0	0
Brine071106	780	114000	146.15	196260	NA	Brine	2	0	0
Brine281106	740	124000	167.57	196104	NA	Brine	2	0	0
Brine261206	580	139600	240.69	217432	NA	Brine	2	0	0
Brine090507	680	144500	212.50	198534	NA	Brine	2	0	0
Brine020707	560	140500	250.89	195834	NA	Brine	2	0	0
Brine220108	500	133500	267.00	191108	NA	Brine	4	0	0

Notes for Table 6:
SOE: Standard Oil-Contaminated Soil Equivalents; NA: Not available
Cluster Group: Clusters are based on Cl/SO_4 and TDS;
Disc.Match A: Discriminant analysis categorization success (0) or failure (>0) based on Cl/SO_4 and TDS;
Disc.Match B: Discriminant analysis categorization success (0) or failure (>0) based on Cl/SO_4 and TDS (Quadratic relation).

TABLE 7 CLASSIFICATION MATRIX (CASES IN ROW CATEGORIES CLASSIFIED INTO COLUMNS)

	Oilfield Brine	Polluted Groundwater	Seawater	Unpolluted Groundwater	% Correct
Oilfield Brine	14	0	0	0	100
Polluted Groundwater	0	32	2	44	41
Seawater	0	0	4	0	100
Unpolluted Groundwater	0	4	0	32	89
Total	14	36	6	76	62

Cluster and discriminant analysis of only the groundwater samples have also been carried out where apart from TDS and Cl/SO_4mass ratio, hydrocarbon content has been used as a discriminating parameter. The summary results have been presented in Table 8. The overall efficiency of discrimination varied within the range of 56 – 58% (Table 9) with polluted water samples with low hydrocarbon and Cl/SO_4 ratio often classified as unpolluted (Fig. 12). The cluster analysis results again grouped the polluted water samples with low Cl/SO_4 ratio and low hydrocarbon contents with the unpolluted samples (Table 8 and Figs. 13 and 14). Invasion by seawater or brine was not significant in these cases.

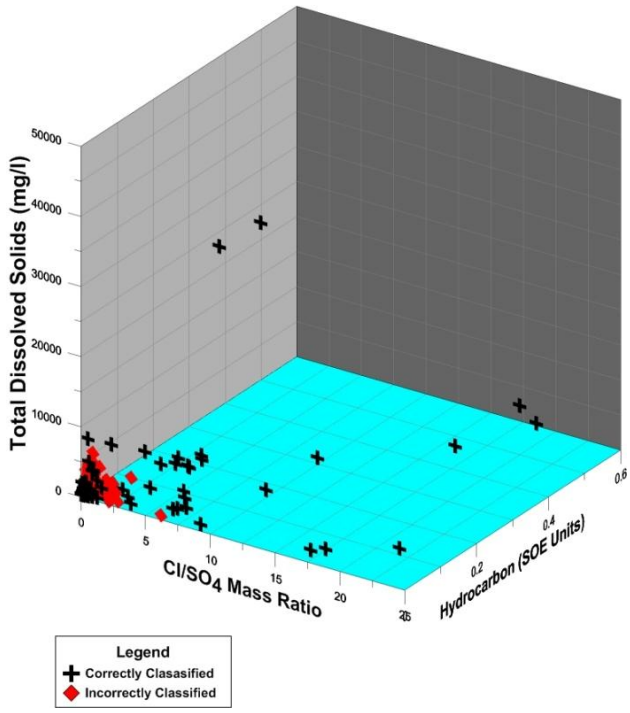

Fig. 12 Classification of groundwater samples using discriminant analysis

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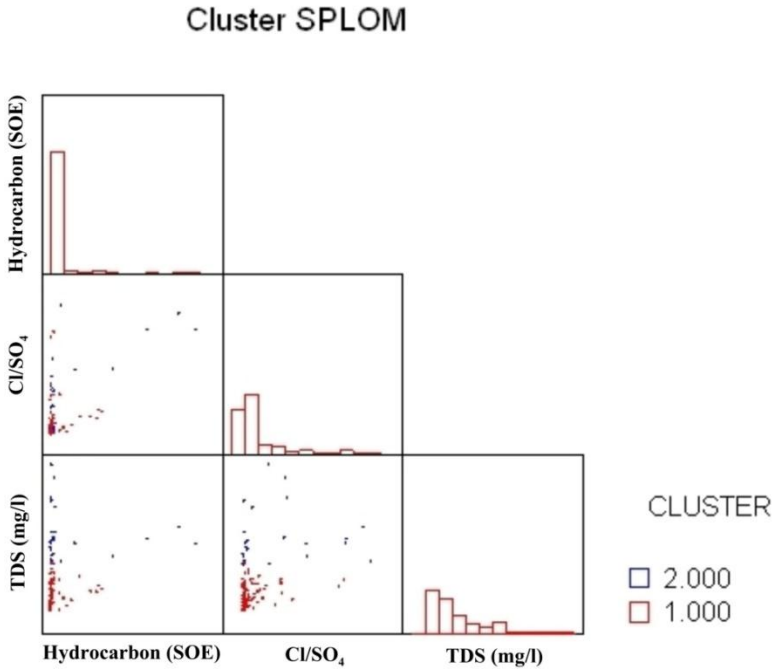

Fig. 13 Cluster analysis results of groundwater samples based on Cl/SO4 mass ratio, total dissolved solids and hydrocarbon contents

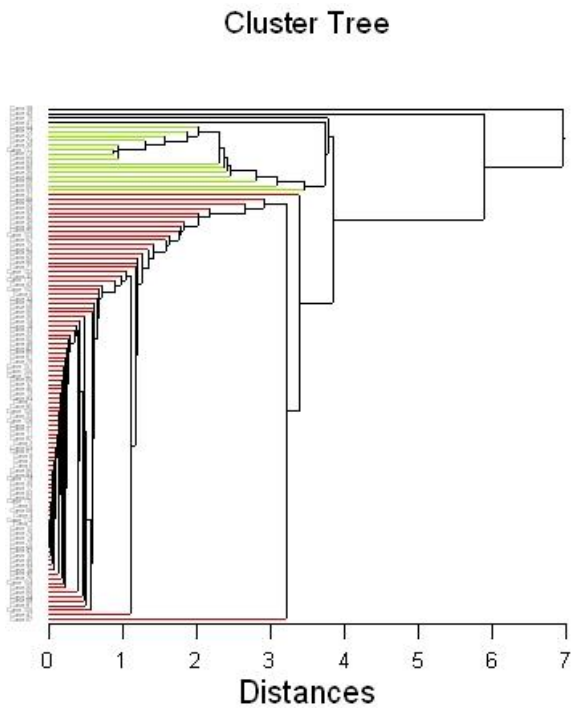

Fig. 14 Hierarchial cluster analysis results of groundwater samples based on Cl/SO4 mass ratio, total dissolved solids and hydrocarbon contents

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TABLE 8 RESULTS OF CLUSTER AND DISCRIMINANT ANALYSES FOR GROUNDWATER SAMPLES FROM NORTH KUWAIT

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster-A	Cluster-B	Cluster-C	Disc.Match A	Disc.Match B	Disc.Match C	Disc.Match D
P-01	151	50	0.33	413	Not	Unpolluted	1	1	1	0	0	0	0
P-02	109	19	0.18	329	Not	Unpolluted	1	1	1	0	2	0	0
P-03	186	41	0.22	416	Not	Unpolluted	1	1	1	0	0	0	0
P-04	234	86	0.37	515	Not	Unpolluted	1	1	1	0	2	0	0
P-05	1314	491	0.37	2265	Not	Unpolluted	1	1	1	0	0	0	0
P-06	1135	481	0.42	2342	Not	Unpolluted	1	1	1	0	2	0	0
P-07	1437	157	0.11	2030	Not	Unpolluted	1	1	1	0	0	0	0
P-08	639	130	0.20	1056	Not	Unpolluted	1	1	1	0	2	0	0
P-09	67	85	1.27	583	Not	Unpolluted	1	1	1	0	0	1	0
P-10	435	140	0.32	876	0.0013	Polluted	1	1	1	1	2	1	1
P-11	419	202	0.48	949	0.0011	Polluted	1	1	1	1	1	1	1
P-12	1662	917	0.55	3027	0.0110	Polluted	1	1	1	1	2	1	1
P-13	215	502	2.34	1510	0.0077	Polluted	1	1	1	1	1	0	1
P-14	258	86	0.33	1555	Not	Unpolluted	1	1	1	0	2	0	0
P-15	4733	2055	0.43	8394	0.0040	Polluted	2	1	2	1	1	0	1
P-16	2590	929	0.36	4313	0.0050	Polluted	2	1	2	1	2	1	1

TABLE 8 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster-A	Cluster-B	Cluster-C	Disc.Match A	Disc.Match B	Disc.Match C	Disc.Match D
P-17	175	63	0.36	620	0.0593	Polluted	1	1	1	1	1	1	1
P-17B	205	174	0.85	810	0.0090	Polluted	1	1	1	1	2	1	1
P-18	126	2407	19.05	5580	0.3550	Polluted	2	2	2	0	0	0	0
P-19	145	593	4.09	1836	0.1887	Polluted	1	1	1	0	1	0	0
P-20	602	303	0.50	1299	0.0049	Polluted	1	1	1	1	1	1	1
P-21	361	269	0.74	1038	Not	Unpolluted	1	1	1	0	2	0	0
P-22	323	41	0.13	602	Not	Unpolluted	1	1	1	0	0	0	0
P-23	1884	1821	0.97	5385	0.0014	Polluted	2	1	2	1	2	0	1
P-24U	144	1026	7.14	2558	0.0327	Polluted	1	1	1	0	0	0	0
P-	557	567	1.02	1725	0.0050	Polluted	1	1	1	1	2	1	1
P-	600	5002	8.34	8631	0.0014	Polluted	2	1	2	0	0	0	0
P-26U	168	355	2.12	433	0.0017	Polluted	1	1	1	1	2	0	1
P-27U-	175	2080	11.88	4255	0.2300	Polluted	2	2	2	0	0	0	0
P-	203	348	1.72	1032	0.0787	Polluted	1	1	1	1	1	0	1
P-	298	1522	5.11	3723	0.0095	Polluted	2	1	2	0	0	0	0
P-	793	1002	1.26	2998	Not	Unpolluted	1	1	1	0	2	0	0
P-29U	637	515	0.81	1730	0.0100	Polluted	1	1	1	1	1	1	1

TABLE 8 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster-A	Cluster-B	Cluster-C	Disc.Match A	Disc.Match B	Disc.Match C	Disc.Match D
P-30U	125	113	0.91	526	Not Detected	Unpolluted	1	1	1	0	2	0	0
P-30UB	131	51	0.39	406	Not Detected	Unpolluted	1	1	1	0	0	0	0
P-31U	101	287	2.84	843	0.0010	Polluted	1	1	1	0	1	0	1
P-31UB	111	63	0.57	414	Not Detected	Unpolluted	1	1	1	0	0	0	0
P-32U	54	1272	23.55	3912	0.0387	Polluted	2	2	2	0	1	0	0
P-32UB	260	758	2.92	2225	0.0117	Polluted	1	1	1	0	0	0	0
P-33U	430	1369	3.18	2797	0.1080	Polluted	1	1	1	0	1	0	0
P-33UA	106	2011	18.97	5254	0.5367	Polluted	2	2	2	0	0	0	0

DOI: 10.5963/JWRHE0401003

P-33UB	147	3246	22.03	6452	0.4733	Polluted	2	2	2	0	1	0	0
P-34R	1957	584	0.30	3712	0.0033	Polluted	2	1	2	1	1	1	1
P-34RB	1674	661	0.39	3852	0.0033	Polluted	2	1	2	1	2	1	1
P-35R	3318	1749	0.53	6057	0.0150	Polluted	2	1	2	1	1	0	1
P-35RB	1610	914	0.57	3977	0.0015	Polluted	2	1	2	1	2	1	1
P-36R	2086	3963	1.90	7932	0.0170	Polluted	2	1	2	0	1	0	0
P-37R	450	314	0.70	1123	0.0016	Polluted	1	1	1	1	2	1	1

TABLE 8 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster-A	Cluster-B	Cluster-C	Disc.Match A	Disc.Match B	Disc.Match C	Disc.Match D
P-38RA	2636	691	0.26	4477	0.0110	Polluted	2	1	2	1	1	0	1
P-38RB	2459	1588	0.65	5298	Not	Unpolluted	2	1	2	0	2	1	0
P-39R	1863	374	0.20	2597	0.0092	Polluted	1	1	1	1	1	1	1
P-40R	217	291	1.34	1271	0.0015	Polluted	1	1	1	1	2	1	1
P-40RB	143	289	2.03	1018	0.0009	Polluted	1	1	1	1	1	0	1
P-41RA	324	2495	7.71	4638	0.0090	Polluted	2	1	2	0	1	0	0
P-41RB	56	513	9.22	980	0.0010	Polluted	1	2	1	0	0	0	0
P-41RC	555	223	0.40	1179	Not	Unpolluted	1	1	1	0	2	0	0
P-42R	350	897	2.56	1896	0.0047	Polluted	1	1	1	0	0	0	1
P-43R	265	312	1.18	1054	0.0477	Polluted	1	1	1	1	2	1	1
P-43RB	147	1039	7.09	2007	0.0010	Polluted	1	1	1	0	0	0	0
P-44RA	715	507	0.71	1608	Not	Unpolluted	1	1	1	0	2	0	0
P-44RB	420	266	0.63	1148	Not	Unpolluted	1	1	1	0	0	0	0
P-45RA	850	324	0.38	1879	Not	Unpolluted	1	1	1	0	2	0	0
P-45RB	204	93	0.45	675	Not	Unpolluted	1	1	1	0	0	0	0

TABLE 8 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster-A	Cluster-B	Cluster-C	Disc.Match A	Disc.Match B	Disc.Match C	Disc.Match D
P-46 RA-1	270	918	3.40	1562	0.0085	Polluted	1	1	1	0	1	0	0
P-46 RB	425	246	0.58	1118	0.0010	Polluted	1	1	1	1	1	1	1
P-46 RC	319	1977	6.20	668	Not Detected	Unpolluted	1	1	1	0	1	0	0
P-47RA-1	1040	284	0.27	1888	0.0015	Polluted	1	1	1	1	1	1	1
P-47-RB	1068	300	0.28	1864	Not Detected	Unpolluted	1	1	1	1	2	1	1
P-48RA	915	282	0.31	1828	0.0020	Polluted	1	1	1	1	1	1	1
P-48RB	1019	315	0.31	1759	Not Detected	Unpolluted	1	1	1	0	2	0	0
P-49UA-1	474	944	1.99	2218	0.0120	Polluted	1	1	1	1	1	0	1
P-49UB	561	4437	7.91	8189	0.0133	Polluted	2	1	2	0	1	0	0
P-50UA-1	1802	19031	10.56	41200	0.0049	Polluted	2	2	2	0	0	0	0
P-50UB	1730	23728	13.72	46231	0.0061	Polluted	2	2	2	0	1	0	0
P-51-UA	3264	1061	0.33	3614	0.0087	Polluted	1	1	1	1	1	1	1
P-51UB	1941	1112	0.57	4946	0.0040	Polluted	2	1	2	1	2	1	1
P-52UA	751	380	0.51	1609	0.0050	Polluted	1	1	1	1	1	1	1
P-52UB	768	910	1.19	2751	0.0046	Polluted	1	1	1	1	2	1	1
P-53UA	322	204	0.63	846	Not Detected	Unpolluted	1	1	1	0	0	0	0
P-53UB	436	232	0.53	981	0.0015	Polluted	1	1	1	1	2	1	1

TABLE 8 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster-A	Cluster-B	Cluster-C	Disc.Match A	Disc.Match B	Disc.Match C	Disc.Match D
P-54RA	1517	1572	1.04	3928	0.0017	Polluted	2	1	2	1	1	1	1

DOI: 10.5963/JWRHE0401003

P-54RB	414	275	0.66	955	Not Detected	Unpolluted	1	1	1	0	2	0	0
P-54RC	941	511	0.54	1727	0.0010	Polluted	1	1	1	1	1	1	1
P-55RA	579	147	0.25	1168	Not Detected	Unpolluted	1	1	1	0	2	0	0
P-55RB	835	546	0.65	2018	0.0013	Polluted	1	1	1	1	1	1	1
P-56R	202	408	2.02	1924	0.0033	Polluted	1	1	1	1	2	0	1
P-57R	2135	1012	0.47	3152	0.0024	Polluted	1	1	1	1	1	1	1
P-58UA	152	676	4.44	1812	0.1767	Polluted	1	1	1	0	1	0	0
P-58UB	91	654	7.21	1866	0.0097	Polluted	1	1	1	0	0	0	0
P-59UA	174	490	2.81	1420	0.1700	Polluted	1	1	1	0	1	0	0
P-59UB	143	317	2.22	1090	0.0026	Polluted	1	1	1	1	1	0	1
P-60UA	134	425	3.18	1473	0.1487	Polluted	1	1	1	0	1	0	0
P-60UB	42	788	18.61	2128	0.0110	Polluted	1	2	1	0	0	0	0
P-61UA	70	513	7.30	1336	0.0307	Polluted	1	1	1	0	1	0	0
P-61UB	35	613	17.69	1760	0.0024	Polluted	1	2	1	0	0	0	0
P-62U	219	257	1.17	905	Not Detected	Unpolluted	1	1	1	1	2	1	1
P-63U	695	3392	4.88	8933	0.0033	Polluted	2	1	2	0	0	0	0

TABLE 8 (CONTD.)

Sample ID	Sulfate (mg/l)	Chloride (mg/l)	Cl/SO4 Ratio	TDS (mg/l)	Hydr.Carb. (SOE)	WATERTYPE	Cluster-A	Cluster-B	Cluster-C	Disc.Match A	Disc.Match B	Disc.Match C	Disc.Match D
P-64RA	1609	1613	1.00	4408	Not Detected	Unpolluted	2	1	2	0	2	0	0
P-64RB	1565	1389	0.89	4062	Not Detected	Unpolluted	2	1	2	0	0	0	0
P-65RA	225	288	1.28	1258	0.0025	Polluted	1	1	1	1	2	1	1
P-65RB	57	35	0.61	366	0.0340	Polluted	1	1	1	1	1	1	1
P-66RA	374	677	1.81	1935	0.0100	Polluted	1	1	1	1	2	0	1
P-66RB	96	369	3.83	1055	0.0015	Polluted	1	1	1	0	0	0	0
P-67RA	1455	905	0.62	3132	0.0049	Polluted	1	1	1	1	2	1	1
P-67RB	1542	1752	1.14	4481	0.0120	Polluted	2	1	2	1	1	1	1
P-68RA	665	28	0.04	320	Not Detected	Unpolluted	1	1	1	0	2	0	0
P-68RC	322	192	0.59	764	Not Detected	Unpolluted	1	1	1	0	0	0	0
U-04	457	61	0.13	589	Not Detected	Unpolluted	1	1	1	0	2	0	0
U-10	588	308	0.52	1353	Not Detected	Unpolluted	1	1	1	0	0	0	0
U-11	452	170	0.38	1021	0.0056	Polluted	1	1	1	1	2	1	1
U-54	144	1704	11.80	4295	0.0903	Polluted	2	2	2	0	0	0	0
R-52	321	99	0.31	813	Not Detected	Unpolluted	1	1	1	0	2	0	0
R-63A-PW	1075	1725	1.60	2145	Not Detected	Unpolluted	1	1	1	1	0	0	1
R-64	197	77	0.39	513	Not Detected	Unpolluted	1	1	1	0	2	0	0

Notes for Table 8:
SOE: Soil oil equivalent;
Cluster-A: Clusters based on Cl/SO_4 and TDS; Cluster-B: Clusters based on Cl/SO_4 and Hydrocarbon; Cluster-C: Clusters based on Cl/SO_4, Hydrocarbon and TDS;
Disc.Match A: Discriminant analysis categorization success (0) or failure (>0) based on Cl/SO_4 and TDS; Disc.Match B: Discriminant analysis categorization success (0) or failure (>0) based on Cl/SO_4 and Hydrocarbon; Disc.Match C: Discriminant analysis categorization success (0) or failure (>0) based on Cl/SO_4 and TDS (Quadratic relation); Disc.Match D: Discriminant analysis categorization success (0) or failure (>0) based on Cl/SO_4, hydrocarbon and TDS

TABLE 9 CLASSIFICATION MATRIX FOR GROUNDWATER ONLY (CASES IN ROW CATEGORIES CLASSIFIED INTO COLUMNS)

	Polluted Groundwater	Unpolluted Groundwater	% Correct
Classification Parameters: TDS and Cl/SO_4 Mass Ratio			

DOI: 10.5963/JWRHE0401003

Polluted Groundwater	29	49	37
Unpolluted Groundwater	1	35	97
Total	30	84	56
Classification Parameters: Hydrocarbon and Cl/SO_4 Mass Ratio			
Polluted Groundwater	31	47	40
Unpolluted Groundwater	1	35	97
Total	32	82	58
Classification Parameters: TDS, Hydrocarbon and Cl/SO_4 Mass Ratio			
Polluted Groundwater	30	48	38
Unpolluted Groundwater	1	35	97
Total	31	83	57

C. Cl/SO_4 Ratio in the Contaminated Groundwater of North Kuwait

It may be concluded from the above that in the study area, a Cl/SO_4 mass ratio greater than about 1.5 should indicate contamination of shallow groundwater either by seawater or by brine produced with oil from deeper levels. When this mass ratio is higher than 7.5, significant contamination by brine coproduced with oil should be indicated. Where the infiltrating water has carried the salts from seawater and brine along with the hydrocarbon contaminants, the correlation between the concentrations of total dissolved solids and Cl/SO_4 mass ratio is strong, as seen in the Umm Al-Aish Field (Fig. 5). The relations between organic concentration and parameters like TDS and Cl/SO_4 mass ratio are also relatively strong under these circumstances (Figs. 15 and 16). The Cl/SO_4 mass ratio can thus be used to map the extent and degree of intensity of contamination by seawater or brine where the groundwater is fresh to brackish.

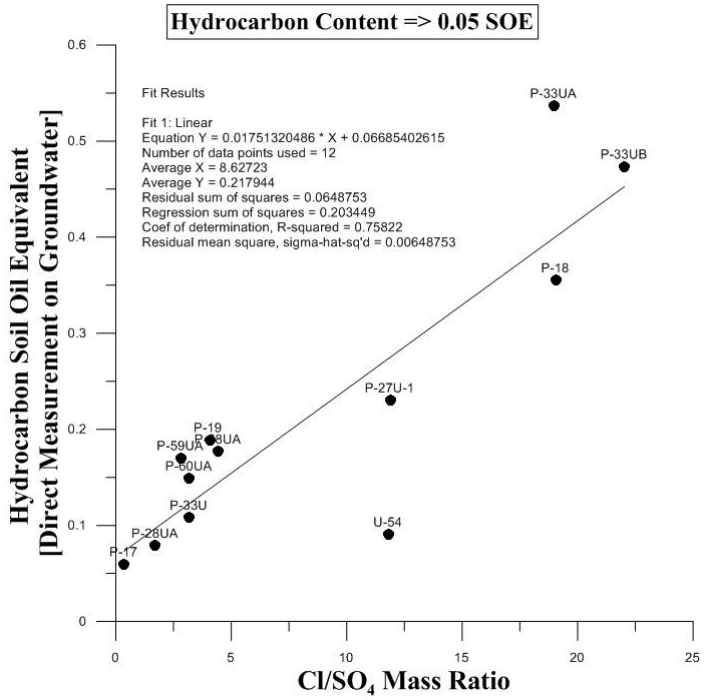

Fig. 15Cross-plot of organic concentration against Cl/SO_4 mass ratio in polluted groundwater

DOI: 10.5963/JWRHE0401003

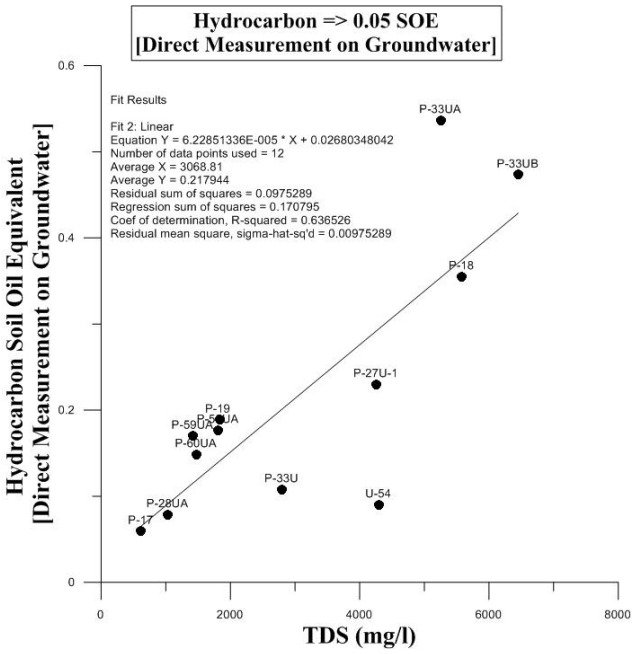

Fig. 16Cross-plot of organic concentration against TDS in polluted groundwater

In general, the intensity of pollution by both hydrocarbon and seawater/brine, is lower in the Raudhatain Field than that in the Umm Al-Aish Field. This is clearly shown in the separate cross-plots for the two fields (Figs. 17-28). As can be seen from these plots, the maximum value of Cl/SO_4 mass ratio in Raudhatain Field is 9.22 (Fig. 17) whereas that for Umm Al-Aish Field reaches 23.55 (Fig. 18). Similarly, the maximum level of organic contents measured in the Raudhatain Field is 0.05 SOE (soil oil equivalent) units (Fig. 19). Actually, except for the two wells (P-43R and P-65RB), organic contents in Raudhatain monitoring wells does not exceed 0.02 SOE. In contrast, that for the Umm Al-Aish Field is 0.54 SOE units (Fig. 20).

It can be further observed that in unpolluted and slightly polluted groundwater, the correlations amongCl/SO_4 mass ratio, hydrocarbon content and TDS are not very strong,in general (Figs. 4, 21,22, 23 and 27).The exception to this observation is the relation between hydrocarbon content and TDS in the Raudhatain Field for hydrocarbon content in the range of 0.006 and 0.02 SOE (R^2 = 0.81; Fig. 25). The correlations are much better above a hydrocarbon concentration value of 0.05 SOE (Figs. 15, 24, 26 and 28). This suggests that the lower values of hydrocarbon content (estimated through fluoroscopic measurements) is indicating the presence of other types of organics (possibly humic acids) that is not associated with the recent contamination.In both the fields, there are wells that display high (> 1.5)Cl/SO_4 ratios without significant (> 0.005 SOE units) hydrocarbon contents (Figs. 21 and 22) that may suggest contamination by seawater or oil co-produced brine only without accompanying hydrocarbon pollution.

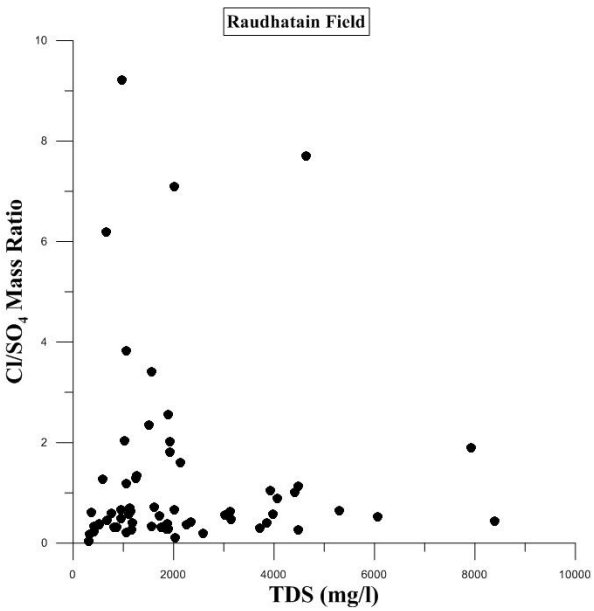

Fig. 17 Cross-plot of CL/SO_4 mass ratio against total dissolved solids (TDS) in Raudhatain Field

DOI: 10.5963/JWRHE0401003

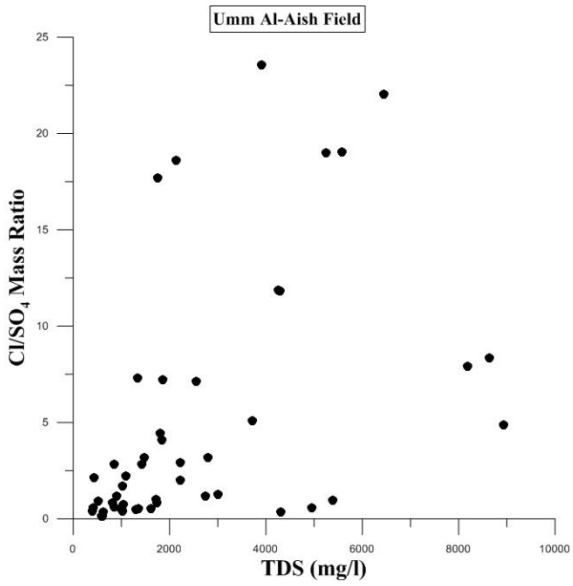

Fig. 18 Cross-plot of CL/SO_4 mass ratio against total dissolved solids (TDS) in Umm Al-Aish Field

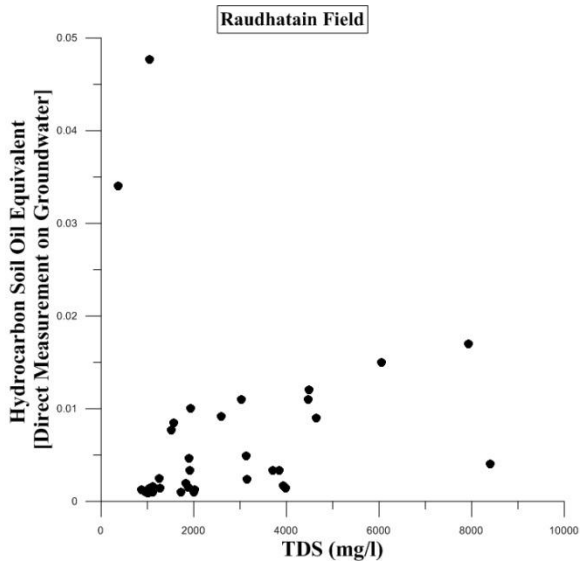

Fig. 19 Cross-plot of hydrocarbon content against total dissolved solids (TDS) in Raudhatain Field

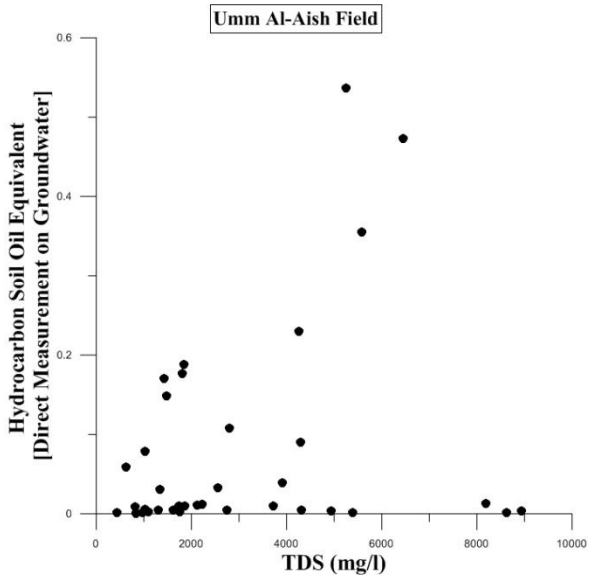

Fig. 20 Cross-plot of hydrocarbon content against total dissolved solids (TDS) in Umm Al-Aish Field

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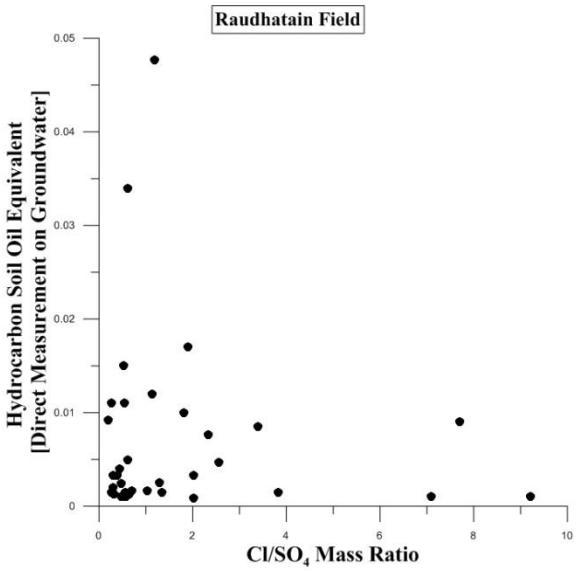

Fig. 21 Cross-plot of hydrocarbon content against Cl-SO_4 mass ratio in Raudhatain Field

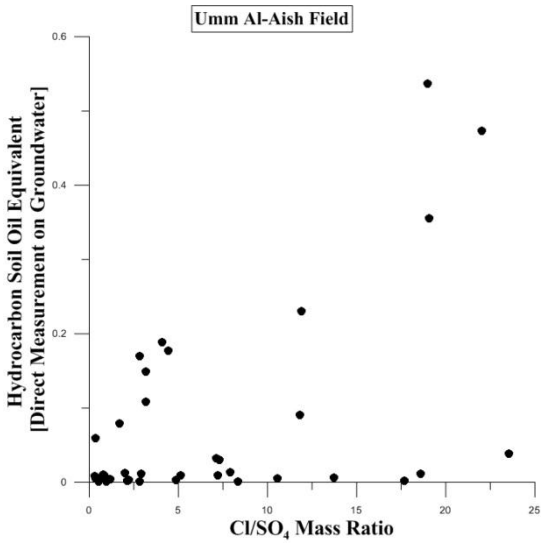

Fig. 22 Cross-plot of hydrocarbon content against Cl-SO_4 mass ratio in Umm Al-Aish Field

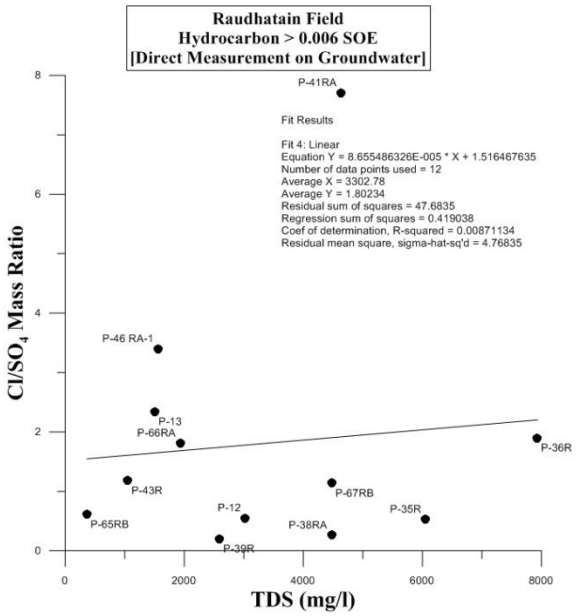

Fig. 23 Relation between Cl/SO_4 mass ratio and total dissolved solids (TDS) in polluted groundwater of Raudhatain Field

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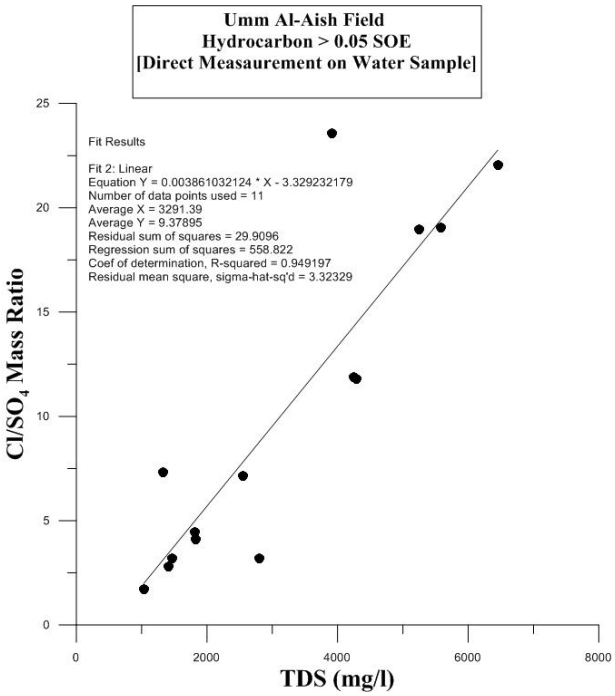

Fig. 24 Relation between Cl/SO_4 mass ratio and total dissolved solids (TDS) in polluted groundwater of Umm Al-Aish Field

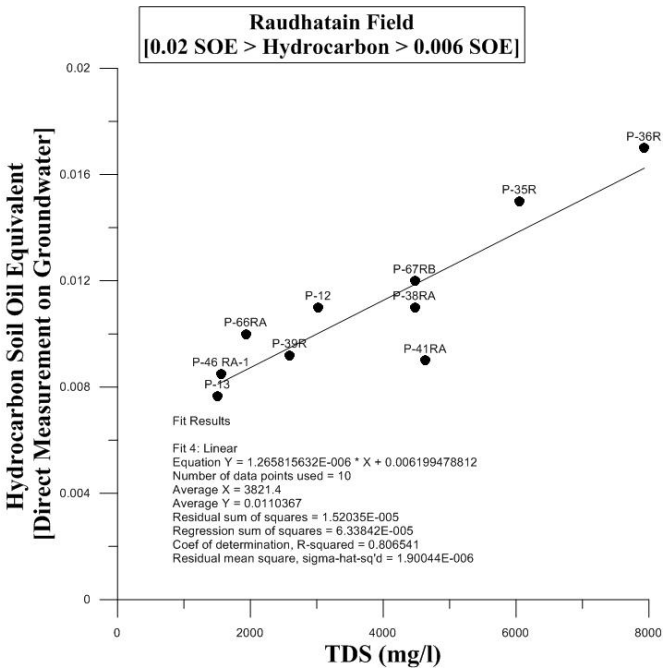

Fig. 25 Relation between hydrocarbon content and total dissolved solids (TDS) in slightly polluted groundwater of Raudhatain Field

DOI: 10.5963/JWRHE0401003

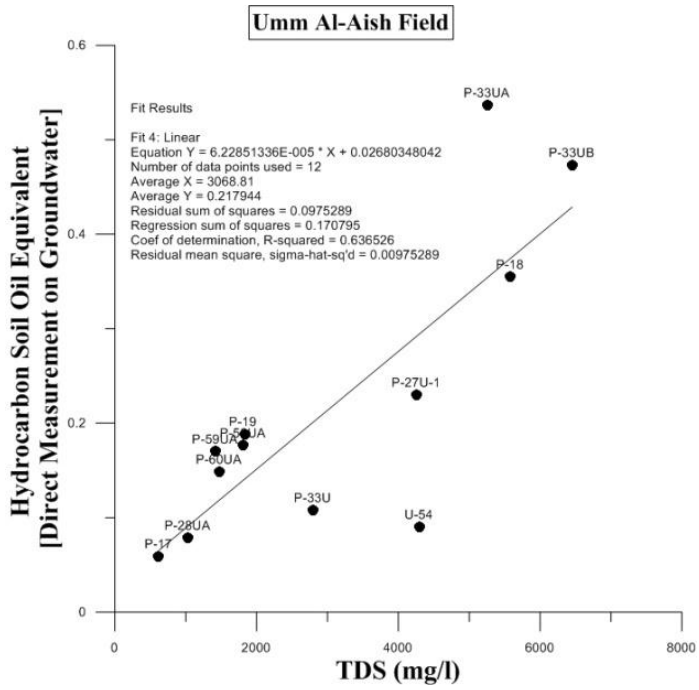

Fig. 26 Relation between hydrocarbon content and total dissolved solids (TDS) in polluted groundwater of Umm Al-Aish Field

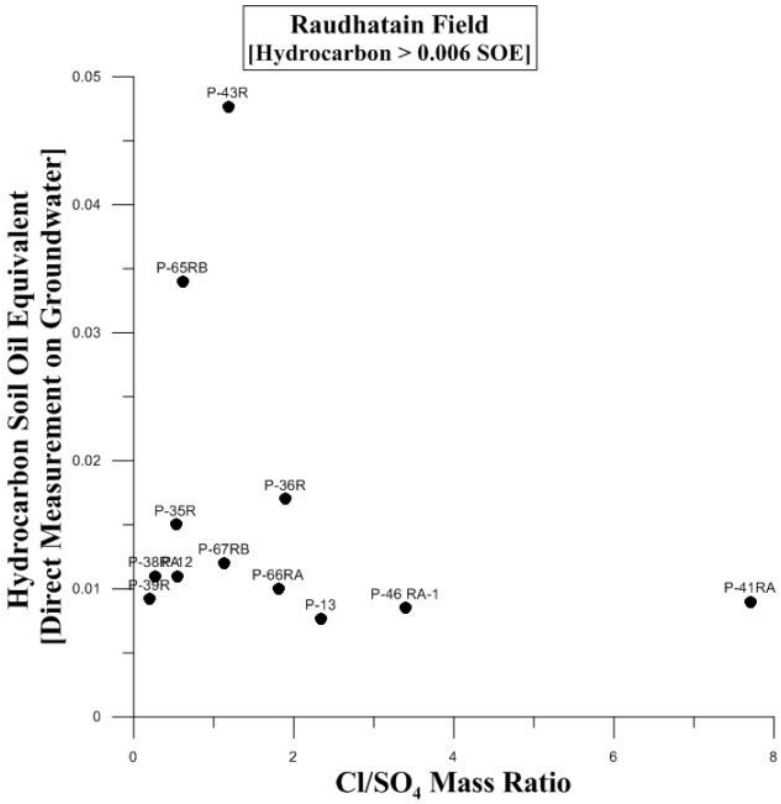

Fig. 27 Relation between hydrocarbon content and Cl/SO_4 mass ratio in slightly polluted groundwater of Raudhatain Field. (No apparent relation between hydrocarbon and seawater pollution)

DOI: 10.5963/JWRHE0401003

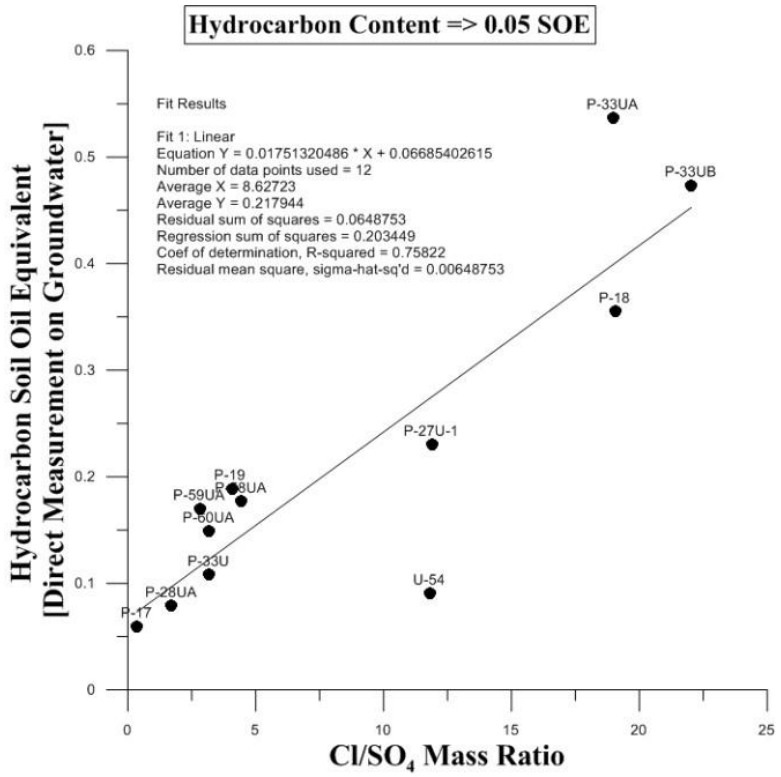

Fig. 28 Relation between hydrocarbon content and Cl/SO_4 mass ratio in polluted groundwater of Umm Al-Aish Field

IV. SUMMARY AND CONCLUSIONS

In the unpolluted (not contaminated by petroleum hydrocarbon) fresh to brackish groundwater of Raudhatain – Umm Al-Aish area with TDS values in the range of 300 to 5,500 mg/l, the Cl/SO_4 mass ratio does not exceed a value of 1.3. The same parameter has a value of 7.19 for the water of the Arabian Gulf (TDS 45,000 mg/l) used for extinguishing the oil well fires of 1991 Gulf War. The brines produced with oil in the Sabriya and Raudhatain oil fields adjacent to these water fields are characterized by the Cl/SO_4 mass ratio in the range of 118 to 267. Thus a Cl/SO_4 mass ratio higher than 1.5 in the groundwater of this area should indicate contamination either by seawater or the brine produced with oil. If this value exceeds 7.5, contamination by oilfield brine should be inferred. In fact, high values of Cl/SO_4 mass ratio that reached 23.5, have been observed in the hydrocarbon contaminated (petroleum hydrocarbon contents higher than 0.005 SOE units) groundwater in these fields. It has been concluded from this observation that the salts from seawater used for fire fighting and those from brine that flowed along with oil from the damaged oil wells have been left in the soil along with the petroleum hydrocarbons. Subsequently, rainwater infiltrating through the soil has picked up these salts along with the petroleum hydrocarbons and/or their degradation products and carried these contaminants to the groundwater. There are some instances of groundwater having high (> 1.5) Cl/SO_4 ratio without significant (> 0.05 SOE units) hydrocarbon content. This suggests contamination by seawater and/or oilfield brine only that has flowed independently of oil flows from the damaged wells. There are also instances of hydrocarbon contamination without significant salt pollution (Cl/SO_4 ratio ≤ 2).

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