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ORIGINAL PAPER

Assessment of sulfurous springs in the west of Iraq for balneotherapy, drinking, irrigation and aquaculture purposes

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Abstract This research deals with the sulfurous spring waters flow along the course of the Euphrates River in western Iraq in the area extended between Haqlaniya and Hit within the Al-Anbar governorate. Eleven springs (3 in Haqlanya, 4 in Kubaysa and 4 in Hit) have been addressed for the purpose of water evaluation for balneology, drinking, irrigation and aquaculture (fish farming). In order to meet the objectives of this research, all springs were sampled and analyzed for the total dissolved solid, electrical conductivity, pH, temperature, major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}), major anions (SO_4^{2-}, Cl^{-}, HCO_3^{-} and CO_3^{2-}), minor anions ($PO_4^{3-}$and NO_3^{-}) as well as the trace elements that included Pb, Zn, Cd, Ni, Fe, Mn, Cu, Br, F, Ba, B, Sr, Al, As, Cr, Hg and Se. The International Standards of World Health Organization are used for assessing the water quality. The results revealed that the springs belong to the tepid springs of 27–30 °C and classified as hypothermal to the thermal springs. Lithochemistry and geochemical processes clearly affected the water chemistry. The hydrogeochemical processes are responsible for the element enrichment in water by the chemical dissolution of carbonate and gypsum and evaporation as well. The results of the study indicate the possibility of using spring water for therapeutic purposes, but not allowed for drinking and aquaculture (fish farming), except those free of H_2S gas. On the other hand, it can be used for irrigation with risk. However, soil type as well as proper selection of plants should be taken into consideration.

Keywords Aquaculture · Balneotherapy · Iraq · Irrigation · Springs

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Introduction

The study area is located close to the western bank of the Euphrates River that can be seen in Fig. 1. The geographic coordinates are listed in Table 1. The area is characterized by undulated plateau plain. Sissakian and Salih (1994) divided the geomorphologic units into five types: first, mesas and plateau (originated due to erosion factors with structural effect); second, hills and pediment (originated due to erosional factors); third, alluvial terraces, flood plains, depression and valley fill sediments (originated due to erosional and depositional factors); fourth, karst, depressions and valleys (originated due to physical and chemical weathering); and fifth, sabkhas and salt crusts (originated due to climatic factors, such as temperatures and evaporation).

The arid climate is characteristic of the region. The climatological factors are derived from the meteorological station in Haditha, Ramadi and Rutbah, during the long-term period (1971–2000), which indicates

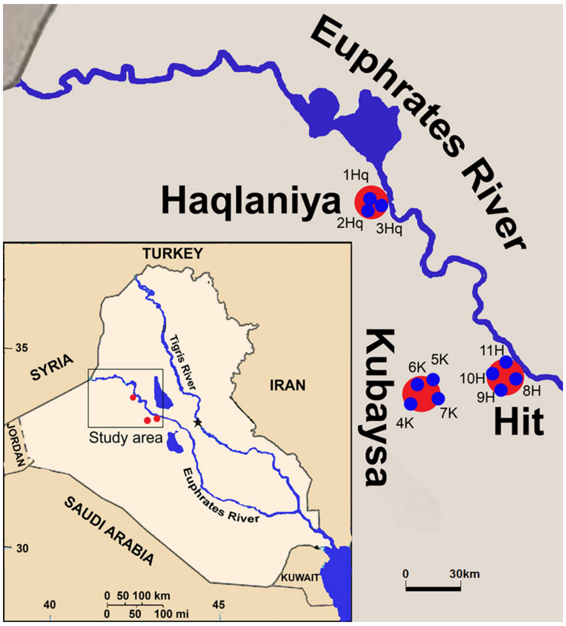

Fig. 1 Location map shows the study area and sampling sites

Table 1 Area name and geographic coordinates of study area

Spring no.	Area	Coordination		
		Longitude	Latitude	Elevation (m)
1Hq	Haqlaniya	E42°21 59.8	N34°05 24.7	89
2Hq		E42°21 59.8	N34°05 24.7	89
3Hq		E42°21 59.8	N34°05 24.7	89
4 K	Kubaysa	E42°27 53.7	N33°26 14.4	168
5 K		E42°36 47.5	N33°34 6.7	120
6 K		E42°36 40.3	N33°34 3.9	115
7 K		E42°35 36.7	N33°35 53.4	114
8H	Hit	E42°44 18.3	N33°39 53.5	85
9H		E42°48 51.9	N33°38 20.9	60
10H		E42°49 51.4	N33°37 48.8	56
11H		E42°50 10.3	N33°38 19.8	50

that the investigated area is characterized by an arid climate (Gharbi 2005). The mean annual minimum and maximum temperature ranges between 12.3 and 29.15 °C. The mean annual rainfall is 142 mm, varies between 138.6 and 143.2 mm; the mean annual evaporation is 106 mm, ranges between 100.1 and 113.3 mm (Hussien and Gharbie 2010a). The main aquifer in the study area is recharged by precipitation and runoff water, and the discharge amount of springs, within the studied area, ranges between 0.5 and 230 l/s (Hussien and Gharbie 2010a). The average of groundwater temperature for all the studied springs is 27 °C, and their range varies between 22 and 34 °C. According to Laboutka (1974), the waters of the springs are classified as subthermal to thermal waters (Hussien and Gharbie 2010a). A set of springs in the study area are used for farm irrigating only. Thus, the possibility of investing these springs for other purposes such as balneotherapy, drinking, irrigation and aquaculture purposes is a suitable subject for prospecting. Al-Dulaymie et al. (2011) studied spring water in Hit and Kubaysa and concluded that the spring waters are classified as brackish to salty, genetically, originated from connate fossil water of marine origin mixed with water of meteoric origin. Balneologically, they classified springs into two potential sites: the first one located in the region of the Hit city (east of the Abu-Jir Fault Zone) and the second potential site representing the region of the Kubaiysa city (west of the Abu-Jir Fault Zone). Balneotherapy and spa therapy emerged as an important treatment modality in the first decade of the nineteenth century, first in Europe and then in the United States (Matz et al. 2003). The effects of spa therapy can be divided into three categories: mechanical, thermal and chemical effects. Immersion allows the patient to mobilize joints and strengthen muscles with minimal discomfort. It has been shown that immersion for 1 h increases water excretion by about 50 % (O'Hare et al. 1985). The hot water causes superficial vasodilation, and it has been shown to reduce vascular spasm and stasis in the nail bed and conjunctiva (Adler 1961). Absorption of minerals through the skin seems to be limited. The dermatological therapeutic effect would therefore appear to lie in a local interaction between the mineral water and the structure of the skin surface (Ali and Sadanobu 2005).

Water can heal many diseases; also, acne vulgaris is another dermatologic disease that benefits from balneotherapy, psychological effects of balneotherapy being to relax and strengthen the body and mind, and to prevent the development of disease (Ali and Sadanobu 2005). Hydrochemical evaluation of groundwater systems is usually based on the availability of a large amount of information concerning groundwater chemistry (Hussien 2004). It is very necessary to investigate the physiochemical specification of water to evaluate its suitability for drinking, irrigation and aquaculture (fish farming) purposes.

Water quality criteria for assessing fish farming may take into account only physical–chemical parameters that tend to define a water quality that protects and maintains aquatic life.

To establish water quality criteria for a specific subject, parameters of physical and chemical constituents must be specified. In this paper, an attempt has been made to assess the spring water for the purposes of balneotherapy, drinking, irrigation and aquaculture (fish farming).

Geology

Geological map of the study area and surroundings is shown in Fig. 2. The area is of low-hilly structure. A number of karst features of circular to elliptical shape that are 20–50 m deeper than the surroundings along the fault zone can be observed. These topographic depressions are formed as a response to the dissolution process played on carbonates. On the other hand, it contains few uplifted parts that are relatively higher both topographically and stratigraphically than the surroundings. Stratigraphically, it is very simple. Miocene–Holocene deposits are exposed in the studied area. Lithostratigraphy can be described from the oldest to the youngest as follows: Baba Formation (U. Oligocene) comprised of hard dolomitic limestone of white color with thickness varying between 99 and 149 m. The formation overlies Baba is Anah Formation which has thickness ranging between 7 and 99 m composed of chalky limestone, coral reef and breccia belong to the U. Oligocene. The Euphrates Formation (L. Miocene) of neritic environment is mainly

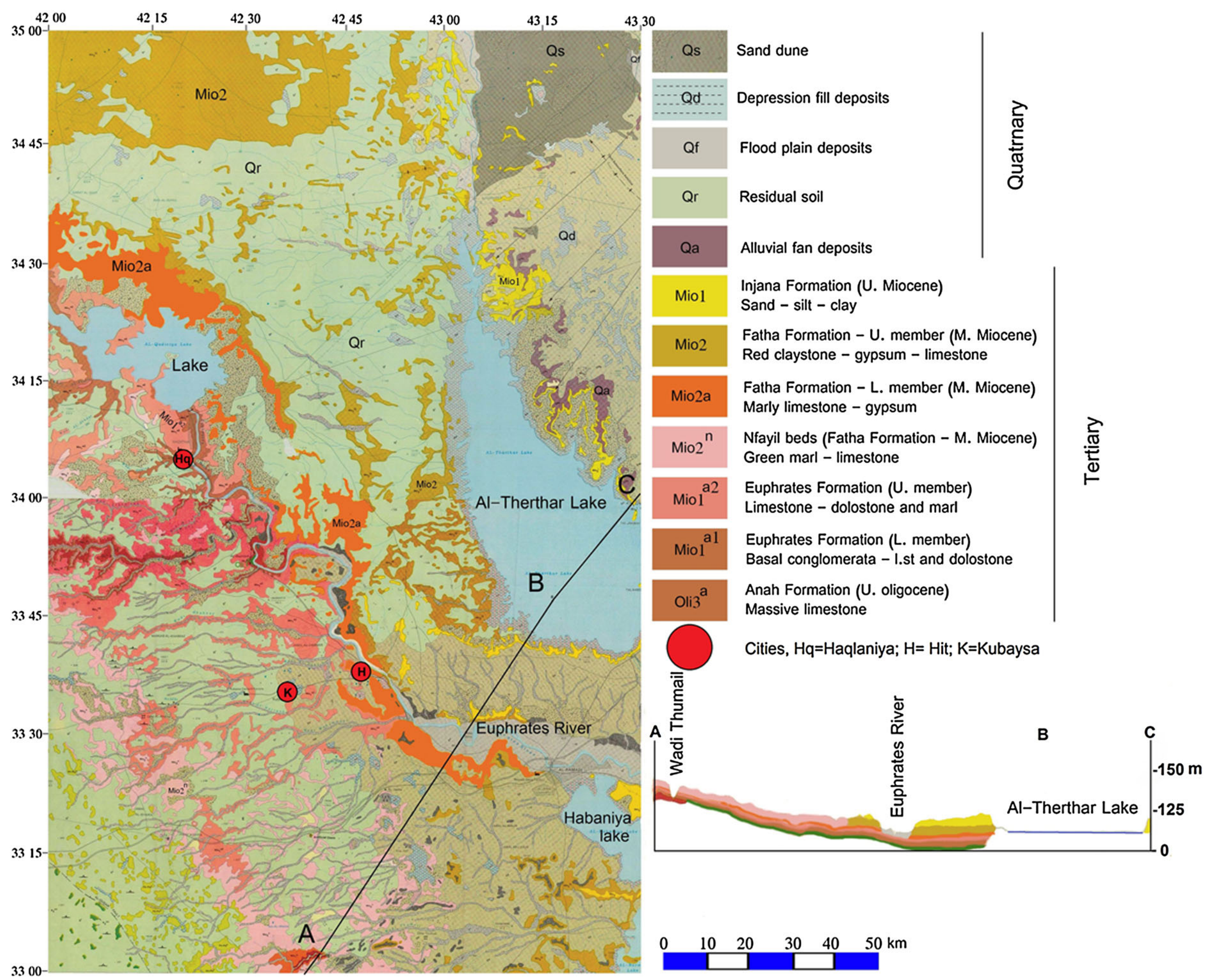

Fig. 2 Geological map and cross section of the study area

composed of basal conglomerate, dolomitic limestone, chalky limestone and marly limestone with thickness ranging between 28 and 75 m. The Fatha Formation (M. Miocene) is a lagoonal environment composed of marl, limestone, gypsum, bituminous gypsum and clay stones. This formation extends on both banks of the Euphrates River. The thickness of this formation ranged between 5 and 28 m, where the formation is underlain by Euphrates Formation and overlain by Quaternary deposits. Quaternary deposits comprised river terrace (sandy gravel) sediments of Pleistocene; Pleistocene–Holocene deposits are represented by slope sediments (clays, sands, gravels, cobbles, rock fragments and boulders), floodplain sediments (clays, sands and silts), valley and depression fill sediments, organic soil sediments (clays, silts and sands containing secondary gypsum and bitumen) and sabkhas sediments including salt crust mixed with silt and clay.

The amount of groundwater inflow to the hydrogeologic system is 32.32 × 106 m^3/year, while the groundwater outflow from the system is 10.74 × 106 m^3/year (Hussien and Gharbie 2010b). The annual loss of the amount of water is 21.58 × 106 m^3/year. Limestone of Fatha Formation is a perched aquifer. The main aquifer in the study area is multi-water-bearing horizons, Euphrates (35 m thickness), Anah (16–23 m thickness) and Baba Formations (50 m thickness), which consist of carbonate rock that is the main aquifer in the study area (Hussien and Gharbie 2010b). Aquifers of Baba and Anah are confined to semiconfined aquifers. Aquifer of Euphrates is unconfined, but it changes to confined aquifer where underlies the gypsum of Fatha Formation.

Structurally, the study area lies in the Abu-Jir Fault Zone, which is part of the stable shelf within the Afro-Arabian platform (Jassim and Goff 2006). Complicated fault zones underwent for the several tectonic events are present in the study area; Fouad (2004) describes this fault as a right lateral strike slip fault, and it is considered as a proposed boundary between the stable and unstable shelves. Awadh et al. (2013) determined the geometrical shape of Abu-Jir Fault Zone and computed its width in three sections (Haqlania, Ramadi and Najaf) using the geochemical simulation model to be 48 km. Another fault system of NW–SE trends classified as a part of the Najid Fault System, including Ramadi-Musaiyab Fault (Jassim and Goff 2006), is activated during the Early Mesozoic. From the geophysical results, it is indicated that the depth of the footwall reaches 600 m, while the depth of the hanging wall reaches 150 m below the land surface. Also, both the shallow and deep faults are present in the study area.

Methodology

Eleven springs in the study area were sampled during October (2011), which represents the drought period in Iraq. The sampling sites are shown in Fig. 1. The coordinates of each spring have been accurately determined using GPS device (Table 1). One water sample was collected from each spring using polyethylene bottle of 1.5 l according to the procedures of Shelton (1994). The pH, electrical conductivity (EC), total dissolved solid (TDS) and temperature were immediately measured after sampling process in the field using the portable digitized device. Samples were then carefully sealed and labeled. All equipment used for sample collection, storage and analysis of chemical components was precleaned using deionized water. Such cleaning and storage procedures ensure that there are no detectable contaminants in the sampling equipment (Shafer et al. 1997). Water samples collected were transferred to the laboratory and analyzed for all ions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^- and PO_4^{3-}) using the standard methods as suggested by the American Public Health Association (APHA 1995). Elements (Ca, Mg, Na, K, Pb, Zn, Cd, Ni, Fe, Mn, Cu, Br, F, Ba, B, Sr, Al, As, Cr, Hg and Se) are determined by inductively coupled plasma-atomic emission spectrometry in the Global ALS Laboratory Group in the Czech Republic-Prague Laboratory. The analytical accuracy of cations and anions in the water samples was done by calculating the absolute difference between total cations and anion concentration in EPM unit (Hem 1985). The accuracy of major ions was evaluated from ionic balance differences percentage (IB %) (UN/ECE 2002). It is calculated from the equation below:

$$\mathrm{IB}\,\% = 100 \times \left| \left(r \sum \mathrm{cat} - r \sum \mathrm{Ani} \right) \middle/ \left(r \sum \mathrm{cat} + r \sum \mathrm{Ani} \right) \right|$$

where $r\ \Sigma$Cat and $r\ \Sigma$Ani are the sum of cations and anions (EPM), respectively. The accepted limit of relative differences or ionic balance (IB) is between 0 and 5 %. It is considered as certain data considerable for hydrochemical interpretation. Then, accuracy (A %) was computed from the equation below; it is also acceptable:

$$A\,\% = 100 - \mathrm{IB}\,\%$$

Results and discussion

Spring water is assessed for balneotherapy (balneology), drinking, agriculture and aquaculture purposes. The geochemistry of spring water and assessments are discussed here:

Spring water geochemistry

Spring water samples are slightly alkaline, with a pH varied between 7.1 and 7.5, showing an average value of 7.3 (Table 2). Electrical conductivity ranges from 3,553 to 35,418 µS/cm with an average of 10,656 µS/cm. The large variation between the minimum and maximum of ions in the spring water indicates a heterogeneous water due to the influences of the subsurface geology and geochemical process. All springs formed as a result crosscutting with the Abu-Jir Fault Zone, where a set of aquifers find their way along the fault planes. Consequently, this fault is an attractive area for geologist for the sake of petroleum, mineral and spa exploration due to a huge number of bitumen, H_2S gas, sulfurous and saline water seepages. Lithology in the study area partially reflected the chemistry of spring water. Na and Ca are the dominant cations present in the spring water next to Mg and K. Similarly, sulfate and Cl are predominant, and bicarbonate is also present in considerable amounts. Carbonate rocks (limestone, dolomitic limestone and dolomite) of Baba, Anah and Euphrates Formations have been partially dissolved and released Ca, Mg and CO_2 into the aquifer. Gypsum and anhydrite of Fatha Formation also contribute to providing Ca and SO_4^{2-}. The equivalent ratio of dissolved Ca^{2+} and HCO_3^- in the spring water is not fit with ratios 1:2 and 1:4; therefore, Ca^{2+} and HCO_3^- in spring water are not originated from calcite and dolomite only (Garrels and Mackenzie 1971; Holland 1978). Similarly, if the Ca^{2+} and SO_4^{2-} in spring water derive from the dissolution of gypsum or anhydrite, the Ca^{2+}/SO_4^{2-} ratio is almost 1:1 (Das and Kaur 2001). Since the ratios in the water were different, this evidence for the diversity of sources of ions and the high concentration of Na and Cl in the spring water supports this conclusion, as it contributes to partial mixing of connate water of marine origin with the meteoric water. Since the study area experiences dry and semiarid climatic condition, evaporation may also contribute to water chemistry causing increased ion concentration.

The evaporation process is a common phenomenon not only in surface water but also in groundwater systems (Subramani et al. 2010). Na/Cl ratio can be used for the function identification of the evaporation process in groundwater and spring water. Evaporation will increase the concentration of total dissolved solid in groundwater, and the Na/Cl ratio remains the same, and it is one of the good indicative factors for evaporation. If evaporation is the dominant process, Na/Cl ratio should be constant when EC rises (Jankowski and Acworth 1997). The EC versus Na/Cl scatter diagram of the spring water samples of the study area in Fig. 3 shows that the trend line is inclined, and Na/Cl ratio decreases with increasing salinity (EC), which seems to be removal of sodium by ion exchange reaction. This observation indicates that evaporation may not be the major geochemical process controlling the chemistry of groundwater and spring water in the study area, or ion exchange reaction dominating over evaporation.

Balneotherapeutic assessment

Water quality plays an important role in balneology, since the chemical properties of the water determine the possible adverse effects on human health. Water chemical properties also determine the curative properties of water for skin diseases and other kinds of therapeutic uses (Manuel and Carvajal 2010). According to Komatina (2004), medicinal water can be classified on the basis of a number of criteria such as total mineralization, ion and gas composition, content of active therapeutic components, acidity or alkalinity, and temperature. For assessing the spring water for balneotherapy, some physicochemical parameters must be compared with the global famous guideline such as the European Union (2009) and US spas. Major cations, anions and the components such as Fe, As, Mn, Al, Cu and Zn give medicinal properties to mineral waters (Saman 2000). For this reason, the physicochemical parameters including trace elements

Table 2 Physicochemical parameters of the spring water during dry period compared with guideline (EU spa) and (US spas)

Parameters	Unit	Criteria (EU and US spas)	WHO 2008	1Hq	2Hq	3Hq	4 K	5 K	6 K	7 K	8H	9H	10H	11H
pH		7.2–7.6	6.5–8	7.3	7.1	7.2	7.3	7.2	7.4	7.2	7.4	7.5	7.1	7.2
EC[a]	µS/cm	>2,308	2,500	5,523	5,068	5,038	3,553	5,704	12,029	6,102	11,867	35,418	12,768	14,152
T_w	°C	29–35	–	29	29	29	29	27	28	29	30	31	29	28
T_a		>27	–	38	38	38	39	39	39	39	40	36	36	36
TDS[a]	ppm	>1,500	600	3,452	3,148	3,110	2,180	3,478	7,290	3,667	7,106	21,082	7,555	8,325
Ca^{2+a}		>150	100	288	320	312	225	300	712	262	780	1,010	711	925
Mg^{2+a}		>50	50	134	146	144	94	125	378	129	400	367	410	375
Na^{+a}		>200	50	709	480	472	396	688	1,294	854	900	6,690	1,145	1,385
K^{+b}		0-90		94.1	22	21	8.1	4.9	70	102	16	479	145	65
$SO_4^{=a}$		>200	250	674	1,260	1,253	389	1,080	1,236	226	2,300	326	2,730	1,420
Cl^{-a}		>200	5	1,330	650	643	565	888	2,220	1,640	1,670	11,800	1,934	2,930
NO_3^-		–	50	3	2	3	5	4	10	2	9	9.5	7	6.2
HCO_3^b		>600	–	223	270	265	503	392	1,380	463	1,040	410	480	1,225
CO_2		>250	–	8.4	8.3	8.1	9.8	10	10	9.9	40	44.8	30	25
F[c]		>1	1.5	1.1	1.2	1.1	0.6	0.8	0.7	0.9	1	2	1.5	1.9
Pb[c]		<4	0.01	0.1	0.1	0.1	0.09	0.1	0.27	0.06	0.16	0.26	0.17	0.17
Zn[c]		<5	4	0.03	0.07	0.07	0.13	0.08	0.22	0.12	BDL	BDL	BDL	BDL
Cd[d]		3×10^{-6}	0.003	0.02	0.02	0.02	BDL	BDL	0.01	BDL	BDL	0.04	0.004	0.005
Ni		–	0.07	0.04	0.04	0.04	0.1	0.08	0.22	0.07	0.18	0.21	0.13	0.13
Fe[d]		>1.0	0.3	0.01	0.01	0.01	0.04	0.05	0.08	0.03	0.08	0.26	0.1	0.09
Mn[d]		0.023	0.4	0.0009	0.0009	0.0009	0.01	0.01	0.01	0.01	0.03	0.03	BDL	BDL
Cu[d]		5×10^{-6}	2	0.0026	0.0025	0.0025	0.003	0.003	0.003	0.002	0.002	0.0036	0.002	0.002
Br[d]		9.7	–	10.4	10.2	10.3	11.1	13.2	14	12.7	80	89.2	66	60
B[c]		0.08	0.5	1.34	1.32	1.3	1.5	1.6	1.6	1.5	6	7	5	5.4
Sr[d]		5.3	–	4.27	4.44	4.55	7.07	9.59	20.2	7.07	38.84	48.58	26.76	30.3
Al[d]		0.02	0.2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
As[d]		6×10^{3}	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr[d]		35×10^{-5}	0.05	<0.002	<0.002	<0.002	<0.002	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Hg[d]		7×10^{-6}	0.006	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Se[c]		3×10^{-5}	0.01	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30
Ba		–	0.7	0.0177	0.061	0.016	0.01	0.025	0.019	0.0296	0.01	0.186	0.1	0.09

T_w, T_a = water and air temp, respectively

[a] EU spa according to European Union 2009, [b]US spas according to Lund 1996; Eaton 2004. Trace elements compared with [c]American spa = Agishi and Ohatsuka (1998) and Parish and Lotti(1996), [d]Iceland spa = Kristmannsdóttir et al. (2005)

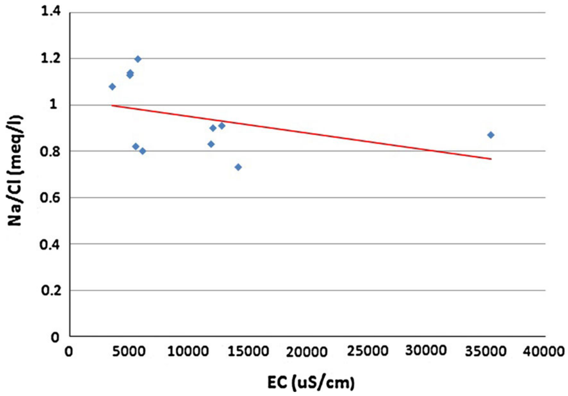

Fig. 3 Relation between EC and Na/Cl in the spring water

are compared with the European Union 2009 and US spas (Lund 1996; Eaton 2004) as shown in Table 2. Trace elements were compared with the guideline of Americans spa and Iceland spa. For the purpose of a comparison with the standard limits, it should be noted here that the standard refers to the minimum. Consequently, pH, TDS, EC, Ca, Mg, Na, SO_4, Cl, Pb, Zn, Fe, Mn, Al, As, Cr, Hg and Se seem to be within the standard referring to the acceptance for balneotherapy. TDS (1,500 mg/l) and EC (2,308 µs/cm) mean a mineral salt-rich water.

Spring temperatures are permissible except for three springs (5 K, 6 K and 11H). Balneologists generally classified the mineral springs as follows: cold springs (below 25 °C), tepid springs (25–34 °C), warm springs (34–42 °C) and hot springs (above 42 °C). For typical condition of spa therapy, the air temperature ranges between 27 and 29 °C and water temperature ranges between 27 and 31 °C. According to ASHRAE (1999), the desirable temperature for swimming pools is 27 °C. The water temperature is described as being cold (<20 °C), hypothermal (20–30 °C), thermal (>30–40 °C) or hyperthermal (>40 °C) (Matz et al. 2003). Air temperatures in the study area seem to be warmer than standard; this may encourage people to swim, while the water temperature seems to be suitable in all springs except three springs (5 K, 6 K and 11H) that have temperature less than the standard required. Bone structure can be healed with aerobic exercise in a spa resort pool with water temperature of 29–30 °C (Ay and Yurtkuran 2003). Spring waters are suitable for swimming according to the swimming limits proposed by Nelson (1978), which states pH should be ranged from 5 to 9. Hydrogen number (pH) is an important element for proper spa maintenance. The ideal pH for spas is between 7.2 and 7.6. If the pH is below 7.6, water is acidic and creates eye and skin irritation and is accompanied by a strong chlorine odor. If the pH is above 7.6, water is alkaline and creates eye and skin irritation. Hydrogen number (pH) in all springs is very suitable for balneotherapy (Table 2) except one spring (2Hq) has 7.1, which may cause irritation to eyes and skin. Mineral waters have a balneological effect on humans as a result of the ionic composition and mineralization (Manuel and Carvajal 2010). Many elements are essential to human health in small doses. Most of these elements are taken into the human body via food, water, air and skin absorption. K concentration appears permissible, except three springs (1Hq, 9 and 10H), where K concentration was more than 90 ppm. HCO_3 tends to be permissible in three springs (6 K, 7 K and 8H), but CO_2 creates suitable condition for balneotherapy. Therapeutic activities of CO_2 water baths (700–1,300 mg/l) are explained by a synergism between hydrostatic pressure and the chemical properties of carbon dioxide that acts directly on the blood vessels of the skin, causing vasodilation and increased oxygen utilization (Hartmann et al. 1997). All springs contain F within acceptable limit except 4, 5, 6 and 7 K in which F was less than 1.0. Sr is acceptable just in three springs (1, 2 and 3Hq). All springs are characterized by high concentrations of Cd, Cu, B and Br. Bromine is another important element for balneotherapy; the high concentration of beer prevents bacterial or algal growth in the spa. Selenium with a relatively high concentration in the spring water helps to heal patients with psoriasis and inflammatory skin, where Pinton et al. (1995) pointed out that patients with psoriasis, inflammatory reactions in the skin, may lead to loss of selenium. The net benefit of immersion in medicinal water is probably the result of a combination of factors, with mechanical, thermal and chemical effects (Sukenik et al. 1999). The chemical effects of balneotherapy are less clear than the physical effects. Balneotherapy may have beneficial effects on muscle tone, joint mobility and pain intensity. The buoyancy under hydrostatic pressure during immersion in the medicinal water causes many physiological changes such as increase in diuresis, natriuresis and cardiac output (Epstein 1992). The spa bathing influences muscle helping to reduce muscle spasm and pain intensity. Also, it stimulates a series of neuroendocrine reactions. Sometimes present in trace amounts, these minerals can be absorbed through the skin and then act at a systemic level. Shani et al. 1985 documented a significant increase in serum concentrations of bromine, rubidium, calcium and zinc in patients with psoriatic arthritis who bathed in the Dead Sea. Many factors may contribute to the beneficial effects observed after spa therapy including anti-inflammatory, chondroprotective immunologic aspects and effects on cardiovascular system. Skin can adsorb the trace elements present in mineral water. This process may affect the immune system where bathing in the sulfurous springs has been successfully used in various skin immuno-mediated afflictions. The applications of balneotherapy, especially with sulfurous waters, can normalize lipid in the arteries and reduce the cholesterol, triglycerides and non-esterified cholesterol and show a significant increase in HDL cholesterol (Strauss-Blasche et al. 2003). Plasma homocysteine may be reduced in the blood of patients after a cycle of bathing in the sulfurous waters (Leibetseder et al. 2004).

SO_4^{2-} tends to be dominant besides Cl^- in all springs. The sulfur that penetrates the skin is oxidized and evokes various physiologic responses in the skin, such as vasodilation in the microcirculation, an analgesic influence on the pain receptors and inhibition of the immune response. It also interacts with oxygen radicals in the deeper layers of the epidermis, producing sulfur and disulfur hydrogen, which may be transformed into pentathionic acid; this may be the source of the antibactericidal and antifungal activity of sulfur water (Matz et al. 2003). Sulfur baths (2,000 mg/l) are recommended to patients with fibromyalgia (Buskila et al. 2001). Magnesium rich in spring water is used in the treatment for inflammatory skin diseases (Schempp et al. 2000). Important processes in the body mediated by magnesium are, for example, synthesis of protein, nucleic acid and fat, glucose use, neuromuscular transmission, muscular contraction and transport over the cell membranes (Strauss-Blasche et al. 2003). Magnesium is essential to the cardiovascular system. Therapeutic uses of spring water include the treatment for arthritis, central and peripheral circulation troubles, chronic constipation, muscle cramp and construction, general health recovery, respiratory system troubles, rheumatism, inflammation of respiratory apparatus and any skin disease (Saman 2000). In Iraq, local people used the spring water to treat a variety of diseases. Attempts and experiences have proved the effectiveness of these water springs on healing, which treated dermatological and allergy diseases and ulcers, nervous diseases, muscle contraction, rheumatism, arthritis, central and peripheral circulation troubles, urinary lithiasis, chronic constipation and intestinal troubles, general health improvement sedative, diuretic and regulation of gland secretions. Also, to treat plasma lipids and cholesterol, spa therapy (CO_2), exercise therapy and dietary measures are recommended.

Drinking permissibility assessment

Human health is directly linked to geology. Water travels through rocks and soils as part of the hydrological cycle, and many of the elements are of geological origin via the dissolution (Selinus et al. 2005). The spring waters have been assessed to ascertain the suitability of spring water in the study area for drinking and agricultural purposes. Water coming from different natural sources contains many chemical species that are undesirable for drinking. Sometimes, these constituents have direct adverse impacts on the human health; others are responsible for an unpleasant taste and odor. Generally, Iraqi specialized institutions accept the standards prepared by the World Health Organization (WHO) for acceptable maximum concentrations of relevant chemicals in drinking water. The WHO (2008) standards have been used as guidelines to assess the water quality for drinking purpose. For comparison with these standard guidelines, the physicochemical parameters were determined and are listed in Table 2. Since TDS is directly related to conductivity, WHO gives guideline values only for TDS and not for conductivity; however, a guideline value of 2,500 μS/cm is provided by the European Commission (2007).

The results display that just pH and trace elements were within permissible limits, whereas parameters of TDS, EC, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^-, Pb and B have concentration higher than the standard of WHO (2008). Some chemical components (NO_3^-, Zn, Fe, Mn, Cu, Al, As, Cr, Hg and Se) appear to be permissible. Cd, Ni and F are permissible in some springs, while impermissible in the other. It is clear that the F in all springs has concentration lower than the standard of WHO (2008) except in one spring (11H). Cd has a concentration lower than the standard of WHO (2008) except in five springs (1Hq, 2Hq, 3Hq, 6 K and 9H). Consequently and according to the above, the spring water is not safe to drink because the amount of all major cations and anions was higher than the standard limits set by the World Health Organization (WHO). Here, it is worthy to note that most of the springs are characterized by inadmissible odor resembling the smell of rotten eggs, because of emitting hydrogen sulfide gas. Also, some springs, especially those in Hit area, contain light bitumen floats on the water surface. These characteristics cause the deterioration of the physical specifications of water such as color, taste and odor.

Irrigation assessment

The chemical composition of groundwater is the response to hydrogeochemical processes; therefore, it varies with respect to space and time. Everywhere, groundwater has specific chemistry due to surface flow, aquifer–water interaction during recharge and flow, prolonged storage in the aquifer and dissolution of mineral species (Hem 1985). Dissolution processes in carbonate, gypsum and anhydrite played an important role in spring water chemistry. The chemical composition of the samples is diverse with regard to water quality for irrigation purposes. Different kinds of salts are normally found in irrigation water; amounts and combinations of these substances define the suitability of water for irrigation and the likelihood of plant toxicity. Two types of salt problems exist, which are very different: those associated with total salinity and those associated with sodium. Soils may be affected only by salinity or by a combination of salinity and sodium (Texas A and M University 2003). A preliminary step for assessing the irrigation water quality is to classify these prospects according to salinity. Salinity on its own does not define the suitability of irrigation water; it represents only a general guide, and other factors must be considered (ANZECC 2000). Five classes of irrigation water based on electrical conductivity and TDS are defined in Table 3. TDS varies between 2,180 and 21,082 mg/l, and EC varies between 3,553 and 35,418 µs/cm. Consequently, all springs appear to be unsuitable for irrigation, except one spring (4 K) that appears doubtful in terms of TDS, but it is still unsuitable for irrigation in terms of EC. Electrical conductivity (EC) and sodium adsorption ratio (SAR) are the two most

Table 3 Water classification based on salinity (Texas A and M University 2003)

Class	Category	Electrical conductivity (µS/cm)	TDS (mg/l)
Class 1	Excellent	<250	<175
Class 2	Good	250–750	175–525
Class 3	Permissible	750–2,000	525–1,400
Class 4	Doubtful	2,000–3,000	1,400–2,100
Class 5	Unsuitable	>3,000	>2,100

Table 4 The well-known Wilcox SAR classification scheme

Quality of water	Electrical conductivity (µs/cm)	Sodium adsorption ratio
Excellent	<250	<10
Good	250–750	10–18
Doubtful	750–2,250	18–26
Unsuitable	>2,250	>26

important water quality parameters for irrigation. The sodium hazard is usually expressed as SAR, which relates to infiltration problems. The relationship between EC and SAR is shown in Table 4. The values of SAR in all springs appeared less than ten, except for one spring (7 K) that was higher than ten (Table 5). On this basis, and for integrating water assessment, an assessment of the water according to Richards (1954), who strongly recommended that the water type is a relationship between EC and SAR, is done. SAR was calculated from the ratio of Na to Ca and Mg according to Hem 1985 by the formula below:

$$\mathrm{SAR} = \frac{\mathrm{Na}}{2\sqrt{(\mathrm{Ca} + \mathrm{Mg})/2}}$$

where Na^{+}, Ca^{2+} and Mg^{2+} represent concentrations expressed in mill equivalents per liter for each constituent. The soil structure is changed by the reaction of the Na^{+}, which is the major cation dominant in water with high salinity. The Na^{+} replaces the Ca^{2+} and Mg^{2+} in the soil. These cation exchanges cause the deterioration of the soil structure, making the soil impermeable to water and air. High concentrations of exchangeable sodium shift the pH to alkaline values, reducing the availability of micronutrients such as Fe and P (Phocaides 2007). In Fig. 2,

Table 5 Sodium hazard of water based on SAR

Spring No	SAR	SAR class	Comments
1Hq	8.65	Low	Use on sodium-sensitive crops must be cautioned
2Hq	5.58	Low	Use on sodium-sensitive crops must be cautioned
3Hq	5.54	Low	Use on sodium-sensitive crops must be cautioned
4 K	5.38	Low	Use on sodium-sensitive crops must be cautioned
5 K	8.42	Low	Use on sodium-sensitive crops must be cautioned
6 K	9.8	Low	Use on sodium-sensitive crops must be cautioned
7 K	10.78	Medium	Amendments (like gypsum) and leaching needed
8H	6.52	Low	Use on sodium-sensitive crops must be cautioned
9H	8.892	Low	Use on sodium-sensitive crops must be cautioned
10H	8.45	Low	Use on sodium-sensitive crops must be cautioned
11H	9.69	Low	Use on sodium-sensitive crops must be cautioned

the categories C1, C2, C3 and C4 indicate low, medium, high and very high salinity, respectively. Samples of spring water occupied C4–S2 and C4–S3. All samples of the spring water have very high salinity hazard (C4) (Fig. 4). Very high-salinity water (C4) is not suitable for irrigation under ordinary conditions but may be used for salt-tolerant plants on permeable soils with special management practices (Richards 1954). As for the electrical conductivity, samples occupied fields that indicate medium and high SAR. The large variation in EC is mainly attributed to lithologic composition and anthropogenic activities prevailing in this region.

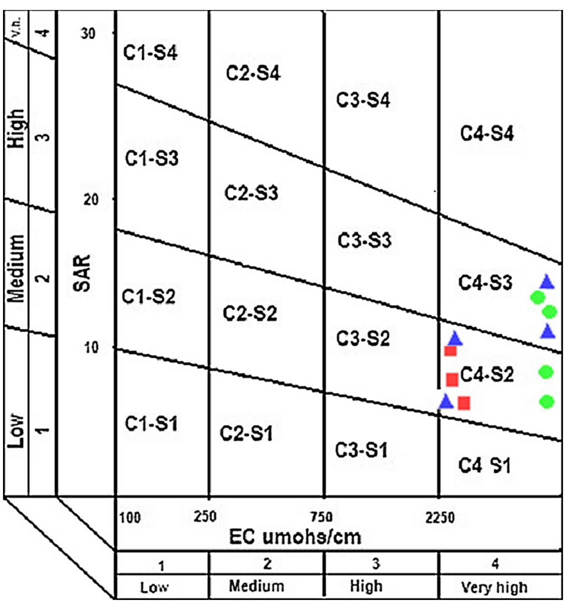

Fig. 4 Classification of the irrigation water according to the Richard classification (1954)

Aquacultural assessment

Many authors used fishes for assessing the effects of environmental pollution on aquatic ecosystem since early times (Gernhofer et al. 2001). Here was a vice versa, where spring water assessed for fish living. The original toxicity data of Water Quality Guideline for Toxicants were essentially depended on (ANZECC 2000; Svobodova et al. 1993). The guidelines include the physicochemical parameters that are very important in aquaculture, for example, temperature affects the growth of fish, and hardness is important for bone and exoskeleton. The chemical aquatic form of metals determines their effect on fish (Zweig et al. 1999). Metals have the property of bioaccumulation in sediments, aquatic flora and fauna. The metals found to be of highest importance to fisheries in practice are aluminum, chromium, iron, nickel, copper, zinc, arsenic, cadmium, mercury and lead (Svobodova et al. 1993). To investigate the suitability of spring water for aquaculture, results have been compared with the standard guideline. The recommended guideline limit values for fish farming provided by Svobodova et al. (1993) are listed in Table 6.

The optimal pH range for fish is from 6.5 to 8.5. Alkaline pH values above 9.2 and acidity below 4.8 can damage and kill salmonids, and pH values above 10.8 and below 5.0 may be rapidly fatal to cyprinids (especially carp and tench) (Svobodova et al. 1993). Fish are poikilothermic animals, that is, their body temperature is the same as, or 0.5–1 °C above or below, the temperature of the water in which they live. The metabolic rate of fish is closely correlated to the water temperature. The fish metabolic rate can continue at

Table 6 General guidelines of water quality for fish farming (Svobodova et al. 1993)

Parameters	Limit (mg/l)	Comments
pH	6.5–8.5	
H_2S	0.002	
NO_3^-	80	Maximum admissible for carb
	20	Maximum admissible for rainbow
Al	0.52	At pH 7.0
Fe	0.2	General acceptable limit
	0.1	For salmonids
Ni	30–75	With short period of exposure, depending on species of fish
Cu	0.001–0.01	Depending on physical and chemical properties of water and species of fish
Zn	0.1	For salmonids
As	3–30	Depending of species of fish
Cd	0.0002	Maximum admissible concentration
	0.001	For cyprinids
Hg (inorganic)	0.3–1.0	Lethal concentration for salmonids
	0.2–4.0	Lethal concentration for cyprinids
Hg (organic)	0.025–0.125	Acute lethal for salmonids
Hg	<0.0003	Maximum admissible concentration of mercury in organic compounds
	0.20–0.70	Acute lethal for cyprinids
Pb	0.008	For salmonids
	0.07	For cyprinids
Cr^{3+}	2.0–7.5	
Cr^{6+}	35–75	

comparatively low temperatures, whereas at high water temperatures, usually above 20 °C, they become less active and consume less food. Water temperature also has a great influence on the initiation and course of a number of fish diseases. The immune system of the majority of fish species has an optimum performance at water temperatures of about 15 °C (Svobodova et al. 1993). The tepid springs of 27–30 °C and hypothermal to thermal springs seem not to be suitable for aquaculture. The toxic action of nitrite in fish is incompletely known; it depends on a number of internal and external factors (such as fish species and age, and general water quality). It is now clear that nitrite ions are taken up into the fish by the chloride cells of the gills. In the blood, nitrites become bound to hemoglobin, giving rise to methemoglobin: This then reduces the oxygen-transporting capacity of the blood (Svobodova et al. 1993). Nitrate content varies from 2 to 10 mg/l in the springs (Table 2); it is lower than that of the guideline. The toxicity of nitrates to fish is very low, and mortalities have only been recorded when concentrations have exceeded 1,000 mg/l; 80 mg/l is considered to be the maximum admissible nitrate concentration for carp and 20 mg/l for rainbow trout (Svobodova et al. 1993). H_2S in the springs was higher than that in the guideline (0.002). It appears impermissible for fish farming. Aqueous aluminum is recognized as the principal toxicant killing freshwater fish in acidified water (Guibaud and Gauthier 2003). It is one of the important factors in the toxicity of acidified water of freshwater fish species (Poleo et al. 1997). A concentration as low as 0.52 mg/l of Al was found to markedly reduce the growth of fish. In the springs, the concentration of Al (0.01 mg/l) is lower than the standard guideline (0.52 mg/l). Ca^{2+} is the predominant cation in most natural waters, and it has been seen that high concentrations of Ca^{2+} can reduce Al toxicity in fish (Playle and Wood 1989). Ca ions have an ameliorating effect on aluminum toxicity in the gills. The Fe lethal content for fish is determined by standard limits based on fish type. In cyprinid culture, it is generally accepted that the concentration of not exceeds 0.2 mg/l; but for salmonids, the limit should not exceed 0.1 mg/l. Consequently, Fe is admissible in all springs, with the exception that spring 9H has 0.26 mg/l Fe. Ni compounds are of medium toxicity to fish. With short periods of exposure, the lethal concentration is between 30 and 75 mg/l. However, it is lower than in spring water.

The maximum admissible Cu concentration in water for the protection of fish is in the range of 0.001–0.01 mg/l, depending on the physical and chemical properties of water and on the species of the fish (Svobodova et al. 1993). All springs contained Cu concentrations higher than the guideline. It has been observed that calcium ions have an ameliorating effect on toxicity in fishes. The exposure of fishes to calcium relieves the copper toxicity (de Vera and Pocssidio 1998; Abdel-Tawwab and Mousa 2005). The elevated levels of Zn and Cu in the water can be harmful, although at lower levels they are essential elements for fish. Zinc poisoning of fish is most frequently encountered in trout culture (Svobodova et al. 1993). The lethal concentrations are around 0.1 mg/l for salmonids. The low content of Zn in the spring water makes all springs admissible, except two springs (6 and 7 K). Zinc can precipitate at high pH and coprecipitate with calcium carbonate (ANZECC 2000). The simplest method for removing Zn is to retain water for 1 or 2 days in a holding pond (Zweig et al. 1999).

Ni compounds are of medium toxicity to fish. With short periods of exposure, the lethal concentration is between 30 and 75 mg/l. The toxic exposure to Ni makes mucus and the lamellae dark in the gill chambers of the fish filled with red.

In terms of As, all springs have a low concentration (<0.01 mg/l), whereas the lethal concentrations are between 3 and 30 mg/l (Svobodova et al. 1993). Accordingly, springs are admissible for fish farming. The maximum admissible Cd concentration in water is 0.0002 mm/l, and for cyprinids 0.001 mg/l. Cadmium in the spring water recorded value higher than the guideline. For fish in general, the maximum admissible concentration of Hg in organic compounds has been suggested to be as low as 0.0003 mg/l. The maximum admissible Pb concentration in water is 0.004–0.008 mg/l for salmonids and 0.07 mg/l for cyprinids. The content of Pb in the springs permits cyprinids for a living.

Cr compounds in the trivalent state are more toxic to fish and other aquatic organisms than are those in the hexavalent state. Cr^{3+} compounds are among those substances with a high toxicity to fish of 2.0–7.5 mg/l, whereas Cr^{6+} compounds are among those substances of medium toxicity of 35–75 mg/l. Chromium appears very low in spring water (Svobodova et al. 1993).

Acute lethal concentrations of inorganic Hg compounds are in the range of 0.3–1.0 mg/l for salmonids and 0.2–4.0 mg/l for cyprinids (Table 6), depending on the physical and chemical properties of the water. The acute lethal concentrations of commonly found organic Hg compounds are from 0.025 to 0.125 mg/l for salmonids and from 0.20 to 0.70 mg/l for cyprinids. For salmonids, the maximum admissible concentration of inorganic forms is about 0.001 mg/l and for cyprinids about 0.002 mg/l. For fish in general, the maximum admissible concentration of Hg in organic compounds has been suggested to be as low as 0.0003 mg/l (Svobodova et al. 1993). H_2S has a high to very high toxicity to fish; the lethal concentrations in the different fish species range from 0.4 (salmonids) to 4 mg/l (crucian carp, tench and eel). H_2S content in Hit area is very high.

Conclusions

From this study, the following conclusions can be drawn:

1. The subsurface geology and lithochemistry are the dominant factors in the spring water chemistry, where both the dissolution and evaporation processes played a key role in the ion enrichment.
2. Depending on the temperature of the water, and according to the viewpoint of balneologists, spring water has been classified into tepid ranges from hydrothermal to the thermal springs.
3. The chemical and physical specifications of the spring water match the spas of the world. Consequently, springs are suitable to use as spas for therapeutic purposes, while avoiding bathing and swimming in those that contain hydrocarbon floating on the water's surface. Hydrocarbon is a sticky substance may stick to the body, causing drowning. The benefits of using spring water reflect on human health; particularly, it has proved a high efficiency in the treatment and healed a

variety of diseases, may be difficult to treat with traditional medicine. Water springs are successful in the treatment for dermatological and allergy diseases, acne vulgaris, nervous diseases, muscle cramp and contraction, rheumatism, arthritis, central and peripheral circulation troubles, urinary lithiasis, chronic constipation and intestinal troubles, general health improvement in sedative, diuretic and regulation of gland secretions.

4. In terms of drinking water suitability: The spring water is poorly and deteriorated water due to the high salinity (TDS), undesirable taste and odor resulting from the dissolved H_2S gas. Fr, Cd and Ni are acceptable in some springs, while unacceptable in other. The mismatch between the spring water and the standards required announced that it is non-permissible for drinking.
5. In terms of irrigation purposes: Spring water falls under the doubtful and unsuitable categories because of the intense salinity and the SAR value. Consequently, it is preferable not to be sued for irrigation. But, in fact, the local farmers use the water of these springs to irrigate their crops, especially palm trees. This causes problems in the growth as well as leads to the deterioration of some soil characteristics. The adoption of inappropriate water for irrigation is causing problems in the growth of trees.
6. For aquaculture (fish farming) purposes: The properties of spring water were divided into two categories: The first category includes pH, NO_3^-, Ni, Zn and As. It is suitable for fish farming. The second category includes H_2S, Fe, Cu, Cd and Pb; it is clear that it was outside the permissible limits. Iron and zinc are within admissible limits in each spring, except iron in spring 9H and zinc in spring 6 and 7 K, which are non-permissible. Accordingly, and due to the lack of all the requirements of the revival living, therefore, the spring water is no longer suitable for fish farming.

Recommendation

Springs could be expressed as natural heritage in Iraq, particularly that they have unique characters. Establishing spa therapy near the spring site to be medical sites having lifestyle pattern and offer exercise, massage and fitness, herbal medical benefits and dietary is possible. Iraq is moreover famous by its archeological sites and ancient civilizations. Springs enable it to be a therapeutic center allowing visitors and tourists to investigate its different archeological sites and enjoy a treatment in its spas and mineral springs. These steps will develop the tourism programs and encourage people to visit these springs that eventually will be an economic project.

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