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HYDROCHEMISTRY AND ISOTOPES OF THE SPRING WATER IN SOREQ CATCHMENT/ RAMALLAH / WEST BANK

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MSc Thesis

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HYDROCHEMISTRY AND ISOTOPES OF THE SPRING WATER IN SOREQ CATCHMENT/ RAMALLAH/ WEST BANK

دراسة هيدروكيميائية و نظائرية المياه لحوض سوريك /رام الله / الضفة الغربية

Submitted By

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This thesis was prepared under the main supervision of Dr. Marwan Ghanem and has been approved by all members of the examination committee.

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The findings, interpretations and the conclusions expressed in this study do not necessarily express the views of Birzeit University, the views of the individual members of the MSc. Committee or the views of their respective employers.

ABSTRACT

This thesis contains the results of hydrochemical and isotopes studies conducted between dry of 2013 to wet season of 2014 on Soreq catchment /West Bank. The study area is located in the western part of the West Bank. Its location is within the western catchments. The study catchment with an area of 70 km^2. This work aims to compensate for the lack of information about hydrochemical characteristics of the springs water، as well as to identify the different pollutants and impact on the spring water, and assessment of the environmental recharge of spring water. The hydrochemical study which involved collection and analysis of water samples from the springs. The EC, pH, TDS and temperature were measured in the field. The chemical and microbiological analyses, including determination of the cations, anions and heavy metals, as well as total and fecal coliform bacteria count, were carried out in the laboratory. The spring water quality is generally low. The pH of all spring water ranged between 7-8 with mean temperature of 20.2 ^oC, which is neutral to slightly basic. Electrical conductivity and total dissolved solids for spring water ranged from 421-1385 µs/cm, 185-763 mg/L, respectively. The concentration of anion and cation of the spring water within the allowable WHO limits except in Ein Beit Soreq and Ein Albalad. The water of most of the springs in the Soreq catchment is contaminated fecal Coliform and total Coliform were found in springs water. The concentration of nitrate show moderate values below the WHO limits. Hardness of water between hard to very hard types. 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 in both seasons. The water of springs in the study area is polluted with some heavy metals like (Zn^{+2}, Cd^{+2}, Mn^{+2}, As^{+2}, Co, Cu, Ni, Pb, Al, Fe^{+2}, and V) because their concentrations are higher than the permissible limits according to WHO (2007) and PWA (2001). Most springs in the study area have water type of (Ca-Mg- HCO_3^-) and the other springs range between (Ca-HCO_3^-) and (Ca-Cl-HCO^-_3). According to Piper's classification the spring water in the study area between the areas of earth alkaline water with increased portion of alkali with prevailing bicarbonate and alkaline water with prevailing bicarbonate in both

seasons. Comparing the quality of spring water with standards for different uses proved that some springs unsuitable for human drinking purposes like Ein Beit Soreq and Ein Albalad, but it's suitable for agricultural and irrigation, except some samples which are poor due to high salinity.

Stable isotopes (^{18}O, ^{2}H) are used to study the recharge of spring water. The study shows that the isotopic composition, ranges for $\delta\ ^{18}O$ between (-5.06 ‰) to (-5.89 ‰) and for $\delta\ ^{2}H$ between (-20.28 ‰) and (-24.44 ‰). The mean is about (-5.53 ‰) and (-22.59‰), in oxygène-18 and deuterium respectively. The relationship between ($\delta\ ^{2}H$, $\delta\ ^{18}O$) contents in spring water samples are used to define the Local Meteoric Water line (LMWL), according to the equation: ($\delta\ ^{2}H = 4.74\ \delta\ ^{18}O + 3.65$). The isotopic content of the analyzed water samples plot on the Mediterranean Meteoric Water Line, signifying recharge from recent precipitation.

الخلاصة

تحتوي الأطروحة على نتائج الدراسات الهيدروكيميائية والنظائر التي تم إجرائها خلال الفترة، ما بين قبل نـزول المطـر في عام 2013 الى ما بعد نزول المطر في عام 2014، في حوض سوريك / الضفة الغربيـة. يعتبر هذا الحـوض جزءاً من الحوض الغربي للضفة الغربية . تبلغ مساحة هذا الحوض قرابة 70 كم^{2}.

تهدف هذه الدراسة إلى التعويض عن نقص المعلومات حول الخصائص الهيدروكيميائية للينابيع ، بالإضافة إلى تحديد اشكال التلوث وتاثيرها على الينابيع، وهدفت ايضا الى تقييم فاعلية تغذية مياه هذه الينابيع. تتمثل الدراسة الهيدروكيميائية بجمع وتحليل عينات المياه من الينابيع.

الايصالية الكهربائية، درجة الحموضة، المواد الصلبة الذائبة ودرجة الحرارة، تم قياسها في نفس الموقع للنبع ، التحاليل الكيميائية والميكروبيولوجية، والتي تشمل الايونات السالبة والايونات الموجبة والمعادن الثقيلة، بالاضافة الى البكتيريا القولونية، جميع هذه التحاليل تم تحليلها في المختبر. جودة مياه الينابيع بشكل عام متدنية، درجة الحموضة لجميع الينابيع تتراوح ما بين 7-8 مع متوسط درجة حرارة 20.2 وهي متعادلة الى قاعدة قليلا، الايصالية الكهربائية والمواد الصلبة الذائبة لمياه الينابيع تتراوح من 421-1385 µs/cm، 185-763 mg/L بالترتيب.

تركيز االايونات السالبة والموجبة لمياه الينابيع تقع ضمن الحد المسموح به في منظمة الصحة العالمية، ما عدا عين بيت سوريك وعين البلد، معظم مياه الينابيع في منطقة الدراسة ملوث بالبكتيريا القولونية. تركيز النيترات تقع ايضا ضمن حدود الصحة العالمية، عسر المياه لهذه الينابيع يقع بين الصعب والصعب جدا.

ترتيب الايونات الموجبة من حيث الاكثر و فرة ,($Ca^{+2} > Mg^{+2} > Na^{+} > K^{+}$). ولكن بالنسبة للايونات السالبة فالترتيب كان ($HCO_3^{-} > Cl^{-} > SO_4^{-2} > NO_3^{-}$) , وهذا الترتيب متماثل في كلا الموسمين.

مياه الينابيع ملوثة ببعض المعادن الثقيلة مثل (Zn^{+2} و Cd^{+2}, Mn^{+2}, As^{+2}, Co, Cu, Ni, Pb, Al, Fe and V) .

نوع الماء في اغلب ينابيع منطقةِ الدراسةِ (Ca-Mg- HCO_3^{-}) بينما بقية الينابيع كانت تَتفاوتُ بين ، (Ca-HCO_3^{-}) و (Ca-Cl-HCO_3).

تدل نتائج التحليل الكيميائي وحسب تصنيف Piper بأن سمة مياه الينابيع في منطقة الدراسة ما بين، ذات سمة قلوية ترابية مع زيادة في القلويات وسيطرة ايونات البايكربونات، وذات سمة قلوية مع زيادة في ايونات البايكربونات

واللفترتين. مقارنة نوعيةَ مياه الينابيع في منطقة الدراسة مع مواصفات قياسية للاستعمالاتِ المختلفةِ اظهرت بأن بعض الينابيع غير مناسبة لشرب الانسان مثل عين بيت سوريك وعين البلد، ولكن صالحة للزراعة والري، ما عدا بعض العينات سيّئة بسبب الملوحةِ العاليةِ.

استخدمت النظائر البيئية المستقرة ($^{18}O,^{2}H$)، لدراسة مصدر التغذية لهذه الينابيع ، أظهرت الدراسة أن القيم النظائرية لمياه الينابيع في منطقة الدراسة، فقد تراوحت بين (-5.06‰) الى (-5.89‰) للاكسجين - 18 وبين (-20.28‰) الى (-24.44‰) للدتيريوم ، وبمعدلات (-5.53‰) ، (-22.59‰) على التوالي

تم تحديد الخط المطري المحلي الاولي وفق المعادلة ($\delta\,^{2}H = 4.74\ \delta\,^{18}O + 3.65$) باستخدام العلاقة بين تراكيز الاكسجين – 18 والدتيريوم لعينات مياه الينابيع. وجد أن المحتوى النظائري لعينات المياه المحللة يقع على خط مياه البحر المتوسط، ومنها فان مصدر التغذية لمياه الينابيع من هطول الامطار.

بسم الله الرحمن الرحيم

" أَلَمْ تَرَ أَنَّ اللَّهَ أَنْزَلَ مِنَ السَّمَاءِ مَاءً فَسَلَكَهُ يَنَابِيعَ فِي الْأَرْضِ

ثُمَّ يُخْرِجُ بِهِ زَرْعًا مُخْتَلِفًا أَلْوَانُهُ ثُمَّ يَهِيجُ فَتَرَاهُ مُصْفَرًّا ثُمَّ يَجْعَلُهُ حُطَامًا

إِنَّ فِي ذَٰلِكَ لَذِكْرَىٰ لِأُولِي الْأَلْبَابِ"

"***Do you not see that Allah sends down rain from the sky and makes***
it flow as springs [and rivers] in the earth; then Allah produces thereby crops of varying colors; then they dry and you see them turned yellow;
then Allah makes them [scattered] debris. Indeed in that is a reminder for those of understanding. "

صدق الله العظيم

Az -Zummar -21– الزمر

Dedication

I Dedicate My Work

To the tree that shaded my path and provided with

Shelter, my mother "Muna" and to my father "Abde- Alfatah"

To Brothers & Sisters "Ali, Tahani and Hanadi"

To all those who love me

With my love and respect

***Hassan*.......**

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Hassan….

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LIST OF ABBREVIATIONS	
Cm	Centimeter
Δ	Delta
E	East
EC	Electrical Conductivity
Eq	Equation
Evap	Evaporation
FC	Fecal Coliform Bacteria
Fig	Figure
G	Gram
GIS	Geographical Information System
^{2}H	Deuterium
Km	Kilometer
km^2	Kilometer Square
L	Liter
LMWL	Local Meteoric Water Lines
M	Meter
M^3	Cubic Meter
Max	Maximum
Meq	Mille Equivalent
Mg	Milligram
Ml	Milliliter (volume)
N	North
^{18}O	Oxygen – 18
ºC	Degree centigrade

pH	Acidity value
PWA	Palestinian Water Authority
SAR	Sodium adsorption ratio
SSP	Soluble Sodium Percentage
TC	Total Count Bacteria
T.Col	Total Coliform Bacteria
TDI	Total Dissolved Ions
TDS	Total Dissolved Solids
TH	Total Hardness
Tem	Temperature
M	Micro
WAB	Western Aquifer Basin

Chapter One

Introduction

1.1 General Background

Water is essential to sustain life and a safe of satisfactory supply that must be available to all people. Improving access to safe drinking-water can result in tangible benefits to health and every effort should be made to achieve a drinking-water quality as safe as practicable (WHO, 2006).

Water resources in the West Bank are scarce. This is due to the fact that the West Bank as well as the Jordan River basin is lying within an arid region. Groundwater is considered to be the main fresh water resource in the West Bank. This study considerable importance as there is a lack of detailed information concerning water quality and related issues. This in spite of the fact that these springs are the major source of water for both domestic and agricultural purposes. In some Palestinian communities a spring is the only source of water. There are three main aquifers in the West Bank, i.e. the northeastern, the western and eastern. The sole source of groundwater in West Bank is in the Mountain Aquifer System, which is divided into three basins: Northeastern; Western and Eastern (Ghanem, 1999).

The chemical characteristic of spring water is very important for municipal, agriculture, and drinking water supplies. The chemical composition of water is based on the minerals which have dissolved in it. In addition, the chemical composition of water is modified by ion-exchange equilibrium. There are some environmental conditions affecting the water chemistry such as type of rock, climate, relief, vegetation and time (WHO,2006).

The growing demand of Palestinians, the lack of sewer systems, the wide distribution of cesspits, and septic tanks, the common practice of wastewater disposal into gardens and road ditches, and the uncontrolled disposal of untreated municipal sewage into wadis may cause rapid contamination pollution of aquifer systems through karstic conduits in the area (Shalash and Ghanem 2007).

This study aims at studying the hydrochemical and microbiological parameters to the spring water in Soreq catchment/SW of Ramallah. Twenty two heavy metals are analyzed including (Fe^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, B, As^{2+}, Be, Se, Ba, Tl , Cr, Al, V, Co, Cu , Ni, Sr, Bi, Mo, Ag and Li). Chemical changes in spring water between dry and wet seasons were determined to locate possible sources of pollution and their impact on the spring water quality for domestic and agricultural uses.

1.2 Problem Identification

There is a lack of information about hydrochemical parameters as well as of the chemical changes in the spring's water constituents between dry and wet seasons of Soreq catchment. The sources of pollution and their impacts on the water quality of spring's water for domestic and agricultural uses are absent in Soreq catchment. The hydrochemical characteristics of the springs in Soreq catchment has to be determined. The springs are located at the direct effect of the human activities. So, their microbiological organisms as well as hydrochemical parameter concentrations will be the indicators of man- made pollution if existed.

The springs are emerging from limestone terrains of perched aquifers. Their relation to each other as well as to springs in the nearby catchments should be studied from the hydrological and hydrochemical environmental point of view. This should be done through determination of the isotopic analyses of oxygen 18 as well as of the Deuterium of the spring water in the study area.

1.3 Research Objectives

The objectives of this study are**:**

1 - Determination the suitability of the spring's water for domestic and agricultural uses.

2- Study the origin of the spring water.

3- Determination of the hydrochemical characteristics of the springs.

4- Assessment of the Environmental Recharge of spring water via isotope fingerprinting.

1.4 Research Motivations

The followings are the research motivations:

1- The need for potable water for drinking and domestic use, agricultural and industrial.

2- The quality and the degree of contamination of the water in the springs through chemical and microbiological.

3- Ease of data manipulation and know the type and degree of contamination of water by using geographic information systems technology and Aquichem program.

4- Represents the first isotopic investigation of the area and will serve as a basis for the promotion of strong science based management practices in the region.

1.5 Research Methodology

1.5.1 Structured Interviews

Interviews and personal communications with Palestinian National Authority (PNA) officials, particularly members of the Palestinian Water Authority (PWA) and the Head of Ramallah and Albirah Agricultural Department, with municipal mayors, chairpersons of local councils, local water engineers, health field officers.

1.5.2 Lab analyses

The samples that were collected from springs, in a 1- Liter high density Polyethylene bottles, stabilized with ultrapure nitric acid (0.5% HNO_3), preserved in a cool place (about 4 ^oC). Temperature, pH, electrical conductivity, total dissolved solids were measured in Onsite, using Hanna Field Multimode Meter, For Total Coliform and Faecal Coliform tests, were collected in sterile 100ml, glass bottles, then cooling in an icebox and transferred to the laboratory on the same day for biological tests.

1.5.2.1 Methods of laboratory analysis

The cations, anions and heavy metals were determined in the labs of the Al-Quds University, while microbiological parameters: Fecal Coliforms and Total Coliforms were analyzed in water and environmental lab at Birziet University.

1. Major cations in mg/L: Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}.
2. Major anions in mg/L: HCO_3^-, Cl^- , $SO4^{2-}$ and NO_3^- .
3. Trace inorganic constituents in µg/L: Fe^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, B, As^{2+}, Be, Se, Ba, Tl, Cr, Al, V, Co, Cu, Ni. Sr, Bi, Li, Mo, Ag.

1.5.2.2 Isotopic analyses

A 12 water samples was taken from three catchment, Soreq, Natuf and Sarida catchment, and their isotopic of ^{18}O as well as of the Deuterium ^{2}H was done in the isotopic labs at Freiberg University /Germany.

1.5.2.3 Software application

- Aquichem, the leading software package designed for managing, analyzing and plotting of water quality data.

1.6 Literature Review

Palestinian environment in the West Bank and the Gaza Strip suffers from the waste of natural resources, environmental pollution in all its forms and the low level of water quality. In addition to the continuing population growth, as well as to the continued neglect and ignorance of the environmental issues. Studying, the drinking water management of sources is a top priority in terms of quality of drinking water and places of existence and the mechanism of exploitation.

The hydrochemistry of the West Bank springs water were thoroughly investigated in a study carried out from Abdul-Jaber (1995) evaluated the chemistry of some springs and groundwater wells from the central and northern parts of the West Bank. He showed that there are four water types represented in the West Bank. The most abundant type is the earth alkaline with prevailing bicarbonate, then the earth alkaline water with increased portions of alkalis and prevailing chloride and lastly the alkaline water with prevailing chloride.

Abdul-Jaber and Aliewi (1996) studied the water quality and chemistry of the springs of Nablus city, especially those used for domestic purposes. They concluded that the major springs in the city are suitable for domestic use from the chemical point of view and can be relied on for any future development.

Scarpa et al. (1998) introduced the results of a chemical and biological study of the wells extracting water from the unconfined aquifer system in the northern West Bank. The excessive use of fertilizers, wide distribution of cesspits and uncontrolled disposal of wastewater were considered probable sources of the wide spread biological contamination and the alarming nitrate, chloride, and potassium levels that were found in many of the wells studied.

Most of the West Bank wells are suitable for irrigation and drinking purposes, but some wells show higher of heavy metals concentrations than the recommended level by WHO and having a low to medium hazard salinity (Abdul-Jaber et al., 1999).

There has been a number of groundwater studies conducted on the West Bank aquifers. In the north eastern aquifer, Ghanem (1999) studied the hydrogeology and hydrochemistry of the Faria drainage basin and environmental isotope analyses, and revealed that the Faria springs were found to be of calcium bicarbonate type and not polluted.

Wishahi and Khalid (1999) gave an idea about the chemistry and quality of the Jordan Valley aquifers through collecting and analyzing (for all main ions) 58 groundwater wells for penetrating the Jordan Valley aquifers. The study presented that the main chemical parameters showed high levels of concentration, where the Jericho wells showed the higher concentrations of the dissolved solids.

Qannam (2003), studies of hydrological, hydrogeological, geomorphological and hydrochemical that conduct during the period between 1998 and 2002 in the basin and Aroub Valley / Palestine. The hydrochemical study showed that the rain water is the only source of ground water recharge. Mixing with the waste water leaking from the poorly designed cesspits and the waste water conduit and/or the infiltration of the leachates from washing the piles of animals dung by the rainfall in winter are the main factors responsible for the modifications in the water types and quality recorded in the area.

Awadallah and Owaiwi (2005) studied the hydrogeology and hydrochemistry of springs and groundwater of Hebron District. Extremely polluted springs and wells with nitrate and no significant salinity problem are found. The microbiological quality test of the water indicates that only 20% of the springs and dug wells are coping with the standard value. The wide distribution of cesspools and septic tanks in the West bank cause rapid contamination of aquifer systems through karstic conduits in the area.

Khayat (2005) studied the hydrochemistry and isotope hydrogeology in the Jericho Area/ Palestine, chloride and TDS concentrations in the shallow Pleistocene aquifer systems in the Jericho area indicate a general trend of increasing salinity eastward and southward, and the groundwater quality varies from fresh carbonate groundwater in the springs in the west. The analyses of major ions, hydrogen and oxygen isotopes as well as carbons, and sulfur isotopes indicate that primary sources of the salinity.

Western Basin has several studies around it, from one of the studies, a study done by Shalash and Ghanem (2007) about Natuf drainage basin. The study involved collection and analysis by conventional and available instrumental methods for the hydrochemical parameters of water from twelve springs before and after recharge. Most of the springs in the study area are of good water quality for domestic and agricultural uses. The study show higher values of EC, SSP, SAR and TH. These springs contain uncountable colonies of Total Coliform and Fecal Coliform.

The chemical composition of the springs' water as well as stable isotopes $\delta\ ^{18}O$ and $\delta\ ^{2}H$ was studied by Abu Hilou (2008). Water quality study of Al Qilt springs showed moderate levels of major ions and higher concentrations of lead and cadmium than allowable concentrations for drinking water in three spring samples, whereas, some springs were microbial contaminated, which indicate the infiltration of pollutants in the recharge area of the springs.

Daghrah, (2009) studied the Pollution and water quality assessment of wadi Al-Qilt , results showed higher concentrations of lead and cadmium than allowable for drinking water in three spring samples, whereas, five samples out of ten were contaminated with fecal coliform, which indicate the presence of pollution sources in the recharge area. While results showed three samples from wadis were contaminated with aluminum, cadmium and lead.

Samhan et al. (2010) assessed the domestic water quality in the West Bank aquifers for major parameters such Chloride, Nitrate, Sodium, Potassium, Sulfate, and other biological indicators such as T. Coliform and F. Coliform. About 90 springs and wells used for domestic purposes were analyzed. The study showed that the main sources of contamination encountered in domestic sources in the West Bank aquifers are from domestic wastewater, agriculture activities and direct discharge of wastewater in wadis without any type of treatment.

Ghanem and Ghannam (2010) studied spring water hydrochemistry along the North- South profile in the Jordan valley, they concluded that an increase in the concentration trend of Na^+, SO_4^{2-}, NO_3^-, as well as of Fe, Co, Bi, Li was noticed towards the South. The majority of the spring water samples fall into the normal earth alkaline water group with prevailing bicarbonate and sulfate or chloride. The springs further to the South are classified as normal earth alkaline water with prevailing bicarbonate having high TDS concentrations and of Na-Cl water type.

Through search and viewing it is clear that there are many previous studies on the subject of the study, out some of the results that can be relied upon and utilized in order to complete this study, are as follows:

Ramesh (2012) studied the hydrochemical analysis and evaluation of groundwater quality in and around Hosur, Krishnagiri District, Tamil Nadu and India. Groundwater quality in and around Hosur area has been analyzed with work. The groundwater is alkaline in nature and total hardness is observed in all samples fall under hard to very hard category. The TDS falls under fresh water to saline categories. The fluoride concentration in the south region exceeds the permissible limit. The concentration of iron, lead, chromium is below the detectable limit in most of well samples except in the wells in industrial area (SIPCOT) has exceeds the safe limit. Major hydro chemical facies were $CaHCO_3$ type, mixed CaMgCl type and NaCl type facies identified using piper trilinear diagram.

Chindo et al (2013) studied the physicochemical analysis of groundwater of selected areas of Dass and Ganjuwa local government areas, Bauchi State, Nigeria, the physicochemical characteristics for groundwater sample such as pH, colour, odour, Hardness, chloride, alkalinity, total dissolved solids (TDS) and others , this parameter has been comparing with World Health Organization (WHO), it was found that some of the samples were non-potable for human consumption due to high concentrations of some of the parameters determined. An attempt was made to find whether or not the quality of ground water in the areas of study suitable for human consumption. All studies didn’t deal with the issue of Soreq catchment either directly and indirectly. Therefore, this study came as an answer for the quality of water in this important area.

Chapter Two

Description of the Study Area

2.1 Location of the study area

The area of the study is Soreq catchment which is located in the western part of the West Bank. Its location is within the western catchments and it has an area of 70 km^2. The selected catchment area lies within the coordinates between 134 – 146 E and 161-173 N, referenced on the Palestinian Grid (Figure 1).

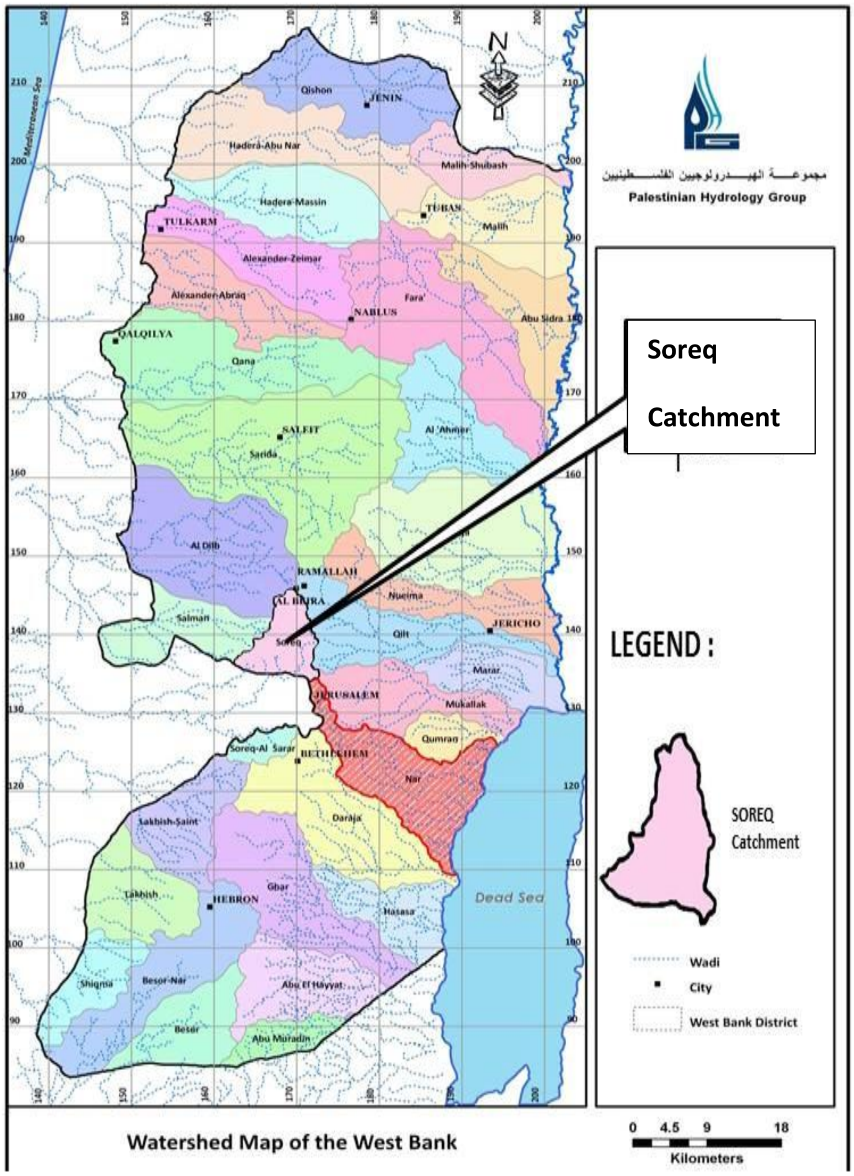

Fig.1: The Soreq catchment borders

The Soreq catchment borders are: Al Dilb catchment from the North, Quilt catchment from the East, Salman drainage basins from the West and Mukallak and Nar catchment from the South East (PHG, 2004).

Soreq catchment includes within its boundaries full or part of the 17 Palestinian communities (Aljib, Bier Nabala, Beit Iksa, Beit Suriek, Biet Hanina, Qalandia, Rafat, kafr aqab, Ala'maary camp, part of Ramallah city, Alraam, Dahiat albarid, Aljadeera, Bidu, Shufat, An Nabi Samwil and Albira) (PCBS, 1999) (Figure 2).

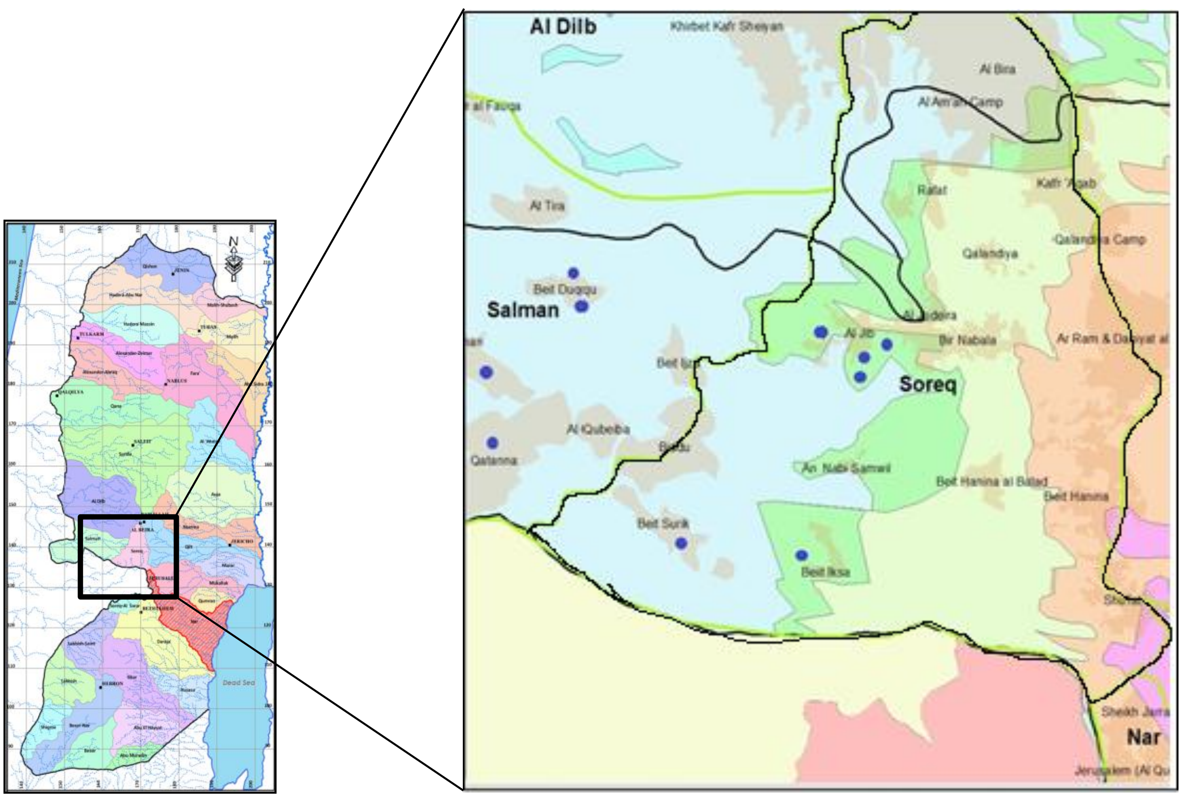

Fig.2: Location map of the Study Area

2.2 Population

Based on the study of the PCBS (2007), the Palestinian population of Soreq Catchment was estimated to be about 125,000.

2.3 Soils

The dominating soil associations in the mountains are Terra Rossas Brown Rendzinas and Pale Rendzinas . The soil associations in western part of the study area Brown Rendzinas and Pale Rendzinas and Brown Lithosols and Loessial Arid Brown soils. While in the eastern part of the study area, Bare Rocks and Desert Lithosols, and Brown Lithosols and Loessial Serozems are the dominated soil types Terra Rossas Brown Rendzinas and Pale Renzinas. (ARIJ, 1998).

2.4 Climate

Climatologically, the West Bank is part of the subtropical zone, which has two climate seasons with a short period of transition: the warm and dry season (summer) and wet cool season (winter). The climate of the West Bank constitutes a transition region from subtropical arid (south) to subtropical wet (north). The climate of the Soreq catchment ranges from arid to semi-arid. The monthly average temperature ranges from 7.5-10 ^{o}C in winter to 22 ^{o}C in the summer. The minimum temperature is -3 ^{o}C in January and the maximum is 40 ^{o}C in August (Ghanem, 1999).

2.5 Rainfall

Rainfall for Soreq catchment is limited to the winter and spring months, mostly between November and May; summer is completely dry. Snow and hail, although uncommon, may occur anywhere in the area especially over the mountains crests. In general, the distribution of rainfall is strongly influenced by the topography, with higher rainfall in the hills and mountains. Rainfall in the area also shows considerable inter-seasonal variation. The rainy days are estimated between 40-70 days per year. (PCBS, 2005).

The average annual rainfall in the eastern part of the district varies from 200 to 450 mm. In the western part of the Soreq catchment, the average annual rainfall is higher than the eastern part; it varies from 350 to 550 mm. In the mountains the average annual rainfalls vary from 550 to 700 m.

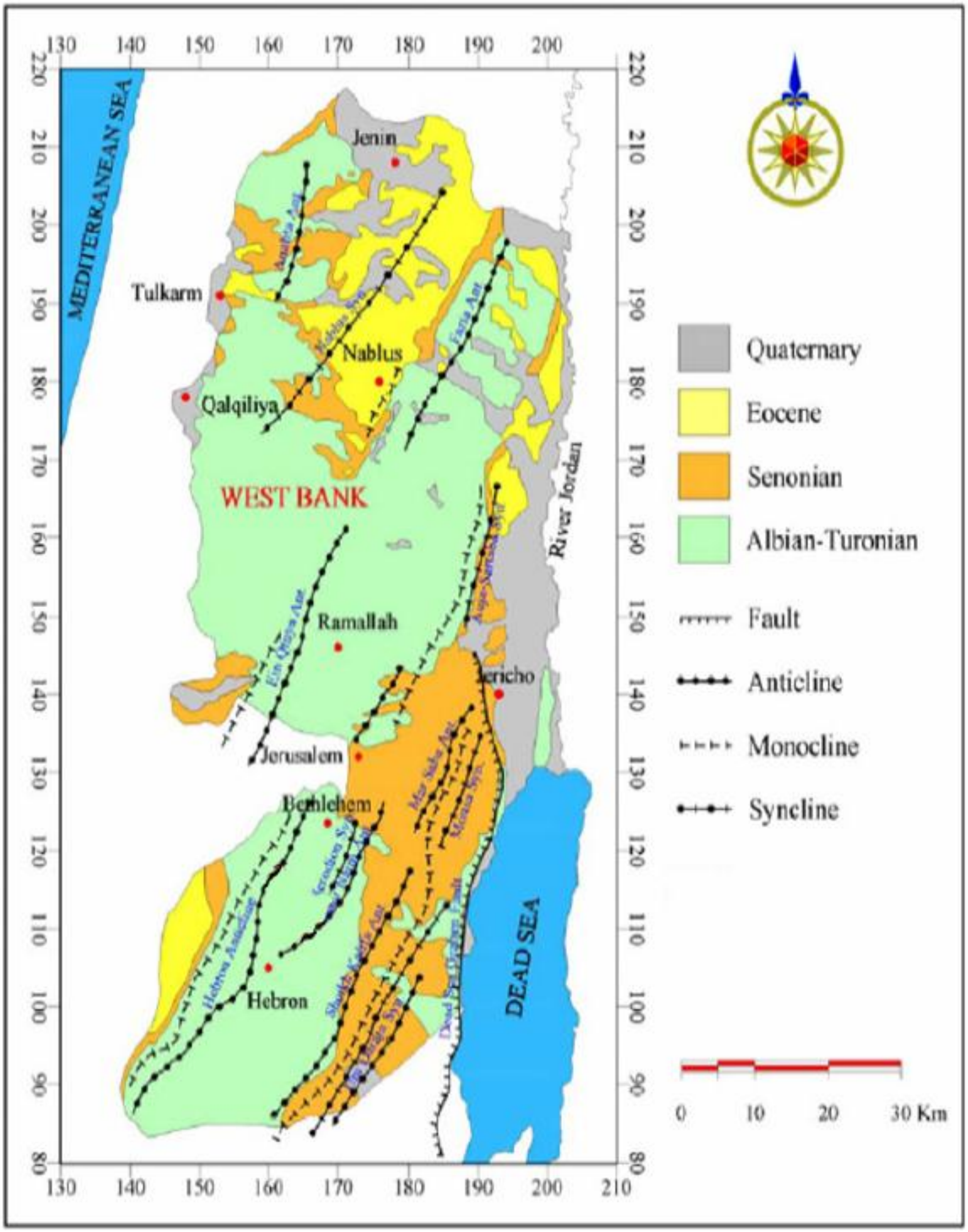

Fig.3: General geological and structural map of the West Bank (modified after Abed Rabbo et al., 1999;)

2.6 Geology and Stratigraphy of Soreq Catchment

The geological formations of Soreq catchment range in age from lower Cennomanian to Albian. Soreq catchment (Figures 4) is mainly covered by sedimentary carbonate rocks of the Cretaceous and Terdiary period. Lithological composition of these formations consists mainly of limestone, dolomite, marl, chalk, chert and alluvium.

The following paragraphs give an introduction to the general lithostratigraphy of the Soreq catchment. The lithology, thickness and other features relevant to the aquifer characteristics are presented briefly.

I. Kopar formation (Aptian to Albian)

It consists mainly of marl, marly limestone, and limestone. In some location it comprises of limestone and intercalation of marl.

II. Lower Beit Kahil formation (Albian)

The Lower Beit Kahil formation consists mainly of limestone, which is well bedded, fine crystalline and highly karstic, and sometimes dolomitic in the upper part. This formation has sometimes intermediate marl layers, and marl increases in downward direction. Its thickness ranges from 120-280 m. In some places the Lower Beit Kahil formation has dark grey dolomite, massively bedded, fine crystalline and hard.

III. Upper Beit Kahil formation (Albian)

The Lower Beit Kahil formation consists mainly of dolomite, marly dolomite, marl and at sometimes chert. Its thickness ranges from 40-220 m. In the study area this formation is exposed in Beit Anan, Katana and Beit Soreq.

IIII. Yatta formation (Lower Cenomanian)

Yatta formation consists of yellowish and brown and contains fine to medium crystalline dolomite and limestone, with marly intercalation, marly at bottom. In some places it consists of marly limestone, usually highly enriched with fossilized fauna. Its thickness lies between 50 m to 130 m. In the study area this formation is exposed in Beit Iksa and AL-Jib.

IIIII. Upper Middle Cenomanian- Turonian Rocks

In this study area these rocks are exposed in Beit Hanina , Bir Nabala , Qalandiya and Kafr Aqab. This formation is divided into three parts:

1- Hebron formation (Upper Middle Cenomanian)

Hebron formation consists of hard and massive dolomite or limestone. It is highly Karstic. Its thickness range from 20-120 m.

2- Bethlehem formation (Upper Cenomanian)

Bethlehem formation consists mainly of limestone and dolomite , chalky limestone, with marl and rich in faunal remains. In some places it is built up of dolomite , massive and coarse crystalline limestone lenses,. The thickness is 80- 270 m.

3- Jerusalem formation (Upper cenomanian – Turonian)

Jerusalem formation consists mainly of limestone, soft, thin- bedded, dolomitic, chalky and marly limestone. In some places it consists of limestone, hard and massive. Its thickness ranges from 90-130 m.

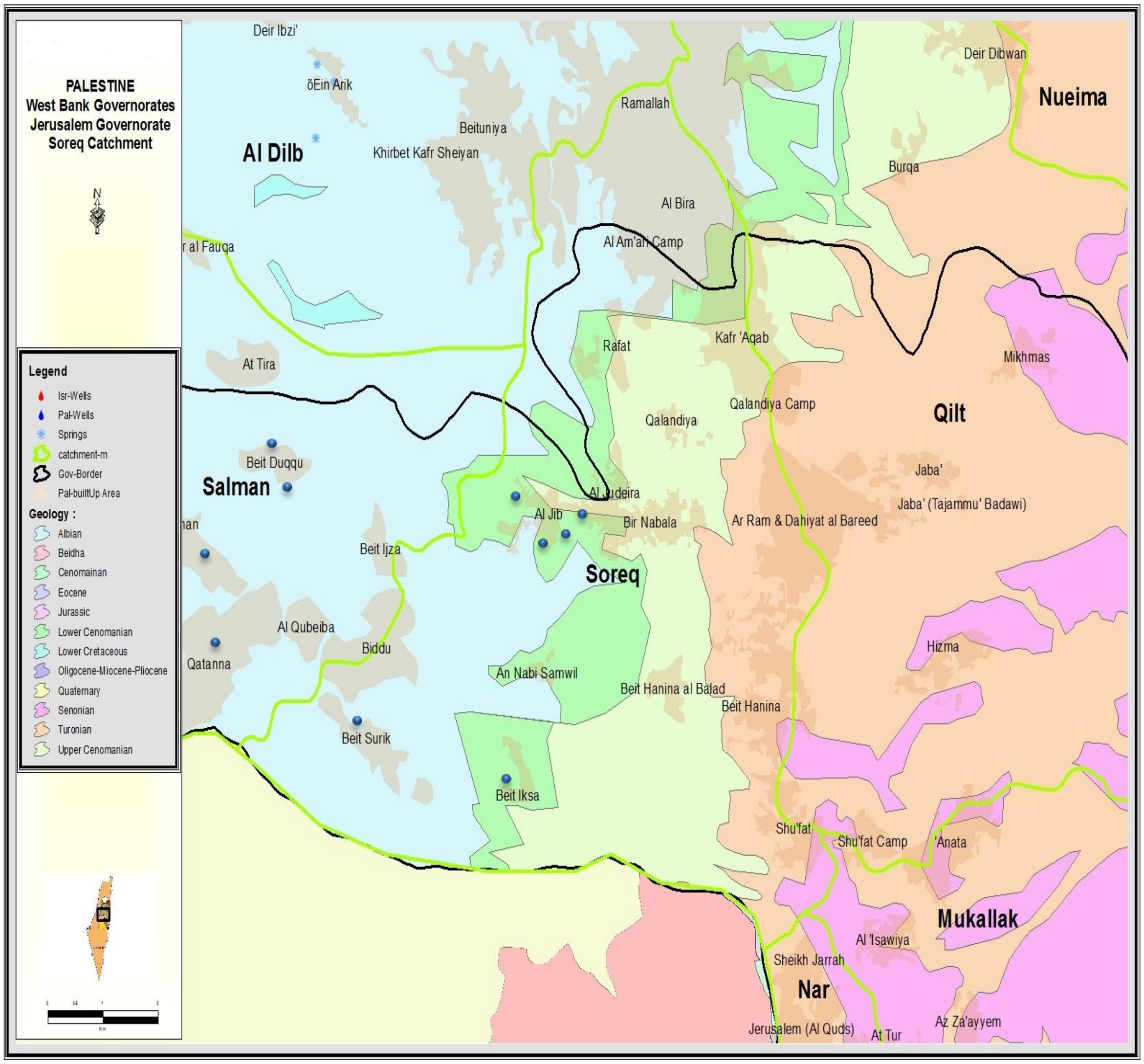

Fig.4: Geological formations in the Soreq catchment. (PWA 2013)

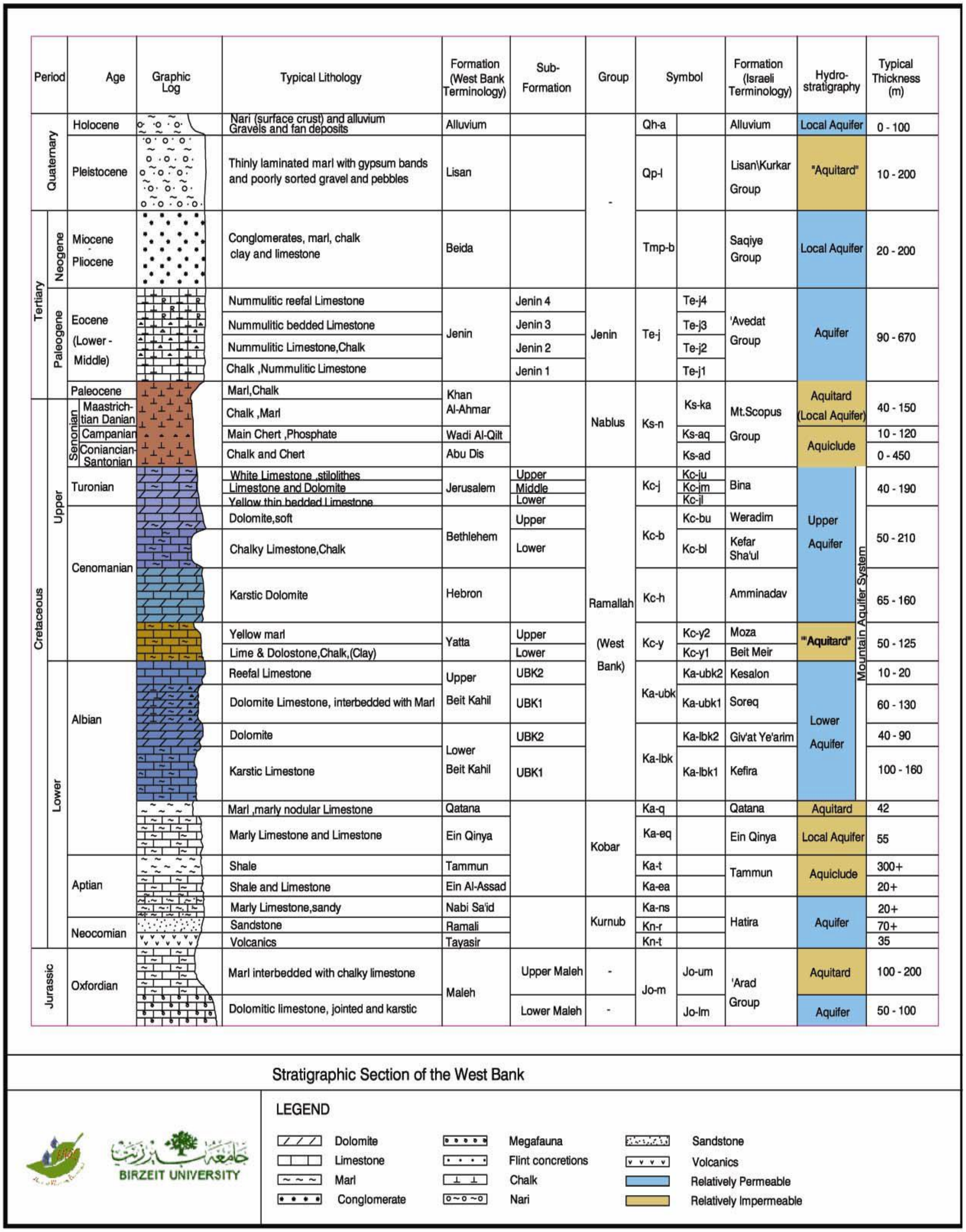

Fig.5: Stratigraphical columnar Section of the West Bank

2.7 Description of the springs

Despite the expansion of the water networks, the inhabitants are still using spring water to satisfy domestic needs, especially in the case of discontinuous supply in the networks. Springs such as Ein Qatana, Ein Beit Soreq and Ein Salman were still a significant source of drinking water. Spring water from Ein Ajab, Ein Jefna and Ein Abu Zaher was consumed from farmers and herdsmen (Table 1). Generally, the water of all the springs in this area is used for domestic purposes other than drinking. The uncontrolled disposal of the raw wastewater, and poorly designed cesspits and in the nearby fields were potential contamination sources endangering the water quality of these resources. Because there is no control on the water quality of the springs with respect to the pathogens and bacteria in the study area although it is very important, such control is highly recommended by this study.

(Table 1): The geological formation spring in the Soreq catchment

Spring Name	**Location**	**Emergent Formation**	**Formation**	**Water Use**
Ein Ajab	Beit Anan	Upper Beit Kahil	Albian	Agricultural
Ein Qatana	Katana	Upper Beit Kahil	Albian	Agricultural and drinking
Ein Beit Soreq	Soreq	Upper Beit Kahil	Albian	Agricultural and drinking
Ein Alshami	Beit Iexa	Yatta	Lower Cenomanian	Agricultural
Ein Salman	Beit Duqqo	Upper Beit Kahil	Albian	Agricultural and drinking
Ein Jefna	Beit Duqqo	Upper Beit Kahil	Albian	Agricultural
Ein Aziz	Aljeeb	Yatta	Lower Cenomanian	Agricultural
Ein Albalad	Aljeeb	Yatta	Lower Cenomanian	Agricultural
Ein Alqeblea	Aljeeb	Yatta	Lower Cenomanian	Agricultural
Ein Abu Zaher	Aljeeb	Yatta	Lower Cenomanian	Agricultural and drinking

Beit Anan Group

- Ein Al-Balad (Ein Ajab)

This spring is located on the eastern side of the village, this spring is dangerous because of pollution by the surrounding human activities such as the presence of cesspits, and extensive use of fertilizer. This spring used as a source of drinking water, and also to irrigate crops.

Qatanna Group

- Ein Qatanna

The Katana spring locates in the village center, the flow of this spring is strong in summer and winter, this spring water collected in big tank and used for drinking and irrigation, but this spring is endangered of pollution by cow dung, coming from cow farms in the settlements.

Beit Eksa Group

- Ein Al-Shami

Beit Eksa village, where many of the important springs, but the Israeli occupation confiscated most of these springs, Ein al-Shami, one of the most important of these spring is this village, is used for drinking and irrigating crops, but this spring is endangered of pollution by the surrounding human activities such as the presence of cesspits or extensive use of fertilizers, or as a result of near by existence of manure.

Beit Soreq Group

- Ein Beit Soreq

Ein Beit Soreq spring located south of the village of Beit Surik, with daily discharge of 70 m^3, the only source of water for the village, but now the water of this spring is used for drinking, plant irrigation and animal breeding, the spring is endangered of pollution by dumping site and fertilizers.

Beit Duqqo Group

- Ein Salman and Ein Jefna

Ein Salman spring located in the north of Beit Duqqo village, was shared between several villages, including Tira, because of the high flow, was used for domestic purposes, for drinking, irrigation, but is now used to irrigate crops, the spring is endanger of pollution by cesspits surrounding houses. Ein Jefna is located to the west of Beit Duqqo, its water is used to irrigate crops, the spring is in danger of pollution by fertilizers.

Aljeeb Group

- Ein Aziz, Ein Albalad, Ein Alqeblya and Ein Abu Zaher

Ein Aziz, Ein Alqeblya and Ein Abu Zaher springs, the water of these springs are used for plant irrigation. The springs are endangered of pollution by the surrounding human activities such as the extensive use of fertilizers, or as a result of near by existence of manure**,** but the Ein Albalad spring in danger of pollution by dumping site and cesspits of surrounding houses.

Chapter Three

Hydrochemistry

3.1 Introduction

Two factors are the fundamental control on water chemistry in drainage basins, the type of geologic materials that are present and the length of time that water is in contact with those materials. Chemical reactions that affect the biological and geochemical characteristics of a basin include acid-base reactions, precipitation and dissolution of minerals, sorption and ion exchange, oxidation-reduction reactions, biodegradation and dissolution and exsolution of gases (Winter et al. 1998). The groundwater quality is nearly of equal importance to quantity. Therefore it's necessary to make chemical, physical and bacterial analyses of groundwater to determine its suitability for different purposes (drinking and agriculture).

3.2 Field work, water sampling, analyses and field measurement

Field work and field surveys were basic modules in every aspect of this study, especially to identify and mapping the existing target water resources, water sampling and measurement that to be taken during the study. The surrounding environmental around each spring was studied. Data about water use and allocation, in addition to the water resource ownership and management was collected. The chemical analysis of spring water includes determination of the major, minor and trace metal constituents, and also the field measurements of the electrical conductance, hydrogen ions activity as well as the water temperature (Karanth, 2008). The physical parameters (EC, pH and temperature) must be taken in the field immediately after sampling, because water chemistry can change rapidly once a sample is extracted from a spring and exposed to light, warm, cold air, or other environmental factors (Sanders, 1998). The hydrochemical study for spring water in the study area involves the major, minor and trace ionic concentrations. Twenty two heavy metals are analyzed. Including, (Fe^2, Cd^2, Pb^2, Zn^{2+}, Mn^{2+}, B, As^{2+}, Be, Se, Ba, Tl, Cr, Al, V, Co, Cu , Ni, Sr, Bi, Mo, Ag, Li). Besides, these ionic concentration study also involves the salinity (total dissolved solids TDS), electrical conductivity (EC) and (pH). The water samples were collected from (10) springs in two periods, their locations are shown in Fig. (3.1), the first period was during November (2013), before rain. The second period was during March (2014), after rain.

3.3 Interpretation of the analyzed parameter

3.3.1 Physical properties

3.3.1.1 Temperature

Temperature affects all physical and chemical characteristics of groundwater, such as EC, pH and DO. Temperature measurements are recorded in degrees Celsius (^oC). All geochemical reactions depend on temperature (SCCG, 2006). Temperature increases with depth, about 2.9 ^oC for each (100 m) depth (Todd, 1980). The average temperature of the whole spring system in dry season is 20.2 ^oC with an average of 20.3 ^oC. Generally it is clear there is no abnormal temperature value recorded. The Temperature reflects the environmental of recharge, in this case, the Temperature reflects the winter Temperature in the study area, and this reflects the perched aquifer recharge of these springs.

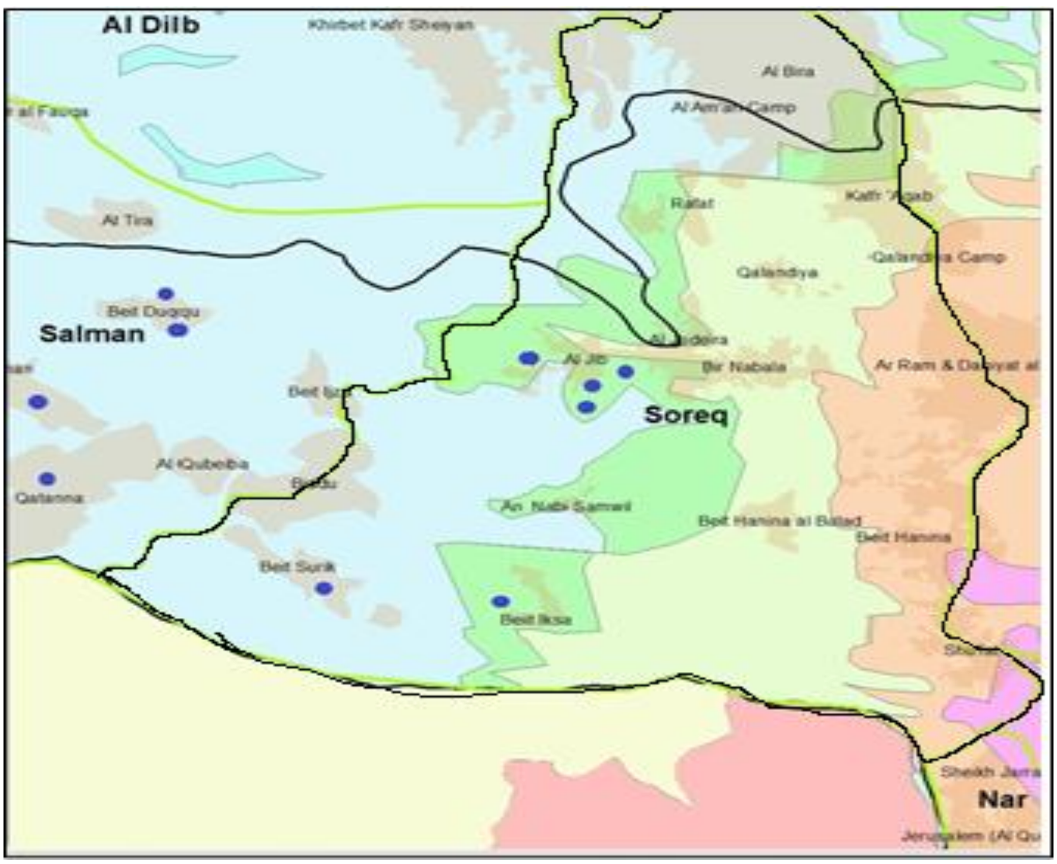

Fig.6: Location map of the springs of Soreq catchment and its surrounding

3.3.1.2 pH

The pH value is a master parameters in water chemistry. The pH of most groundwater results from the balance between the dissolved CO_2 gases derived from the atmosphere as well as biological activity and the dissolved carbonate as well as bicarbonates derived from carbonate rocks (Ghanem 1999). pH of the spring water in Soreq catchment in two period between about 6.5-8 which is neutral to slightly basic and in the allowed limit (6.5-8.5) according to WHO and PWA regulations. The dissolution and mobility of metals in natural water are greatly influenced by the (pH) (Thompson et al, 2007). The pH values of water samples ranges between 7.5-8 in dry season, and 7.1-8 in wet season.

3.3.1.3 Total dissolved solids

Total dissolved solids (TDS) comprise inorganic salts, principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates and some small amounts of organic materials that are dissolved in water. The TDS concentration is a secondary drinking water standard and is regulated because of its esthetic effect rather than a health hazard. Elevated TDS indicate that the dissolved ions may cause the water to be corrosive, of salty or brackish taste, resulting in scale formation, and interfere and decreased efficiency of hot water heaters. It may also indicate that water may contain elevated levels of ions that are above the primary or secondary drinking water standards, such as: elevated levels of nitrate, Arsenic, Aluminum, Copper, Lead, etc. (Qannam, 2003).

A general classification of spring water according to the TDS is shown in (Table 2).

(Table 2): Classification of spring water according to TDS (Todd, 1980)

Water class	TDS (mg/L)
Fresh	<1000
Brackish	1000-10,000
Saline	10,000-100,000
Brine	>100,000

The TDS for all water of springs samples were less than (1000 mg/L) in both periods, which means that water from all springs in Soreq catchment can be classified according to (Table 2) as fresh water, ranging in value of TDS for spring water between 550 mg /L and 200 mg /L.

3.3.1.4 Electrical Conductance (EC)

The electrical conductivity (EC) is a numerical expression of the ability of an aqueous solution to carry electrons. It is a function of the presence of ions and their total concentration, temperature of the solution and the valence of ions and their mobility's. The EC is the reciprocal of resistivity (R): EC = 1/R and is reported in millisiemens/cm (mS/cm) or µS/cm. The measurements conducted during this study for water samples from springs of Soreq catchment range between 440 – 1200 µS/cm in dry period, and range between 421 – 1385 µS/cm in wet period. The highest value of 1200 µS/cm, in dry period, and 1385 µS/cm in wet period, was recorded in Ein Biet Soreq in Soreq Village. The variation in EC in spring water is caused mainly by the variation in total dissolved solid, (Figure 7 and 8) from which shows the relation between TDS and EC values for both periods, it can be observed that linear correlation between them for the dry and wet periods. Since the EC and TDS are measurements of the total salt content, they must be directly proportional. The correlation between these two parameters for the analyzed samples in this study was plotted in (Figure 7 and 8), which showed a linear correlation with a mathematical approximation of (TDS mg/L = 0.55 EC µS/cm). The relationship between (EC) and (TDS) in the spring water of the study area is strong and the value of correlation coefficient (R) is close to one by equations (TDS = 0.46 EC + 20.2 with R^2 = 0.99)

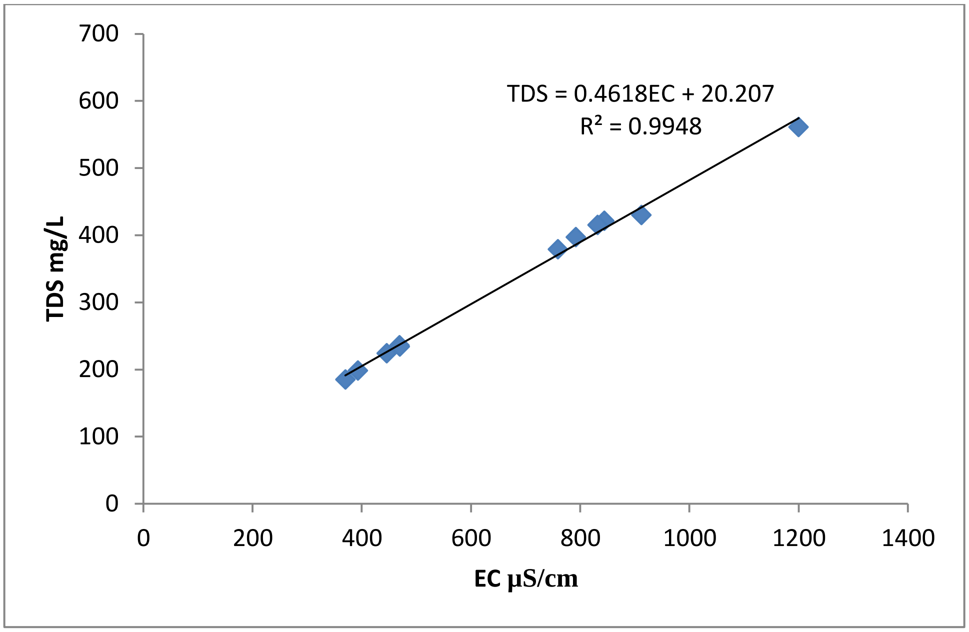

Fig.7: EC - TDS relationship of springs water samples in the study area for dry period

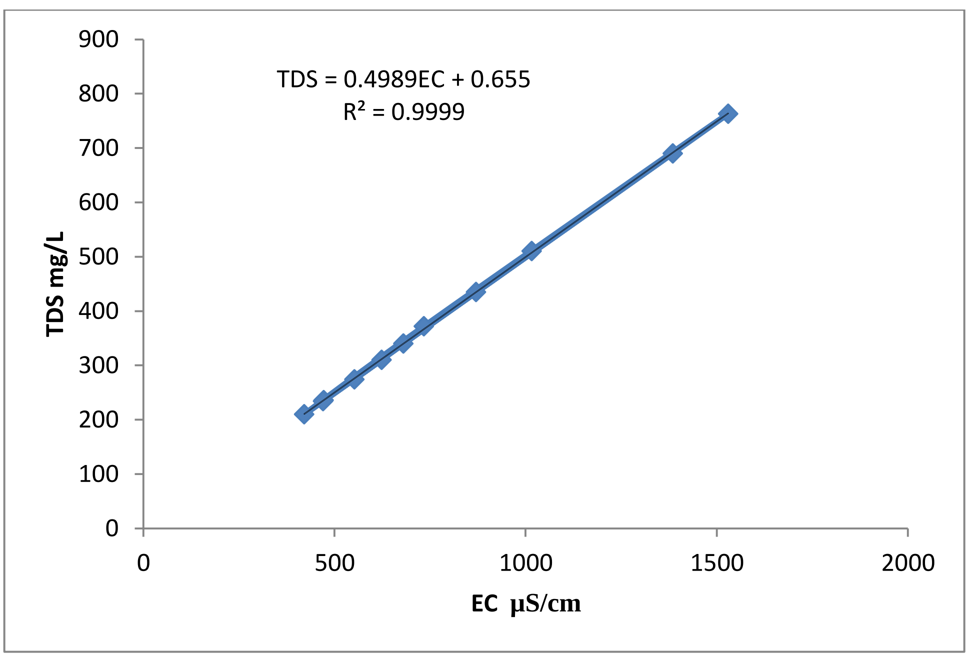

Fig.8: EC - TDS relationship of springs water samples in the study area for wet period

When comparing EC values for both periods with (Table 3) which shows the relationship between electrical conductivity and water mineralization, the type of Ein Jefna, Ein Abu Zaher, and Ein Jarut spring water is as moderately mineralized water, and the type of Ein Salman, Ein Albalad, Ein AlQebleya, Ein Alsahmi, and Ein Aziz spring water is highly mineralized water, and the type of Ein Ajab and Ein Katana spring water is slightly mineralized water, and the type of Ein Biet Soreq spring water is excessively mineralized water.

(Table 3): Relationship between electrical conductivity and water mineralization

EC µS/cm	Mineralization
<100	Very Weakly Mineralized water
100-200	Weakly Mineralized water
200-400	Slightly Mineralized water
400-600	Moderately Mineralized water
600-1000	Highly Mineralized water
>1000	Excessively Mineralized water

3.4 Hydro-Chemical properties

3.4.1 Cations

Ca^{2+} has a mean of 104.3 mg/L in the study area. A big range of Ca^{2+} is recorded in Ein Biet Soreq springs in both seasons, for Ein Aziz, Ein Albalad, Ein Salman, Ein Alshami, Ein Katana, and Ein Biet Soreq which had the concentration above 100 mg /L were as shown in (Figure 9). The concentration of calcium becomes higher in this spring because of longer residence time, which is the contact time between water and minerals, and because the weathering process of limestone, and dolomite. High levels of calcium and magnesium cause water to be hard, which is objectionable for domestic and industrial uses. The magnesium ion (Mg^{+2}) concentration of spring water samples is within the allowable level. The concentration of magnesium in the samples varies between 57 to 15.17 mg/L in Ein Biet Soreq and Ein Aziz in dry period and 59.3 to 14.24 mg/L the same springs in wet period. The respectively reason for the increase in magnesium in Ein Biet Soreq comes from dissolution of dolomite limestone.

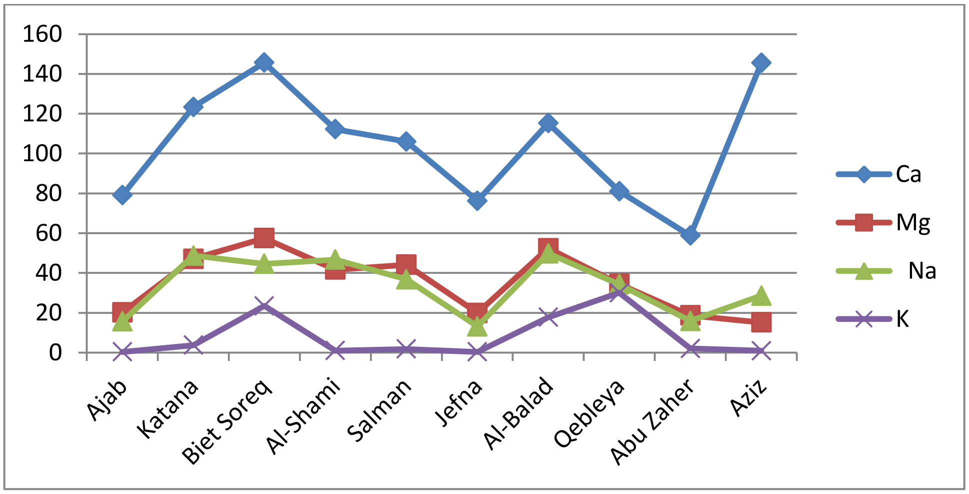

Fig.9: The anions concentrations of water samples of the study area in dry period

The concentration of sodium in the samples varies from a maximum of 49.84 mg/L in Ein Abalad to a minimum value of 13.18 mg/L in Ein Jefna in dry season while in wet season the maximum of 57.94 mg/L in Ein Soreq to a minimum value of 11.67 mg/L in Ein Jefna. The high concentration of sodium in Ein Albalad and Ein Soreq spring water samples comes from rock weathering. In addition of ions exchange. Sodium concentration decreases through the wet season because the dilution of water from rainfall. The concentration of potassium in the samples varies from a maximum of 30 mg/L in Ein AL-Qebleya to a minimum value 0.34 mg/L in Ein Ajab in dry season, and varies from a maximum of 52 mg/L in Ein Biet Soreq to a minimum value 0.29 mg/L in Ein Ajab in wet season. Reason for the increase in potassium in the Ein Al-Qebleya, Ein Biet Soreq and Ein Albalad, because of the Fertilizers. The ranges of potassium in November are less than that of March due to high discharge and dilution by water. By comparing anions concentrations of water samples with standard specification concentration (Table 4), it becomes apparent that all anions for all spring’s water samples, were within the WHO standards in both periods, except calcium which exceed the permissible limit in WHO standards.

(Table 4): Concentration of heavy metals (ppm) in spring's water samples in the study area

parameter	Dry season		Wet season		Average of two periods	PWA Standard 2001	WHO Standard 2007	Exceeding Limits
	Range	**Average**	**Range**	**Average**				
PH	7.5 - 8	7.8	7.1-8.4	7.71	7.7	6.5-8.5	6.5-8.5	**Not exceed**
TDS	200 - 500	335	210-763	414	374.5	1000	1000	**Not exceed**
EC	400 - 1000	680	421-1385	828.3	754.1	1000	1530	**Not exceed**
TH	223.7- 599.8	394.77	228.5-613.4	408.72	401.7	500	500	**Not exceed**
Ca^{2+}	76 – 145	104.3	59.2-148	106.73	105.5	70	75	**Exceed**
Mg^{2+}	15 - 50	35.13	14.2-59.3	34.5	34.8	50	125	**Not exceed**
Na^{+}	13 - 49	33.4	11.6-57.9	32.8	33.1	200	200	**Not exceed**
K^{+}	0.37-30	8.15	0.28-51.83	14.35	11.2	10	12	**Not exceed**
Cl^{-}	31.9 -219.8	105.28	88.63-230.4	127.6	116.4	250	250	**Not exceed**
SO_4	18 - 110	57.9	32-112	63.9	60.9	200	250	**Not exceed**
HCO_3^{-}	183 - 488	354	187.42-498	313.7	333.8	250	200	**Exceed**
NO_3	16 - 49	32	2.52-39.51	17.4	24.7	50	50	**Not exceed**
Fe	0 - 101.9	19.9	157.6-339	233.5	126.7	0.3	0.5	Exceed
Co	0.03 - 0.81	0.207	0.13-0.46	0.25	0.125	0.05	0.05	**Exceed**
Ni	0.13 - 5.87	1.368	0-2.6	0.28	0.824	0.05	0.02	**Exceed**
Cu	0.13 - 3.36	1.016	0-3.2	0.399	0.70	1	1	**Not exceed**
Zn	0.65 - 22.7	5.364	0-48.7	5.54	5.45	5	3	**Exceed**
Cd	0.01 - 0.03	0.013	0-0	0	0.0065	0.05	0.003	**Not Exceed**
Mn	0.01 -15.79	2.053	0-4.7	0.772	1.41	0.5	0.1	**Exceed**
Pb	0.04 - 0.4	0.15	0-1	0.162	0.15	0.1	0.01	**Exceed**
Be	0- 0.01	0.001				0.003	0.004	**Not exceed**
B	29.8-159.2	65.9	22.5-168.9	65.8	65.8	1	1.0	**Exceed**
As	0.27- 11.29	2.7				0.05	0.05	**Exceed**
Se	0.38 - 1.15	0.83				0.05	0.05	**Exceed**
Ba	8 - 63.77	24.9	11.5-69	32.1	28.5	2	1	**Exceed**
Tl	0.02 - 0.20	0.55	0-0.48	0.05	0.3	0.005	0.002	**Exceed**
Al	0.06- 23.09	10.46	0-27.1	7.06	8.76	0.3	0.2	**Exceed**
Cr	0.04 - 1.38	0.41	0-1.1	0.22	0.305	0.05	0.05	**Exceed**

3.4.2 Anions

Concentrations of bicarbonate in groundwater is acceptable by the value of 500 mg/L (Todd, 1980), It is clear from (Figure 10) the concentration of the both season is less than 500 mg/l, the concentration bicarbonate in springs is acceptable for drinking purposes. The ranges of bicarbonate in March are less than that of November due to high discharge.

For sulfate, the acceptable levels of sulfate in groundwater are up to 250 mg/L (Todd, 1980), The concentration of sulfate in the samples varies from a maximum of 110 mg/L in Ein Albalad to a minimum value of 18 ppm in Ein Ajab in dry season, and varies from a maximum of 112 mg/L in Ein Biet Soreq to a minimum value 18 mg/L in Ein Ajab in wet season. It is clear from (Figure 10) and (Table 4) the concentration of the both season is less than 250 mg/L. The increase of sulfates in Ein Albalad and Ein Biet Soreq because of the intensive agriculture surrounding springs.

A big range of Cl^- is recorded in Ein Albalad is due to concentrations of because intensive agriculture surrounding springs. Chloride in spring water is acceptable when less than 250 mg/L (WHO, 1996). It is clear from (Figure 10) and (Table 4) that concentration of chloride in the dry season is less than 250 mg/L, the concentrations of chloride in springs is acceptable for drinking purpose. But in wet season some springs are higher than 250 mg/L like Ein Albalad spring, due to of pollution by domestic waste and human activities. The concentration of anion and cation in Ein Biet Soreq and Ein Albalad is higher as it is clear in (Figure 10); the main sources of those concentrations in the spring water are dumping sites and cesspits of surrounding houses, and human activities and use of fertilizers in addition to concentration weathering process.

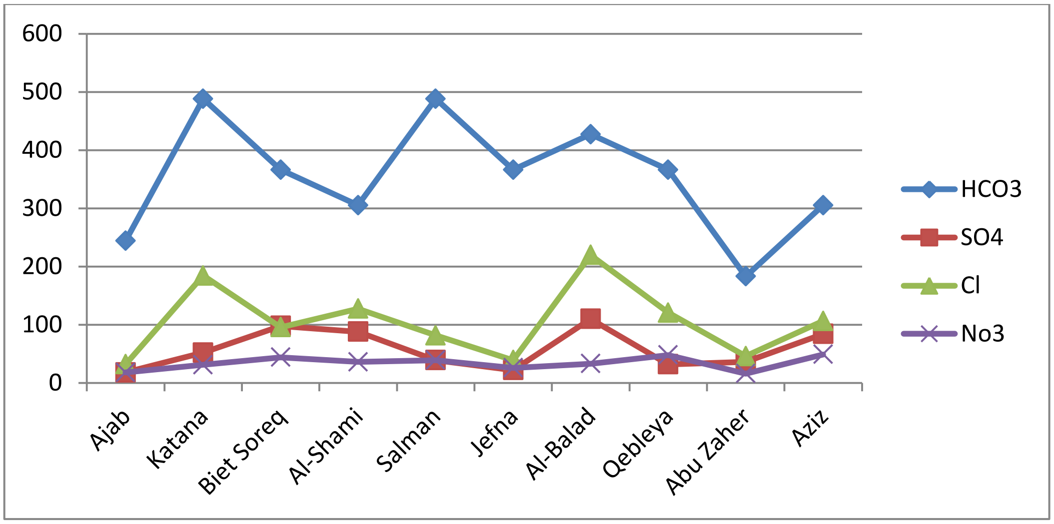

Fig.10: The cations concentrations of water samples of the study area in dry period

The presence of nitrates in groundwater above the WHO guidelines of 45 mg/L makes water toxic for humans, poultry and cattle (Manahan, 2001). The NO_3^- has a mean of 32 mg/L for the samples; the concentration of nitrate varies from 16 mg/L in Ein Abu Zaher to 49 mg/L in Ein Aziz for dry season and between 2.5 mg/L in Ein Jefna to 39.5 mg/L in Ein Biet Soreq in wet season. The concentrations of NO_3^- show moderate values below the WHO limits <50 mg/L. The increases of nitrate in some springs such as Ein Aziz and Ein Biet Soreq due to fertilizes process and cesspits near these springs, recorded in the analyzed water samples is presented in (Figure 10) and (Table 4) . The concentration of nitrite in wet season is less than concentration in dry season due to the dilution by water and short residence time.

3.4.3 Heavy elements (Trace elements)

Represent a common type of chemical pollution in water. Heavy elements can be found naturally in bedrock and sediment or they may be introduced into water from industrial sources and household chemicals. Heavy metals harm humans through direct ingestion of contaminated water or through accumulation in the tissues of other organisms that are eaten by humans. Heavy metals and trace elements in subsurface environments come from natural and anthropogenic sources. The weathering of minerals is one of the major natural sources. Anthropogenic sources include fertilizers, industrial effluent and leakage from service pipes (Tood, 2007). In the area, industrial and agricultural activities are the major contamination of water sources, the following are some common heavy metals found in water: Twenty two heavy metals are analyzed in both seasons. Include, (Fe^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}. Mn^{2+}, B, As^{2+}, Be, Se, Ba, Tl, Cr, Al, V, Co, Cu, Ni, Sr, Bi, Mo, Ag, Li). These samples were analyzed by using ICP emission instrument, the concentration of Heavy metals in spring water samples are presented in appendix (3a and 3b) and (Table 4).

The manganese concentration in spring samples in the current study varies from 0.01 - 15.79 ppm in dry season and between 0.05 – 4.69 ppm in wet season. The high concentration of magnesium in spring samples in the study area comes from dissolution of dolomite limestone, depends on CO_2 solution. The cadmium concentration varies from (0.01 - 0.03) ppm in dry season and between (0-0) ppm in wet season. It is clear that all springs of the study area are polluted with cadmium ion in dry season because its concentration exceed the permissible limit in comparison with (Table 4), except the spring Ein Alsami, Ein Jefna and Ein Abu Zaher). This is attributed to agricultural activities (fertilizers uses) in the recharge areas, and waste disposal in the study area. All springs of the study area are not polluted with cadmium ion in wet season because there is not enough time for water to react with rocks.

Zinc concentration in spring samples ranges from 0.65 - 22.7 ppm in dry season, but in wet season three springs water polluted in zinc. The highest value recorded in Ein Katana is 48.76, 4.26 in Ein Albalad and 2.48 in Ein Abu Zaher. Zinc concentration in this spring water is higher than the permissible limits in comparison with (Table 4). This means zinc pollution in this spring water of the study area. Pollution due to persistent leaching along the top layers of the soil and these springs are also contaminated solid waste, such as cans. The high occurrence of zinc in the sampled water implies that the water is not safe for human consumption particularly drinking and cooking.

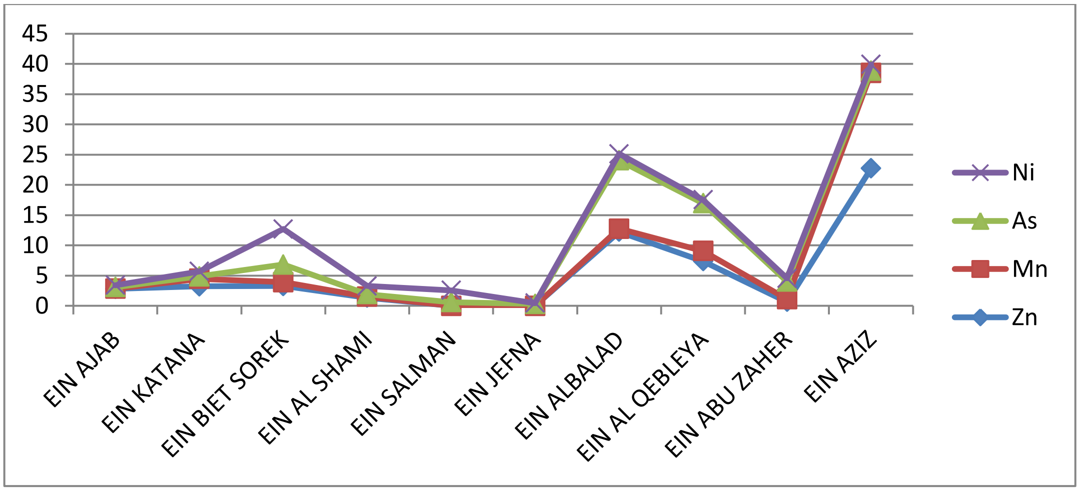

Fig.11: The concentration of (Ni, As ,Mn, Zn) in springs water – dry

The iron concentration in spring samples varies from 0 - 101.97 ppm in dry season and between 154.08- 300.23 ppm in the wet. It is clear that the Ein Aziz, Ein Ajab and Ein AL-Qebeya, contain higher iron ion than the permissible concentration in dry season, but in wet season all springs of water contain high amount of iron. This high concentration of iron can be attributed to the agricultural activities (fertilizers uses) because these springs are located within agricultural regions, in addition to weathering of clay minerals in Quaternary deposits which cover the study area. The high Fe content is related to the weathering of mineral grains, and in some places high concentration of iron in this spring is due to iron pipe placed inside these springs.

The lead concentration varies from 0.04 to 0.4 ppm in dry season and between 0 to 1.01 ppm in wet season. In wet season two spring water contain high amount of lead , Ein Jefna 1.01 ppm and Ein Aziz 0.62 ppm . It is clear that some springs of the study area contain high amount of lead ion like Ein Aziz , Ein Ajab , Ein Biet Soreq and Ein Jefna in dry season, because its concentration exceed the permissible limit about the WHO standards. This is attributed to agricultural activities (fertilizers uses) in the recharge areas, in addition to agricultural and human activities in the study area, and the presence of some old plumbing in these springs, in addition to leakage household sewage.

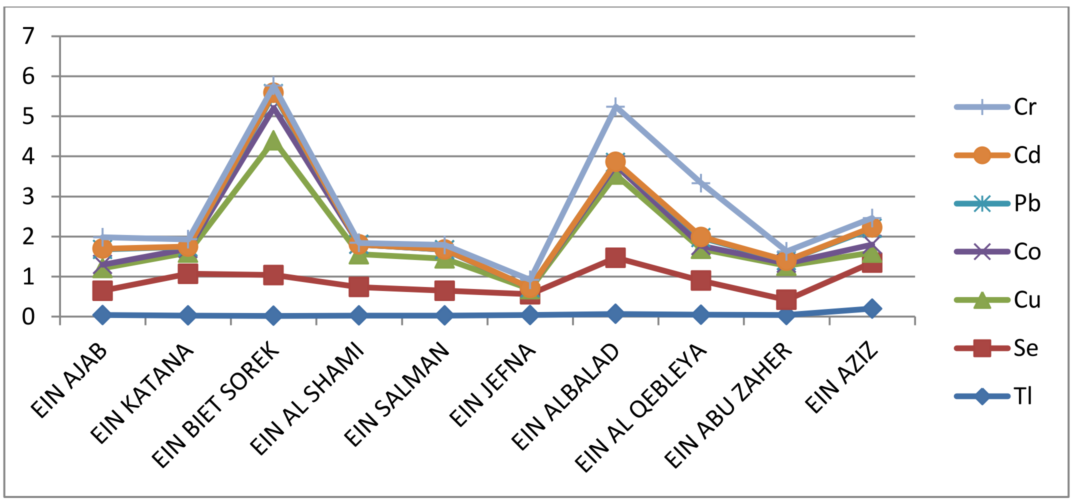

Fig.12: Represents the concentration of heavy metals in spring – dry

The arsenic concentration varies from 0.27- 11.29 ppm in dry season. It is clear the all springs of the study area contain high amount of arsenic, because its concentration exceed the permissible limit about the WHO standards. But the higher of these springs are Ein Albalad and Ein AL-Qebleya. This is attributed to agricultural activities (fertilizers uses) and Industrial effluent which received within these springs.

The Boron concentration varies from 29.8-159.2 ppm in dry season and between 22.53-168.91 ppm in wet season. The high concentration of heavy metal in studied area caused mainly by the pollution of domestic effluents. It can also be dispersed in spring through fertilizer application.

Cobalt concentrations of water samples of the studied area range between 0.03 - 0.81 ppm with an average of 0.21ppm in dry season, and between 0.13- 0.69 ppm in wet season. It is clear that all springs of the study area contain high amount of cobalt ion in both seasons and this is attributed to agricultural activities (fertilizers uses) in the recharge regions, in addition to agricultural activities and waste disposal in the study area. Nickel concentration in water samples of the studied area range between 0.13 - 5.87 ppm with an average of 1.37 ppm in dry season. While in wet season just three springs polluted in Nickel, the higher value recorded in Ein Beit Soreq 2.67 ppm, is clear in (Figure 13), Ein Albalad 0.22 ppm and Ein Salman 0.05 ppm as. By comparing nickel concentrations of water samples with standard specification concentration (Table 4), it becomes apparent that all spring of the study area are polluted with nickel ion in dry season and three in wet season. Copper concentration of water samples of the studied area range between 0.13 - 3.36 ppm with an average of 1.016 ppm (Table 4), in wet season just two spring water contained copper , Ein Albalad 3.2 ppm is polluted and Ein Biet Soreq 0.8, and the other springs did not contain copper ions. Ein Biet Soreq and Ein Albalad are polluted with copper ion in both seasons, because its concentration exceeds the permissible limit, and this is attributed to lay waste inside these springs, such as metallic materials, iron and copper in addition to fertilizer.

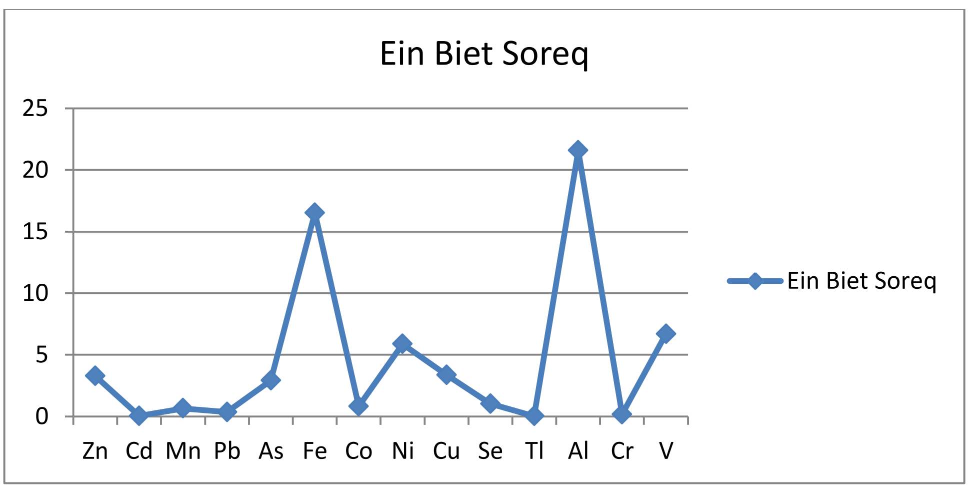

Fig.13: Some of heavy metals for Ein Biet Soreq in dry period

Barium concentration in water samples of the studied area range between 8 - 63.77 ppm with an average of 24.9 ppm, and between 69.04 – 11.52 ppm in wet season. The higher value from Barium ion recorded in both seasons, in Ein Biet Soreq spring water. All springs of the study area are polluted with Barium ion because its concentration exceed the permissible limit, this is attributed to discharge of drilling wastes, discharge from metal refineries, and erosion of natural deposits in the recharge areas, in addition to agricultural and industrial activities and waste disposal in the study area.

Selenium concentration in water samples of the studied area range between 8 - 63.77 ppm with an average of 24.9 ppm in dry season. Chromium concentration in water samples of the studied area range between 0.04 - 1.38 ppm with an average of 0.41ppm in dry season, and 0.01 - 1.1ppm in wet season. Barium concentration in water samples of the studied area range between 8 - 63.77 ppm with an average of 24.9 ppm in dry season, and 11.52 - 69.04 ppm in wet season. Thallium concentration in water samples of the studied area range between 0.02 - 0.20 ppm with an average of (0.55 ppm) in dry season, in wet season just two springs water contain Thallium , Ein Aziz 0.48 ppm and Ein Albalad 0.02 ppm.

The World Health Organization has recommended that aluminum levels in community water supplies should not exceed 0.2 ppm. Aluminum concentration in water samples of the studied area range between 0.06- 23.09 ppm with an average of 10.46 ppm in dry season, and 0 - 27.08 ppm in wet season. it becomes apparent that all spring of the study area contain high amount of Aluminum ion, but higher concentration in Ein Beit Soreq, Ein Albalad and Ein Qebleya, this is attributed to discharge of drilling wastes, discharge from metal refineries, and erosion of natural deposits in the recharge areas, in addition to agricultural and industrial activities and waste disposal in the study area.

The concentration of heavy metals (Zn^{+2}, Cd^{+2}, Mn^{+2} Pb^{+2}, B, As^{+2}, Co, Cu, Ni , Se, V and Fe^{+2}) in all spring water samples of the study area exceed with WHO (2007), as shown in (Figure 12 & 13), Especially in Ein Aziz , Ein Albalad, Ein Alqebleya and Ein Biet Soreq, the main sources of those concentrations in the spring water are human activities and use of fertilizers and industrial activities (metal) in addition to concentration weathering process (WHO, 2006) .

3.5 Microbiological analysis

The discharge of wastes from municipal sewers is one of the most important water quality issues world-wide. It is of particular significance to sources of drinking-water. Municipal sewage contains human waste and water contaminated with these effluents may contain pathogenic (disease-causing) organisms and, consequently, may be hazardous to human health if used as drinking-water or in food preparation. Fecal contamination of water is routinely detected by microbiological analysis. Different micro-organisms can be found in natural groundwater and surface water. The most important organisms are bacteria, viruses, fungus and algae, which makes water objectionable for domestic purposes and health threatening. The presence of pathogenic bacteria in water indicates the degree of contamination in the water and is a common indicator of water polluted by human wastes. The coliform group is the principal indicator of suitability of water for domestic and other uses (Ghanem 1999). Analyses for fecal Coliform (FC) and total Coliform (TC) is shown through the (Table 5).

(Table 5): The Fecal and Total Coliforms of water samples of the study area

Name of the spring	Dry season		Wet season	
	T.C Cfu/100ml	F.C-Cfu/100ml	T.C Cfu/100ml	F.C-Cfu/100ml
Ein Jefna	62	Nil	42	Nil
Ein Ajab	40000	32	7	Nil
Ein Jaruot	2740	Nil	1500	Nil
Ein Katana	11000	Nil	500	3
Ein Abu Zaher	3590	Nil	5401	Nil
Ein Albalad	56000	1175	18900	Nil
Ein Biet Soreq	1290	8	350	2
Ein Alshami	3490	Nil	312	Nil
Ein Aziz	2200	Nil	70	Nil
Ein Salman	8900	3	13990	16

3.5.1 Fecal Coliform Bacteria

The standard value of Fecal coliform bacteria according to WHO is zero, in this study for the dry period, only Ein Albalad spring had uncounted number of fecal coliform bacteria, Also Three springs (Ein Ajab, Ein Beit Soreq and Ein Salman) had fecal coliform bacteria Respectively 32, 8, 3. The other of the springs had not any fecal coliform bacteria. For the water samples analyzed in wet period three springs (Ein Beit Soreq, Ein Katana and Ein Salman) had fecal coliform bacteria Respectively 2, 3, 16 CPU/100ml. The other of the springs had not any fecal coliform bacteria.

3.5.2 Total Coliform Bacteria

According to WHO (2001), the standard value of total coliform bacteria is zero. In this study for the dry period, three springs (Ein Ajab, Ein Katana and Ein Albalad, had uncounted number of coliform bacteria. 80% of the springs had total coliform bacteria between 62 – 8900 col/100ml water. For the water samples analyzed in wet period three springs (Ein Albalad, Ein Salman and Ein Abu Zaher) had uncounted total coliform bacteria, and four springs had total coliform bacteria between 312-1500 col/100ml, (Ein Alshami, Ein Beit Soreq, Ein Katana and Ein Jaruot) and three springs had total coliform between 7-70 col/100ml, (Ein Ajab, Ein Jefna and Ein Aziz).

It is shown that Ein Albalad, Ein Ajab, Ein Biet Soreq and Ein Salman contain uncountable colonies of FC and TC, which reveals contamination from wastewater from sewerage system near Ein Al-Balad and cesspits near Ein Ajab, Ein Biet Soreq and Ein Salman. For Ein Katana, Ein Abu Zaher and Ein Al-Shami spring show uncountable TC, this is referred to sheep herds and manure piles near the spring outlet, especially katana spring, located under dairy farms belonging to the Israeli settlements. It could be concluded that all the springs are contaminated with coliform bacteria; therefore they are not suitable for drinking unless being treated. Boiling, sun disinfection, or chlorination of the water are possible treatment techniques.

3.6 Water origin

The change of groundwater chemistry is very slow due to the effect of nature of rocks and movement of groundwater (Hem, 1985). Knowledge of groundwater quality can provide important insights into the nature of the resource. Also evaluation of groundwater can provide inferences of the reactions that produce natural water chemistry. The quality of groundwater depends on the purpose; it will be used for drinking water, industrial and irrigation. In order to set criteria for quality of water, measurements of chemical, physical and biological properties must be done under standards methods (Winter et al. 1998).

3.6.1 Springs water classification

3.6.1.1 Piper diagram

According to Langguth (1966), using piper diagram, this is trainer plot that permits the classification of water samples into seven water types. On a piper diagram, the chemical results of samples from the springs in Soreq catchment were plotted on such diagram using special software for windows Aquachem. The Piper - plot shows that these springs are located between the areas of earth alkaline water with increased portion of alkali with prevailing bicarbonate and alkaline water with prevailing bicarbonate in both seasons (Figure 14 & 15).

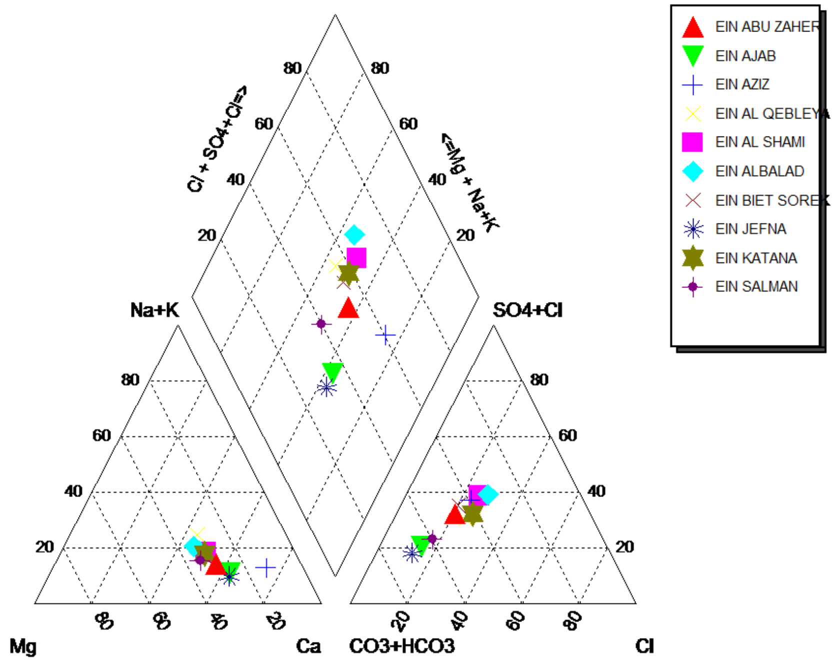

Fig. 14: The Piper diagram in the dry period

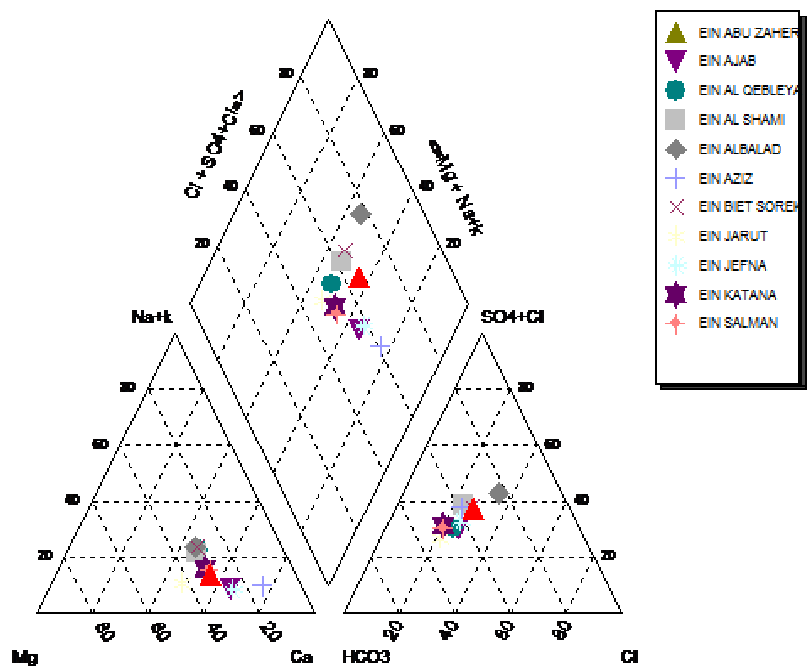

Fig.15: The Piper diagram in the wet period

3.6.1.2 Water Type

The hydrochemical characteristics and water types of spring's water based on the percentages of anions and cations are illustrated by Piper trilinear diagram, (Appendix 6) show that 52% of the samples have a water type of Ca-Mg-HCO^-_3, 48% of the samples show water type of Ca-HCO^-_3 and Ca-Cl-HCO^-_3. nature which indicates interaction with limestone rocks. Based on classification for water types (Figure 14 and 15), there are no obvious changes in the chemical composition of spring's water, during the study period 2013- 2014.

The that HCO_3^- is the dominant anion in all springs and ranges between 183 to 497 mg/L and Cl^- is the second abundant anion which ranges between 31.9 -301 mg/L. SO_4 is the third abundant anion while, NO_3^- concentrations are moderate compared to the dominant anions. The sequence of anions concentration is $HCO_3^- > Cl^- > SO_4^{-2} > NO_3^-$.
The sequence of cations in the study area is $Ca^{+2} > Mg^{+2} > Na^+ > K^+$. As shown in (Figure 16) for Ein Beit Soreq.

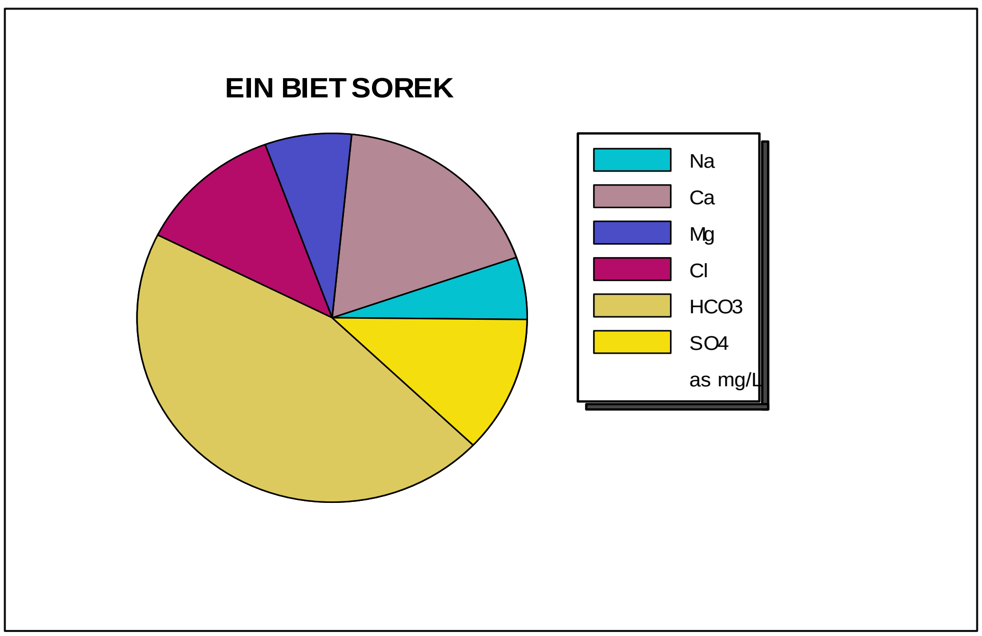

Fig.16: Cations and anions concentrations for Ein Beit Soreq spring

3.7 Spring water suitability for different purposes

Water quality refers to the chemical, biological and physical characteristics of the water. The required water quality is determined by the purpose for which the water is to be used (domestic, urban, agricultural or industrial). The evaluation of the water, for any purpose, is based on the characteristics of the water compared to standard for that use. By standard it is meant the consumer over the life of consumption (WHO, 2007). Therefore it is necessary to evaluate groundwater suitability for these purposes and especially for human drinking .This evaluation is normally carried out by comparing its hydrochemical parameters with some standard limits set for the different purposes as follows:

3.7.1 Spring water suitability for human drinking purposes

The hydrochemical investigation is the first aim to assess of groundwater suitability for all purposes. Groundwater suitability depends on several parameters (major and minor elements, inorganic, organic chemicals and biological constituents). For the purpose of evaluating the suitability of groundwater for human drinking, Palestine standard (PWA, 2001) and World Health Organization standard (WHO, 2007) were used to determine its suitability as drinking water in the study area.

The average of two periods (dry and wet) for the analyzed water samples by (ppm) unit are compared with WHO, (2007) and PWA (2001) standards as shown in (Table 4). As a result the spring water in study area of some springs is unsuitable for human drinking purposes like Ein Beit Soreq and Ein Albalad, where in the case of suitable ones element, another element is not suitable.

3.7.2 Spring water suitability for agricultural and irrigation purposes

The productivity of agricultural crops depends on the quality of plants, its resistance to environmental conditions, its ability to retain water, the properties of the soil structure, the irrigation method used and other factors. The plants tolerance for total dissolved solids and electrical conductivity in water which uses in irrigation are different depends on the quality of plants (Todd, 1980). Salts in the irrigation water could negatively affect the growth of plant by changing the osmotic conditions in the root zone which would decrease or limit the water uptake (a physical effect). Some toxic constituents such as boron might influence the metabolic reactions (a chemical effect). Salt may also affect the soil by changing the soil structure and aeration, which would indirectly affect the growth of plants (Tood, 1980).

3.7.2.1 EC

According to classification proposed by Todd (2007) as shown in (Table 6) all water samples of the study area are suitable for growing most types of crops. The suitability of water for irrigation is determined by its mineral constituents and the type of the plant and soil to be irrigated.

(Table 6): Todd classification (2007) for the tolerance of crops by relative salt concentrations for agriculture.

Crop Division	Low Salt Tolerance crops **Ec (µS /cm)**	Medium Salt Tolerance crops **Ec (µS /cm)**	High Salt Tolerance crops. **Ec (µS /cm)**
Fruit Crops	**0 - 3000** Limon, Strawberry, Peach Spricot, Almond, Plum Orange, Apple, Pear	**3000 - 4000** Cantaloupe, Olive, Figs, Pomegranate	**4000 - 10,000** Date palm
Vegetable Crops	**3000 – 4000** Green beans, Celery, Radish	**4000 - 10,000** Cucumber, Peas, Onion Carrot, Potatoes, Sweet Corn, Lettuce, Cauliflower, Bell pepper, Cabbage, Broccoli, Tomato	**10000 - 120,000** Spinach, Garden beets
Field Crops	**4000 – 6000** Field beans	**6000 - 10,000** Sunflower, Corn (field) ,Rice, Wheat	**10,000 - 16,000** Cotton, Sugar beet.

3.7.2.2 Salinity / TDS

According to the classification in (Table 7), Ein Biet soreq, Ein Salman , Al-Balad and Aziz spring are considered as high saline and cannot be used for irrigation. Other springs in the area are of medium salinity and can be used for irrigation purposes. Classification of Soreq springs according to salinity during the study period is listed in Appendix (4). Graphical representation of EC- SAR is illustrated by Wilcox diagram (Figure 17 & 18).

(Table 7): Grouping of irrigation water based on EC and TDS (Richard, 1954)

TDS (mg/L)	EC μS/cm	Water Class	Remarks
<200	<250	C1	Low salinity hazard: can be used for irrigation With most crops on most soils.
200-500	250- 750	C2	Medium salinity hazard: can be used to irrigate plants with moderate salt tolerance if moderate amounts of leaching occur.
500-1500	750- 2250	C3	High salinity hazard: can not be used on soils with restricted drainage. Can be used to irrigate plants with high salt tolerance.
1500-300	2250- 5000	C4	Very high salinity hazard: not suitable for irrigation under ordinary conditions. It can be used for irrigation occasionally under very special circumstances.

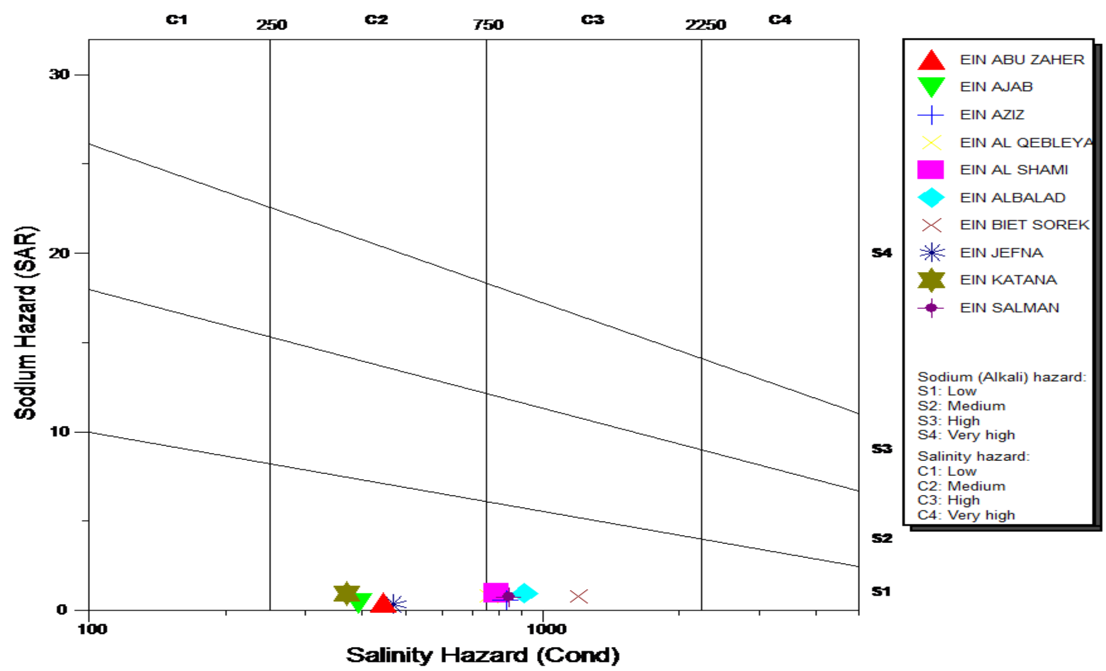

Fig.17: Wilcox classification of the water samples in dry season

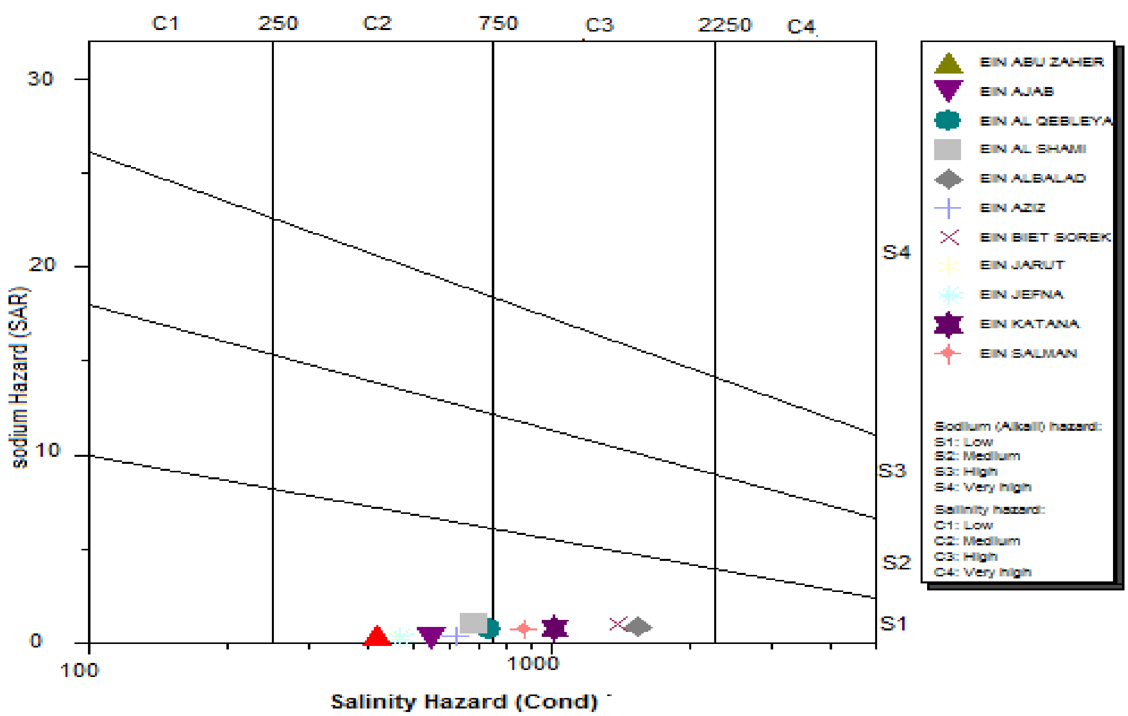

Fig.18: Wilcox classification of the water samples in wet season

3.7.2.3 Soluble sodium percentage (SSP) or % Na

Soluble Sodium Percentage (% Na) is calculated using the equation:

$\% \ Na = [(Na^{+} + K^{+}) *100] / (Ca^{+2} + Mg^{+2} + Na^{+} + K^{+})$ in meq/L. WILCOX (1955) classified the water according to its % Na (mS/cm) from excellent to unsuitable water.

(Table 8): The classification of water according to Wilcox (1995).

Class	%Na	EC µS/cm
Excellent	‹ 20	‹ 250
Good	20 – 40	250 -750
Permissible	40 – 60	750 – 2000
Doubtful	60 80	2000 – 3000
Unsuitable	› 80	› 3000

.

Accordingly, the following are the main conclusions:

1. According to Ec values for the groundwater, the Ec of 6 springs (55%) between 750 and 1200 µs/cm, therefore those springs are permissible for irrigation for both seasons while other water springs samples are good for irrigation for both season.

2. Depend on Na%, Ein Katana, Ein Beit Soreq, Alsami, Ein Salman, Ein Albalad and AL-Qebleya water springs for both seasons are good for irrigation, while the Ajab, Jefna, Abu Zaher and Aziz spring water is excellent for irrigation.

3.7.2.4 Total Hardness (TH)

The hardness of water is defined as its content of divalent metallic ions which react with sodium soaps to produce solid soaps or scummy residue and which react with negative ions when the water is heated in boilers to produce solid boiler scales. The evaluation of hardness could help in determining the need for water softening required to reduce the amount of detergents consumed, thus helping to protect the environment through the reduction of the use of non-biodegradable detergents. It could also help in avoiding the extensive scale formation (precipitation of carbonates) from hard water. Total hardness is expressed as $CaCO_3$ in mg/L, which is calculated according to the following equation (Todd, 1980)

TH ($CaCO_3$) mg/L = 2.497 Ca^{+2} + 4.115Mg^{+2} ---------------------- (3.1)

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 (Table 9).

(Table 9) Sawyer and McCarty (1967) classification of water based on hardness

CLASS OF WATER	HARDNESS AS $CaCO_3$ mg/L	WATER TYPE
I	0-75	Soft
II	75-150	Moderately Hard
III	150-300	Hard
IV	>300	Very Hard

In the study area, the lowest value of TH recorded was 223.7 mg/L for Ein Abu Zaher, and the highest value was 599.8 mg/L for Ein Biet Soreq spring in dry season. Water types according to the average TH in the study area range from hard to very hard water with prevailing very hard water in 80% of the samples. Classifications of the spring's water in the study area based on Sawyer and McCarty classification are listed in Appendix (5).

3.7.2.5 Sodium Adsorption Ratio (SAR)

The sodium adsorption ratio (SAR) indicates sodium concentration in water. (SAR) is considered an important parameter for the evaluation of water suitability for irrigation where the sodium accumulation in the soil will affect the rate of water infiltration through the soil. (SAR) values are calculated according to the following equation (Todd, 2007):

$$S.A.R = \frac{Na^{+}}{\sqrt{\frac{1}{2}(Ca^{2+} + Mg^{2+})}}$$

Where:

SAR: Sodium Adsorption Ratio.

Na^{+}, Ca^{+2} and Mg^{+2}: Concentration of ions by (meq/l.) units.

Winner (2000) classification, represent the classification of water for irrigation purpose (Table 10), acceptable SAR values for irrigation water depend on the particular water and soil characteristics.

(Table 10): Classification of irrigation water based on SAR values according to (Winner, 2000).

SAR	Water Class
<10	Excellent
10-18	Good
18-26	Fair
>26	Poor

According to the winner classification in (Table 10), most of spring water samples in study area fall in the zone of excellent water type for both seasons.

(Table 11): Values of (SAR, Na %) for water samples of the study area

Spring Name	**Dry season**	**Wet season**
	SAR	**SAR**
AJAB	2.2	1.7
KATANA	5.3	4.6
BIET SOREK	4.4	5.7
AL SHAMI	5.3	5.7
SALMAN	4.2	4.4
JEFNA	1.9	1.6
ALBALAD	5.4	5
AL QEBLEYA	4.5	4
ABU ZAHER	2.5	2
EIN AZIZ	3.2	2.3

3.7.3 Ion Distribution and chemical composition

Total Dissolved Ions (TDI) = Total cations (mg/L) + Total anions (mg/L).

The total dissolved Ions (TDI) for the major ions in the area of study is calculated to be 297.5 meq/l in the dry season and 234.6meq/l for the wet season, the higher content of TDI during dry season confirms the effect of contact time of water with minerals hence more dissolution of minerals. As clear in (Figure 19).

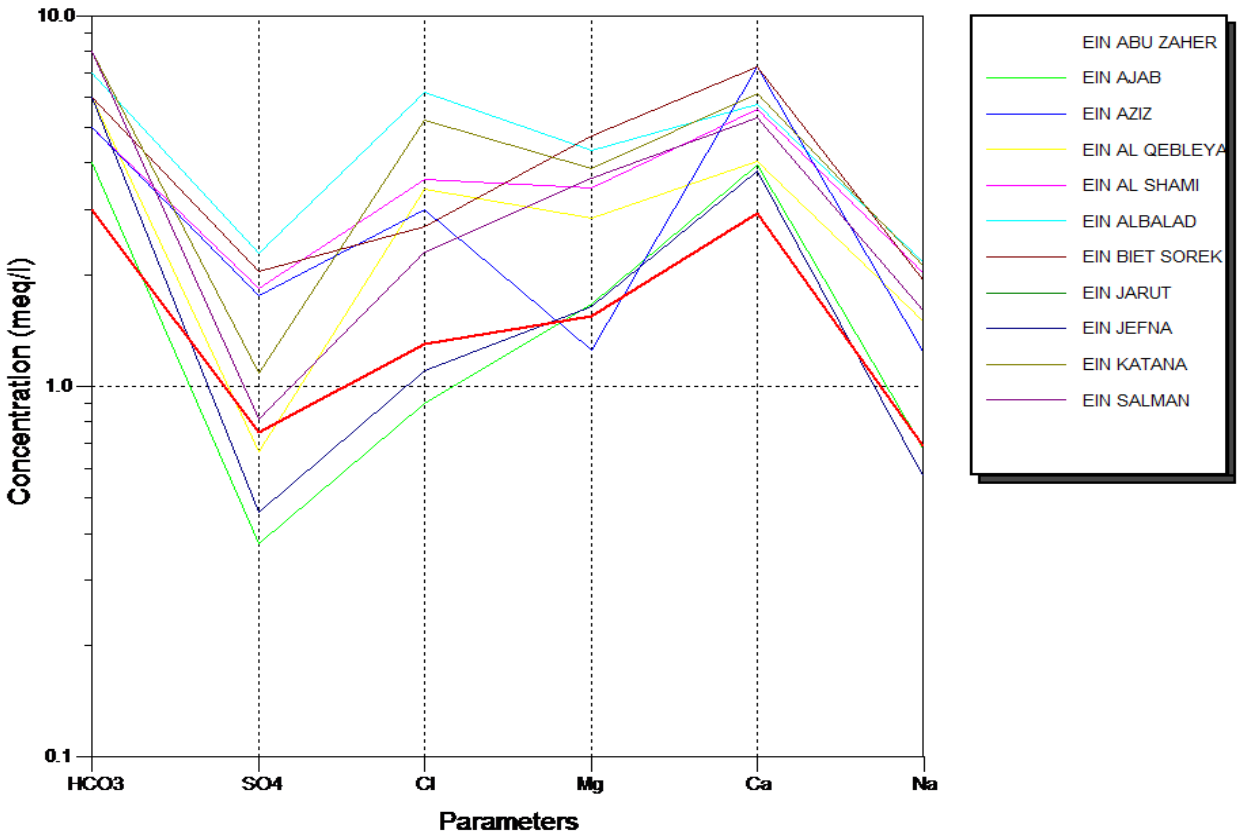

Fig.19: Schoeller Diagrams for springs in Soreq Area

3.8 Hydrochemical characteristics between Albian and Lower Cenomanian formation

Albian formation, this formation contains five springs, Ein Ajab, Ein Qatana, Ein Beit Soreq , Ein Salamn and Ein Jefna , this formation has an Ec average of 655 μS/cm in dry period, while in wet period Ec average 859 μS/cm. For Lower Cenomanian formation, this formation contains five springs, Ein Alshmi,Ein Aziz, Ein Albalad and Ein Abu Zaher .this formation has an Ec average of 748 μS/cm in dry period, while in wet period Ec average 746 μS/cm. The average TDS value is found to be 320 and 369 for the Albian and the Lower Cenomanian formation, respectively. The cations and anion in Albian formation are higher than in Lower Cenomanian in two periods.

3.9 Soreq catchment compared with Salman catchment

In this study, were taken, four springs from Salman catchment, which are Ein Ajab, Ein Katana, Ein Salman and Ein Jefna, most of these springs, similar to Soreq catchment by pollutions and uses, but generally the spring water quality in Salman catchment better than Soreq catchment.

Chapter Four

Isotopes

4.1 Environmental Isotopes

Isotopes are widely used in research and practice in ground water hydrology. They can be divided broadly into stable and radiogenic varieties. The stable isotopes are used mainly for flow system tracing and climate reconstruction; the radiogenic isotopes are used to date ground water.

Isotopes of a particular element have the same atomic number but different atomic weights due to varying number of neutrons in the nucleus. Stable isotopes are not involved with any natural radioactive decay process. Radioactive isotopes undergo spontaneous radioactive decay to form new elements or isotopes. Radiogenic isotopes are the stable product of radioactive decay. Certain stable isotopes of hydrogen, oxygen, carbon, nitrogen, and sulfur can be used to study geologic processes that affect ground and surface water. Radioactive isotopes can be used to determine the age of ground water. Environmental isotopes are those that are naturally occurring (Clark, and Fritz, 1997).

4.2 Stable Isotopes of Water

Stable isotopes studies are based on the tendency of some pairs of isotopes to fractionate, or separate into light and heavy fractions. This fractionation occurs during some geologic process, such as evaporation or heating. The five elements that are used in stable isotope studies are able to fractionate readily are fairly common have a relatively large difference in mass between the two isotopes, and have one isotope that is much more abundant than the other. If R is the ratio of the heavy isotope to the light one, then the relative fractionation is expressed in del notation as:

$$(\delta, ‰) = \{R_{sample} - R_{standard} / R_{standard}\} * 1000 \quad \ldots\ldots\ldots\ldots (4.1)$$

Where:

R_{sample} ratio in the samples

$R_{standard}$ ratio in the standard

There are two stable isotopes of hydrogen, ^{1}H and ^{2}H (deuterium), as well as three stable isotopes of oxygen, ^{16}O, ^{17}O, ^{18}O. There are nine different combinations of these isotopes that make stable water molecules with atomic masses ranging from 18 to 22. The most abundant water molecule, $^{1}H\ ^{16}O$, which is the lightest, has a much higher vapor pressure than the heaviest form, $^{2}H\ ^{18}O$.

The use of mass spectrometry can determine the ratio of isotopes in a water sample. Important isotope ratios include $^{18}O/^{16}O$ and $^{2}H/^{1}H$. These isotopic ratios from an environmental water sample can be compared with the isotopic ratio of standard mean ocean water (SMOW). The comparison is made by means of the parameter δ, which is defined as

$$\delta^{18}O\ (‰) = \{(^{18}O/^{16}O)_{sample} / (^{18}O/^{16}O)_{SMOW} - 1\} * 1000 \qquad (4.2)$$

$$\delta^{2}H\ (‰) = \{(^{2}H/^{1}H)_{sample} / (^{2}H/^{1}H)_{SMOW} - 1\} * 1000 \qquad (4.3)$$

When $\delta^{2}H$ is plotted as a function of $\delta^{18}O$ for water found in continental precipitation, an experimental linear relationship is found that can be described by the equation (Allison, 1984)

$$\delta^{2}H = 8\ \delta^{18}O + 10 \qquad (4.4)$$

This is known as the global metric line. Continental precipitation samples will tend to group close to this line. Precipitation falling in areas with lower temperatures or at higher latitudes will tend to have lower $\delta^{2}H$ and $\delta^{18}O$ values. Naturally, oceanic water will fall below the meteoric water line as it is isotopically enriched. Deviations from the meteoric water line can be interpreted as being caused by precipitation that occurred during a warmer or colder climate than at present or by geochemical changes that occurred when the water was underground (Craig, 1961).

Geothermal water tends to be isotopically enriched with respect to $\delta^{18}O$ owing to equilibration of the oxygen in the ground water with respect to oxygen in the rocks (Mayo, Muller, &Ralston 1985) .(Figure 20) shows the meteoric water line.

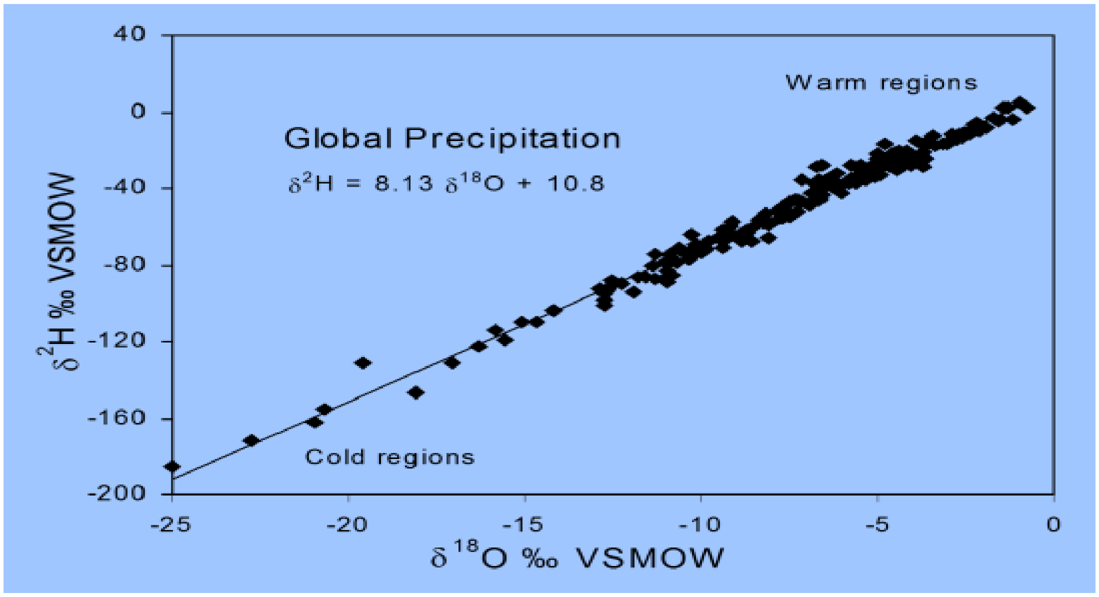

Fig.20: The relationship between $\delta\ ^{18}O$ and δ D (GMWL)

4.3 Sampling Methods and Isotope Analyses

Sample of spring water were obtained from different places, the 50 ml dark glass bottles for ^{2}H and ^{18}O. The complete analyses and separation of stable isotopes were carried out at the laboratory of Freiburg University in Germany.

4.3.1 Deuterium and ^{18}O

The isotopic composition ^{2}H and ^{18}O of spring water are listed in (Table 12).

4.3.1.1 Deuterium

The highest and lowest Deuterium values were found in the Soreq catchment, ranging between -24.44 and -20.28 ‰ with a mean of -21.71 ‰. Whereas, the mean for all catchment spring is -22.59 ‰.

4.3.1.2 Oxygen – 18

Delta ^{18}O values in the study are varied between -5.87 ‰ to -5.06 in the Soreq catchment with a mean of -5.3‰. The Natuf catchment has a range of -5.89 to -5.21‰ with a mean -5.63. The Sarida catchment has a range of -5.52 to -5.43‰ with a mean of -5.47 ‰. The mean is - 5.53 ‰ for all spring water with small variation in Deuterium. The stable isotopes are good tracers for determining the recharge of spring water in hilly areas

4.4 Comparison with other catchments

The sample of Natuf and Sarida catchment show high ^{2}H and ^{18}O compared with the Soerq catchment, due to the combined effect of rainwater and accompanying flood flows (Table 12). This reflects all spring recharge comes from rainfall directly.

(Table 12): Environmental Isotopes Data of Selected, springs for the Studied Area

Name	Date	Location	$\delta^{18}O$	$\delta\ ^{2}H$	Catchment
Ein Ajab	29/11/2013	Biet Anan	-5.06	-20.28	Soreq
Ein Katanah	29/11/2013	Katanah	-5.07	-20.42	Soreq
Ein Salman	29/11/2013	Biet Duqqo	-5.87	-24.44	Soreq
Ein Jariot	29/11/2013	Batounia	-5.75	-23.23	Natuf
Ein Arik – Alfuqa	29/11/2013	Ein Arik	-5.57	-23.02	Natuf
Ein Arik –Altehta	29/11/2013	Ein Arik	-5.62	-23.18	Natuf
Ein Al-Zarqa- Aboud	29/11/2013	Aboud	-5.58	-22.6	Natuf
Ein Al-Zarqa – Beitillu	29/11/2013	Beitillu	-5.89	-24.31	Natuf
Ein Qinia	29/11/2013	Ein Qinia	-5.21	-21.2	Natuf
Ein Bobbin	29/11/2013	Deir Bzei	-5.79	-23.83	Natuf
Ein Al-Fawwar	29/11/2013	Kafr ad-Dik	-5.43	-22.12	Sarida
Ein Al- Matwi	29/11/2013	Salfit	-5.52	-22.49	Sarida

4.5 Relationship between ^{18}O and ^{2}H

Delta ^{2}H with ^{18}O could be used to identify water bodies that are affected by rapid evaporation. A linear relationship is found, after plotting δ ^{2}H as a function of ^{18}O for the water in continental precipitation (MAYO, MULLER and RALSTON 1985):

$\delta\ ^{2}H = 8\ \delta\ ^{18}O + 10$ (meteoric water line MWL) where d is constant and the results are given in terms of permils deviation form SMOW (δ ‰) (Craig, 1961). Deviation from the MWL may cause by precipitation that occurred during warmer and colder climate than at present or by subsurface changes. The whole catchment area was found to be: $\delta\ ^{2}H = 4.74\ \delta^{18}O + 3.65$ ‰. These values lie on the local meteoric water line.

Deviation from the MWL (Craig, 1961) is well known and documented for this area by (Gat & Carmi 1970). Measured ^{2}H values of all catchment plot parallel to but higher the MWT. The values lie on the local meteoric water line as defined by Gat and Dansgaard (1972). The most depleted isotope content is found in springs, such as Ein Al-Zarqa, which has ^{18}O of -5.89 0/00 and ^{2}H of -24.31 0/00.

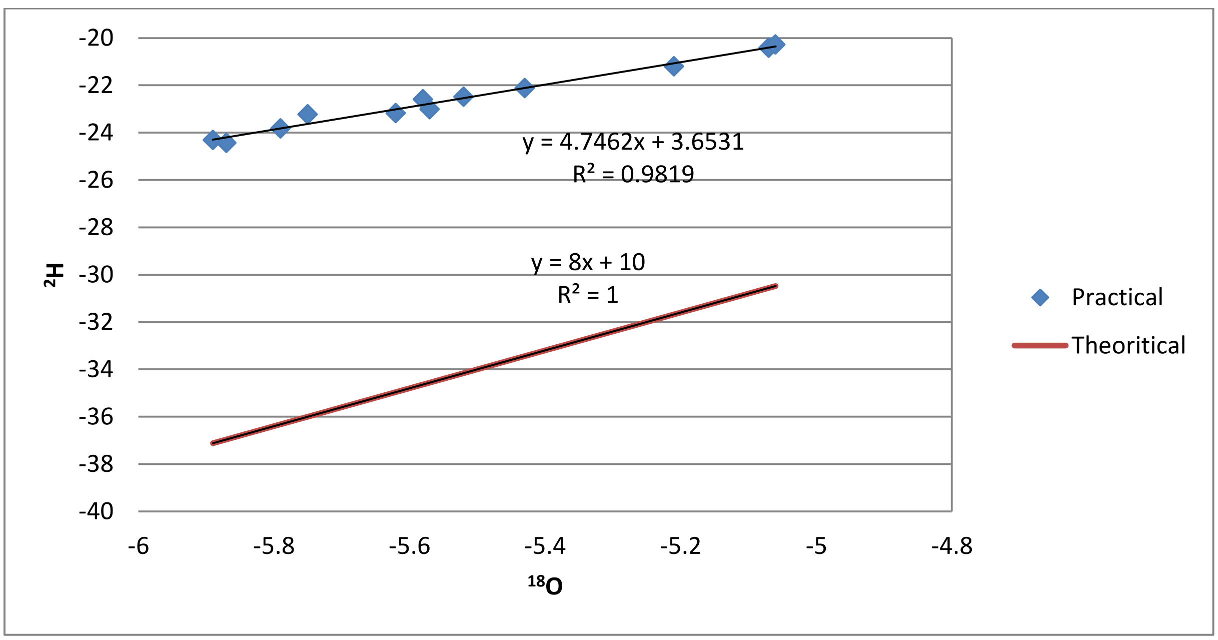

Fig.21: The relationship δ18 O and δD in the spring water samples with LMWL

Chapter Five

Conclusion and Recommendations

5.1 Conclusion

The spring water quality assessed through the analysis of physical parameters (pH, EC, T, TDS) and major cations (Ca^{2+}, K^{+}, Na^{+}, Mg^{2+}), major anions (Cl^{-}, SO_4^{-}, HCO_3^{-}, No_3) and heavy metals (Zn^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+}, B^{2+}, As^{2+}, Be , Se , Ba , Ti , Cr, Al , V, Co, Cu , Ni, Sr , Bi , Mo , Ag , Li). The spring water in the study area is generally of low alkalinity with (pH) average ranging between (7.8) for dry period and (7.7) for the wet period. The maximum TDS value was 763 ppm recorded in Ein Albalad in March and the minimum is 210 ppm recorded in Ein Abu Zaher, while the maximum TDS value is 561 ppm recorded in November in Ein Biet Soreq and the minimum is 185 ppm recorded in Ein Katana. (EC) and (TDS) averages in wet period are higher than dry period due to dilution process. Depending on (TDS) values for both periods the spring water in the area is classified as fresh water. The relationship between (EC) and (TDS) in the spring water of the study area is strong and the value of correlation coefficient (R) is close to one by equations (TDS = 0.46 EC + 20.2 with R^2 = 0.99). The concentration of Ca^{2+} is higher than the other major cations and HCO_3^{-}concentration is higher than the other major anions in both seasons. The water of the area is between highly mineralized and excessively mineralized. EC values are higher in Ein Beiet Soreq as a result of the applications of fertilizers uses in the recharge areas, in addition to human activities.

Concentrations of cations and anions in wet period are greater than in dry period due to the dilution process except bicarbonate ion (HCO_3^{-}) which is lower in the wet period due to the recharge process, where the carbonate is associated with water converted to (HCO_3^{-}).

The NO_3^{-} has a mean of 32 mg/L for all spring water in the study area; nitrate concentration in dry period is greater due to agricultural activities fertilizers and sewage effect.

According to Total Hardness (TH) the spring water in the study area is classified as very hard to hard water due to the presence of dissolved calcium and magnesium salts.

The results of the analysis of heavy elements in the spring water of the study area confirm that springs water contains higher values of heavy metals like (Zn^{+2}, Cd^{+2}, Mn^{+2}, As^{+2}, Co, Cu, Ni, Pb, Al, Fe^{+2} and V) because their concentrations are higher than the permissible limits according to WHO (2007) and PWA (2001) as a result of weathering and solution action, in addition to the effect of the fertilizers and human activities.

The results of hydrochemical formula show that most springs in the study area have water type of ($Ca\text{-}Mg\text{-}HCO_3^-$) and the other springs range between ($Ca\text{-}HCO_3^-$) and ($Ca\text{-}Cl\text{-}HCO_3$) for the two periods. The spatial distribution of water quality in the study area for both dry and wet periods shows difference in water quality between both periods as a result of recharge and dilution processes in the wet period. Piper classification showed that the type of groundwater in the study area for both periods is located between the areas of earth alkaline water with increased portion of alkali with prevailing bicarbonate and alkaline water with prevailing bicarbonate, with prevailing sulfate and chloride for the two periods.

These springs are located close to populated areas and have agricultural activities nearby. Recorded values of SAR, SSP, and EC in the springs of Soreq drainage basin indicate that there is a pollution risk. Uncountable FC and TC were found in these springs which make the water of these springs unsuitable for drinking purposes according to WHO (2007) and PWA (2001) standards, but it is suitable for agriculture, use irrigation water. Municipal solid wastes may increase the risk of trace elements contamination in Soreq springs. Water genesis in the springs of Soreq catchment is mainly originates from the recharge area of limestone and dolomitic limestone and affected by dry and wet seasons as well as leakage from wastewater. Changing the type of water in some springs is due to the fact that the spring water mixes with wastewater and runoff water.

The relationship between ($\delta\ ^{2}H$, $\delta\ ^{18}O$) contents in spring water samples are used to define the Local Meteoric Water line (LMWL), according to the equation: ($\delta\ ^{2}H = 4.74\ \delta\ ^{18}O + 3.65$). The isotopic content of the analyzed water samples plot on the Mediterranean Meteoric Water Line, signifying recharge from recent precipitation.

5.2 Recommendations

It is important to take the following points into consideration at any level in the planning and management programs which aim to improve the water quality of the springs and to prevent further contamination:

- Population in study area depends mainly on agriculture so, priority should be given to the quality of water, design and new techniques of irrigation, kinds of plants, soil properties, training farmers, fertilizers and pesticides education in order to rising the agriculture efficiency

- Spring rehabilitation and provision of proper storage facilities. This would protect the immediate surroundings of the springs discharge points from contaminating activities (watering livestock, domestic laundering, etc.). It would also facilitate upgrading of the water to good potable standards by disinfection and any other appropriate methods of treatment.

- Legislation to protect the aquifers, including controlling urban expansion over the recharge area and preventing illegal disposal of sewage into the fields and wadis.

- Strict regulation requiring well designed cesspits or their replacement with proper sewage networks where possible.

- Long term spatial and temporal monitoring of the water quality, especially the fecal coliform count, EC, NO_3 and Cl^- concentration in major springs.

- It is recommended to long-term monitoring of rainwater will give a better understanding of distribution environmental isotopes in rain water in Palestine.

- Where the disinfection of drinking water (chlorination) is not possible, boiling water before use is highly recommended.

- Springs should be cleaned from solid waste, especially in the Ein Albalad and Ein Aziz.

- Where the contaminated springs are the major or the only water source for domestic purposes, it is recommended to supply pregnant women and infants with low nitrate bottled water.

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Appendix

Appendix 1

Names and Locations of samples springs of the study area

Spring No.	Spring Name	Location		Elevation
		Latitude	Longitude	
1	Ajab	31°5048.2	350743.4	605
2	Katana	314933.8	350627.1	598.7
3	Biet Soreq	314931.4	350915.7	758
4	Al- Shami	314917.4	351039.8	782
5	Salman	315144.2	350915.7	521
6	Jefna	315156.9	350654.6	445.4
7	Aziz	315112.9	351036.6	723.4
8	Al-Balad	315052.8	351103.5	745.8
9	AL-Qebleya	315043.8	351111.3	725
10	Abu-Zaher	315039.7	351106.8	752

Appendix 2

Hydrochemical Parameters in Soreq springs

1- Hydrochemical Parameters in Soreq springs in dry period

Spring Name	Date	pH	TDS	T [in °C]	EC
Ajab	01/11/2013	8	198	20.2	393
Katana	01/11/2013	7.5	185	20.3	370
Biet Soreq	01/11/2013	7.6	561	19.7	1200
Al-Shami	01/11/2013	7.8	397	23.4	792
Salman	01/11/2013	7.9	421	21.4	844
Jefna	02/11/2013	7.7	236	22.9	469
AL-Balad	02/11/2013	8	430	15.6	912
Qebleya	02/11/2013	7.9	379	19.5	759
Abu Zaher	02/11/2013	8.2	224	19.8	446
Aziz	02/11/2013	7.5	415	20	832

2- Hydrochemical Parameters in Soreq springs in wet period

Spring Name	Date	pH	TDS	T [in °C]	EC
Ajab	11/03/2014	7.8	274	21	552
Katana	11/03/2014	7.1	510	22	1016
Biet Soreq	11/03/2014	7.3	690	21.4	1385
Al-Shami	11/03/2014	7.6	340	19	680
Salman	11/03/2014	7.8	435	20.3	870
Jefna	11/03/2014	8	236	20	472
AL-Balad	11/03/2014	7.8	763	19.1	1530
Qebleya	11/03/2014	8	372	20	734
Abu Zaher	11/03/2014	8.4	210	20.2	421
Aziz	11/03/2014	7.5	310	20	623

Appendix 3a

Cations and Anions of the spring water in the Soreq catchment

1- Cations and Anions of the spring water in the Soreq catchment in dry period

Spring Name	Date	Na	K	Mg	Ca	Cl	SO_4	HCO_3	No_3
Ajab	01/11/2013	15.62	0.34	20.17	79.06	31.91	18	244.08	18
Katana	01/11/2013	48.68	3.75	47.08	123.34	184.34	52	488.16	31
Biet Soreq	01/11/2013	44.58	23.48	57.48	145.61	95.72	98	366.12	44
Al-Shami	01/11/2013	46.67	0.98	41.75	112.16	127.62	88	305.1	36
Salman	01/11/2013	36.77	1.8	44.13	106.01	81.54	39	488.16	39
Jefna	02/11/2013	13.18	0.4	19.91	76.2	39	22	366.12	26
Al-Balad	02/11/2013	49.84	17.71	52.45	115.22	219.79	110	427.14	33
Qebleya	02/11/2013	34.33	30.01	34.45	81.07	120.53	32	366.12	48
Abu Zaher	02/11/2013	15.91	2.07	18.73	58.77	46.09	36	183.06	16
Aziz	02/11/2013	28.64	0.96	15.17	145.47	106.35	84	305.1	49

2- Cations and Anions of the spring water in the Soreq catchment in wet period

Spring Name	Date	Na	K	Mg	Ca	Cl	SO_4	HCO_3	No_3
Ajab	11/03/2014	12.4	0.29	19.8	82	88.63	18	251.95	8.85
Katana	11/03/2014	43.6	5.5	48.1	132.6	106.35	78	430.15	20.87
Biet Soreq	11/03/2014	57.9	51.8	59.3	148.1	230.43	112	497.75	39.51
Al-Shami	11/03/2014	43.9	1.0	34.1	84.4	106.35	90	288.82	24.02
Salman	11/03/2014	41.1	2.2	42.5	127.2	88.63	56	359.48	23.18
Jefna	11/03/2014	11.6	0.3	18.3	79.5	88.63	35	245.8	2.52
Al-Balad	11/03/2014	48.8	52.02	54.4	131	301.33	102	337.98	22.05
Qebleya	11/03/2014	33.4	27.7	35.4	91.5	88.63	32	285.74	17.16
Abu Zaher	11/03/2014	15.8	1.8	19.6	59.2	88.63	40	187.42	3.95
Aziz	11/03/2014	20.09	0.7	14.2	131.1	88.63	76	251.95	12.08

Appendix 3b

Trace Elements (ppm) in Soreq Springs

1- Trace Elements (ppm) in Soreq Springs in dry periods

Spring Name	Zn	Cd	Mn	Pb	B	As	Fe	Co	Ni	Cu	Se	Ba	Tl	Al	Cr	V	Be
Ajab	2.81	0.02	0.01	0.38	30.42	0.27	31.37	0.09	0.33	0.56	0.61	11.57	0.04	4.19	0.28	1.88	0
Katana	3.22	0.01	1.26	0.04	35.92	0.38	1.81	0.1	0.82	0.53	1.04	30.07	0.03	4.17	0.18	2.54	0
Biet Soreq	3.27	0.03	0.65	0.35	133.87	2.91	16.52	0.81	5.87	3.36	1.02	63.77	0.02	21.57	0.17	6.69	0
Al-Shami	1.35	0	0.16	0	50.39	0.41	0.75	0.24	1.35	0.82	0.71	29.26	0.03	3.11	0.04	2.5	0
Salman	0	0.01	0	0	53.94	0.62	1.12	0.22	1.95	0.8	0.62	23.22	0.03	1.08	0.11	2.97	0
Jefna	0	0	0	0	29.82	0.31	0	0.03	0.13	0.13	0.52	12.58	0.04	0.06	0.2	2.69	0
Al-Balad	12.24	0.01	0.5	0.07	159.25	11.29	11.56	0.24	1.09	2.07	1.4	30.4	0.07	17.01	1.38	31.49	0
Qebleya	7.37	0.02	1.69	0.2	93.7	7.9	28.47	0.08	0.57	0.79	0.85	17.7	0.05	23.09	1.34	29.59	0.01
Abu Zaher	0.65	0	0.47	0.07	36.71	2.89	5.54	0.06	0.54	0.85	0.38	8.02	0.04	12.15	0.23	10.6	0
Aziz	22.73	0.03	15.79	0.4	35.51	0.36	101.97	0.2	1.03	0.25	1.15	22.87	0.2	18.23	0.23	0.79	0.01

2- Trace Elements (ppm) in Soreq Springs in wet periods

Spring Name	Zn	Cd	Mn	Pb	B	Li	Fe	Co	Ni	Cu	Sr	Ba	Tl	Al	Cr	Bi	Mo	Ag
Ajab	<0.0	<0.0	<0.0	<0.0	22.5	0.3	188.8	0.16	<0.0	<0.0	110.8	15.8	<0.0	<0.0	<0.0	<0.0	0.2	<0
Katana	48.7	<0.0	4.7	<0.0	39.3	0.9	272.1	0.22	<0.0	<0.0	178.9	51.6	<0.0	<0.0	<0.0	<0.0	0.08	<0
Biet Soreq	<0.0	<0.0	0.3	<0.0	148.5	4.8	339.9	0.68	2.6	0.79	194.0	69.0	<0.0	27.1	0.05	<0.0	4.05	<0
Al-Shami	<0.0	<0.0	0.77	<0.0	45.6	0.8	197.4	0.25	<0.0	<0.0	140.1	29.9	<0.0	4.9	<0.0	<0.0	0.16	<0.
Salman	<0.0	<0.0	<0.0	<0.0	52.1	1.2	222.5	0.46	0.05	<0.0	140.1	33.5	<0.0	1.1	0.03	<0.0	0.1	<0
Jefna	<0.0	<0.0	0.05	1.0	24.2	0.5	157.6	0.13	<0.0	<0.0	106.0	16.5	<0.0	0.8	0.01	<0.0	0.17	<0
Al-Balad	4.25	<0.0	0.29	<0.0	168.9	7.5	276.9	0.19	0.2	3.2	176.6	44.2	0.02	3.7	1.02	0.0	6.5	<0
Qebleya	<0.0	<0.0	0.74	<0.0	90.7	3.8	194.1	0.14	<0.0	<0.0	128.2	24.8	<0.0	20.4	1.1	<0.0	3.7	<0
Abu Zaher	2.48	<0.0	0.24	<0.0	32.01	1.2	186.2	0.15	<0.0	<0.0	86.4	11.5	<0.0	2.4	<0.0	<0.0	0.18	<0.
Aziz	<0.0	<0.0	0.63	0.62	34.1	1.7	300.2	0.13	<0.0	<0.0	152.4	24.2	0.48	10.2	0.01	0.98	0.6	<0

Appendix 4

Classification of water salinity in Soreq springs, based on EC and TDS

Spring Name	**Date**	**EC µS/cm**	**TDS mg/L**	**Water Class & Remarks**
AJAB	1/11/2013	393	198	C2: Medium salinity water
KATANA	1/11/2013	370	185	C2: Medium salinity water
BIET SOREK	1/11/2013	1200	561	**C3: High salinity water**
AL SHAMI	1/11/2013	792	397	C2: Medium salinity water
SALMAN	1/11/2013	844	421	**C3: High salinity water**
JEFNA	1/11/2013	469	236	C2: Medium salinity water
ALBALAD	2/11/2013	912	430	**C3: High salinity water**
AL QEBLEYA	2/11/2013	759	379	C2: Medium salinity water
ABU ZAHER	2/11/2013	446	224	C2: Medium salinity water
AZIZ	2/11/2013	832	415	**C3: High salinity water**
JARUT	2/11/2013	470	234	C2: Medium salinity water
AJAB	11/3/2014	552	274	C2: Medium salinity water
KATANA	11/3/2014	1016	510	**C3: High salinity water**
BIET SOREK	11/3/2014	1385	690	**C3: High salinity water**
AL SHAMI	11/3/2014	680	340	C2: Medium salinity water
SALMAN	11/3/2014	870	435	**C3: High salinity water**
JEFNA	11/3/2014	472	236	C2: Medium salinity water
ALBALAD	11/3/2014	1530	763	**C3: High salinity water**
AL QEBLEYA	11/3/2014	734	372	C2: Medium salinity water
ABU ZAHER	11/3/2014	421	210	C2: Medium salinity water
AZIZ	11/3/2014	623	310	C2: Medium salinity water
JARUT	11/3/2014	470	234	C2: Medium salinity water

Appendix 5

Classification Water of Soreq springs according to TH (mg/L)

SPRING NAME	Dry season			Wet season		
	AVERAGE TH(MG/L)	CLASS	WATER TYPE	AVERAGE TH (MG/L)	CLASS	WATER TYPE
AJAB	280.3	III	Hard	286.05	III	Hard
KATANA	501.5	IV	Very Hard	529.13	IV	Very Hard
BIET SOREK	599.8	IV	Very Hard	613.38	IV	Very Hard
AL SHAMI	451.6	IV	Very Hard	351.26	IV	Very Hard
SALMAN	446.1	IV	Very Hard	492.19	IV	Very Hard
ALBALAD	503.3	IV	Very Hard	551	IV	Very Hard
JEFNA	272	III	Hard	273.83	III	Hard
AL QEBLEYA	244	III	Hard	374.1	IV	Very Hard
ABU ZAHER	223.7	III	Hard	228.46	III	Hard
AZIZ	425.4	IV	Very Hard	387.8	IV	Very Hard

Appendix 6

Water type in Soreq springs (dry and wet season)

Spring Name	Date	Season	Water type
EIN AJAB	01/11/2013	Dry	Ca-Mg- HCO_3
EIN KATANA	01/11/2013	Dry	Ca-Mg-HCO_3
EIN BIET SOREK	01/11/2013	Dry	Ca-Mg- HCO_3
EIN AL SHAMI	01/11/2013	Dry	Ca-Mg-HCO_3
EIN SALMAN	01/11/2013	Dry	Ca-Mg-HCO_3
EIN JEFNA	02/11/2013	Dry	Ca- HCO_3
EIN ALBALAD	02/11/2013	Dry	Ca-Mg-HCO_3
EIN AL QEBLEYA	02/11/2013	Dry	Ca-Mg- HCO_3
EIN ABU ZAHER	02/11/2013	Dry	Ca-Mg- HCO_3
EIN AZIZ	02/11/2013	Dry	Ca-HCO_3
EIN AJAB	11/03/2014	Wet	Ca- HCO_3
EIN KATANA	11/03/2014	Wet	Ca- Mg-HCO_3
EIN BIET SOREK	11/03/2014	Wet	Ca- HCO_3
EIN AL SHAMI	11/03/2014	Wet	Ca- Mg-HCO_3
EIN SALMAN	11/03/2014	Wet	Ca-Mg- HCO_3
EIN JEFNA	11/03/2014	Wet	Ca- HCO_3
EIN ALBALAD	11/03/2014	Wet	Ca- Cl-HCO_3
EIN AL QEBLEYA	11/03/2014	Wet	Ca- HCO_3
EIN ABU ZAHER	11/03/2014	Wet	Ca- HCO_3
EIN AZIZ	11/03/2014	Wet	Ca- HCO_3