Impact of Natural and Human Activities on the Groundwater Quality in the Southern Part of Al Madinah Al Munawwarah, Saudi Arabia

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ABSTRACT

Groundwater in the southern part of Al Madinah Al Munawwarah area exists in the Quaternary alluvial deposits of Wadi Al Aqiq as well as the basaltic lava flows and the buried sediments of the Harrat Rahat Plateau. The basaltic and sub-basaltic aquifers are mainly confined to semi-confined, with a saturated thickness of 30m. On the other hand, the Wadi Al Aqiq aquifer is unconfined, and the saturated thickness ranges between 30-40m. The groundwater flow is generally toward the north and northwest.

The TDS values range widely from 1515 to 7292 mg/l (average 4083 mg/l). Such a wide range of TDS values indicates the effect of several major processes acting either individually or collectively. Among these; recycling of saline irrigation water, water-rock interaction and anthropogenic activities. Hydrochemical facies is of Na-Cl type in Harrat Rahat. Values of Na/Cl ratio indicate that silicate weathering and halite dissolution are the main sources that release Na into groundwater.

Hydrochemical facies in Wadi Al Aqiq groundwater is of Ca-SO$_4$ type. Calcium-rich silicate minerals and gypsum in the alluvial deposits of Wadi Al Aqiq are the major sources of Ca and SO$_4$ in groundwater. Groundwater from this aquifer contains high levels of toxic heavy metals, such as As, Pb, Cd, Fe and V, which render it unsafe for drinking purposes as compared with WHO guidelines. These high concentrations are mainly derived from leakage of industrial wastewater from the unlined disposal site located to the west of Wadi Al Aqiq.

Enrichment of NO$_3$ in groundwater in the study area is most likely related to intensive usage of fertilizers and leakage of sewage.

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Hydrochemical facies in Wadi Al Aqiq groundwater is of Ca-SO₄ type. Calcium-rich silicate minerals and gypsum in the alluvial deposits of Wadi Al Aqiq are the major sources of Ca and SO₄ in groundwater. Groundwater from this aquifer contains high levels of toxic heavy metals, such as As, Pb, Cd ,Fe and V, which render it unsafe for drinking purposes as compared with WHO guidelines. These high concentrations are mainly derived from leakage of industrial wastewater from the unlined disposal site located to the west of Wadi Al Aqiq.

Enrichment of NO₃ in groundwater in the study area is most likely related to intensive usage of fertilizers and leakage of sewage.

INTRODUCTION

The investigated area lies in the southern part of the Al Madinah Al Munawwarah area between Lat. 24° $24''$ to 24° $28''$ N (Northing 2695000-2708000) and Long. 39° $22''$ to 39° $42''$ E (Easting 550000-571000) (Fig. 1). Two main types of aquifers exist in the study area; namely the Tertiary–Quaternary basaltic lava flows and underlying sediments of Harrat Rahat and the Quaternary alluvial deposits of Wadi Al Aqiq. Harrat Rahat is an extensive plateau composed of four lava flows of basaltic composition underlain in certain parts by buried sediments. Weathered and jointed lavas, bedding planes between successive lava, lava tubes, vesicles and buried sediments constitute the most permeable zones in the harrah. Herein, groundwater occurs under various hydraulic conditions, varying from confined to semi-confined and possibly unconfined. Piezometric surface ranges from relatively deep in the inner parts (>100m) to shallow in the peripheries (<50m) due to difference in topography.

Groundwater in Wadi Al Aqiq is found at depths ranging between 30 to 45m. It flows in a north to a northeasterly direction along the main course of the wadi. The aquifer is unconfined and underlain by Precambrian basement rocks.

Groundwater in the investigated area is mainly of meteoric origin, hence it acquires its chemical constituents through water-rock interactions where dilute CO_2-charged precipitation with low pH attacks different types of silicate and other minerals to produce major and trace constituents.

Since the study area is both residential and agricultural, it has been affected by various types of anthropogenic contaminations varying from agricultural in the Harrat Rahat plateau, to industrial in the areas surrounding the Wadi Al Aqiq main course. Agricultural pollution results from the excessive usage of nitrogen fertilizers and saline water recycling. Whereas, industrial contamination is caused by wastewater disposal in unlined landfills at a dumping site 4 km to the west of Wadi Al Aqiq. This disposal site is considered the major point source affecting the groundwater quality through releasing high concentrations of toxic trace metals (e.g. As, Cd, Pb, Cu, Zn, Fe, Mn, and V). Other types of pollution may be resorted to infiltration of sewage and waster water from cesspools and other sources.

The present study aims at identifying the hydrochemical characteristics of groundwater in Al Madinah Al Munawwarah area and its relation to the various natural processes, which are responsible for the observed groundwater compositions. Impact of anthropogenic activities on groundwater quality is also a specific objective.

GEOLOGICAL SETTING

Geologically, the study area lies within the Arabian Shield. The lithological units outcropping in the investigated area are the Precambrian basement rocks in the west and the Tertiary-Quaternary lava flows of Harrat Rahat in the east (Fig. 2). The basement complex rocks exposed herein are the Al Ays and Furayh Groups (Pellaton 1981). The Al Ays Group crops out north and northwest of the area and is composed of silicic volcanic lava, epiclastic breccia, sandstone and rhyolite. The Fuaryh Group crops out west of the study area and consists of andesite, volcanic breccia, tuff, conglomerate, sandstone and marble. These groups are intruded by younger granitic plutons in the north and northwest.
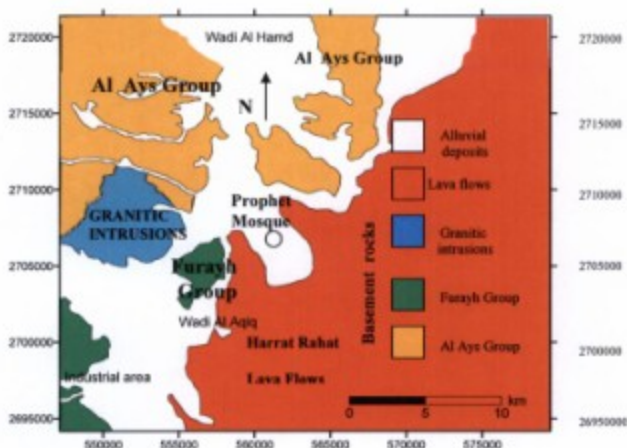
Fig.1. Location map of study area.

Fig. 2 Geological map of the study area (modified after Pellaton 1981).

Harrat Rahat comprises five basaltic lava flows of varying ages ranging from Tertiary to Recent (Moufti 1985). The oldest is 3 Ma years old, whereas, the youngest is only a few hundred years old and is outcropping in the northern most parts of the plateau. Old lavas have been severely subjected to fracturing and weathering. In places, alluvial deposits exist below the lava flows (sub-basaltic deposits) covering the courses of the old buried valleys.

The thickness of the lava flows varies from more than 400m in the central parts near the volcanic cones, to less than 5m in the peripheries.

Quaternary deposits cover the drainage patterns everywhere in the area and especially in the central area around the Prophet's Mosque. It consists of wadi alluvium terrace, fan eluvial and eolian deposits. They range in size from gravel, sand to clay and their thickness varies from about 8m in the central area to more than 80m in Wadi Al Aqiq.

HYDROGEOLOGICAL SETTING

The climate of the study area is of the desert type, whereby summer is extremely hot and dry and winter is cold. Rainfall takes place mainly in winter and. The average annual rainfall is about 60mm (Bayumi, et al. 2007).

The main aquifer systems in the Al Madinah area exist in the Harrat Rahat and the drainage basins within the Precambrian outcrops. The lava flows of Harrat Rahat together with the old sub-basaltic alluvial deposits comprise two inseparable hydrogeological units of regional scale. Weathered and jointed lavas, bedding planes between successive lava, lava tubes, vesicles and buried sediments constitute the most permeable zones. Groundwater occurs under various hydraulic conditions, varying from confined to semi-confined and possibly unconfined. Piezometric surface is relatively deep in the inner parts (>100m) to shallow in the peripheries (<50m). Regional groundwater movement is to the north and northwest, i.e. towards Al Madinah (Fig. 3).

The major valley system in the study area is that of Wadi Al Aqiq, which runs parallel to the western side of Harrat Rahat. It drains an area of about 3300 km^2 (Al-Doaan 1999). The aquifer is unconfined consisting of unconsolidated Quaternary alluvial deposits in addition to the weathered part of the underlying basement rocks. The thickness of the saturated zone ranges between 30-40m and the average depth to water level is 35m. Groundwater flow is toward north and northeast (Fig. 3). The average annual recharge rate was calculated using the chloride-mass balance method. It is estimated about 0.72 mm/yr (Bazuhair, et al. 2002).

Several wells pump both aquifers for irrigation purposes. An inventory of the sampled wells is given in Table1.

ANALYTICAL METHODS

Groundwater samples were collected from 43 wells during March 2007 (Fig.4). These samples were collected after pumping the wells for at least 10 minutes. Electrical conductivity was measured at the well sites. Water samples were later on analyzed for major and trace constituents. Minerals saturation indices were calculated using PHREEQC (Parkhurst and Appelo 1999) interfaced with AquaChem software.
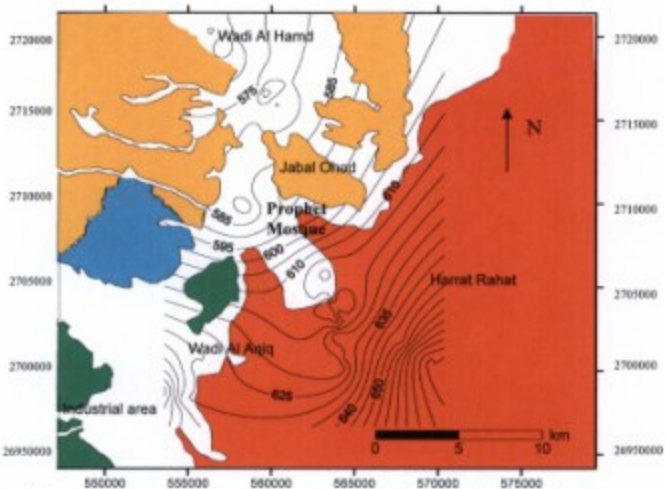
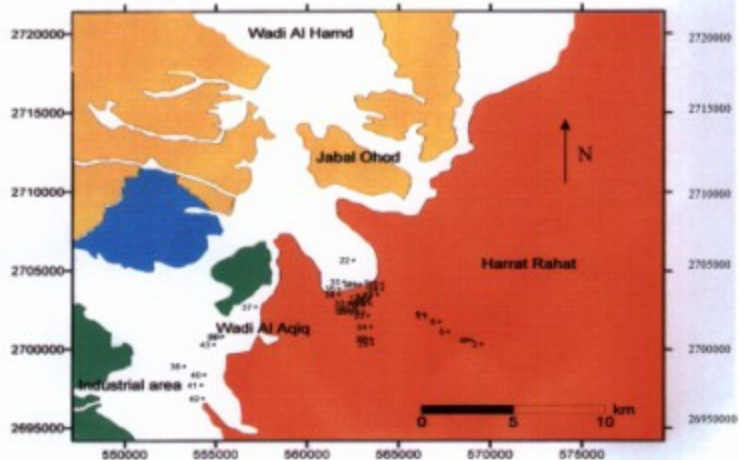Fig. 3 Piezometric surface map of the study area (meters above sea level).

Fig. 4. Well location map of the study area.

Table 1. Well inventory of the study area.

Well No	Location (UTM)		Total Depth of Well (m)	Elevation of Well Top(m above sea level)	Total Depth to Water Level (m)
	Easting	Northing			
1	2703872	564372	90	612	78
2	2700279	570365	190	690	150
3	2700534	569811	178	683	148.5
4	2700537	569628	183	688	146.5
5	2701086	568503	160	672	?
6	2701748	568009	175	650	143.5
7	2702080	567215	182	646	?
8	2702247	567149	?	644	?
9	2704282	564282	?	611	?
10	2704218	564799	95	605	62
11	2703886	564805	75	913	65
12	2703519	564497	?	614	66
13	2703417	564116	?	618	?
14	2703242	564043	?	616	55
15	2703083	563948	?	614	?
16	2702895	564090	?	610	42
17	2703290	563704	60	605	24
18	2702935	563620	67	613	43
19	2702884	563720	?	614	48
20	2704144	563363	55	607	23
21	2704170	563576	52	606	22
22	2705761	563157	45	610	20
23	2702149	563986	100	618	50
24	2701402	564140	90	622	59
25	2700276	564231	72	624	61
26	2700571	564205	72	630	65
27	2700618	564098	80	624	64
28	2702389	563712	60	616	45
29	2702427	563083	?	625	?
30	2702468	562884	58	619	46
31	2702620	563224	60	617	47
32	2702935	562886	52	614	44
33	2704337	562623	?	615	36
34	2703487	562327	46	616	?
35	2703888	562345	60	611	42
36	2698784	553582	75	658	41
37	2702692	557628	95	631	33
38	2700706	555649	110	630	39
39	2700776	555773	100	631	40
40	2698221	554747	95	630	42
41	2697544	554563	?	641	45
42	2696667	554656	85	639	44
43	2700216	555268	?	629	38

Hydrochemistry

Chemical analysis results of major and trace elements of representative wells are given Tables 2 and 3, respectively. The EC and TDS values range widely from 3140 to 10930 µS/cm (average 6604 µS/cm) and from 1515 to 7292 mg/l (average 4083 mg/l), respectively. This indicates slightly to moderately brackish water. High salinity water exists in the upper parts of Harrat Rahat and becomes fresher northward, possibly due to mixing with groundwater from other aquifers. Relatively fresher water is found in the alluvial deposits aquifers, such as Wadi Al Aqiq. Wide range of TDS values may reflect that various environmental and artificial processes, such as cycling salting, water-rock interaction, excessive pumping of groundwater, and human activities, control the groundwater quality in the study area. On the other hand, pH values (average 7.39) indicate that the groundwater is alkaline.

Major Ion Distribution

Table 2 shows the concentrations of major dissolved constituents are quite variable. The general ionic dominance of groundwater of Wadi Al Aqiq (Ca>Na>Mg>K and SO$_4$>Cl>HCO$_3$), is different from that of Harrat Rahat, which is characterized by the following ion dominance: Na>Mg>Ca>K and Cl>SO$_4$>HCO$_3$.

To understand the spatial control of major ions, the relationships between TDS, as a useful indicator of cyclic salting, and major ions are shown in Fig.5. Concentrations of most ions in Harrat Rahat samples tend to have strong relationship with TDS, to the contrary of those in Wadi Al Aqiq.

Relatively low concentrations of Na, averaging 440mg/l, are found in Wadi Al Aqiq. Moving toward Harrat Rahat, higher concentrations reaching up to 1500 mg/l are found, particularly in the inner zones. This increase is most likely attributed to recycling of irrigation water rich in evaporite salts.

Ca, however, is dominant in Wadi Al Aqiq, where most of the samples form a cluster deviating from other samples. Ca enrichment in this area may be attributed to dissolution of calcium-rich silicate minerals and carbonate minerals as well as gypsum, which were proved to occur in the alluvium (Bayumi, et al. 2007). Other possible sources of Ca in the Wadi Al Aqiq area may be attributed to polluted water infiltrating from a dumping site of industrial wastewater west of the wadi (Somasundaram et al. 1993; Reimann and Caritat 1998). Ca is replaced by Na through its flow path from Wadi Al Aqiq towards Harrat Rahat by the influence of cation exchange where clay exchangers are common in the aquifer matrix.

Mg content in the study area ranges between 29 to 500 mg/l. Groundwater samples from Harrat Rahat tend to have high Mg contents, which may be due to weathering of basaltic lava enriched in Mg. High Mg concentrations in Wadi Al Aqiq area is most likely derived from the metal industry in the industrial area west of the Wadi. Similar conclusion was reached by Pitt et al. (1999)

Concentration of K ranges between 2.9 and 28.4 mg/l. Highest K contents were observed in groundwater of Harrat Rahat, possibly originating from agricultural fertilizers (Trauth and Xanthopoulos 1997).

Table 2. Hydrochemical results of major constituents in the collected groundwater samples (in mg/l).

Well #	pH	EC μS/cm	TDS	Ca	Mg	Na	K	HCO₃	SO₄	Cl	NO₃
1	7.13	8610	5854	240	509	900	28.4	543.1	1025	2075	231
2	7.95	8240	5740	290	263	1080	20.3	65.2	629	2433	55.3
3	7.77	10570	7716	402	445	1280	24.1	91.7	912	3139	221
4	7.44	9310	6612	370	327	1160	23.3	90.5	724	2773	142
5	7.37	6600	4426	361	108	895	14.9	71.2	521	1831	127
6	7.43	4850	3168	222	80	697	12.2	88.1	416	1273	94
7	7.46	5550	3610	243	162	685	16.5	112.2	498	1447	124
8	7.30	5130	3284	191	142	705	13.8	124.3	481	1320	116
9	7.43	5490	3630	139	154	890	15.8	422.4	683	1198	171
10	7.58	4810	3086	164	126	730	13.3	237.8	483	1151	132
11	7.32	8580	5928	283	310	1270	20.8	493.6	916	2150	205
12	7.26	9160	6252	287	294	1480	21.0	494.8	1064	2277	181
13	7.37	6770	4500	160	180	1180	16.8	494.8	857	1557	112
14	7.32	5830	3868	144	153	1000	14.6	453.8	743	1313	98.4
15	7.47	5170	3408	126	112	910	13.3	458.6	687	1081	90.4
16	7.30	6710	4298	186	181	1015	18.0	526.2	875	1383	115
17	7.16	5790	3772	124	117	1050	16.4	527.4	765	1208	95.6
18	7.42	6530	4324	107	135	1230	16.5	582.9	957	1343	113
19	7.68	5430	3556	120	102	980	14.2	446.6	740	1128	95.6
20	7.47	3590	2246	80	74	650	11.7	374.1	421	732	61.5
21	7.25	5310	3364	96	112	930	17.2	554	622	1078	83.7
22	7.67	5580	3642	139	143	950	18.5	418.8	691	1198	121
23	7.33	6040	4078	192	136	1050	15.6	446.6	896	1238	112
24	7.07	10300	6888	387	303	1500	23.3	439.3	1544	2258	183
25	6.99	11930	7996	563	440	1350	23.4	253.5	1544	2917	202
26	7.01	10400	6996	488	348	1250	20.3	289.7	1455	2446	179
27	7.14	8800	5796	307	254	1390	17.4	458.6	1311	1923	164
28	7.15	6660	4492	167	129	1220	17.1	550.4	1016	1365	139
29	7.18	3980	2780	157	102	590	12.9	382.6	716	650	141
30	7.19	4430	3090	150	132	670	13.0	410.3	826	727	154
31	7.12	5430	3813	160	129	870	14.2	474.3	926	980	180
32	7.19	4060	2730	113	84	560	10.9	417.6	647	685	136
33	7.44	5000	3200	83	61	1050	8.9	358.5	475	1221	79.2
34	7.33	3780	2545	108	80	570	10.7	412.8	641	610	117
35	7.50	2360	1525	75	41	320	7.8	284.8	348	361	79
36	7.24	2760	1770	301	50	110	13.9	177.4	334	436	83
37	7.15	6100	4220	752	29	520	5.5	45.9	1574	971	106
38	7.18	5900	4106	641	77	550	16.4	120.7	1372	1006	137
39	7.51	6300	4296	661	76	600	2.9	130.3	1766	828	97.4
40	7.83	2400	1564	115	45	340	13.7	113.4	501	406	31.2
41	7.76	5100	3636	689	36	350	3.2	64	1576	602	106
42	7.09	6400	4488	758	70	550	5.9	134	1679	947	113
43	7.39	6000	4198	667	72	525	4.6	100.2	1713	797	129

Table 3. Concentrations of trace constituents in the collected groundwater samples (in mg/l).

Well #	Al	Sr	Ba	As	Cd	Pb	Cu	Fe	Mn	Zn	V
1	0.410	3.906	0.015	0.0200	0.0015	0.0100	0.0003	0.1050	0.0620	0.0030	0.0090
2	0.490	5.444	0.057	0.0130	0.0012	0.0300	0.0003	0.0950	0.0700	0.0029	0.0050
3	0.520	6.732	0.045	0.0160	0.0012	0.0620	0.0004	0.0620	0.0350	0.0029	0.0030
4	0.650	7.197	0.450	0.0140	0.0015	0.0690	0.0003	0.0700	0.0028	0.0033	0.0060
5	0.820	9.629	0.780	0.0100	0.0012	0.0720	0.0004	0.0400	0.0003	0.0029	0.0050
6	0.820	5.554	0.510	0.0050	0.0000	0.0220	0.0003	0.0500	0.0028	0.0031	0.0110
7	0.410	3.938	0.087	0.0040	0.0012	0.0310	0.0003	0.0610	0.0028	0.0029	0.0120
8	0.420	3.850	0.052	0.0030	0.0000	0.0350	0.0003	0.0600	0.0028	0.0034	0.0170
9	0.007	2.410	0.010	0.0050	0.0012	0.0290	0.0003	0.0800	0.0060	0.0036	0.0200
10	0.390	2.958	0.030	0.0130	0.0000	0.0310	0.0003	0.6500	0.0028	0.0035	0.0140
11	0.410	4.868	0.010	0.0000	0.0012	0.0450	0.0004	0.1500	0.0028	0.0036	0.0140
12	0.405	4.610	0.032	0.0030	0.0015	0.0390	0.0004	0.0620	0.0060	0.0036	0.0110
13	0.110	2.817	0.017	0.0050	0.0012	0.0220	0.0003	0.0590	0.0028	0.0036	0.0170
14	0.190	2.284	0.019	0.0001	0.0013	0.0230	0.0003	0.0550	0.0028	0.0036	0.0200
15	0.160	1.832	0.012	0.0050	0.0012	0.0270	0.0003	0.0010	0.0090	0.0036	0.0190
16	0.220	2.744	0.013	0.0070	0.0013	0.0250	0.0004	0.0450	0.0028	0.0033	0.0140
17	0.180	2.030	0.012	0.0020	0.0012	0.0190	0.0002	0.0420	0.0060	0.0028	0.0270
18	0.120	2.106	0.030	0.0004	0.0014	0.0210	0.0002	0.0350	0.0028	0.0032	0.0160
19	0.160	1.925	0.030	0.0130	0.0012	0.0220	0.0003	0.0310	0.0090	0.0033	0.0130
20	0.110	1.282	0.013	0.0002	0.0000	0.0290	0.0003	0.0220	0.0028	0.0029	0.0500
21	0.130	1.841	0.007	0.0010	0.0012	0.0185	0.0002	0.0350	0.0028	0.0028	0.0280
22	0.240	2.664	0.026	0.0090	0.0030	0.0340	0.0003	0.0410	0.0028	0.0033	0.0240
23	0.210	2.989	0.039	0.0070	0.0012	0.0370	0.0004	0.0460	0.0090	0.0035	0.0140
24	0.520	6.340	0.550	0.0150	0.0000	0.0410	0.0005	0.0120	0.0120	0.0028	0.0040
25	0.680	8.747	0.920	0.0190	0.0012	0.0550	0.0006	0.0450	0.0420	0.0011	0.0005
26	0.720	7.370	0.870	0.0150	0.0000	0.0480	0.0006	0.0580	0.0620	0.0028	0.0020
27	0.390	4.896	0.056	0.0060	0.0014	0.0390	0.0005	0.0320	0.0000	0.0033	0.0080
28	0.190	2.436	0.018	0.0070	0.0000	0.0330	0.0004	0.0090	0.0028	0.0033	0.0270
29	0.210	2.467	0.031	0.0070	0.0009	0.0250	0.0003	0.0010	0.0010	0.0026	0.0170
30	0.180	2.325	0.030	0.0003	0.0008	0.0022	0.0003	0.0110	0.0028	0.0034	0.0170
31	0.220	2.387	0.033	0.0009	0.0080	0.0240	0.0028	0.0085	0.0100	0.0084	0.0180
32	0.120	1.603	0.022	0.0011	0.0070	0.0170	0.0031	0.0092	0.0100	0.0085	0.0130
33	0.090	1.065	0.017	0.0011	0.0080	0.0120	0.0035	0.0052	0.0100	0.0083	0.0100
34	0.140	1.616	0.020	0.0015	0.0080	0.0101	0.0028	0.0075	0.0100	0.0084	0.0110
35	0.075	0.999	0.022	0.0014	0.0080	0.0040	0.0030	0.0065	0.0090	0.0084	0.0080
36	0.780	8.220	0.985	0.1200	0.0900	0.1800	0.0500	0.8500	0.6200	2.0100	1.0300
37	0.950	13.500	1.850	0.0900	0.1050	0.2500	0.0540	1.0200	0.5800	2.5000	1.3000
38	0.890	14.600	1.100	0.0950	0.0800	0.2020	0.0620	0.9500	0.3500	1.2000	0.8900
39	0.620	8.080	2.050	0.0010	0.1200	0.5000	0.1000	1.5000	0.5500	1.8000	0.7500
40	0.200	2.828	0.013	0.0017	0.0080	0.0150	0.0025	0.0091	0.0100	0.0081	0.0220
41	0.720	8.118	0.550	0.0004	0.0030	0.3400	0.0035	0.1500	0.0350	0.0490	0.0410
42	0.920	12.020	0.750	0.0008	0.0080	0.3900	0.0028	0.0950	0.0070	0.5210	0.0430
43	0.750	8.467	0.480	0.0020	0.0120	0.2900	0.0042	0.1990	0.0090	0.0580	0.0370

All anions, except SO_4, have lower concentrations in Wadi Al Aqiq. In particular, Cl ions show a positive relationship with TDS (Fig. 5), suggesting that it can be used as effective indicator of salinity. Cl tends to be enriched in Harrat Rahat groundwater, which has geochemically evolved from groundwater of Wadi Al Aqiq through natural flow paths. This probably has been caused by cyclic salting from farm areas along the flow path toward northeast (Bayumi, et al. 2007), as well as mixing with sewage water.

SO_4 contents show increasing trend with increasing TDS. Samples having high SO_4 concentrations from Wadi Al Aqiq cluster together. High SO_4 contents may be derived from dissolution of gypsum in the aquifer matrix or from industrial effluents and phosphate fertilizers (Subbarao et al. 1996; Cortecci, et al. 2002). High SO_4 contents in groundwater of Wadi Al Aqiq may be attributed to the effect of the disposal site of industrial wastewater, which is located at 4 km to the west.

HCO_3 shows weak relationship with TDS as shown in Fig. 5, indicating diverse sources of this ion. High HCO_3 concentration results from dissolution of CO_2 gas likely formed by the anoxic biodegradation of organic matter that can be derived from leaky industrial and domestic sewage water (Canter 1997; Jeong 2001; Zilberbrand et al. 2001).

NO_3 content in groundwater samples range between 31-231 mg/l. Most of those samples have nitrate concentrations exceeding the WHO (2004) drinking water standards of 50 mg/l. NO_3 has most likely originated from fertilizers application and leakage of sewage, which tends to increase along the flow path. NO_3 concentrations may be further affected by complex hydrochemical processes such as nitrification and denitrification (Arnade 1999; Rosen et al. 1999; Silva and Williams 2001).

Hydrochemical Facies

Major ion concentrations of all groundwater samples, which represent the two main aquifers in Harrat Rahat and Wadi Al Aqiq are shown in a Piper's diagram (Fig. 6). Hydrochemical facies of groundwater in the study area change broadly from a Ca-SO_4 type in Wadi Al Aqiq to a Na-Cl type in Harrat Rahat. This may suggest that the groundwater quality is controlled by water-rock interaction and anthropogenic activities. The distribution of cations and anions in groundwater of each aquifer in the ternary diagrams indicates dominance of Ca and SO_4 for Wadi Al Aqiq samples and of Na and Cl for Harrat Rahat samples. All samples are characterized by dominance of Cl and SO_4 over HCO_3. The change of the hydrochemical facies of groundwater from Ca-SO_4 in Wadi Al Aqiq to Na-Cl in Harrat Rahat may be attributed to cation exchange where Ca is removed from groundwater and Na is released from the clay exchangers.
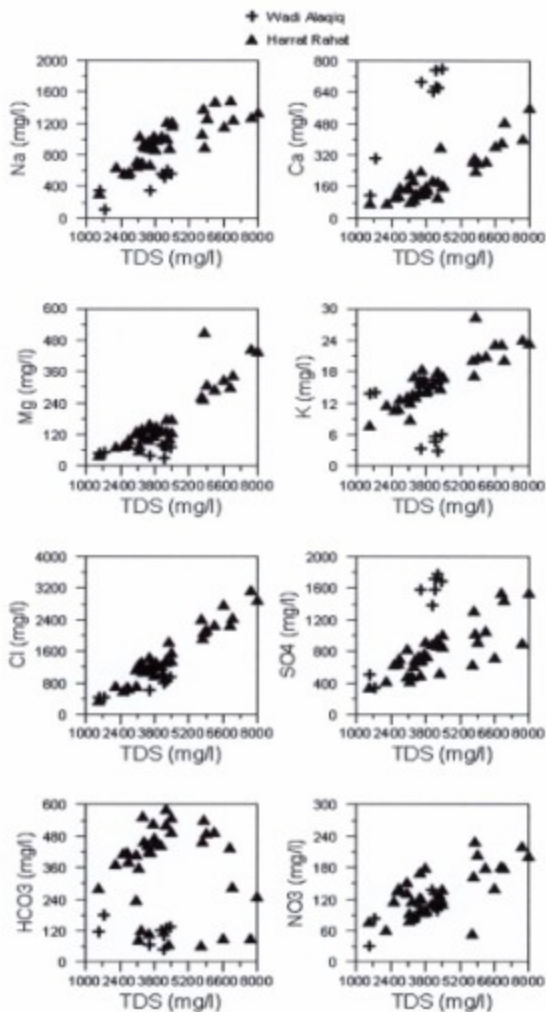
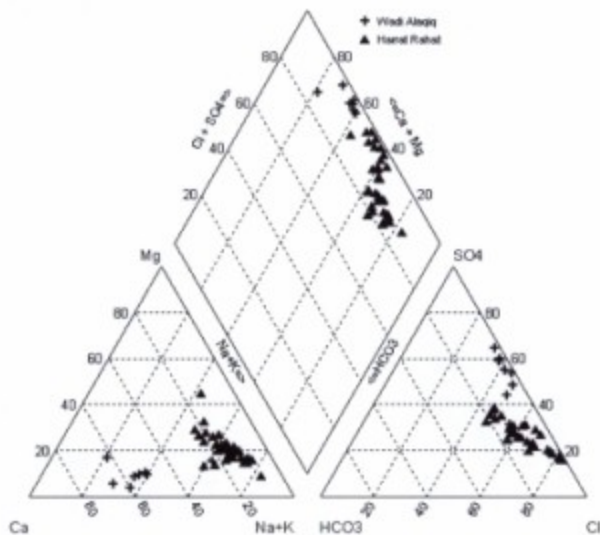Fig. 5. Relationships of TDS versus major ions concentrations.

Fig. 6. Piper's diagram showing hydrochemical facies of the collected samples.

Dissolution and Deposition

Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity (Deutsch, 1997). If certain minerals such as calcite and dolomite are commonly found in equilibrium with groundwater, it is then reasonable to assume that these minerals are reactive in typical groundwater environments and that they can control solution concentration. By using the saturation index approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy. In the present study, saturation indices (SI) of some common minerals were calculated to determine the chemical equilibrium between minerals and water. If the groundwater is saturated (SI>0) with respect to a mineral, it is prone to precipitate some of the solute load. On the other hand, if it is undersaturated (SI<0) it will take more mineral into the solution. If the saturation index of a specific mineral is equal to zero, it means that groundwater is in equilibrium with the mineral.

The SI values of aragonite, calcite and dolomite of groundwater of the study area indicate that the groundwater is mostly oversaturated with respect to these minerals. Very few samples are slightly undersaturated with respect to these carbonate minerals ($SI_{aragonite}$ -0.37 - 0.52, $SI_{calcite}$ -0.23 - 0.66, $SI_{dolomite}$ -1.50 - 1.65).

Groundwater of the study area is also moderately undersaturated with respect to gypsum and anhydrite and strongly undersaturated with respect to halite (SI_{gypsum} - 0.03 - -1.31, $SI_{anhydrite}$ -0.23 - -1.50, SI_{halite} -4.16 - -5.97). All these minerals were found as salt aggregates in the soil zone (Bayumi, et al. 2007). These salts are concentrated in the soil due to high rates of evaporation and therefore they are deposited. Recharge of rainwater during the rainfall events and/or irrigation water dissolves these minerals, and evaporation enriched water in the soil zone is flushed into the groundwater. This increases the SI of groundwater.

POTENTIAL SOURCES OF SALINITY

The complex nature of groundwater chemistry in the study area suggests an interaction of water with the hydrogeological environment. Various natural and human activities, such as water-rock interaction, cycling salting, and anthropogenic activities, can be thought of as possible factors causing deterioration of groundwater quality. Those factors are discussed below:

1- Rock – Water Interaction

Weathering of silicate rocks in the study area is one of the important processes responsible for the higher concentration of Ca and Na in groundwater. Relationship of Na/Cl molar ratio versus EC can be used as an indicator of silicate weathering. A ratio greater than one is typically interpreted as Na released from a silicate weathering reaction (Mayback 1987). On the other hand, if halite dissolution is responsible for sodium, the Na/Cl molar ratio should be approximately equal to one.

In this study, most of the Na/Cl ratio values range around or exceeding 1.00, indicating that silicate weathering and halite dissolution are the main processes resulting in release of Na into groundwater (Fig. 7).
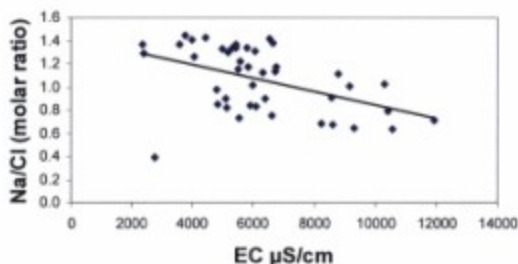

Fig. 7. Na/Cl molar ratio versus EC.

The country silicate rocks in the region are mainly composed of basalt, andesite, rhyolite and granite. It is ,therefore, expected that Ca and Na are released during weathering reactions of these rocks according to the following reactions:

$$2.33NaAlSi_2O_8 + 8.64H_2O + 2O_2 \longrightarrow Na_{1.33}Al_{2.33}Si_{3.6}O_{10}(OH)_2 + 2Na^+ + 2HCO_3^- + 3.32H_4SiO_4$$
Albite   Na-montmorillonite

Or

$$2NaAlSi_2O_8 + 11H_2O + 2CO_2 \longrightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + H_4SiO_4$$
Albite   Kaolinite

For pyroxene:
$$CaMg(Si_2O_6) + 4CO_2 + 6H_2O \longrightarrow Ca + Mg + 4HCO_3 + 2Si(OH)_4$$

In addition, for amphiboles:
$$Ca_2Mg_5Si_8O_{22}(OH)_2 \longrightarrow 14CO_2 + 22H_2O + 2Ca + 5Mg + 14HCO_3 + 8Si(OH)_4$$

Calcite and dolomite are common minerals in the alluvium, where their dissolution yields Ca and Mg ions to the groundwater. Relationship between Ca/Mg ratio and Cl concentration in groundwater samples may help in determining the sources of both ions. That is, if the ratio Ca/Mg =1, dissolution of dolomite should occur, whereas a higher ratio is indicative of greater calcite contribution (Maya and Loucks, 1995). Higher Ca/Mg molar ratio (>2) indicates the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater (Katz et al. 1998). Fig. 8 shows such relationship in which the points lie closer to the value of Ca/Mg =1 indicating the dissolution of dolomite. Samples having ratios between 1 and 2 indicate the dissolution of calcite. Those with values greater than 2 indicate the effect of silicate minerals.

Furthermore, Sr and Ba are common elements replacing Ca or K in igneous- rock minerals in minor amounts (Hem 1970). Dissolution of carbonate minerals can be another source for Sr. Fig. 9 shows plots of Ca and Al concentrations versus Sr and Ba. Those relationships are identical to Al versus Sr and Ba, indicating the influence of silicate weathering as a major source of these ions.
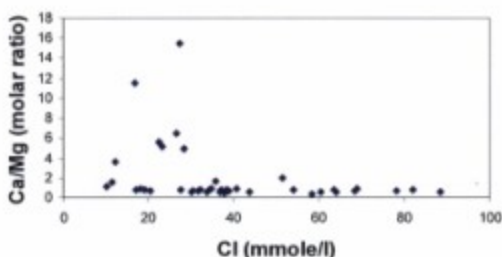

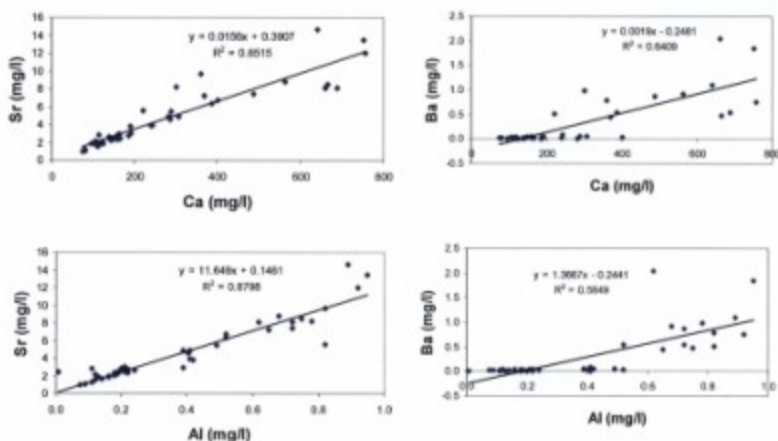Fig. 8. Ca/Mg molar ratio versus Cl.

Fig. 9. Relationships of Ca and Al versus Sr and Ba.

2- Cycling Salting

Intensive pumping of groundwater for irrigation purposes in quantities exceeding rates of recharge, particularly in Harrat Rahat resulted in serious consequences to the quantity and quality of groundwater. Water levels continue to lower down with time causing dryness of shallow aquifers. Most of the wells are now pumping water from deep aquifers, which hardly receive recharge from the surface. Pumping rates range between 500 to 800 m^3/day, whereas pumping durations vary between 6 to 12 hours daily. This yields an average abstraction rate of about $6000m^3$/day. If we consider 6% recirculation rate of irrigation water, it means that approximately $360m^3$ moves through the soil to reach the saturated zone every day.

Recirculation of irrigation water plays an important role in increasing the salinity of groundwater. Irrigation water tends to precipitate evaporite salts, such as halite, calcite and gypsum, within the soil column. Those salts are later on washed down by irrigation water, which becomes highly mineralized, to the saturated zone.

3- Anthropogenic Activities

High concentrations of several trace elements in groundwater samples from Wadi Al Aqiq aquifer are mainly attributed to the anthropogenic influence of the industrial area located to the west of the Wadi (Fig. 2). Near this area, industrial wastewater from various industries such as tannery, paints, rock wool...etc, are disposed of in unlined landfill (Fig. 10).

Leakage of industrial wastewater loaded with high concentrations of harmful trace constituents is the main point source of groundwater pollution in Wadi Al Aqiq. Several death cases and serious diseases for local inhabitants were recorded in newspapers, which reflect the impact of this industrial area on the public health. Although there are environmental legislations for preventing such undertakings, they do not seem to be applied here.

High NO_3 contents in groundwater are most likely attributed to excessive application of fertilizers in agriculture in addition to leakage of sewage from septic tanks.

Fig. 10. Dumping site of industrial disposal waste in Al-Hamra District, south of Al-Madinah Al-Munawwarah.

TRACE ELEEMENTS CONCENTRATIONS

Eight trace elements were analyzed in the collected groundwater samples; namely As, Cd, Pb, Cu, Fe, Mn, Zn and V. Analytical results of these constituents are given in Table 3 and illustrated in Fig. 11. Samples collected from Wadi Al Aqiq (Nos. 36-43) contain noticeably high concentrations of most examined trace constituents. The rest of samples show normal concentrations of these elements.

Arsenic is an important drinking-water contaminant known to cause cancer, skin damage and circulatory system problems to humans (Steinmaus, et al., 2005). Relatively high concentrations of As were found, in three samples (nos. 36-38) from Wadi Al Aqiq, exceeding the WHO (2004) maximum contaminant level (MCL) of 0.05mg/l. The possible source of this contaminant is the tannery factory waste that is disposed of in the Al Hamra area, west of the wadi. Number of the inhabitants in the area has died and others have suffered serious diseases as a result of this problem.

Cadmium metal is used in steel industry, paints, plastics and batteries. Contamination in drinking water may also be caused by corrosion of galvanized pipes and some metal fittings. Cd contents in groundwater samples from Wadi Al Aqiq range between 0.003 and 0.120 mg/l, which exceeds the MCL of 0.01mg/l. The possible sources of this pollutant are the paint factory and the car workshops in the industrial area.

Lead is used principally in the production of lead-acid batteries, solder and alloys. The organolead compounds tetraethyl and tetramethyl lead are used extensively as lubricating agents in petrol. Lead is rarely present in tap water as a result of its dissolution from natural sources; rather, its presence is primarily from household plumbing systems containing lead. It is known to cause kidney problems and high blood pressure (EPA 1999). Average Pb level in the study area (of 0.075 mg/l) exceeds the maximum permissible limit of 0.05 mg/l. Highest concentrations were met in Wadi Al Aqiq (sample nos. 36-43).

Copper is both an essential nutrient and a drinking-water contaminant. It is used to make pipes, valves and fittings and is present in alloys and coatings. Copper concentrations in drinking water vary widely, with the primary source most often being the corrosion of interior copper plumbing. Copper concentrations in treated water often increase during distribution, especially in systems with an acid pH or high-carbonate waters with an alkaline pH (WHO 2004). Consumption of standing or partially flushed water from a distribution system that includes copper pipes or fittings can considerably increase total daily copper exposure, especially for infants fed formula reconstituted with tap water.

The measured Cu concentrations in groundwater from the investigated area are generally less than the MCL set by WHO of 1 mg/l. However, Wadi Al Aqiq groundwater has higher values of Cu contents due to the effect of leakage from the industrial wastewater landfill.

Iron is one of the most abundant metals in the earth's crust. It is found in natural fresh waters at levels ranging from 0.5 to 50 mg/l. Iron may also be present in drinking water as a result of the corrosion of steel and cast iron pipes during water distribution. Iron is an essential element in human nutrition and the minimum daily requirement for it depends on age, sex and physiological status. Average Fe concentration in the collected groundwater samples is 0.16 mg/l, which is less than the recommended value for drinking water of 0.3 mg/l (WHO 2004). High Fe concentrations were recorded in for Wadi Al Aqiq groundwater where the maximum concentration was 1.5 mg/l.

Manganese is one of the most abundant metals in the Earth's crust, usually occurring with iron. It is used principally in the manufacture of iron and steel alloys. More recently, it has been used as an octane enhancer in petrol in North America. Manganese is an essential element for humans and other animals and occurs naturally in many food sources. Manganese is naturally occurring in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions. Mn content in groundwater of the Al Madinah area ranges from 0 - 0.62 mg/l. Part of the Wadi Al Aqiq samples exceeded the MCL for drinking water of 0.05 mg/l (WHO 2004); this is also attributed to the impact of the industrial wastewater landfill.

Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. Although levels of zinc in surface water and groundwater normally do not exceed 0.01 and 0.05 mg/l, respectively, concentrations in tap water can be much higher as a result of dissolution of zinc from pipes. Groundwater samples from the investigated area have Zn concentrations ranging between 0.001 to 2.5 mg/l, which lie below the MCL of drinking water of 5 mg/l.
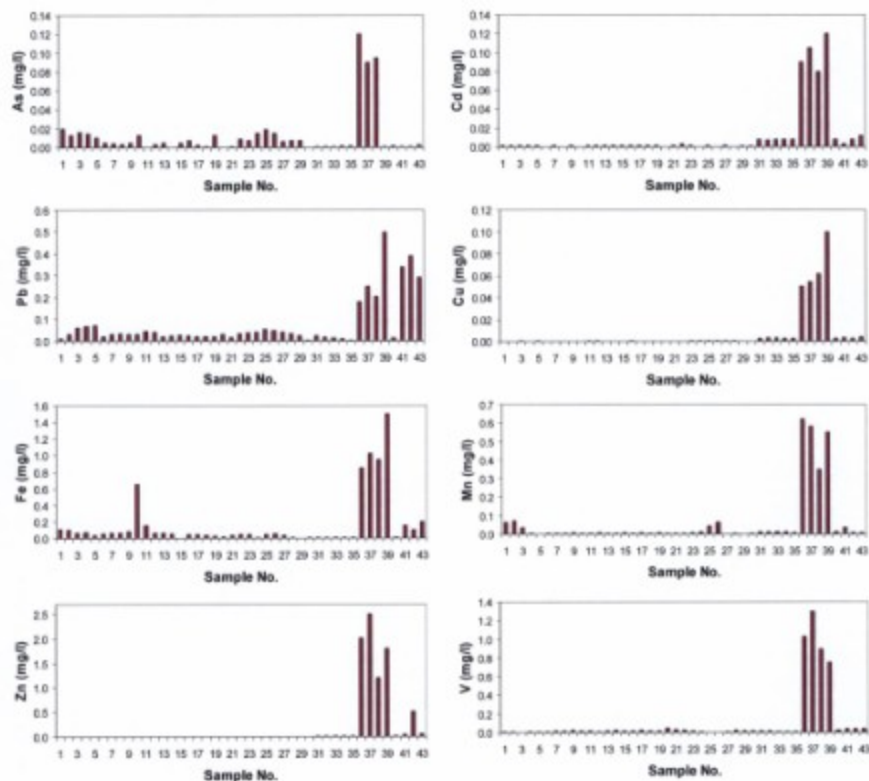
Fig. 11. Concentrations of trace constituents in the collected groundwater samples.

Significant sources of vanadium include the dumping of sewage sludge, discharge of domestic wastewater and the industrial effluents specially fertilizers containing materials with high vanadium content. Groundwater from Wadi Al Aqiq has abnormally high values of V concentrations, varying between 0.022 to 1.3 mg/l in sample nos. 43 and 37, respectively. This high values is due to leakage from the industrial wastewater landfill, where spent oils from car workshops are disposed.

CONCLUSIONS

The main aquifers in the southern parts of the Al Madinah Al Munawwarah area are the lava flows and intervening sediments of Harrat Rahat and the drainage basin of Wadi Al Aqiq. Groundwater movement is toward the north and northeast and the average annual recharge rate is about 0.72 mm/yr.

The groundwater quality in these aquifers has deteriorated greatly as a result of several major processes acting either individually or collectively. Cyclic salting or dissolution of the readily soluble salts in the soil zone, intensive pumping, water-rock interaction and the intensive application of fertilizers are the main possible causes for increasing groundwater salinity. Weathering of silicate minerals controls the major ions such as Na, Ca, Mg, and K in groundwater. Groundwater is oversaturated with respect to carbonate minerals and undersaturated with respect to gypsum, anhydrite and halite. The ionic ratios of Na/Cl and Ca/Mg explain the contribution of halite, calcite, dolomite and silicate minerals to the groundwater.

The hydrochemical facies of groundwater changes from $Ca - SO_4$ in Wadi Al Aqiq to Na-Cl in Harrat Rahat. This may be attributed to cation exchange where Na is released into groundwater from clay exchangers.

Chemical composition of groundwater in the Wadi Al Aqiq area is mainly influenced by leakage of industrial wastewater from the unlined dumping site to the southwest. The groundwater herein is characterized by noticeably elevated concentrations of As, Cd, Pb, Cu, Zn, Fe, Mn, and V. It is, therefore, strongly recommended to stop disposal of the untreated industrial wastewater in this insecure landfill. Moreover, conservation of groundwater resources in this area can be accomplished through using of subsurface drip irrigation methods, which will also help in decreasing the possibility of salt precipitation in the soil zone and hence cyclic salting.

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