Academia Journal of Environmental Science 6(1): 001-010, January 2018
DOI: 10.15413/ajes.2017.0122
ISSN: ISSN 2315-778X

Research Paper

Environmental spring water qualitative assessment in Natuf catchment - West Bank

Accepted 13th December, 2017

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ABSTRACT

Assessment of groundwater quality is essential to ensure sustainable use of it for drinking and agricultural purposes. This study was carried out to assess the overall water quality and identify major variables affecting the groundwater quality in the Natuf catchment of West Bank. Groundwater quality indicators were determined and integrated with spatial information about the surrounding environment. Three sampling campaigns were conducted at 19 springs in the Natuf surface water basin in Western Ramallah, and samples were analyzed for physico-chemical parameters, major ions, trace elements and total and fecal coliform bacteria. Relationships between different hydrochemical parameters reflect the carbonate nature of the aquifers. Hydrochemical evaluations show that most springs in the study area are of water type (Ca-Mg-HCO_3). The presence of coliform bacteria and elevated concentrations of trace elements point to human impacts on water quality, and indicate the need for groundwater protection efforts in the study area.

Key words: Natuf catchment, spring water, hydrochemistry, water quality, pollution

INTRODUCTION

Most of the important springs in Palestine are located in Natuf catchment, and many communities are dependent upon springs as their only source of drinking water. Springs have long been a critical water resource for communities in the West Bank, and many communities are dependent upon springs as their only source of drinking water. The value of water is evident as the names of many communities are synonymous with the name of the nearby spring ("ein" in the Arabic language) or stream ("wadi"). In the West Bank, the use of spring water for domestic purposes has increased in recent decades (PWA, 2012) due to increase in population, and decreasing availability of freshwater from other sources. The quantity and quality of spring water varies over time and space, and is influenced by natural and man-made factors including climate, hydrogeology, management practices, and pollution. The area of interest for this study is the Natuf catchment, which is located in the west of the city of Ramallah. It contains springs in the villages of Beitillu, Deir Ammar, Jamala, Deir Ibzai, Ein Arik, and Ein Qania. Like other areas in the West Bank, the Natuf drainage basin, which is part of the Auja-Tamaseeh sub-basin (SUSMAQ, 2003) in the Western subsurface drainage basin, suffers from scarcity of water. The average water consumption rate in Ramallah district is 108 L per capita daily (PWA, 2012). The overall water consumption in Ramallah District is 11.855 million cubic meters and the total supply is 16.195 million cubic meters, leading of a total loss of 4.340 million cubic meters (PWA, 2012).

There are 130 springs located within the Natuf catchment. The wide distribution of cesspools and septic tanks with inadequate quality controls, graywater 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

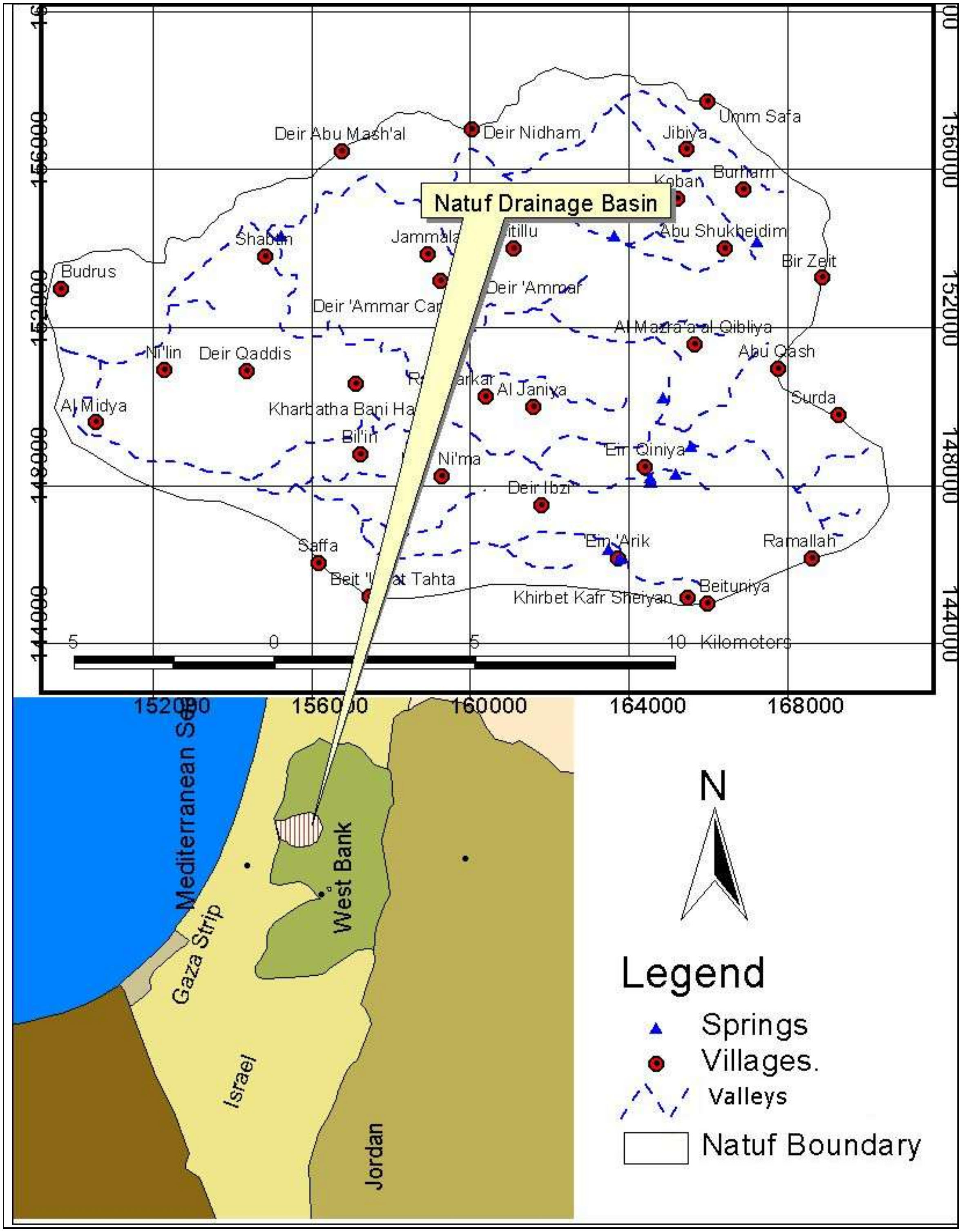

Figure 1: Location of the Natuf drainage basin in the West Bank (Shalash and Ghanem, 2007).

in the area (Qannam, 1997). There have been very few hydrochemical studies conducted in the study area, leaving environmental managers and advocates with little data to use in groundwater protection efforts. Therefore, a chemical and biological investigation is essential for the authorities to implement successful management plans. The Natuf drainage basin is located in the Western part of the West Bank between 149.3 W-170 E and 144.5 S -158 N in Palestinian national coordinates (Figure 1). It drains from the mountains of Western Jerusalem into the coastal

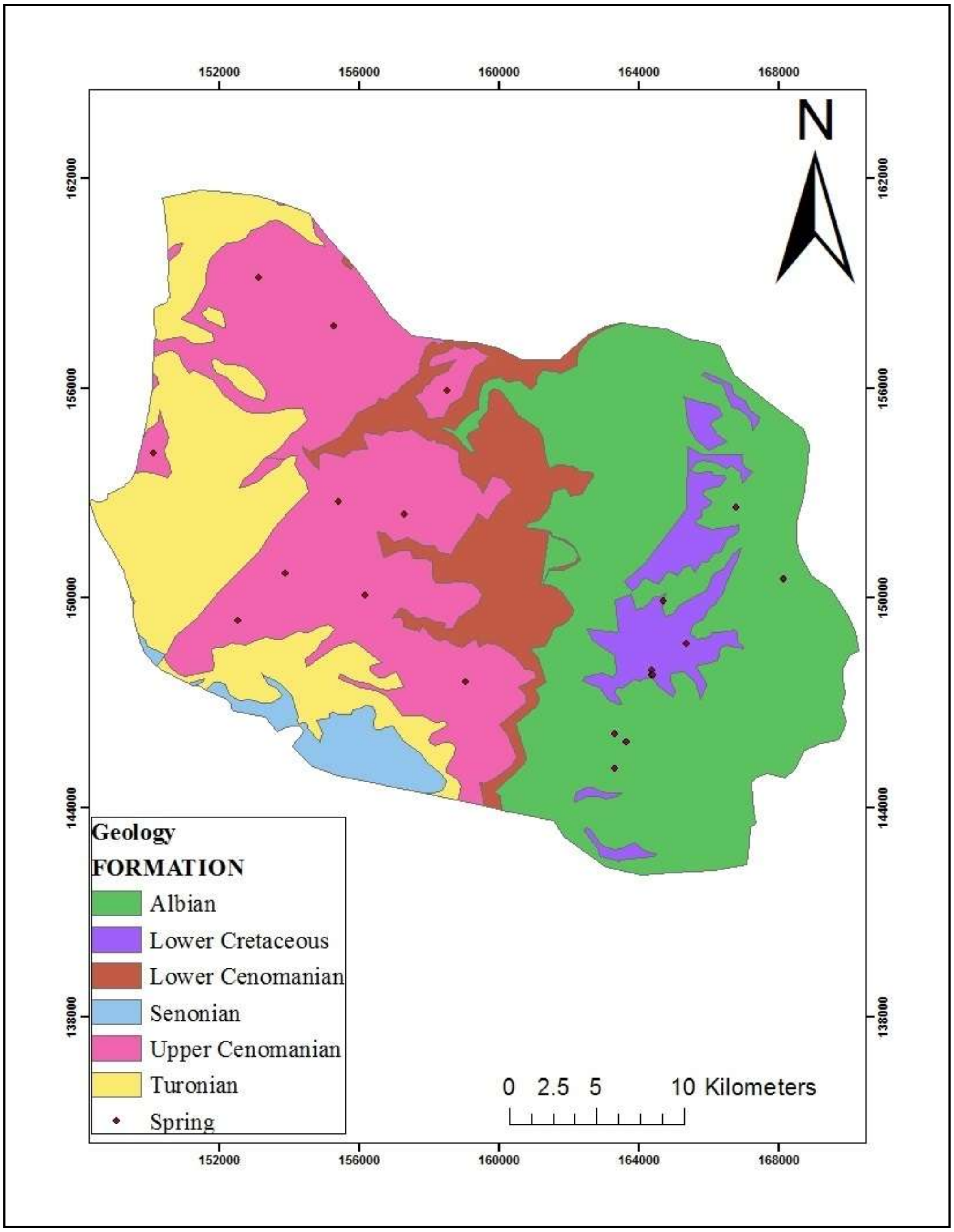

Figure 2: The geological map of the Natuf catchment.

plains of the Mediterranean Sea and has a surface area of about 204 km^2. In 2014, there were 110 thousand people living in the study area (PCBS, 2014). The Natuf basin is one of the main sensitive recharge areas within the Western Aquifer Basin (WAB). It is also the site of one of the world's oldest cultures, the Natufian civilization, (8,000 B.C), where humans first engaged in domestic agriculture. The area is expected to be listed by UNESCO as one of the world's cultural reserves for its historic and cultural heritage (Ministry of Archeology and Tourism, 2004).

The geology of the Natuf drainage basin comprised thick sequences of layered limestone, dolomite, chalk, and marl. The main outcrop formations are Albian to Turonian age (SUSMAQ, 2003) (Figure 2).

The groundwater is recharged mainly from precipitation falling on the mountains at the middle of West Bank by direct infiltration along the karstified outcrops in the mountainous and sloped areas in the eastern part of the aquifer system (Figure 3). The springs are the natural outlets of the aquifer in the study area, due to the

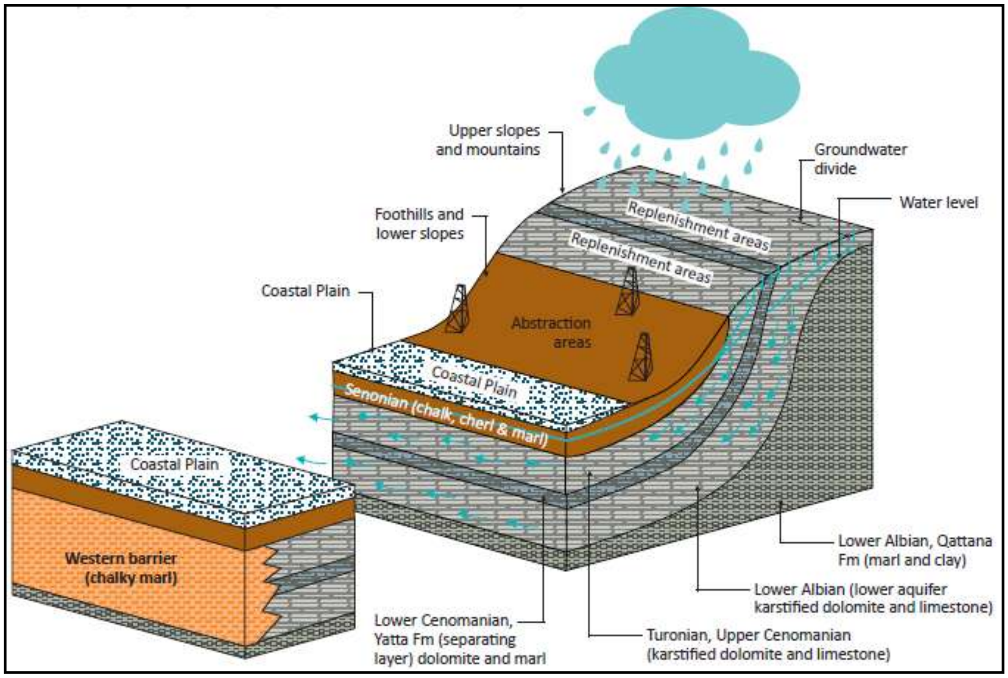

Figure 3: The hydrogeological setting of the WAB aquifer (Abu Saada and Sauter, 2012).

karstified nature of the limestone and dolomite outcroppings. Most of the springs are distributed in the middle part of the study area and the flow discharge of these springs is greatly affected by the intensity of precipitation. Springs in the study area are an outcrop of perched aquifers.

METHODOLOGY

Samples were collected from springs in the study area in 2008, 2010 and 2011 (R1, R2, R3, respectively). Spring water sampling was taken from the emerging source of the springs. A total of 19 samples spring water were collected. Analyses included physical parameters pH, temperature, and EC, and concentrations of chemical constituents Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-}. Chemical analyses were conducted at the water laboratory of Birzeit University. The concentrations of trace elements Fe, Cd, Pb, Zn, Mn, B, As, Cr, Al, Co, Cu, Ni and Hg were assessed in the laboratory at Purdue University in USA. Samples were collected from the springs in one-liter polyethylene bottles and refrigerated in the laboratory at 2°C. *In-situ* tests for pH, total dissolved solids (TDS), electrical conductance (EC), and temperature (T) were carried out for each site using a Hanna field multimode meter. The meter was calibrated before and during the field campaign using buffer solutions recommended by the manufacturer. Major anions (NO_3^-, SO_4^{2-}, and Cl^-) were analyzed using HP liquid chromatography. The concentrations of the major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) were determined by ICP-MS. Alkalinity and HCO_3^- analysis was measured onsite by titration. For the analysis of trace elements, about 100 ml of each sample was acidified with Aristar Concentrated 69% Nitric Acid (14.4M HNO_3) after filtration. Trace elements analyzed by ICP/MS, each samples were prepared by dilution of 1.0 mL of the water samples to 10.0 mL with 0.3% ultrapure nitric acid after filtration. Each sample was analyzed three times and the results are expressed as mean ± SD (SD: standard deviation). Relative standard deviation (RSD) of the three results are calculated and found to be less than 5% for all samples for all metals analyzed in this study, reflecting the precision of the method for the analysis of these trace elements. Microbiological tests of total coliform (TC) and fecal coliform (FC) were carried out at the Birzeit University laboratory. Samples were collected in sterile 100-mL glass bottles, cooled, and transferred to the laboratory on the same day for biological testing.

RESULTS AND DISCUSSION

Physicochemical parameters

This study investigated the physical (pH, EC, TDS) and chemical (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $HCO3^-$, SO_4^{2-}, NO_3^-) parameters for the spring water over three years (2008, 2010, 2011). The pH of the spring water ranged between 7.1 – 8, which is neutral to slightly basic and within the allowed limit (6.5-8.5) according to WHO regulations. The TDS for all spring water samples were less than 1000 mg/L, with value ranging between 133 and 407 mg/L. As such, the water from all the sampled springs in the

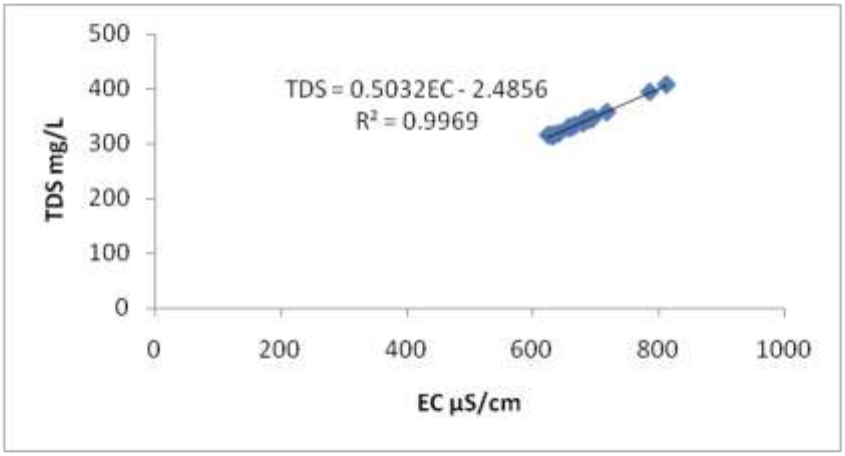

Figure 4: EC - TDS relationship of springs water samples in the study area.

catchment can be classified as fresh water (Todd, 2007). The conductivity measurements during this study for water samples from springs ranged from 263 - 813.2 µS/cm. The highest value of 813.2 µS/cm, was recorded in Ein Abu Esam in (Bitllou village). The variation in EC in spring water is caused mainly by the variations in total dissolved solids. (Figure 4). The relationship between (EC) and (TDS) in the spring water of the study area is strong and the TDS versus EC values show that the value of the linear correlation coefficient (R^2) is close to one (Figure 4). The relationship between electrical conductivity and water mineralization indicate that the spring water is moderately to highly mineralized.

Hydrochemistry

Cations

The concentration of calcium was found to be higher in Ein Massour and Ein Arik Al Tehta due to longer contact residence time between water and minerals and also, due to the weathering process of limestone and dolomite. High levels of calcium and magnesium cause water to be hard, which is undesirable for domestic and industrial uses. The magnesium ion (Mg^{+2}) concentration of spring water samples varies between 15 - 56 mg/L which is within the allowable level of the WHO standards (1996). The increased magnesium concentration in Ein Arik Al Fuqa emanates from dissolution of dolomite limestone.

The concentration of potassium in the samples varies from a maximum of 155 mg/L in Ein Arik Al Fuqa in 2011, to a minimum value of 0.15 mg/L in Ein Al Khaneq in 2008. The high concentration of potassium in Ein Arik Al Fuqa emanates from rock weathering. In addition to ion exchange, the concentration of sodium in the samples varies from a maximum value of 59 mg/L in Ein Majoor (Deir Bzei village) to a minimum value 13.6 mg/L in Ein Abu Aqla. By comparing the cation concentrations of water samples with the WHO standard, it becomes apparent that all anions for all spring's water samples were within the WHO standards over the three years of sampling, with the exception of calcium in some springs, such as Ein Majoor and high concentration of the potassium in Ein Arik Al Fuqa which exceed the permissible limit of WHO standards (Figure 5).

Anions

As shown in Table 1, the concentration of (HCO_3^-) in groundwater is below the threshold value of 500 mg/L, rendering it suitable for consumption (Todd, 1980). For sulfate, the acceptable levels of sulfate in groundwater are up to 250 mg/L (Todd, 1980), The concentration of sulfate (SO_4^{2-}) in the samples varies from a maximum value of 67 mg/L in Ein Al Zarqa (Bitllou village), to a minimum value of 1 mg/L in Ein Al Qus (Ein Qinya village), which are below the 250 mg/L WHO standard (WHO, 1996). The concentrations of chloride (Cl^-) of 250 mg/L in springs is acceptable for consumption. The concentration of the anions and cations in Ein Majoor and Ein Arik Al Fuqa is higher; the main sources of those concentrations in the spring water are dumping sites and cesspits of surrounding houses, human activities, and use of fertilizers, in addition to natural weathering processes. The concentrations of NO_3^- for all samples show moderate values below the WHO limits <50 mg/L with a mean 11.2 mg/L. The order of cation abundance (mg/L) was (Ca^{2+} > Mg^{2+} > Na^+ > K^+), but that of anions (HCO_{3-} > Cl^- > SO_4^{2-} > NO_3^-) was similar over the three years, where calcium was the dominant cation and (HCO_{3-}) the dominant anion (Figure 6). Thus we concluded that the water type is calcium-, which reflects the calcic nature of the spring's reservoirs.

The suitability of water for irrigation has been assessed using various properties or ratios. These include electrical conductivity (EC), Sodium Adsorption Ratio (SAR), and

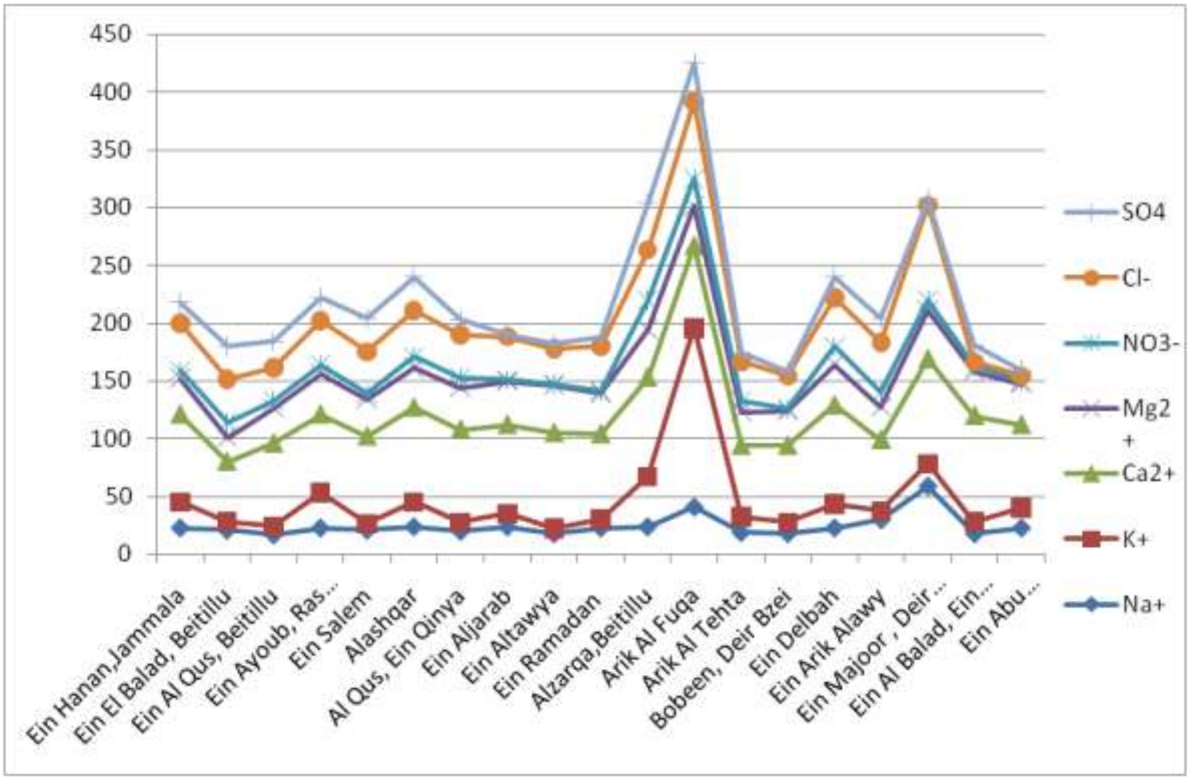

Figure 5: Average cation and anion concentrations for sampled spring water over three years.

Table 1: Descriptive statistics for physico-chemical parameters of spring water (in mg/L) over three years of sampling.

Parameter	Min			Max			Mean		
	R (1)	R (2)	R (3)	R (1)	R (2)	R (3)	R (1)	R (2)	R (3)
Na^+	13.6	14.2	17	18.9	46.6	59	15.33	20.9	24.6
K^+	0.15	0.24	4	1.15	12.7	155	1.97	1.89	21.7
Ca^{2+}	68.4	40	52	72.4	147	92	70.74	61.4	75.2
Mg	24.7	15	21	33.1	56	33.1	29	39.7	33.8
Cl^-	23.3	33	3	35.6	133	82	27.5	48.5	37.2
SO_4^{2-}	2.1	1	2	20.1	67	41	13.6	12	17.1
HCO_{3-}	254	118	90	265	195	270	259.6	144.9	213.3
NO_3^-	3.2	1	1	12.1	53	26	8.1	16.4	9.1
pH	7.6	7	7.1	8	7.6	7.9	7.8	7.5	7.5
EC	624.5	251	263	813.2	504	636	681.3	421	459.1
TDS	313.9	204	133	407.4	307	318	340.3	241	230.4

Residual Sodium Carbonate (RSC). EC and SAR play a vital role in suitability of water for irrigation. The EC values in 95% of the analyzed samples were less than 500 µS/cm and SAR values were less than 3; thus, classifying the water into the medium salinity hazard class (C2) and low sodium hazard class (S1), respectively (Figure 7).

As illustrated in Figure 8, ternary plots for major cations (Mg^{2+}, Ca^{2+}, Na^+ and K^+) and anions (SO_4^{2-}, HCO_{3-} and Cl^-) in all the water samples revealed different water types with different proportions (Piper, 1944). According to Xu and Usher (2006), when fresh water is enriched with Ca^{2+} and depleted with Na^+, an initial sodium chloride type becomes calcium chloride in nature as in the study area (Ca-Mg-Cl) in a process of inverse cation exchange. Piper diagram in Figure 8 shows the water types with proportions in the three years rounds catchment, as the alkali metals (Na^+ + K^+) exceed the alkali earth metals (Ca^{2+} + Mg^{2+}). The Piper plot shows that the spring water is located between the Normal earth alkaline water with prevailing type and sulfate or chloride type (Figure 8).

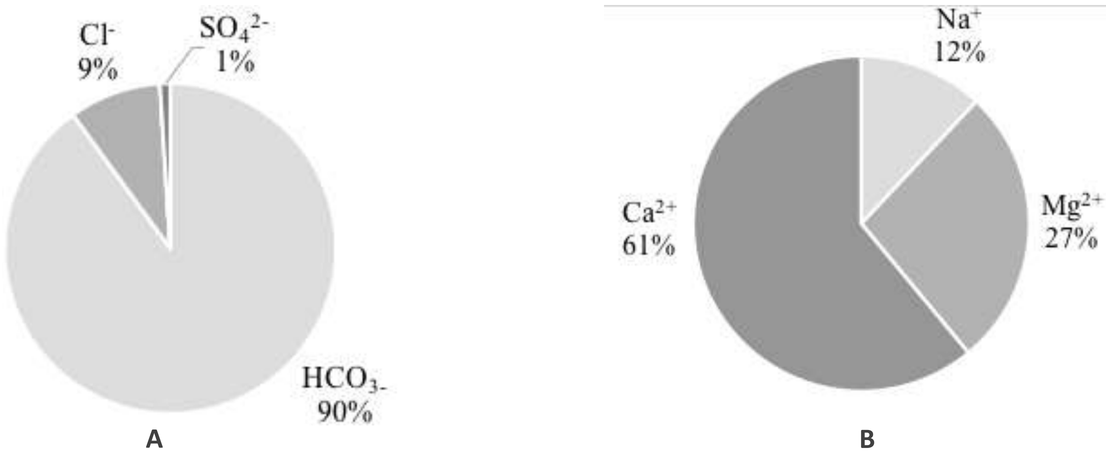

Figure 6A: Anion concentration as a percentage of the composition for water samples of the study area; **B.** Cation concentration as a percentage of the composition for water samples of the study area.

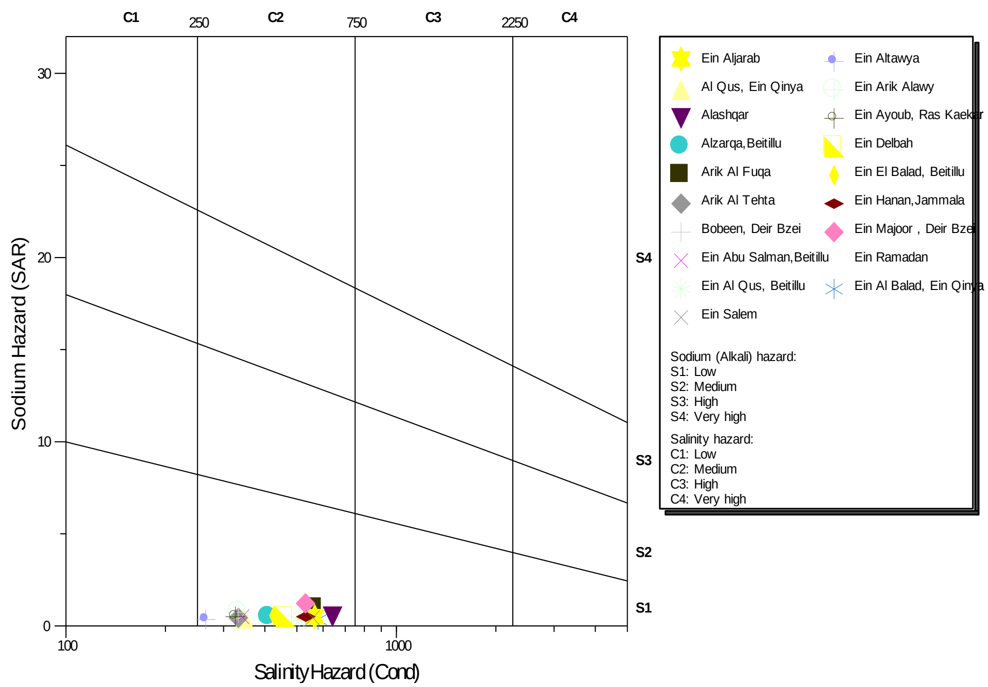

Figure 7. Wilcox classification of the water samples.

The hydrochemical characteristics and water types of the spring's, based on the percentages of anions and cations, are illustrated by Piper trilinear diagram. The water type in the study area is Ca-Mg-HCO$^{-}_{3}$, 20% of the samples showed water type of Ca-HCO$^{-}_{3}$ and Ca-Cl-HCO$^{-}_{3}$ as shown in Schoeller diagram (Figure 9). The majority of them indicate interaction with limestone rocks. The samples showing higher amount of Cl^{-} indicate an input of fertilizers within the recharge zone of these springs. Based on classification of water types, there are no obvious changes in the chemical composition of spring's water during the three year sampling period.

Trace elements

The occurrence of trace elements in natural water is affected both by hydrochemical factors, such as mineral composition of the rocks, soil characteristics etc, and anthropogenic activities, resulting in both temporal and spatial variations. In the study area, wastewater and agricultural activities are the major contamination of water sources, the following are some common heavy metals found in water: Twenty-two heavy metals including (Fe, Cd, Pb, Zn, Mn, B, As, Cr, Al, Co, Cu, Ni, Hg) were analyzed in both seasons,. These samples were analyzed

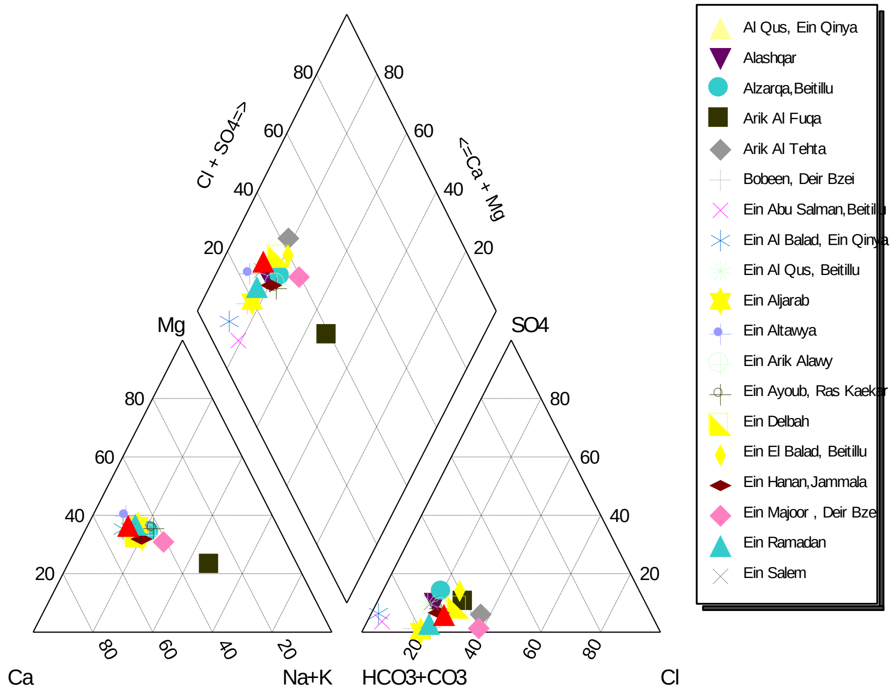

Figure 8: The Piper diagram of the spring water in the study area.

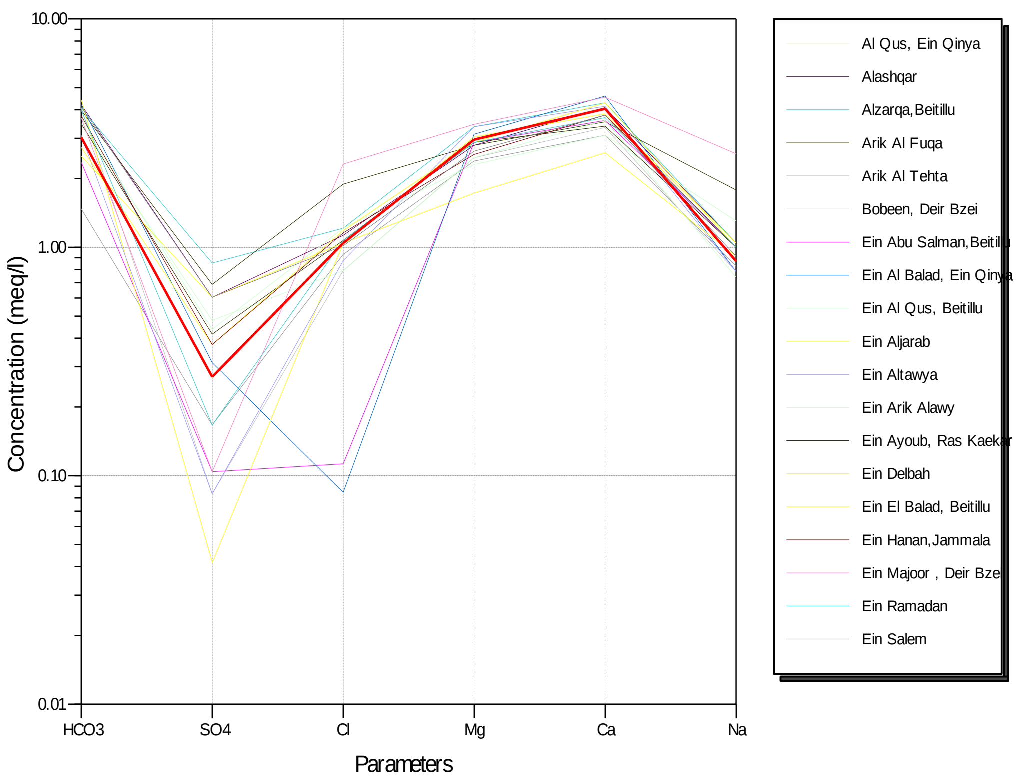

Figure 9: Schoeller Diagrams for springs in Soreq Area.

using ICP-MS and the concentration of these heavy metals in the spring water samples are presented in Table 2.

The results were compared with EPA and WHO standards. Results showed that concentration of all trace

Table 2. Heavy metals concentrations which are detected in the groundwater samples analyzed in this study (minimum, maximum, median, standard deviation (SD), mean in (μg/L)).

Heavy metal	Min	Max	Median	SD	Mean
Fe	4.216	380.503	229.8	90.8	225.3
Cd	0	0.861	0.007	0.34	0.16
Pb	0.72	5.524	1.58	1.2	2.169
Zn	0.114	79.22	6.2	25.2	14.28
Mn	0.064	18.538	0.74	3.63	1.79
B	22.589	53.581	30.2	8.1	33
As	0.22	0.95	0.38	0.19	0.45
Cr	0.083	11.107	7.04	2.8	6.42
Al	1.51	75.4	8.5	17.4	16.6
Co	0.112	0.819	0.16	0.18	0.25
Cu	0.006	19.411	1.14	3.6	2.03
Ni	1.552	6.109	3.55	1.11	3.79
Hg	0.103	1.749	0.25	0.39	0.37

metals (Fe, Cd, Pb, Zn, Mn, B, As, Cr, Al, Co, Cu, Ni, Hg) is within the allowed WHO limits in drinking water (3, 10, 300, 3000, 2400, 10, 50, 200, 50, 2000, 70, and 6 ug/L, respectively), except (Fe), which exceed the limits in some springs, such as Ein Abu Zama'a , Ein Al Kaikaba(in Beitllou village), and Ein Al Ghazal (in Jamalla village). The high Fe content can be attributed to weathering of mineral grains. In some places, the high concentration of iron in these springs can be attributed to iron pipe placed inside the springs. Some of the springs have concentrations significantly higher than other springs in the catchment, and even exceed the EPA limit. Abu Esam spring has Aluminum concentration of 75.49 μg/L > EPA standard limit of 50 μg/L.

The result for selected trace elements constituents show that some sampled springs water contain very low concentrations that are far below the WHO standards and in many cases, even below the detection limits. This leads to the suggestion that the above named trace elements in the water resources in the study area have no health hazard potential. The geological formation of the rock have significantly impact on the water quality of the springs included in this study.

The hydrochemical characteristics of springs co-located in the same village is similar, because the same geological formations are present, and sometimes the source of pollution is the same (Figure 5).

Conclusion

The hydrochemical characteristics of 29 springs of Natuf catchment were determined in order to understand the their qualitative manners against pollution. This study investigated the physical (pH, EC, TDS) and chemical (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_{3-}, SO_4^{2-}, NO_{3-}) parameters of spring water for over three years of sampling (2008, 2010, 2011). The TDS and EC of water in all the springs range between 133 and 407 mg /L, and 263 and 813.2 μS/cm, respectively. The ionic concentrations are generally within the WHO drinking water standards, with the exception of a few springs. The concentration of the anions and cations in Ein Majoor and Ein Arik Al Fuqa is higher; the main sources of those concentrations in the spring water are dumping sites and cesspits of surrounding houses, human activities and use of fertilizers in addition to concentration of the weathering processes. The concentrations of NO_3^- for all sample showed moderate values below the WHO limits <50 mg/L with a mean 11.2 mg/L. The order of cation abundance (mg/L) was ($Ca^{+2} > Mg^{+2} > Na^+ > K^+$), but that of anions ($HCO3^- > Cl^- > SO_4^{-2} > NO_3^-$), which was similar over the three years of sampling. This results in calcium water type, indicating the calcic nature of the spring's reservoirs. The EC values in 95% of the analyzed samples were less than 500 μS/cm, and the SAR values were less than 3; thus, classifying the water into the medium salinity hazard class (C2) and low sodium hazard class (S1), respectively. The Piper - plot shows that these springs are located in the Normal earth alkaline water with prevailing bicarbonate and sulfate or chloride. The concentration of trace metals (Cd, Pb, Zn, Mn, B, As, Cr, Al, Co, Fe, Cu, Ni and Hg) was within the allowed WHO limits in drinking water with the exception of F, which exceeded the limits in some spring such as Ein Abu Zama'a , Ein Al Kaikaba (in Beitllou village) and Ein Al Ghazal (in Jamalla village). The majority of springs are reliable and safe for drinking purposes, especially those located outside the populated areas. Some springs showed an increase in the

Table 3: The spring water in the study area.

Village	Spring Name							
Beittlou	Ein Abu Zama'a	Alashqar	Ala'qaleh	AlKaikaba	Salem	Abu Esam	Twisah	Ein Al-Balad
Ein Qinya	AlSaqia	Ein Al Balad	AlJnanin	Al'awinah	Abu Sm'an	Abu Kinan		
Ein Arik	Ein Arik Al Tahta	Ein Arik Al Foqa	Al Sheikh Hussein					
Jamalla	Ein Al Teen	Ein Al Ghazal	Ein Al Dawaheen					
Dair Bzeea	Bobin	Majoor						
Aboud	Al Zarqa	Lemon						
Dair Amar	Ein Al Shakhariq							
Dair Ndam	Rayia							
Ras Karkar	Ein Ayoub	Ein Al Jooz						
Al Jania	Ein Al Jania							

amount of ion concentrations due to manmade pollution including cesspits, landfills, pesticides and herbicides.

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Cite this article as:

Ghanem M, Dare A, Jebreen H (2018). Environmental spring water qualitative assessment in Natuf catchment - West Bank. Acad. J. Environ. Sci. 6(1): 001-010.

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