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Hydrochemical Processes and Metal Composition of Ain Umm-Sabah Natural Spring in Al-Hassa Oasis Eastern Province, Saudi Arabia

Ahmed A. Al-Naeem
Department of Soil and Water, King Faisal University, Al-Hassa, Saudi Arabia

Abstract: This study was carried out to determine the hydro-chemical processes and the metal concentration of spring water to evaluate its suitability for irrigation and other purposes. A total of 10 water samples were collected from Ain Umm Sabah at different times and from different locations from the spring basin. EC (dS m^{-1}), pH, temperature, total cations (Na, Ca, Mg, K) and anions [Cl, CO_3, HCO_3, SO_4, NO_3, Fluoride (F)] were determined. Some trace and heavy metals (Al, As, Ba, B, Br, Mo, Ni, Si, Cd, Cu, V, Fe, I, Pb, Mn, Zn, Sr, Se, Sb, La and Se were determined. The Spring water is classified as C4S2 (high salinity with medium sodicity problem water). Chloride (Cl) and nitrate (NO_3) concentrations were higher than the permissible limits according to World Health Organization Standards. The Ain Umm Sabah water is Na-Cl dominant water and can create soil sodicity problems and cause Na and Cl ion toxicity to plants if used for irrigation of sensitive crops. The spring water is under-saturated (negative SI) with respect to calcite, dolomite, gypsum, anhydrite, halite, fluorite and aragonite and oversaturated (positive SI) with respect to goethite, siderite and hematite minerals. The concentration of all the estimated trace metals was within the permissible limits for its use as drinking water and other purposes according to WHO. Since the spring water contains high concentration of NO_3, hence can not be used for drinking purposes without prior treatment. The study findings suggest careful use and pumping of water from the spring. Further studies are required on regular basis to monitor the depletion in the spring water level and the temporal change in water salinity.

Key words: Hydrochemical processes, water salinity, ion concentration, trace metals, nitrate, fluoride, saturation index, water classification

INTRODUCTION

Al-Hassa Oasis is situated about 60 km to the West of the Arabian Gulf in the Eastern Province of Saudi Arabia. The total land area is approximately 20000 ha. Its geographical location is between 49° 10′ and 49° 55′ Eastern longitude and 25° 05′ and 25° 40′ Northern latitude (Al-Taher, 1999) which is around 130-160 m above sea level (Al-Barrak, 1993). An extreme maximum air-temperature of 51.3°C was recorded at Hofuf in June 1983. Mean annual rainfall is about 70.3 mm (Al-Kuwaiti and Ahmed, 2003).

Natural water springs were widespread along the western edge of the Oasis from south of Al-Hofuf to north of Al-Mutirifi village and divided under four main groups. Three of these groups are located within the jurisdiction of Al-Hassa Irrigation and Drainage Authority (HIDA) and the fourth group is situated out of this organization. These groups are over three main sectors i.e., Eastern, middle and Northern sectors. Ain Umm Sabah was classified under third group and is located south of Al-Mutirifi village. Previously, Al-Hassa Oasis was irrigated by limited groundwater resources represented by a hundred water wells and natural springs.

Al-Kuwaiti and Ahmed (2003) stated that the total water discharge of free flowing springs was 10 m^3 sec^{-1}. according to BRGM (1977a) and 15.2 m^3 sec^{-1} as recorded by HIDA in cooperation with Waste Water Authority and the Directorate of Agriculture and Water. Leichtweiss-Institute Research Team (1978) reported that the discharge of all free flowing water springs was 10.3 m^3 sec^{-1}.

Ain Umm Sabah is one of the major springs in the Al-Hassa Oasis. Its geographical location is between 49° 35′ eastern longitude and 25° 28′ northern latitude (BRGM, 1977b). It is situated about 6 km north of Mubarraz and 2.5 km South-East of Mutairifi. The basin of the spring is a square concrete pond having dimensions of 18×18 m. Possibly, it is recharged through the broken and cracked rocks from the bottom of the Neogene rocks. It was a natural artesian spring. Currently, water from Ain Umm Sabah spring is being pumped through a well drilled upto 300 m depth. Water discharge of Ain Umm Sabah was 1.26 m^3 sec^{-1} (Twitchell, 1944) and 0.145 m^3 sec^{-1} (Wakuti Consulting Engineers, 1964).

Water salinity of the Ain Umm Sabah natural spring was measured as 1536 mg L^{-1} in 1979 (Anonymous, 1984), 1540 and 1560 mg L^{-1} by Leichtweiss-Institute (1975, 1978), respectively, 1750 mg L^{-1} (top of Ghawar Structure) to 2200 mg L^{-1} (east of Shedgam Plateau) in 1978 and 1690 mg L^{-1} by Hussain and Sadiq (1991) and 2579 mg L^{-1} by Al-Hawas (2002). The temporal changes in water quality especially the total water salinity may be the result of intensive pumping to meet water requirements for various uses (Blaszyk and Gorski, 1981; Appelo and Postma, 1994).

The suitability of water for irrigation, drinking and other purposes is determined by many factors such as the solubility constants of different ions present in water coming through rock-water interaction in the aquifer. Water may not be suitable for all purposes if certain elements such as chloride, nitrates and other trace metals (Cr, Pb, Cu, etc.) exceed the permissible limits according to APHO (1998). Montgomery (1985) reported that 80% of world's well water samples contain less than 50% chloride concentration. A strong relationship was found between human health and the fluoride contents in water. Fluoride is well known for its help in protecting tooth decay (Al-Shemi and Al-Minawi, 1988).

Also, the chemical reactions in water play a minor role in influencing the blood heart vessels, in spite of main factors not be specified yet (Montgomery, 1985). More than 80% world diseases were linked with water deficiency (WHO, 1971).

The change in water quality of Neogene aquifer in the recent years created some concern for its re-evaluation especially for the Ain Umm Sabah natural spring for irrigation, drinking and other purposes. The aim of the study was to determine and evaluate the hydrochemical processes of water of Ain Umm Sabah natural spring and its suitability for irrigation and drinking purposes.

MATERIALS AND METHODS

A total of 10 water well samples were collected from five different locations of the basin of Ain Umm Sabah natural spring during 2006-2007. The pH and EC of water were measured instantly at the time of sample collection. The water samples were collected in sterile plastic bottles, acidified with pure nitric acid, stored in an ice box and transported to the analytical laboratory for chemical analysis. Each sample was filtered through 0.45 mm pore size filter paper, then divided into three portions, (1) for cation analysis, (2) for anion determinations and (3) for some minor and trace elements. The analytical methods used for the determination of cations and anions were those described in USDA (1954) and Page (1982) and shown in Table 1.

Table 1: Analytical methods used to determine cations and anions in the study

Parameters	Methods	References
Electrical conductivity (EC)	Conductivity Bridge	USDA (1954)
pH	Glass electrode	USDA (1954)
Cations	Titration method	Page (1982)
Anions	Titration method	Page (1982)
Sulfate	Turbid metrically	USDA (1954)
Total dissolved salts	Gravimetrically	USDA (1954)

The ratio of sodium to other major cations (Ca, Mg, K) is important to maintain soil structure and determine Na ion toxicity to plants. Because plants are sensitive to sodium when its concentration in irrigation waters exceeds the permissible limits for normal plant growth. To assess the magnitude of Na on soil exchange complex, sodium hazard is usually expressed in terms of Sodium Adsorption Ratio (SAR). The SAR was calculated by the following equation (Rogers and Lydon, 1994). The concentration of sodium, magnesium and calcium ions in Eq. 1 is me L^{-1} (Wilcox, 1955).

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}} \quad (1)$$

The sodium adsorption percentage was determined by the following equation.

$$SP\ (\%) = \frac{Na^{+}}{Ca^{++} + Mg^{++} + Na^{+} + K^{+}} \times 100 \quad (2)$$

The cation exchange phenomenon occurs when the ions absorbed on the surface of the soil particle differ from those present in the soil solution. This phenomenon continues until an equilibrium is reached between the cations on the mineral surface and those in the water (Rump and Krist, 1992). The appropriate method for assessing the exchangeable sodium in the Ain Umm Sabah aquifer is to determine the Exchangeable Sodium Percentage (ESP) values on the basis of the SAR of water using the following empirical relationship between the SAR of water and the ESP (USDA, 1954):

$$ESP = \frac{100 \times (-0.0126 + 0.01475SAR)}{1 + (-0.0126 + 0.01475SAR)} \quad (3)$$

Trace and heavy metals were analyzed using Inductively Coupled Plasma, ICP (Moselhy *et al*., 1978), while Arsenic and Selenium were determined using Activation Technique Neutron (Reeves and Brooks, 1978) and (Morgan and Ehmann, 1971). Fluoride (F) and the nitrate (NO_3) groups were determined Spectrophotometrically utilizing the disulphonic acid and alizarin red-S with the Zirconium-Oxychloride Reagent.

Each water sample was run in triplicate and the mean for 10 water samples was calculated. The discharge of Ain Umm Sabah was measured by traditional method i.e., volume container and the stopwatch.

Saturation indices: Saturation Indices (SI) were calculated for the 10 water samples from Ain Umm Sabah spring using the PHREEQC model developed by Parkhurst (1995) to determine the thermodynamic equilibrium of spring water with respect to solid phase of different minerals present in the aquifer rock formation and their effect on water chemistry after dissolution during rock-water inaction process.

RESULTS AND DISCUSSION

The total salinity ranged between 1699-1802 mg L^{-1} with a mean value of 1764 mg L^{-1} at different locations at various period of time (Table 2). The temporal change in water salinity could be due to high rate of pumping water from the aquifer and also to the depletion of water level in the aquifer of Ain Umm Sabah spring area. The water salinity is low as compared to that reported by Al-Hawas (2002). This would mean that the water salinity improved with time and could be attributed to the recharge of the aquifer by the intrusion of low salinity water from below the Neogene aquifer and the surrounding area. However, according to USDA (1954) and Wilcox (1955) water classification schemes, the water of the Ain Umm Sabah natural spring can be classified as C4S2 i.e., very high salinity and medium sodicity hazard water. The cation concentration order is Na followed by Ca > Mg > K and the anion concentration order is Cl followed by SO_4 > HCO_3 > CO_3. This shows that the Ain Umm Saba has Na-Cl dominant ions water. Therefore, the water is not suitable for irrigation under normal soil and water conditions (Yousef, 1999). Also if the Exchangeable Sodium Percentage (ESP) exceeds the level of 15, soil structure deteriorates very rapidly and crates drainage problems due to inadequate soil permeability (Ayers and Westcot, 1985). The water could be used for irrigation on coarse textured soils provided certain management practices such leaching requirements, selection of semi-salt tolerant crops and provision of adequate drainage are adopted (Hussain *et al*., 1994).

Additionally, the use of spring water for irrigation might create some sodicity problem in fine textured soils which could be mitigated by applying appropriate amount of soluble calcium amendments such gypsum, calcium chloride etc if the indigenous gypsum is not adequately present in the soils under irrigation. This water can be used on coarse textured (sandy) soil or organic soils having adequate drainage facilities (Hussain *et al*., 1994).

The fluctuation is water salinity of Ain Umm Saba could be attributed to the intrusion of fresh groundwater from the surrounding water bearing aquifers or recharge of Neogene aquifer during the heavy rainy season. There is also possibility that excess pumping during peak water requirement period might have extracted water from the Al-Khobar aquifer below the Neogene aquifer where the water salinity is less than the Neogen aquifer thus causing fluctuation in water salinity either high or low depending upon the rate of pumping water from Ain Umm Sabah spring.

Comparison of metal composition of Ain Umm Saba water with WHO standards: Table 3 shows that the Cl concentration in Ain Umm Sabah water (966 mg L^{-1}) was higher than the WHO (1971) permissible limits of 250 mg L^{-1} for drinking water and 600 mg L^{-1} as the upper limit of Cl concentration acceptable for other activities.

The concentration of NO_3 ion is slightly higher in the water of Ain Umm Sabah natural spring as compared to the WHO (1993) permissible limits (Table 3). This could be attributed to the application of inorganic fertilizers containing appreciable amount of nitrogen elements and the biological activities taking place in the agricultural farms. These pollutants may stimulate the digestive, urinary and intestinal systems in human being upon consumption of this water.

Table 4 shows the concentration of different ions on percent basis. The high Cl concentration in the water of Ain Umm Sabah spring accounts for 56% of the total cations and is in agreement with the reported Cl

Table 2: Mean chemical composition of water of Ain Umm Sabah spring (mg L^{-1})

Sample No.	Temp. (°C)	TDS (mg L^{-1})	EC (dS m^{-1})	pH	Na	K	Ca	Mg	Na (%)	HCO_3	CO_3	Cl	Cl (%)	SO_4	SAR
1	21	1699	2.655	7.1	418	29	155	58	63	207	0.60	925	59.8	414	7.24
2	21	1779	2.780	7.2	425	29	162	65	62	205	0.80	973	61.6	400	7.39
3	21	1757	2.745	7.2	437	29	144	58	65	210	0.50	962	60.7	412	7.75
4	21	1741	2.720	7.4	418	32	144	62	64	199	0.50	955	60.7	420	7.31
5	21	1763	2.755	7.4	406	34	164	68	60	198	1.70	967	61.3	412	6.70
6	21	1763	2.755	7.3	446	29	139	56	67	202	1.10	968	61.2	412	8.04
7	22	1802	2.815	7.4	470	22	140	54	69	204	1.10	988	61.3	418	8.52
8	21	1757	2.745	7.4	440	30	145	57	65	208	0.50	964	61.0	409	7.81
9	20	1792	2.800	7.2	439	35	141	61	65	206	0.90	978	61.1	417	7.75
10	19	1782	2.785	7.3	478	25	159	49	67	201	0.40	979	61.3	418	8.47
Mean	21	1764	2.756	7.3	438	29	149	59	65	204	0.79	966	61.0	413	7.66

Table 3: Comparison of ions concentration in the water of Ain Umm Sabah with the ion concentration permissible by World Health Organization (WHO, 1971)

Elements	Ain Umm Sabah (mg L^{-1})	WHO	±SD
Na	438.0	600	23.0
K	29.5	10	3.8
Ca	149.0	200	9.7
Mg	59.0	150	5.6
Cl	966.0	600	17.1
SO_4	413.0	250	5.8
NO_3	47.0	45	2.4

Table 4: Comparison of concentration (mg L^{-1}) of different ions on percent basis with the WHO Standards

Elements	WHO	Ain Umm Sabah (mg L^{-1})	(%)
Na	600	438	25
K	10	29	2
Ca	200	159	9
Mg	150	59	3
CO_3		1	0
HCO_3		17	1
Cl	600	966	56
SO_4	400	62	4

Table 5: Mean metal concentration (mg L^{-1}) of water of Ain Umm Sabah spring in Al-Hassa, Eastern Province as compared to the WHO (1993) standards

Treatments	Mean element concentration	International upper permissible limits
Cr	0.018	0.050
Co	0.005	0.100
Al	0.090	0.200
As	0.005	0.050
Ba	0.017	1.000
Cd	0.005	0.001
Cu	0.005	1.500
Fe	0.008	1.000
La	0.005	----
Mn	0.005	0.100
Mo	0.006	0.010
Ni	0.005	0.100
Pb	0.005	0.050
Se	0.005	0.001
Si	9.060	----
Sr	2.250	----
V	0.012	0.100
Zn	0.005	5.000

Source = EEC (European Countries Guidelines)

concentration of Montgomery (1985) who found that the chloride concentration is less than 50% in approximately 80% of world water samples. The sodium (Na) ion concentration was ranked second (25%).

Table 5 shows the mean concentration of heavy metals in the water of Ain Umm Sabah. In general, the concentration of all the heavy metals was within the permissible limits of WHO (1993) standards. The fluoride (F) concentration of spring water was higher than that reported by McClure (1982) and Murray (1976) who found its range between 0.5-1 mg L^{-1}. Therefore, it can be stated that the water of Ain Umm Saba is safe for drinking purposes with respect to F concentration. Furthermore, high concentration of Silicon ions of water may reflect the composition of the Ain Umm Sabah's aquifer rocks.

Table 6: Temporal change in mean chemical composition of water from Ain Umm Sabah (mg L^{-1})

Treatments	Present study (2006-7)	Al-Hawas (2002)	BRGM(1977a)
EC (dS m^{-1})	2.76	2.58	1.66
pH	7.30	7.09	7.50
Na	438.00	348.00	271.00
K	29.00	29.00	20.00
Ca	149.00	163.00	149.80
Mg	59.00	63.00	47.80
SAR	7.66	5.90	4.94
Na (%)	65.00	58.00	49.70
CO_3	0.79	0.00	0.00
HCO_3	204.00	188.00	204.00
Cl	966.00	618.00	469.00
SO_4	413.00	416.00	290.00
NO_3	47.00	---	18.00
TDS	1764.00	2579.00	1470.00

The discharge of Ain Umm Sabah natural spring was measured using traditional method (plastic container of known volume and the stopwatch). Currently, its discharge is 84 L sec^{-1} (0.084 m^3 sec^{-1}) and the depth of well in the spring is more than 300 m. The temporal variation in the spring discharge might possibly affect the water salinity due to the radius of influence during pumping.

Temporal change in Ain Umm Sabah natural spring water: The results of Table 6 indicate that Na, Cl, HCO_3 and SAR of spring water showed increases, Ca ion and total water salinity decreased while K remained unchanged when compared with the results of Al-Hawas (2002). Overall the spring water showed improvement with the passage of time and could be attributed to higher pumping rate of water from the aquifer.

Saturation indices: Saturation Indices (SI) were calculated for the 10 water samples from Ain Umm Sabah spring using the PHREEQC model developed by Parkhurst (1995). The spring water is under-saturated (negative SI) with respect to calcite, dolomite, gypsum, anhydrite, halite, fluorite and aragonite and oversaturated (positive SI) with respect to goethite, siderite and hematite minerals. Actually, the SI is a measure of the thermodynamics state of a solution relative to the equilibrium with a specified solid-phase mineral. This shows that the spring water flow is capable of dissolving the aquifer rock thus increasing its porosity and permeability consequently affecting the water salinity.

CONCLUSIONS

The Spring water is classified as C4S2 (high salinity with medium sodicity problem water). Chloride (Cl) and nitrate (NO_3) concentrations were higher than the permissible limits according to World Health Organization Standards (WHO, 1993). The Ain Umm Sabah water is Na-Cl dominant water and can create soil sodicity problems and Na and Cl ion toxicity to plants if used for irrigation of sensitive crops. The spring water is under-saturated (negative SI) with respect to certain minerals (calcite, dolomite, gypsum, anhydrite, halite, fluorite and aragonite) and oversaturated (positive SI) with respect to goethite, siderite and hematite minerals. All the trace metals were within the permissible limits for drinking and other purposes. Since the spring water contains high concentration of NO_3, hence can not be recommended its use as drinking water without prior treatments. The study findings suggest careful use and pumping of water from the spring. High concentration of silicon ions provide good concept regarding the chemical settings of the aquifer rocks of Ain Umm Sabah (Neogene aquifer) and may relate to the faults arrangements nearby the Al-Gawar's fold convex. In conclusion, careful monitoring, appropriate irrigation scheduling and groundwater pumping strategy should be developed to avoid over pumping of water and minimize aquifer depletion in the Al-Hassa Oasis for sustainable irrigated agriculture.

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