Hydrochemistry of the Natuf drainage basin in Ramallah area/West Bank

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ORIGINAL ARTICLE

Hydrochemistry of the Natuf drainage basin in Ramallah area/West Bank

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Abstract The Natuf drainage basin in the western hills of Ramallah district is about 200 km^2. Many springs emerge in the area from perched aquifers and outcrop from limestone and dolomite limestone formations. This study aims to add more information about hydrochemical parameters and the chemical changes in spring water between dry and wet seasons and to locate possible sources of pollution and their effect on the water quality of water from the springs for domestic and agricultural uses. The study involved collection and analysis by conventional and available instrumental methods for the hydrochemical parameters from 12 springs before and after recharge. Water samples of runoff from two places in eastern and western parts of the study area were collected and analyzed as well. Most of the springs in the study area are of good water quality for domestic and agricultural uses. Variations in the chemical composition between dry and wet seasons, and from one spring to another, were observed. Springs near densely populated areas and agricultural activities show higher values of EC, SSP, SAR and TH. Also uncountable colonies of faecal- and total coliform were detected. Trace amounts, within World Health Organization (WHO) and the Palestinian standard limits, of cadmium, chromium, cobalt and lead are found in some springs; while concentrations of iron and zinc that were detected in springs near populated areas are higher than other springs. Water types of Ein Musbah, Al Alaq and Ein Arik El Tehta are of earth alkaline with increased portion of alkalis with prevailing bicarbonate and chloride in wet and dry seasons. Other springs show a variation in water type between earth alkaline with prevailing bicarbonate in the wet seasons to earth alkaline with prevailing bicarbonate and chloride in the dry seasons.

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Introduction

The continuous supply of high quality water is essential for economic growth, quality of life, environmental sustainability and survival. The quantity and quality of potable water varies over time and space, and is influenced by natural and man-made factors, including climate, hydrogeology management practices and pollution. In the West Bank, the demand for potable water for domestic uses has increased in the last few decades because of the rapid increase of population in the West Bank.

Ground water is the major source of fresh water in the West Bank and provides about 70% of drinking and domestic water needs. The sole source of groundwater in the West Bank is in the Mountain Aquifer System, which is divided into three subsurface drainage basins: Northeastern; Western and Eastern.

The Natuf drainage basin, which is part of the Auja-Tamaseeh sub-basin[1] in the Western subsurface drainage basin, like other areas in the West Bank, suffers from the

[1] SUSMAQ [P1]- NAT#48V0.3 (2003) Field Measurement Campaign for Wadi Natuf Recharge Estimation: Background, Design and Workshop. Palestinian Water Authority, Palestine

scarcity of water as well as other parts in the West Bank. The scarcity of water in the study area has limited land use for agriculture.

Heavy exploitation of groundwater, the shortage of sewer systems, the wide distribution of cesspools and septic tanks with inadequate quality control, the common practice of gray water disposal into gardens and road ditches and the uncontrolled disposal of untreated municipal sewage into valleys, may cause rapid contamination of aquifer systems through karstic conduits in the area (Qannam 1997).

Because of the lack of information about water quality in the area, there is a need for investigation of chemical and biological pollutants in water to determine the sources of pollution, which will help authorities to prepare and to implement successful management plans.

Location and geography of Natuf drainage basin

Natuf drainage basin is in the Western part of the West Bank between 34° 98′ W and 35° 26′ E, it is about 204 km^2, and drains from the mountains of Western Jerusalem into the coastal plain of Mediterranean Sea and serves about 80,000 inhabitants that are distributed into 28 villages and some parts of Ramallah city (PCBS 1999).

Natuf drainage basin is one of the main recharge areas in the Western Aquifer Basin (WB). It has a cultural value as one of the oldest world cultures, Natufian culture, 8000 BC, where man began the first domestic agricultural community. The area will be soon listed by UNESCO as one of the world's cultural reserves in Palestine for its historic and cultural heritage (Ministry of Tourism and Antiquities 2005).

Climate

West Bank is in the Mediterranean climate, which is considered to be semi-arid to arid climate, with dry and wet seasons. The wet season starts approximately in early November and extends to late April. The rainfall in the study area ranges between 400 and 900 mm (Meteorological Service 2003). Out of the rainfall, 2–13% returns to the Mediterranean Sea as surface runoff, 20–26% infiltrates to groundwater aquifers, and the rest is lost by evapotranspiration (Rofe and Raffety 1965)

The study area is part of the hilly regions in the West Bank. Temperatures are lower than other places in the West Bank. The temperature in the coldest month (January) is in the range of 6–13°C and the average temperature in the hottest month (August) was 37.5°C during 1994–1995. The mean annual temperature ranges between 18 and 20°C (Applied Research Institute in Jerusalem 1996).

Hydrology of the study area

Water resources in the Natuf drainage basin originates from rainfall in the winter season and from snowmelt which falls occasionally for a few days on the eastern parts of the study area near Ramallah and Birzeit hills.

The Natuf drainage basin is underlain by the Western aquifer; many springs emerge in the study area (Table 1), with an average annual discharge of 0.3–0.6 million cubic meters (mcm) of fresh water, which is used for domestic and agricultural purposes. There is only one groundwater well from the lower aquifer near Shibteen village downstream Natuf valley, which is controlled by the Israeli Water Authority (Mekarot) and supplies about 0.7 mcm/year of

Table 1 Springs in the Natuf drainage basin

No.	Spring code	East	North	Spring name	Location	Formation
1	BA/152	166.775	152.575	Al-Alaq	Abu Shekhedem	Qatana
2	BA/153	164.700	149.900	Harrashah	Al-Mazr'a Al-Quibliya	Qatana
3	BA/157	159.100	155.410	Akari	Beitillu	Bottom upper beit kahel
4	BA/158	161.440	153.700	Al-Balad	Beitillu	Bottom Lower Yatta
5	BA/159	161.400	154.140	Al-Quos	Beitillu	Lower upper Beit kahel
6	BA/163	165.000	148.680	Old JWU well	Ein Qinia	Lower Ein Qinia
7	BA/170	163.600	145.850	Ein Arik Al-Fuqa	Ein Arik	Lower lower Beit kahel
8	BA/171	163.400	146.180	Ein Arik Al-Tehta	Ein Arik	Lower lower Beit kahel
9	NS/007	159.130	150.580	Ein Ayoub	Ras Karkar	Hebron[a]
10	NS/040	159.410	153.440	Al-Tina	Jammalah	Lower Yatta
11	NS/041	159.740	153.600	Al-Shakhariq	Deir Ammar	Lower Yatta
12	NS/MUS	169.380	146.275	Ein Musbah	Ramallah	Lower upper Beit kahel
13	SHW	155.220	153.250	Shibteen Well	Shibteen	Hebron

[a] The formation in this site is more likely alluvial

fresh water. The apparent surface water is the base flow of the springs and the seasonal flow of valleys during heavy storms (Fig. 1).

Geology of the study area

The geological settings in the Natuf drainage basin are composed of thick sequences of layered limestone, dolomite, chalk and marl. The main outcrop formations belong to formations of the Albian to Turonian age (Fig. 2).[1]

Most of the springs are distributed in the middle part of the study area near Beitillu and Deir Ammar, where Yatta formation, which is an Aquitard, is dominant. The flow discharge of these springs is greatly affected by the intensity of precipitation and by the heavy withdrawal (80 m^3/h) of Shibteen productive well down stream of Natuf Wadi. Springs in the study area are an outcrop of perched aquifers distributed over Ramali, Yatta and Abu Dis Aquitard formations (Fig. 2).

Methodology

The hydrochemistry of the springs in the study area has been monitored by many researchers. Collected hydrochemical data from the springs of the study area from 1999 to 2002 were used in this work for comparison.

Sampling

The sampling protocol was carried out in wet and dry seasons, starting from November 2003 to May 2005; a total of 47 samples were collected. Twelve major springs were assigned for sampling campaign (Table 1). During winter 2005, two samples were collected from Shibteen well, one runoff sample near Birzeit University and one sample from Al-Fawarah, Seasonal Base flow from Natuf valley, giving a total of 51 samples.

The water samples were collected in 1-l polyethylene bottles and refrigerated in the laboratory at 2°C. Onsite

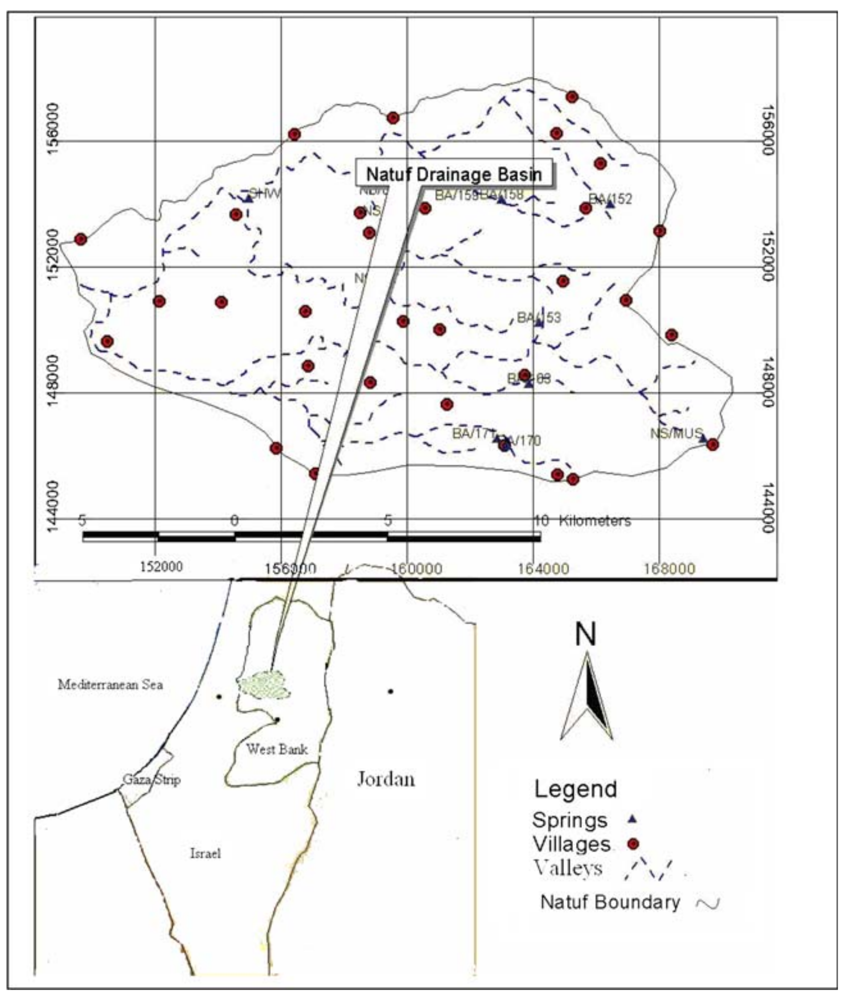

Fig. 1 Location of the Natuf drainage basin

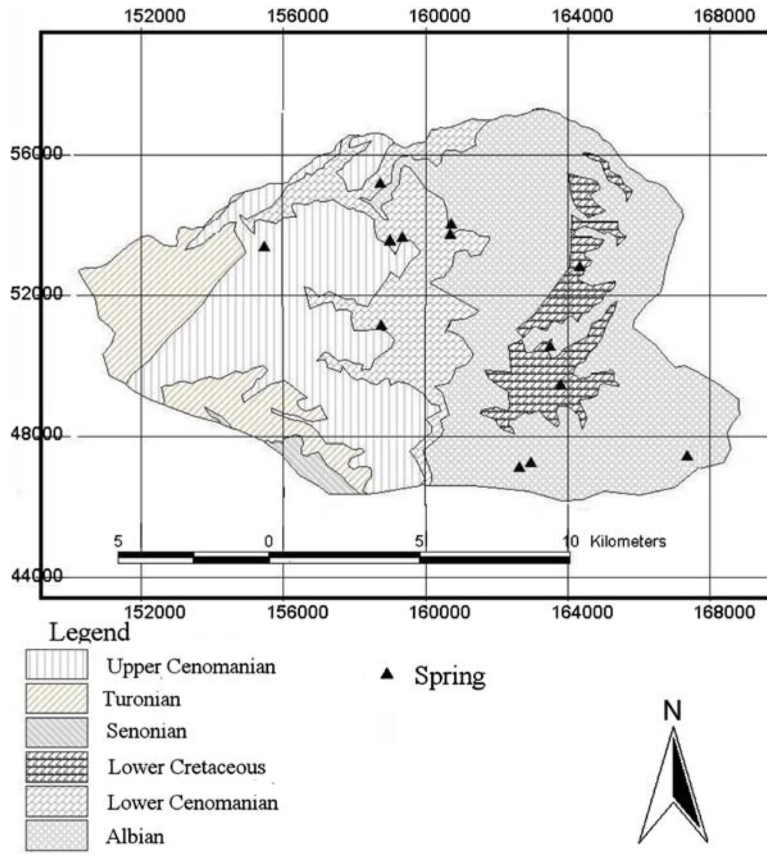

Fig. 2 Geological formations of Natuf area

tests for pH, electrical conductance (EC) and temperature (T) were carried out for each site using Hanna field multimode meter.

Three sites, Ein Musbah, Harrashah and Al Alaq, were chosen for biological tests, to show the possibility of wastewater intrusion from sewer systems and cesspit. Samples from these sites were collected in sterile 100 ml glass bottles, cooled and transferred to the laboratory on the same day for biological tests.

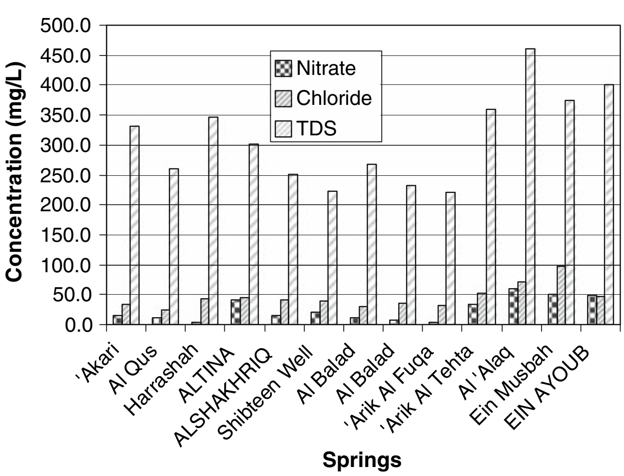

Fig. 3 Average values of nitrate, chloride and TDS in Natuf springs' water 2003–2005

Laboratory tests

All samples were acidified for trace elements analysis, with 69% nitric acid (14.4 M); a Perkin–Elmer ICP Optima 3000 was used to detect iron, copper, zinc, chromium, lead, cadmium, cobalt and magnesium.

A Sharewood 4010 flame photometer was used to determine calcium, sodium and potassium. A HP 8453 Diode Array Spectrophotometer was used to determine nitrate and sulfate concentrations. A Hanna pH multi-meter was used onsite for the determination of pH, TDS, EC temperature. A Metrohm 716 titrator used to determine chloride and bicarbonate concentrations.

Results and discussion

The mean values of major ion concentrations, pH and calculated P_{CO_2} for the 12 springs and Shibteen well for the period from October 2003–May 2005 are listed in Table 2. HCO_3^- is the dominant anion in all springs, and ranges between 174 and 321 mg/l, Cl^- is the second most

Table 2 Average values of hydrochemical parameters from spring water of Natuf drainage basin

Spring ID	Ca^{+2} (mg/l)	Mg^{+2} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl^{-} (mg/l)	HCO_3^{-} (mg/l)	NO_3^{-} (mg/l)	SO_4^{-2} (mg/l)	EC (µS/cm)	pH (mg/l)	P_{CO_2} (atm.)
BA/152	81.2	40.6	35.4	4.1	71.1	321.2	56.3	30	842	7.2	2.10E–02
BA/153	65.1	24.4	11.8	1.5	38.8	259.8	4.2	22.4	555.3	7.5	5.00E–03
BA/157	57.8	24.2	17.2	2	32.7	210.2	14.8	21	514.8	7.6	3.60E–03
BA/158	47.5	24.7	14	1.8	29.5	226.3	13.2	27	502.3	8	8.10E–04
BA/159	41.9	19.7	11.6	1.3	26.2	205.2	12.1	22.4	472	7.5	7.00E–03
BA/163	54.5	15.9	13.5	1.3	34.8	215.5	7	24	512.3	7.4	4.70E–02
BA/170	48.2	15.1	11.6	1	31.6	202.2	4.2	21.2	403	7.9	1.50E–03
BA/171	71	18.6	29	6.1	49.4	244.6	28.5	29.2	612.3	7.1	4.10E–02
NS/007	72.4	23.2	26.6	2.6	48.3	218.3	49.1	25.9	609.5	7.2	2.00E–02
NS/040	54.5	15.6	24.8	1.4	45.7	174.8	41.4	26.7	526.3	7.6	5.30E–03
NS/041	60.9	15.6	17.2	5.6	42	207.2	15.6	26	479	7.6	3.80E–03
NS/MUS	83.4	42.8	61.3	2.1	97.5	310.4	50.9	28	916.7	7.9	5.50E–04
SHW	58.9	16.4	16.7	2.04	39.1	206.6	19.9	17.3	453	8.1	5.60E–04

abundant anion with ranges between 29.5 and 97.5 mg/l. The concentrations of NO_3^- show moderate values below the WHO limits of 45 mg/l (World Health Organization 1996) and Palestinian drinking water standards (Palestinian Standards Institute 2005). Two sites, Al - Alaq and Ein Musbah springs, show average values of nitrate 56.3 and 51.6 mg/l, respectively (Fig. 3). Those two springs are in a densely populated area where cesspits are in the outcrop area of these springs. SO_4^{-2} concentrations are moderate compared to the dominant anions.

The Na^+/Cl^- ranges between 0.26 and 0.8 in all samples except one sample collected in the dry season of 2003 from Akari spring showed a Na^+/Cl^- ratio of 1.79. The high levels of sodium and chloride are assumable to be related to contamination processes (Helena 1998). The high concentrations of sodium and chloride found in Al Alaq, Ein Ayoub and Ein Musbah reveal the probable wastewater leakage from sewer systems and cesspits. All samples lie within the pH range of 7.1–8.1. The calculated values of P_{CO_2} are higher than the atmospheric P_{CO_2} ($10^{-3.5}$ bar), which indicates that the water from the spring is saturated with CO_2 during infiltration of rainfall water.

Saturation indices (SI), listed in Table 3, for anhydrite ($CaSO_4$), aragonite ($CaCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4.2H_2O$) were calculated for 47 samples using PHREEQC.

The SI for anhydrite and gypsum is below zero in all samples, which means that water is undersaturated with respect to anhydrite and gypsum. SI for Aragonite is between –0.7 and 0.9 with 40% of the samples having an SI > 0, which means that they are in saturation and aragonite is precipitated. Around 8.5% of the samples have SI = 0 meaning that water is in equilibrium in these samples with respect to the aragonite.

Table 3 Average values of saturation indices for Natuf drainage basin

Spring ID	Anhydrite	Aragonite	Calcite	Dolomite	Gypsum
BA/152	–2.4	–0.2	0	0	–2.2
BA/157	–2.6	0	0.1	0.2	–2.4
BA/158	–2.5	0.4	0.5	1.1	–2.3
BA/159	–2.7	–0.2	–0.1	0	–2.5
BA/163	–2.5	–0.2	–0.1	0	–2.4
BA/170	–2.7	0.3	0.3	0.5	–2.4
BA/171	–2.4	–0.4	–0.3	–0.9	–2.2
BA153	–2.5	0.1	0.2	–0.2	–2.2
NS/007	–2.4	0	–0.7	–0.4	–2.2
NS/040	–2.4	0	0.1	0.1	–2.1
NS/041	–2.4	0	0.2	0.1	–2.2
NS/MUS	–2.5	0.4	0.5	1.0	–2.2
SHW	–2.8	0.3	0.4	0.5	–2.6

Fifty-one percent of the samples have SI < 0, which means under saturation with respect to the aragonite. SI for calcite ranges between –0.6 and 1.1. Fifty-seven percent of the sample have SI > 0, which means that they are oversaturated for precipitation of calcite. Around 13% of the samples have SI = 0, which means equilibrium and 30% of the samples have SI < 0 which means that they are undersaturated with respect to calcite. For dolomite, SI ranges between –2.2 and 1.9, and 51% of the samples have SI > 0, which means that they are oversaturated and precipitation of dolomite occurs. About 11% of the samples have SI = 0, which means equilibrium conditions and 38% of the samples have SI < 0, which means that they are undersaturated with respect to dolomite.

Statistical analysis

Correlation analysis was performed using SPSS version 11.5, between all parameters. Based on the correlation coefficient value (R), the interrelationships between hydrochemical parameters can be classified from poor ($R < 0.7$) to very high significance ($R > 0.9$) (Abed Rabbo et al. 1999). The results show that (EC) is highly dependent on chloride, magnesium, nitrate, sodium, bicarbonate concentrations, which means that field measurement of EC with a suitable instrument, can be used for quick estimation of other related parameters. The values of EC during the study period for water samples from springs of Natuf drainage basin range between 403 and 917 µS/cm. The highest values of EC were recorded in the dry season of 2003 in Ein Musbah (916.7 µS/cm), which is in a densely populated area in the center of Ramallah city and in Alalaq spring (842 µS/cm), which is near an agricultural area. All other springs have values range between 403 and 600 µS/cm, which is considered as good water for agricultural purposes (Bauder et al. 2005).

Chloride and nitrate show the same trend of variation, which supports the supposition that human activity contributes to high pollution rates in this sensitive area (Ghanem 1999).

The significance of interrelationship between TDS and other ions is an indication of salinity-controlling ions (Abed Rabbo et al. 1999). TDS was high correlated with EC ($R = 0.86$), good correlation with NO_3^- ($R = 0.78$), Cl^- ($R = 0.76$), Na^+($R = 0.79$), Mg^{+2} ($R = 0.75$) and acceptable correlation with HCO_3^- ($R = 0.71$) and Ca^{+2} ($R = 0.70$).

Trace elements are in very low concentrations and below toxic limits in all samples. The highest value (27 µg/l) of Pb^{+2} was recorded in Ein Ayoub in the dry season of 2004, and decreases to 16 µg/l in the wet season of 2005 because of dilution. The location of the outcrop is full of old vehicle dumping sites where old galvanic batteries are disposed. Zinc content shows variations between 1 µg/l at Ein Arik El Tehta in wet season of 2005 and 142 µg/l at Al Alaq in the dry season of 2004. Other springs contain values of zinc within this range.

Biological results for faecal (FC) and total coliform (TC)in the three target springs of Harrashah, Ein Musbah and Al Alaq show that Ein Musbah and Al Alaq contain colonies of FC and TC, which reveals contamination from wastewater from sewerage system near Ein Musbah and cesspits near Al Alaq. Harrashah spring also shows TC colonies, which is probably related to sheep herds and animal manure piles near the spring outlet.

Graphical representation of the hydrochemical data

The chemical composition of the springs in the study area is affected by rainfall chemistry, climate, rock type, rock division, human activities and residence time of water (Cruz and Amaral 2004). The hydrochemical characteristics of spring water based on the percentages of anions and cations can be illustrated by Piper trilinear diagram (Fig. 4) (Fetter 1994). Similar waters are clustered in clearly defined areas, indicating water-mixing phenomena, precipitation and dissolution (Helena 1998).

There is no obvious change in the chemical composition of spring water at Harrashah, Akari, Ein Arik Al Fuqa,

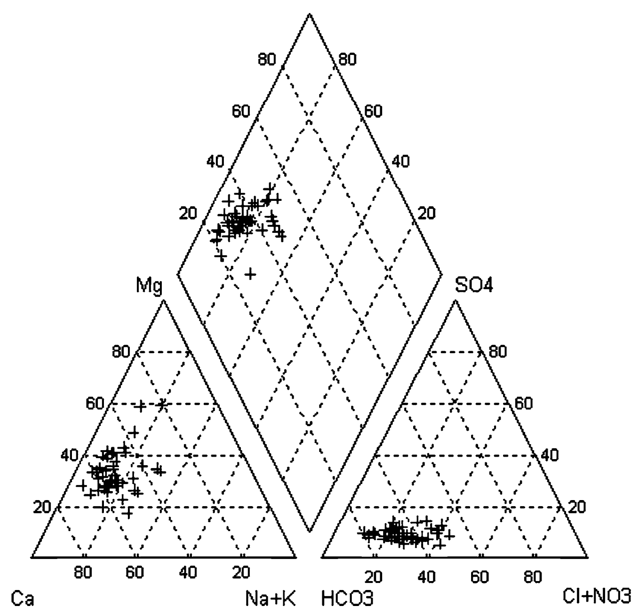

Fig. 4 Piper diagram for hydrochemical parameters of Natuf springs (2003–2005)

Beitillu Al Balad, Alshakhariq and Al Quos springs. The water type remains as normal earth alkaline before and after recharge. The chemical composition also remains as earth alkaline with prevailing bicarbonate and sulfate or chloride for Al Alaq and Al Tina springs. Other springs show different variations in chemical composition before and after recharge. Ein Ayoub and Arik El Tehta show an increase in alkali type with prevailing bicarbonate and chloride after recharge, which indicates human contribution in pollution. Ein Musbah shows an increase in chloride concentrations, which indicates leakage of waste water from a nearby sewerage system.

Ion distribution and chemical composition

The total dissolved ions (TDI) for the major ions in the springs (Table 1) of Natuf drainage basin was calculated as 152 meq/l, in the dry season of 2004 and 144 meq/l, in the wet season of 2005, reveals for the dilution process. The higher content of TDI during dry season confirms the effect of residence time on dissolution process of minerals from rocks.

Water quality parameters and pollution rates are also affected by dry and wet seasons as well as the effect caused by the human activities and agricultural processes. As indicated by Schoeller diagrams (Fig. 5), the concentrations of major cations and anions recorded in dry seasons are higher than those in the wet seasons, which can be explained by the longer residence time of water and lowering of the water table in the dry season. In the wet seasons, the dilution process due to the infiltrated rainfall is the main cause of lowering the concentrations of major cations and anions. Nitrate and chloride concentrations increase in wet season more than dry seasons, which indicates a washing process of pollutants by runoff over agricultural and urban areas.

Water quality parameter

Salinity

Springs in Natuf drainage basin are used mainly for irrigation purposes where many market vegetables are produced such as lettuce, cabbages, bell pepper, beans, parsley and zucchini in addition to many other fruits such as citrus. Many of these crops are sensitive to high water salinity (Todd 1980). Ein Musbah spring in Ramallah city is considered as high saline and cannot be used for unrestricted irrigation in crops sensitive to this parameter. Other springs in the area are of medium salinity and can be used for irrigation purposes in crops of suitable choice.

Total hardness (TH)

Hardness of water is defined as the inhibition of soap action in water because of the precipitation of magnesium and calcium salts such as carbonates, sulfates and chlorides. It can be temporary or permanent hardness. Temporary hardness is mainly due to the presence of calcium carbonate and is removed by boiling water. Permanent hardness is caused by the presence of calcium and magnesium chlorides and sulfates and can be cured only with ion exchange processes.

Hardness of water limits its use for industrial purposes; it causes scaling of pots and boilers, closure to irrigation pipes and may cause health problems to humans, such as kidney failure.

TH is calculated as follows (Todd 1980):

$$\text{TH } (CaCO_3) \text{ mg/l} = 2.497\ Ca^{+2} + 4.115\ Mg^{+2}$$

The concentrations of Ca^{+2} and Mg^{+2} are expressed in mg/l. As a water quality parameter, TH values can be used to classify water for domestic and industrial uses.

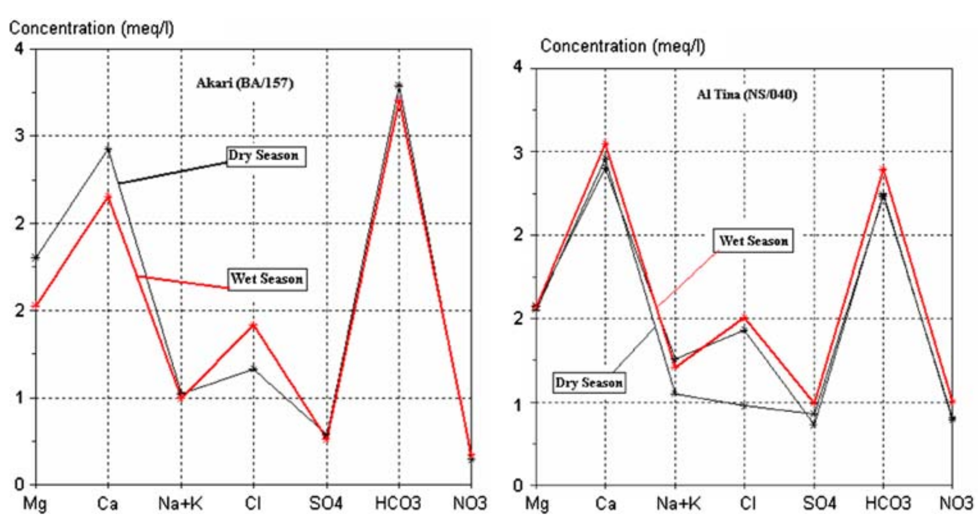

Fig. 5 Schoeller diagrams for some springs in Natuf Area 2003–2005

In the study area, the lowest value of TH recorded was 74.8 mg/l for Wadi Natuf runoff on 6 February 2005, and the highest value was 568.8 mg/l for Ein Musbah spring on 19 October 2004. Water types according to the average TH in the study area range from soft to very hard water with prevailing hard water in 80% of the samples.

Soluble sodium percentage (SSP)

Water quality for agricultural purposes in the Natuf drainage basin shows variation between excellent to good based on Todd' classification of soluble sodium percentage (SSP) values, which is defined as:

$$\mathrm{SSP} = \left(\frac{(\mathrm{Na}^+ + \mathrm{K}^+)}{(\mathrm{Na}^+ + \mathrm{K}^+ + \mathrm{Ca}^{+2} + \mathrm{Mg}^{+2})} \right) \times 100,$$

where all concentrations are in meq/l. SSP values were 16.7 and 13.67 for dry 2004 and wet 2005 seasons, respectively.

Sodium adsorption ratio (SAR)

Sodium adsorption ratio (SAR) is used as an index for sodium hazard in water for irrigation purposes in accordance with EC values. SAR is calculated according to the formula:

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\sqrt{\frac{\mathrm{Ca}^{+2} + \mathrm{Mg}^{+2}}{2}}}$$

where all concentrations are in meq/l.

Sodium hazard starts at values of SAR > 1 and EC values >650 uS/cm, respectively (Bauder et al. 2005). The values of SAR are <1 and <650 uS/cm for EC in most the springs, Ein Arik Al Tehta, Ein Ayoub and Ein Musbah show values of SAR > 1 and >650 uS/cm, which means that water from these springs is not recommended for unrestricted irrigation.

Based on EC and SAR ratio, water from Natuf springs can be classified for irrigation purposes according to Wilcox diagram (Fig. 6; Abed Rabbo et al. 1999).

Microbiological analysis

Water is a good media for microorganism. Groundwater and surface water may contain bacteria, viruses, fungus and algae, which makes water objectionable for domestic purposes and health threatening. In this study, water samples from three springs near densely populated areas, were tested for FC and TC. The results obtained from microbiological analysis of Harrashah, Ein Musbah and Al- Alaq show that Ein Musbah and Al Alaq contain uncountable colonies of FC and TC, which indicates contamination from wastewater

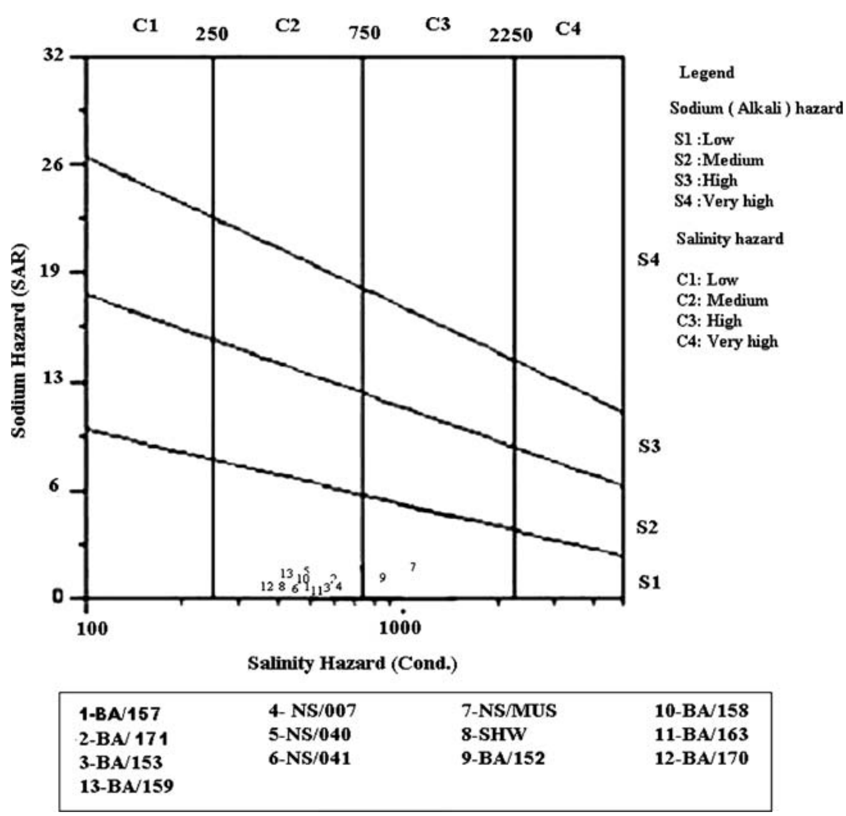

Fig. 6 Classification of Natuf springs according to Wilcox

from sewerage systems near Ein Musbah and cesspits near Al-Alaq. Harrashah spring show uncountable TC, which is referred to sheep herds and manure piles near the spring outlet.

Conclusions

Springs in Natuf drainage basin emerge from perched aquifers and are distributed over Yatta formation in the upper aquifer. The springs are of good water quality, except Ein Musbah, Al Alaq and Ein Ayoub springs which are near populated areas. Samples from these three springs have low water quality for agricultural and domestic uses based on SAR, SSP and EC values. Faecal and Total coliform are found in these springs. The recorded trace elements levels are not harmful according to WHO water quality guidelines.

The recharge areas for the springs in Natuf area are mainly composed of limestone and dolomite. The dominant water types in springs of Natuf drainage basin are earth alkaline with prevailing bicarbonate. Some springs show earth alkaline water type with a little increase in alkalis and prevailing bicarbonate and sulfate or chloride. The change of water types in some springs is related to mixing with wastewater, rainfall and dissolution of minerals.

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