

Deanship of Graduate Studies

Al-Quds University



**Rainwater and Groundwater Chemistry of the Deep
Aquifer System in the North Eastern Basin /West Bank-
Palestine**

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Rainwater and Groundwater Chemistry of the Deep Aquifer System in the North Eastern Basin /West Bank-Palestine

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A thesis submitted in partial fulfillment of requirements for
the degree of Master in Environmental Studies, Department of
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Thesis Approval

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A photograph of three handwritten signatures in blue ink on a light blue background. The first signature is the most prominent and appears to be "Amer Marei". The second and third signatures are less legible but correspond to the names of the internal and external examiners listed in the text.

Jerusalem –Palestine

2015/1436

Dedication

To my father who taught me the value of education

**To my mother who supported me, and trust my ability to succeed
and lights up my life since my birth to this date**

**To my lovely husband Sadeq for his efforts, moral support,
generosity, and endless encouragement**

**To my children, Sara and Majed for the understanding during
my absence**

To All those people who's helped me in this study

Sana Nairokh

Declaration

I certify that this thesis submitted for the degree of Master is the result of my own research, except where otherwise acknowledged and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Name: Sana ‘Mohammad Salem’ Nairokh

Sign: 

Date: 6/5/2015

Acknowledgments:

Thanks God for helping and supporting me.

Foremost, I would like to express my sincere gratitude to my advisor Dr. Amer Marei for the continuous support of my study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis.

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Abstract

The North Eastern Basin consider one of most important water sources for Palestinian in the northern part of the West Bank. To utilize and protect valuable water resources effectively and predict the change in groundwater environments, it is necessary to understand the hydro-chemical characteristics of the groundwater and its evolution under natural water circulation processes, so the main objective of this study is to understand the changes in water chemistry starting from rainwater in to groundwater in deep aquifer system.

The study show that recharge zones for the deep system locate along the flank of the Anabta and Al-Far'a anticline in the west and east respectively.

The results of the chemical analysis for rainwater show that, the arithmetic average for pH and EC is 7.14 and 122.6 $\mu\text{S}/\text{cm}$ respectively and have some high value of EC due to accumulate dust in atmosphere so rise the value to above 200 $\mu\text{S}/\text{cm}$. The abundance of the major cations and anions is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$, high concentration of Ca^{2+} and HCO_3^- due to affect the atmosphere by the dust which rich by carbonate minerals. Low concentration of NO_3^- and SO_4^{2-} is an indication of there is no atmospheric pollution in our study area. Then these value changes for groundwater after water infiltrated into the underground and become as following, pH value range between (6.8 – 7.5) and EC for most samples is below 1000 $\mu\text{S}/\text{cm}$ which is indication of young groundwater with low residence time and minimum water-rock interaction except for two samples have EC value above 1000 $\mu\text{S}/\text{cm}$ because the water level in these wells is close to the current Mediterranean sea level. The abundance of the major cations and anions is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$. High concentration of Ca^{2+} and HCO_3^- are resulting from dissolution of carbonate minerals, which identified in rock type of study area. Low concentration of NO_3^- and SO_4^{2-} is an indication of there is no pollution from wastewater in our study area. Saturation indices show that nearly all the samples saturated with respect to calcite, dolomite and aragonite. Nearly all samples have a water type Ca-Mg- HCO_3 -Cl except for two sample, which have the type Na-Mg-Ca- HCO_3 and Mg-Na- HCO_3 -Cl. The integration of ionic ratio, hydrochemistry and various conventional graphs show there is carbonate weathering and reverse ion exchange for all sample except in two sample-position have ion exchange process. Finally, I recommend making environmental isotopes studies such as ^{18}O , ^2H , ^3H and ^{14}C to identify recharge zones and recharge volume.

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Chapter One:

Introduction:

1.1. Introduction

Water resources in the West Bank are limited to groundwater, surface water and rainwater harvesting. The groundwater and surface water originate from meteoric water. Due to the fact that the access for the Palestinian to the Jordan River is forbidden by the Israeli occupation, only groundwater in form of natural springs and groundwater boreholes and in rural areas rainwater harvesting can consider as water sources. (UNEP, 2003; Anayah, 2006; Marei, 2011)

West Bank consider as part of the Mediterranean climate zone, where rainy season extend from October until April, where the rest of the year can consider as dry. The annual rainfall varied from east to west and from south to north, this is due to the geographical location as well as to the altitude above sea level (Figure 1) (Ghanem, 2010 ; Herut et al,2000 ; Awad,2008).

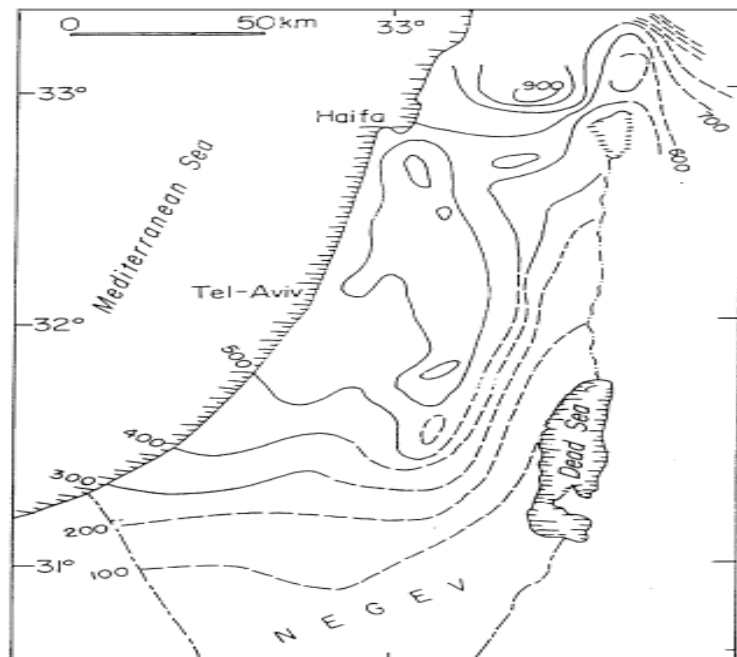


Figure 1: The annual rainfall contours in Israel (Herut et al, 2000)

The average total annual volume of waterfall over the West Bank is about 2700 – 2900 million cubic meter (MCM), the recharge rate varied from site to another depending on the rock formation, intensity of rainfall, land cover as well as land slope. The highest recharge rate was found at the top Hebron-Ramallah anticline as well as in Selfeet area, where the lowest recharge rate is in the Jordan Valley area followed by the Eastern Slopes (PWA, 2008).

According to the regional groundwater flow directions three groundwater basins are presence in the West Bank; these are Eastern, Western and North Eastern Basin (Figure 2) . In each Basin more than sub aquifer systems are presence, these known as Shallow one (Alluvial in The Jordan Valley and Jenin Aquifer in the Northern part of the West Bank), and the Deep Upper and Lower Aquifer of the Mountain aquifer (Rofe & Raffely,1963 ; Anayah,2006) .

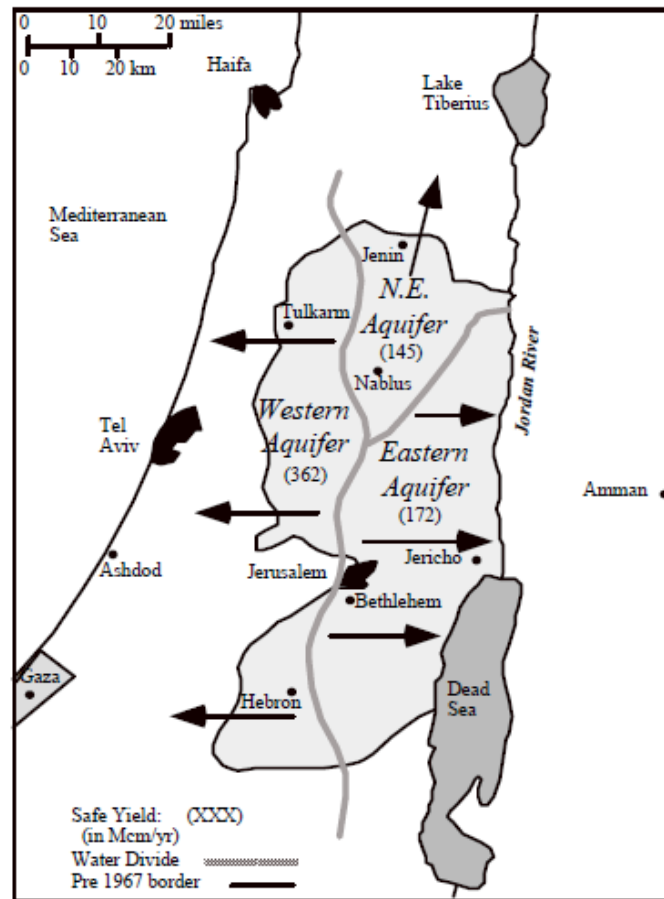


Figure 2: Groundwater basin in West Bank. (Rofe & Raffely,1963)

North Eastern Aquifer Basin (NEAB), it is considered the smallest aquifer basin in West Bank. Its area is about 1424 km². The replenishment rate of this aquifer as it has been agreed upon in Oslo Agreement is 145 MCM/Y, but the actual discharge is 184 MCM/Y (PWA, 2001).

The Eastern Basin and part of the North-Eastern Basin flow east towards the Jordan River and the Dead Sea. The Western Basin and part of the North-Eastern Basin flow westerly towards the Mediterranean Sea (Figure 2). (Scarpa, 1994; Abdul-Jaber et al, 1999; Abed and Wishahi, 1999; PWA, 2001; UNEP, 2003; Anayah, 2006).

The North Eastern Basin (NEB) extend from Zatra - Yetma - Kufur Hares south of Nablus city in the south to the North of Jenin city in the north, this basin has a triangular shape. 385000 Palestinian people are living within the surface watershed boundary of this Basin, cities like Nablus, Jenin, Tubas, Tammon and many small cities and villages overlay this basin.

Within the NEB, two aquifer systems are presence; these are the Jenin Sub-series aquifer system that related to Eocene age, where most of the springs in Nablus and Jenin Districts as well as most of the agricultural wells drain water from this aquifer. And about 17 deep wells (Palestinian and Israeli) abstract water from the Deep Mountain Aquifer with its two sub-aquifer , rock formation of the deep system are related to the upper Cretaceous age. Water production from these deep well estimated to be 15 MCM/Y. Groundwater recharge is driven through the annual rainfall, so groundwater fluctuation as well as discharge fluctuation is common mainly in the Eocene aquifer.

The annual precipitation is critical components in calculating water budgeting. So the high rainfall water quality changes after water infiltrate into the underground depending on different factors, such as the mineralogical composition of soil and rock layers, reaction and duration of pathway, and anthropological influences of man mad activities. (Apodaca, 2002; Martinez, 2002; Nwankwoala and Udom, 2011)

Water chemistry is a major component in water resources management especially in Semi-Arid region, like the study area. Increasing demand for both domestic and agricultural purposes force the stakeholder to provide the population with their water

need, consequently additional groundwater boreholes were drilled during the last 10 years, and additional boreholes are planned to drill.

1.2. Problem Statement:

There are many wells drilled in deep aquifer system and we are still need to drill more wells to provide the population with their water need, so it is important to know the quality of the groundwater in different site in this basin, if the quality including chemistry of these wells are similar or not, the reasons of salinity in some wells and where is the suitable place to drill the new wells.

Therefore, a logical starting point to study the groundwater geochemistry is studying the rainwater composition because it consider as the main input components into the groundwater aquifer.

Dafny (2006) said that it is widely accepted that each of the major ions dissolved in groundwater originates from three possible sources, rainwater, water-soil and water-rock interaction and anthropogenic influences. He proofed that the major ions dissolved in groundwater originated from present rainwater according to the result of isotopes.

So it is important to study the chemical composition of rainwater and ground water which lead to know the chemical reactions that happened underground between rainwater and rocks and effect on the groundwater chemistry in Northeastern Basin.

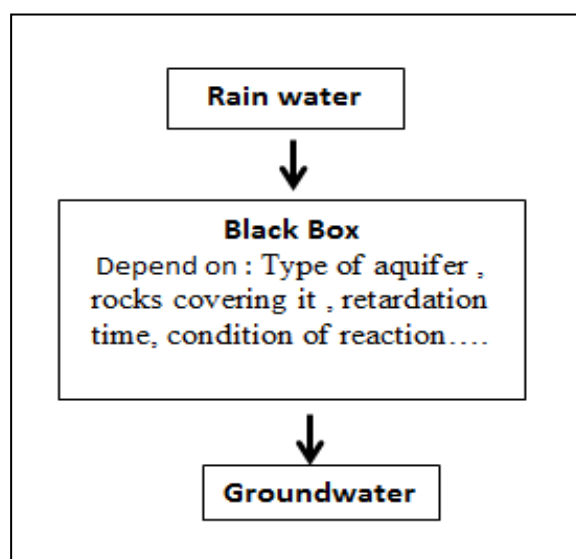


Figure 3: Schematic of the proposed concept of this study.

1.3.Objective:

The main objective of this study is to understand the change in water chemistry starting from rainwater into the groundwater in the Deep Aquifer System.

The main hypothesis of this research is that changes in water chemistry take place along the groundwater flow regimes from south to north direction within the Nablus-Beit Qad syncline which consider as the core of the NEB, and also groundwater chemistry change when water flow from Al- Faria anticline in the East to the center as well as from Anabta anticline in the west to the center of the syncline.

Chapter two

Study Area

2.1. Climate Data

In general, West Bank has a Mediterranean climate characterized by long, hot and dry summers and short, cool and rainy winters. Rainfall is limited to winter months starting with October and ending in May, while summer is completely dry. The average annual rainfall in the Northeastern part of West Bank is 415 mm. Approximately 80% rainfall falls during November through February. (ARIJ, 2002). Figure 4 shows locations of rainfall stations and the distribution of rainfall in the study area. While the annual evaporation is estimated to be 175.2 mm (Najem, 2008).

The quantity of recharge depends mainly on climatic conditions including rainfall, temperature, relative humidity, and wind, in addition to the soil type (infiltration capacity), land use and topography. The North Eastern Basin aquifer expected to be recharged through direct infiltration from rainfall as well as by wadi runoff.

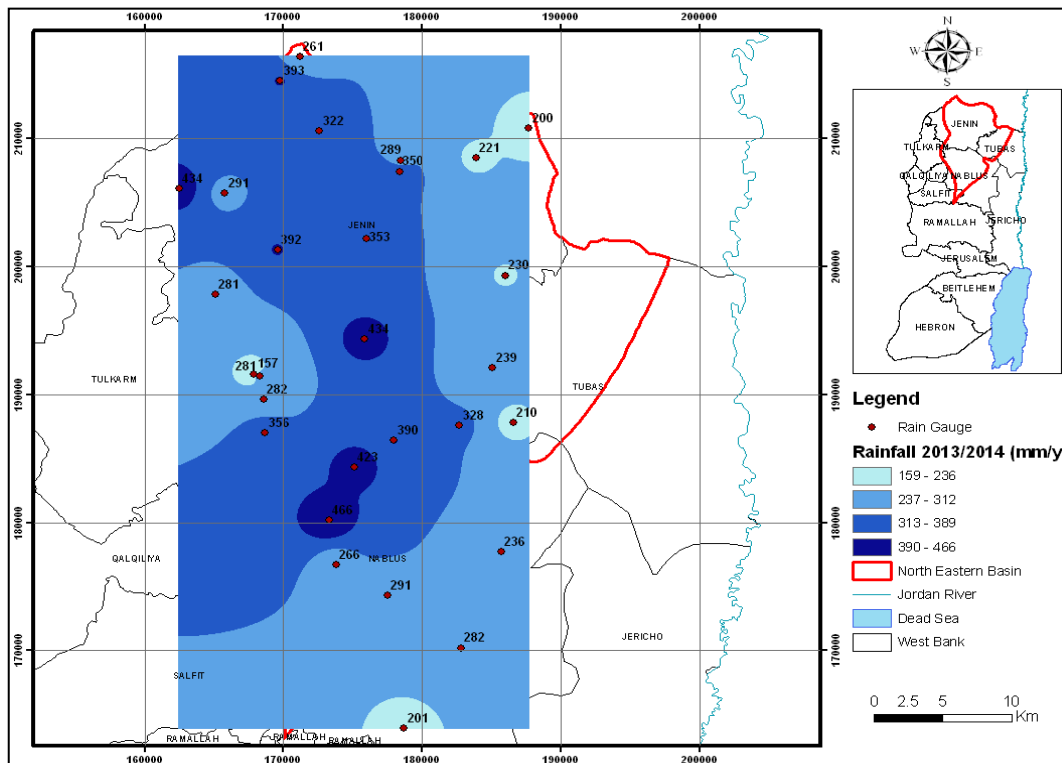


Figure 4: Spatial distribution of the rainfall in the study area

The annual mean of temperature is 20.3 centigrade degrees. January was the coldest month in the year, in which the lowest recorded temperature was 10.4 centigrade degrees, while August was the hottest month with 35.7 centigrade degrees. And the atmospheric pressure mean is 995.8 mbar , the highest value obtain in January and the lowest in June and November .The mean of relative humidity is 64% and mean average wind speed is 7.8 Km/h .The climate data was provided by Palestinian Central Bureau of Statistics (2010).

2.2.Geology and Hydrogeology

2.2.1 Rock Formation

The thickness and lithology of the Eocene Aquifer varies widely in the center and in the west. It is mostly highly karstic reef limestone in the east and soft chalk dominates. The primary hydrostratigraphic formation of the Eocene Aquifer as summarized and arranged from oldest to youngest are as follows (ARIJ, 2002):

1. Limestone, dolomite, and marl (Cenomanian to Turonian).
2. Chalk and chert of Senonian age.
3. Chalk, limestone and chert of Eocene age.
4. Alluvium of Pleistocene to Recent age.

The detailed geological studies for the study area show the following geological formations, figure 5. (Roffe and Rafaty, 1963):

1. Cretaceous Rocks

Cretaceous Rocks can be divided into the following formations:

- Lower Beit Kahil Formation : Outcrops of this formation exist in the core of the Faria anticline. The lower part of the sequence consists of thick and massive limestone and sandy marl shales in the middle and sandy ferruginous limestone at the top. This formation is considered a good aquifer.
- Upper Beit Kahil Formation: Outcrops of this formation exist in the north on the deeply eroded flanks of the Faria anticline. This formation is composed mainly of limestone, marl, dolomite and dolomitic limestone. It is a moderate to good aquifer.
- Yatta Formation: Outcrops of this formation exist in the north of Jenin district. The formation consists of chalky limestone, marl and calcareous karstic limestone. Hydrogeologically, it is regarded as a poor aquiclude.

- Hebron Formation: The main outcrops are exposed mainly in the northwestern part of Jenin district as well as in the Far'a anticline. The lithological composition consists of limestone, dolomite and chalky limestone; it is regarded as the important aquifer in the district.
- Bethlehem Formation: Outcrops exist on the flank of the Anabta anticline. This formation consists of dolomite, limestone and chalky marl.
- Jerusalem Formation: The most extensive outcrops are in the Anabta anticline and in the flanks of the Far'a anticline. It consists of massive, bedded limestone, dolomite and chalky limestone. The formation forms a good aquifer.

2. Rocks of Cretaceous to Tertiary Transition Chalk

The outcrops exist in the western limb of the Nablus-Beit Qad syncline. This formation consist mainly of chalk of Senonian to Paleocene age. The chalk is usually dark colored due to the presence of bituminous materials and has a variable thickness varied from 80 meters near the boundary of the syncline to few hundred meters in the middle of the syncline, due to the earth's movements during its composition. It also include conglomerated, thin-bedded limestone. The chalk faces make the formation a good aquiclude.

3. Tertiary Rocks

These are represented by two lithological units:

- Jenin Subseries: this consists mainly of chalk of Eocene age. Outcrops are widely spread covering large areas of the district. In this formation, five faces of limestone and chalk are described: chalk with minor chert, chalk with inter-bedded limestone, limestone with minor chalk, massivelimestone and reef limestone. Generally, it forms a good aquifer except in the chalk zone, where it forms an aquiclude. Variable thickness reaches about 700 meters in some places of Jenin district.
- Bayda Formation: this ranges in age from the Miocene to Pliocene. Conglomerate forms the main composition of this formation, with some marl and limestone. There is unconformity between the conglomerate and Cretaceous rocks. Outcrops are extensive in the northeast of the district in the Bardala-Bayda area.

4. Quaternary Rocks: this consists of unconsolidated laminated marl with some siliceous sand known as alluvium rocks. It has a red color and fine texture, which is due to its derivation from limestone.

5. Igneous Rocks: These are widespread east of Beit Qad. These rocks are dark, green, fine-grained, basic or sub-basic, and have a strong jointing

2.2.2 Structure and Tectonics

1- Folding

- **Anabta Anticline**

It extends to about 25 km, and trends north-south. Its northern part has southerly pitch but the southern part is broken by faults. The Anabta anticline is symmetrical in structure, figure 5.

- **Far'a Anticline**

It is considered as one of the main folds in Nablus district. It trends north and northwest (NNW) and extends to about 10 km. The east and west limbs of the anticline form two minor folds, Rujeib monocline and Khirbet Fasayil monocline. Its broad axial area is distinguished from the flanks. The anticline has a symmetrical structure, figure 5.

- **Nablus –Beit Qad Syncline**

It covers an area of about 1500 km. The axis trends north and northeast to south and southwest (NNE-SSW), but near Jamm'in it bends sharply westwards. The northern part has a northerly pitch except for the last few kilometers where it tilts southwards. The syncline is symmetrical with a gently dipping west limb and a steep east limb, figure 5.

2- Faulting

Faulting in the area follows the general axes northwest southeast (NW-SE). Faulting has resulted in the formation of several graben structures in the area. The effect of faulting on the Eocene limestone of the western West Bank is less visible.

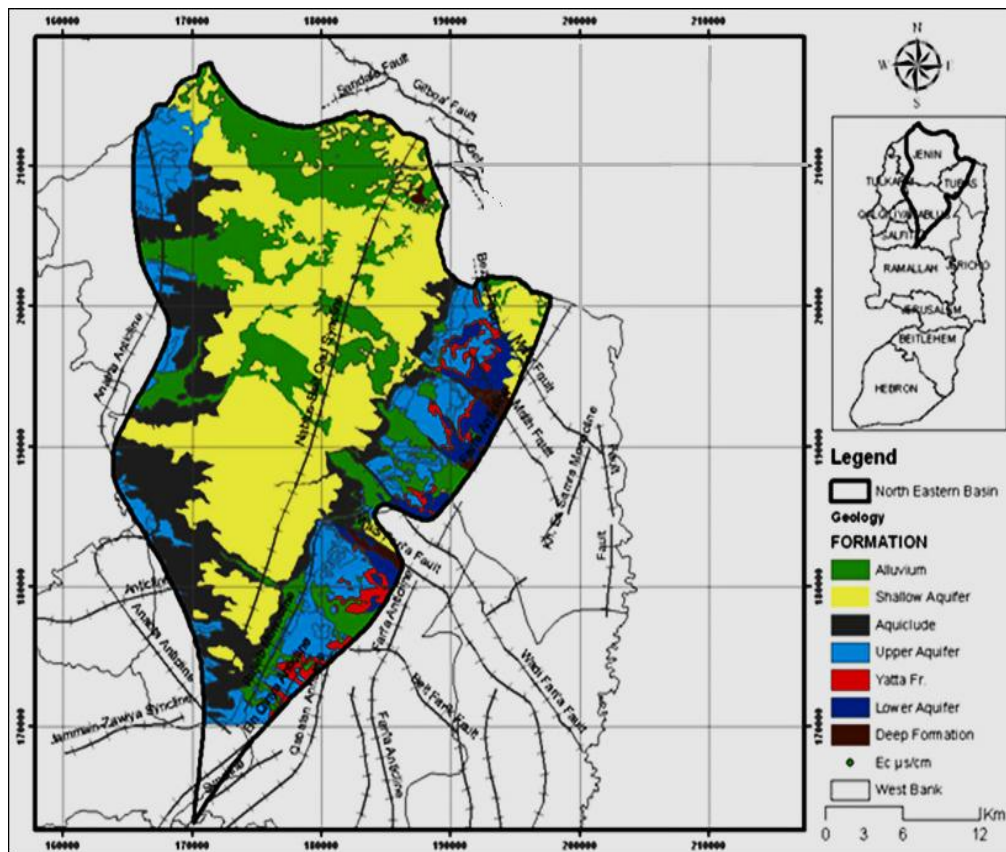


Figure 5: Geological formation of study area.

The geological map, figure 5 and cross sections, figure 6 shows that most of the outcrops in the study area covered with shallow and alluvium deposits that vary with thickness

Jenin formation is the most predominant outcrop with marly limestone. In general Jenin formation can slowing the process of recharge to deep layers, moreover, the presence of the underlying Abu Dis formation make the evidence of direct recharge to the upper and lower aquifers layer very rare, three cross-section were constructed to study area (Figure 7,8,9).

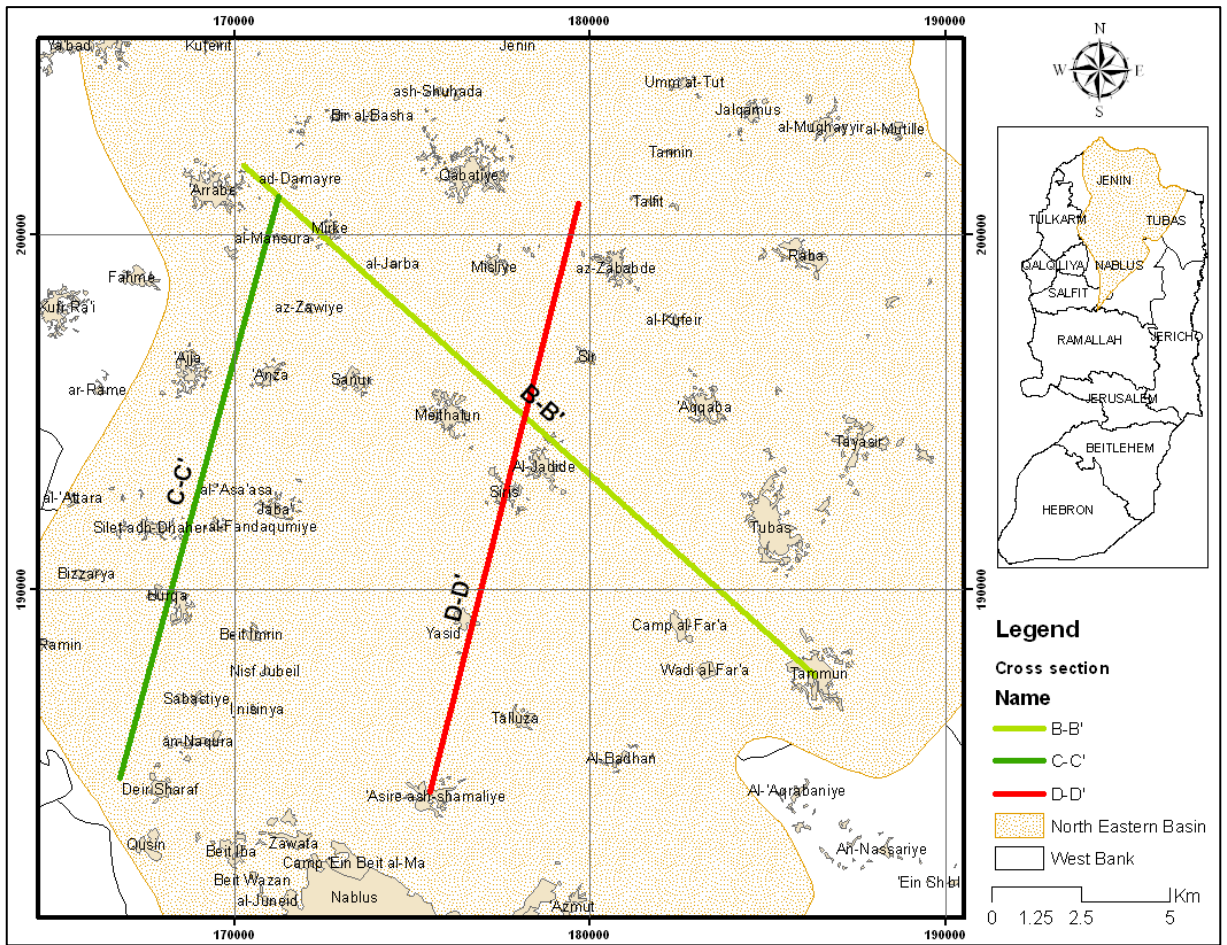


Figure 6: Cross section locations over the study area.

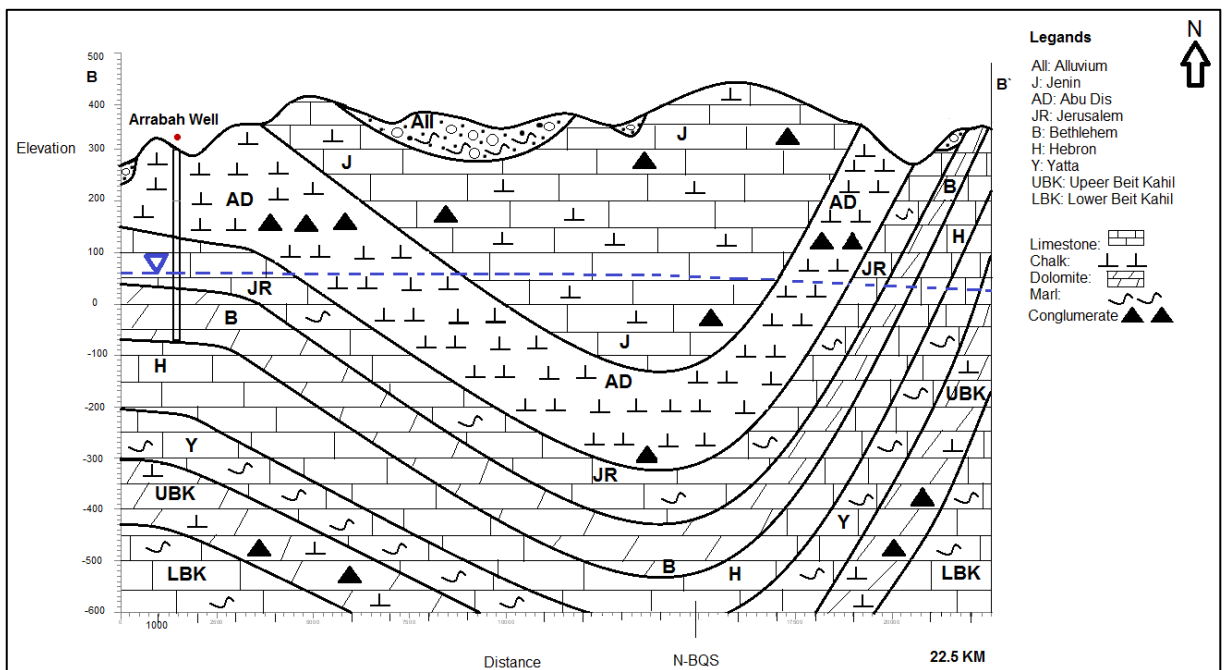


Figure 7: Cross section B-B',

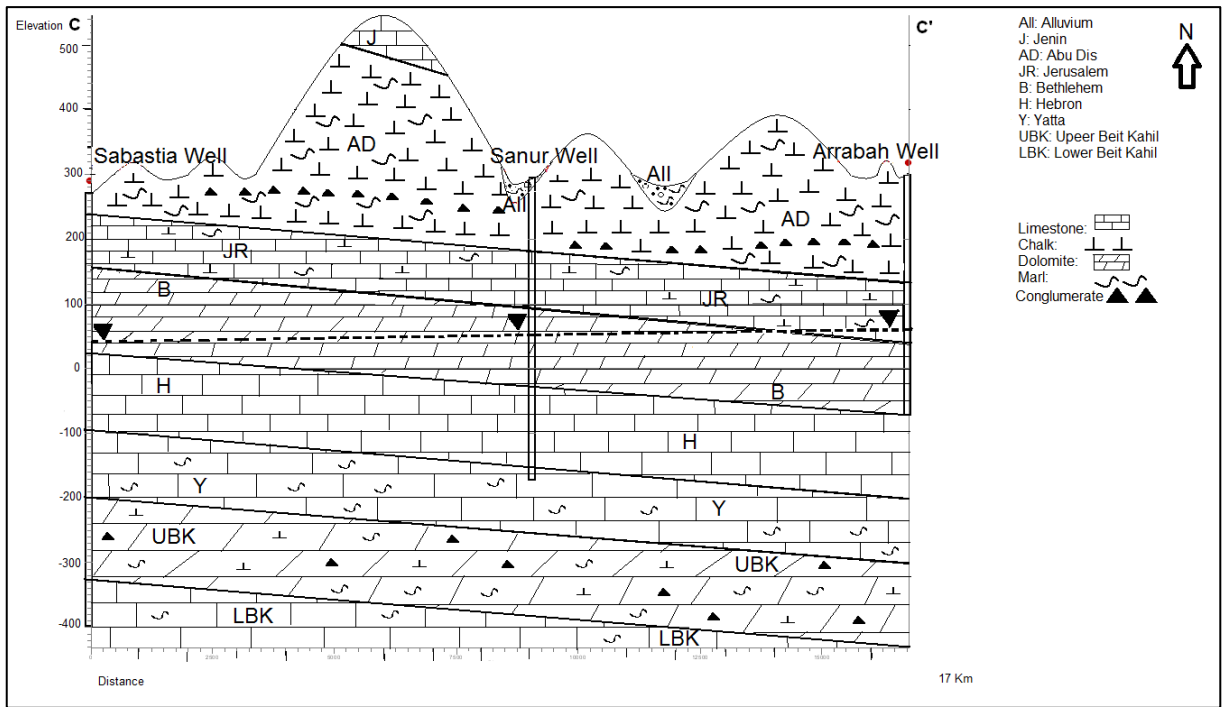


Figure 8: Cross section C-C',

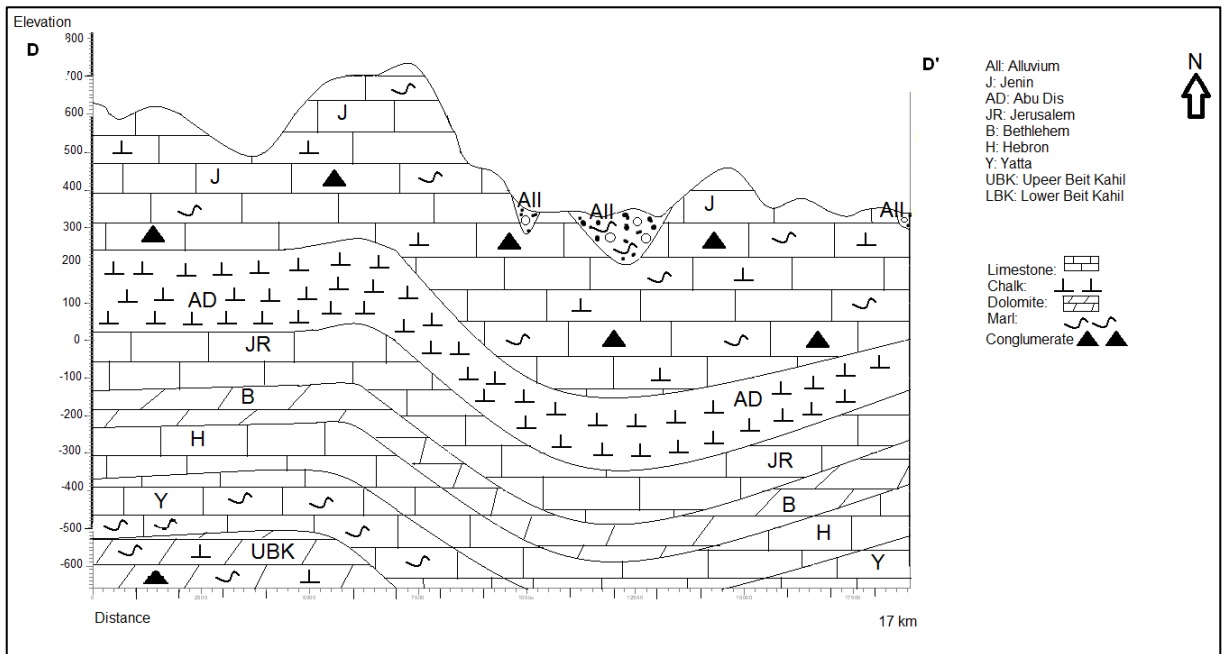


Figure 9: Cross section D-D',

Chapter Three

Literature Review

There are many previous studies that are studying the chemistry of rainwater, and other studied the interaction between rainwater and groundwater, some of these studied and there result are illustrated as follow:

3.1 Literature Review for Rainwater

- **Zhang et al (2011)**; studied the chemical composition of rainwater in central Tibetan Plateau from August 2005 to August 2009 , he found that Ca^{2+} and HCO_3^- have the highest concentration among ions and the source of these ions is terrestrial source due to influence of crustal dust that rich in calcium .
- **Attar et al (2011)**; studied and analyzed samples that collected from rainwater, the resulting runoff in urban drainage channels and the Khoshk River to evaluate their quality and found that existence of deserts around the country can have considerable effects on rainwater quality and alkalinity. The higher concentration of sulphate in rainwater and the alkalinity of the rainwater samples reflect the effect of soil dust originating from deserts, which contains a large fraction of calcite, dolomite, gypsum and halite.
- **Khoon et al (2011)**; analyzed the rainwater chemical composition in Setapak district of Kuala Lumpur using ion chromatography method to evaluate the air quality, It was observed that the nitrate and sulphate ions concentrations have increased over the past two decades mostly due to rapid economic development of Malaysia.
- **Ghanem et al (2010)**; studied the Hydrochemical variation of rainwater in Ramallah District in West Bank by analyzed the samples of rainwater through two rainy seasons (2007-2008), he found that sodium and potassium concentration in western parts more than eastern parts due to the nearest distance to Mediterranean sea, also found three types of rainwater and it was Na-Cl , Na- HCO_3 and Ca- HCO_3 .
- **Al-Khashman (2009)**; studied the chemical composition of rainwater in Ghore El-Safi area western side of Jordan in order to understand factors that affect

the rainwater chemistry and he suggested that rainwater chemistry is strongly influenced by local anthropogenic sources (potash factory and agricultural activities in Ghore El-Safi area) rather than natural and marine sources. The pollutants in rainwater samples were mainly derived from long distance transport, local industry and traffic sources.

- **Qabajeh (2008)**; studied the chemical composition of rainwater in Abu-Dis for the period 2001-2007, 122 samples were analyzed to identify the characteristic and source of main ions and the result shows that Na^+ and Cl^- source mainly from marine, while Ca^{2+} and Mg^{2+} from terrestrial source, and the relative abundance of ions in precipitation is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+$ for cations and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ for anions.
- **Baez et al (2007)**; analyzed rainwater samples collected from two place in Mexico for the periods 1994–2000 and found large variations in rainwater chemical composition in most years, mainly because of the variability of meteorological conditions and also because of changes in source emissions. Concentration of SO_4^{2-} decrease due to decrease in SO_2 emissions resulting from the change of fuel oil to gas fuel.
- **Arsene et al (2007)**; studied the chemical composition of rainwater in the northeastern Romania, Iasi region, and found that the pH of the rainwater is 5.92 suggesting a sufficient load of alkaline components neutralizing its acidity. On average, 97% of the acidity in the collected samples is neutralized by CaCO_3 and NH_3 .
- **Tiwaria et al (2007)**; studied the monsoon precipitation chemistry at eight different locations in Delhi to understand the nature of rainwater and sources of pollution, the order of concentrations of major ions in samples was $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NH}_4^+ > \text{Cl}^- > \text{NO}_3^- > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$.
The source of ions were suspended soil–dust and sea salts, which are natural sources, Acidity, observed at some location is attributed to industrial influence.
- **Li et al (2007)**; analyzed precipitation samples collected from Nam Co Monitoring and Research which located in the central Tibetan Plateau and found high pH value due to large inputs of crustal aerosols in the atmosphere, which contain a large fraction of carbonate. Also found that HCO_3^- and Ca^{2+} are the predominant ions . Correlation and Empirical Orthogonal Function (EOF) analysis indicate that

regional crustal aerosols and species from combustion emissions of residents are the major sources for these ions, lake salt aerosols from the Nam Co nearby and regional mineral aerosols from dry lake sediments are secondary sources, and sea salt contribution is the least due to the long distance transport.

- **Demirak et al (2006)**; studied the chemical composition of the rainwater in Mugla-Turkey, The equivalent concentration of components followed the order: $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Na}^+ > \text{K}^+ > \text{H}^+$. High concentration of Ca^{2+} and SO_4^{2-} due to dust-rich local and surrounding limestone environment and the relatively high concentration of NH_4^+ observed is suspected to be due to surrounding agricultural.
- **Tu et al (2005)**; studied the variations of the chemical composition of precipitation in Nanjing, China, over 12 years and found that the source of ions came from anthropogenic and crustal sources, also decreasing in concentration of SO_4^{2-} because of the abatement strategies for SO_2 emissions and energy policy change, while a significant increasing trend was found in the contribution of NO_3^- to acidification due to the rapidly growing number of motor vehicles. A significant decreasing trend was found in dust-derived cation Ca^{2+} due to more stringent controls of industrial dust emissions and rapid urbanization reducing the amount of open land.
- **Mouli et al (2005)**; studied rainwater chemistry over a one year period at a regional representative urban site, Tirupati, India, and found good correlation between the crustal ions (Ca, Mg, K and NH_4) and SO_4 so he suggested that the ionic composition of rainwater in the region is strongly influenced by terrestrial sources rather than anthropogenic and marine sources.
- **Migliavacca et al (2005)**; studied the chemical composition of precipitation in the Guaíba Hydrographic Basin, in South Brazil, and found that the Cl^- present in samples originated from sea salts and anthropogenic sources.
- **Al-Khashman (2005)**; analyzed precipitation samples collected in Petra –Jordan, and found that rainwater quality is characterized by low salinity and neutralized pH. Factor analysis was used to identify the factors that affect the presence of ions in wet precipitation and suggest three sources, which is crustal dust, sea-salt spray and combustion products.

- **Root et (2004)**; studied the chemical composition of rainwater collected from 48 sites in 31 states throughout the United states ,then he discovered that rainwater usually contains chloride , nitrate and sulfate anions, whereas phosphate and nitrate anion were less prevalent. Chloride concentration correlate with proximity to ocean, which are rich in salt. $\alpha^{18}\text{O}$ are also dependent on geographical location , as well as altitude ,the amount of rainfall and distance from the source of the rain (usually an ocean).
- **Zunckel et al (2003)**; studied the chemical composition of rainwater from 1999 to 2000 in Northeast Uruguay and suggest four contributed factors to rain composition in the area and these are terrigenous (rock, soil, dust), agriculture, marine air influx and biomass burning.
- **Hontoria et al (2003)**; studied the chemical characteristics of precipitation in Madrid, and found that the marine influence did not appear to be relevant, while the soil seemed to play an important role in the composition of precipitation and precipitation chemistry displayed seasonal differences, with higher concentrations of sulphates and chloride in autumn and winter and of calcium and sodium in the summer.
- **Lara et al (2001)**; studied the chemical elements in atmospheric precipitation in south Brazil ,and measure ions concentration and pH levels in rainwater to determine the effect of coal and limestone mining industry of rainwater composition and conclude that rainwater slightly affected by the dust emission from these industries.

3.2 Literature Review for Groundwater

- **Dikeogu et al (2014)**; investigate in geochemical processes of aquifer systems in Port Harcourt ,Nigeria using hydrochemicalfacies and ionic ratios by using hydrogeochemical analysis of groundwater samples collected from ten boreholes. Results of the analysis show that the concentrations of these cations and anions in the groundwater system exhibit spatial and temporal variations. Abundance of these ions is in the following order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$. The dominant facies of the area are Ca-Mg-Cl-HCO₃ and Ca-Mg-Cl-SO₄. Carbonate

and silicate weathering as well as ion exchange processes are mechanisms controlling groundwater chemistry in the area.

- **Singh et al (2013)**; evaluated hydro-geochemical parameters and heavy metals in groundwater in the Rupnagar District of Punjab, The spatial distribution of physico-chemical parameters were studied using Arc GIS 9.2. It was observed that the concentration of parameters, such as NO_3 , Cd, Cr, Mn and Pb was above permissible limit (World Health Organization, WHO) in southern part of the study area. The heavy metal pollution index (HPI) was calculated for all sampling locations and it was found much above the critical limit of pollution. It also suggests that evaporates, ion exchange, dissolution along with anthropogenic activities are controlling the hydro-geochemistry of groundwater in the region
- **Nwankwoala et al (2013)**; studied groundwater systems in Port Harcourt City, Southern Nigeria. Thirty two (32) groundwater samples were analyzed for their physical and chemical properties. The analytical results show the abundance of the ions in the following order: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$, $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^-$. Elevated EC values in some locations are indicative of high ionic activities as well as salinity and suggest possible pollution of groundwater. Chloride concentrations in some boreholes are up to 710mg/l, which shows saltwater encroachment. For determining groundwater types and visualizing trends of groundwater chemistry, Piper trilinear diagrams reveal that there is a mixture of two types of water with variable concentrations of major ions. These are Ca-Mg-Cl- SO_4 type and Na-K-Cl- SO_4 type water.
- **Rina et al (2012)**; studied groundwater in North Gujarat, India. The study attempts to identify the factors and processes controlling the groundwater salinity in the area, based on ionic ratios in integration with various graphical methods, saturation indices and geographical information system. And found that along with natural processes, intensive agricultural and anthropogenic waste water infiltration from industrial activities are the major sources of salinization and the dominant processes which govern the groundwater salinity.
- **Saleem et al (2012)**; analyzed the impact of rainwater harvesting on groundwater quality in Jamia Millia Islamia university, New Delhi India campus, where rainwater harvesting structure is installed and found that the rainwater recharges and

improves the quality of groundwater which is also depends upon the amount of rainwater recharged and the environment of rainwater collection and recharging.

- **Shivasharanappa et al (2012)**; assess the groundwater quality characteristics of Bidar city and its industrial area. The groundwater samples of all the 35 wards were collected and subjected for a comprehensive physicochemical analysis. The following 17 parameters have been considered viz., pH, total hardness, calcium, magnesium, chloride, nitrate, sulfate, total dissolved solids, iron, fluoride, sodium, potassium, alkalinity, manganese, dissolved oxygen, total solids & zinc. The results analyzed by Correlation and Regressions, have been used to suggest models for predicting water quality. The analysis reveals that the groundwater quality status of the study area is good, but it also needs to be protected from the perils of contamination by giving certain degree of treatment.
- **Krishnaraj et al (2011)**; studied the groundwater samples in Thirumani-muttar sub basin the Kerala state of India in order to identifying hydrochemical processes and their relation to groundwater quality and found groundwater is generally neutral to alkaline in nature. The abundance of the major cations and anions in the groundwater are of the following order: $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^- > \text{Br}^- > \text{F}^- > \text{PO}_4^{3-}$ and $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. The sources of ions into the groundwater are from dissolution and leaching from source rocks, cation exchange and anthropogenic activities. The saturation index calculated specify oversaturation of carbonate species and undersaturation of amorphous silica indicating groundwater chemical evolution controlled by water rock interactions. Water type alters from Ca-HCO₃ to Na-Cl indicating groundwater chemistry controlled by rock-water interaction and anthropogenic activities. This suggests that the groundwater hydrochemistry is controlled by water rock interaction and anthropogenic pollution.
- **Nas et al (2008)**; determined the quality of groundwater in Konya City, located in the central part of Turkey, to provide an overview of present groundwater quality and to determine spatial distribution of groundwater quality parameters such as pH, electrical conductivity, Cl^- , SO_4^{-2} , hardness, and NO_3^- concentrations, and to map groundwater quality in the study area by using GIS. The final map shows that the southwest of the city has optimum groundwater quality, and, in general, the groundwater quality decreases south to north of the city; 5.03% (21.51 km²) of the total study area is classified to be at the optimum groundwater quality level.

- **Lee et al (2007)**; studied seawater intrusion in a monitoring well field, located in western coastal area of Buan, Korea using groundwater chemistry and ionic ratios. Most of the study area is paddy fields apart from 200–2,500 m from the coast. The groundwater affected by the seawater intrusion featured high levels of Cl and TDS, which are the simplest common indicators for the seawater influence. High levels of NO₃ at some monitoring wells indicated nitrate pollution of groundwater due to anthropogenic origin such as septic effluents or chemical fertilizers.
- **Olobaniyi et al (2007)**; studied the disparity of physico-chemical and bacteriological quality between rainwater and groundwater within Warri (an oil producing town) and environs, The results of the physico-chemical parameters show lower values in rainwater (pH, 5.10-6.35; total dissolved solids, 12.40-22.00mg/l; conductivity, 14.05-42.10μS/cm; Ca²⁺, 0-0.50 mg/l; Mg²⁺, 0.06-0.70mg/l; Fe, 0.01-0.04mg/l; HCO₃⁻, 8.45-23.25 mg/l; Cl⁻, 19.51-26.95mg/l) when compared to groundwater (pH, 4.70-8.40; total dissolved solids, 21.90-300.50 mg/l; conductivity, 43.51-601.00μS/cm; Ca²⁺, 17.64-94.40 mg/l; Mg²⁺, 1.93-39.85mg/l; Fe, 0.06-0.15mg/l; HCO₃⁻, 10.05-111.90mg/l; Cl⁻, 26.35-128.00 mg/l). However, markedly higher concentration values of Pb (0.05-0.56mg/l), NO₃⁻ (24.00- 38.00 mg/l) and SO₄²⁻, (24.00-42.00 mg/l) were recorded for rainwater than groundwater (Pb, 0-0.10 mg/l; NO₃⁻, 0.05-0.60mg/l and SO₄²⁻, 0.02-0.16 mg/l). Microbiological analysis indicated that while no coliform bacteria were detected in rainwater they occurred in groundwater (0-7.38log₁₀cfu/ml). The observed quality disparity reflected in relative parameter enrichments may be attributed, in groundwater, to natural hydrogeochemical processes and microbial contamination reflecting the unsanitary habits of the inhabitants. In rainwater, it could be related to atmospheric pollution from vehicular exhausts and gas flaring by petroleum industries.
- **Jalali (2006)**; studied the groundwater samples from Tajarak area, western Iran, in order to assess their chemical compositions and suitability for agricultural purposes. All of the groundwater are grouped into two categories: relatively low mineralized of Ca–HCO₃ and Na–HCO₃ types and high mineralized waters of Na–SO₄ and Na–Cl types. The chemical evolution of groundwater is primarily controlled by water–rock interactions mainly weathering of alumino-silicates, dissolution of carbonate minerals and cation exchange reactions. The groundwater is oversaturated with respect to calcite, aragonite and dolomite and under saturated with respect to gypsum, anhydrite and halite. With respect to adjusted SAR, the sodium (Na⁺)

content in 90% of water samples in group A is regarded as low and can be used for irrigation in almost all soils with little danger of the development of harmful levels of exchangeable Na⁺, while in 40 and 37% of water samples in group B the intensity of problem is moderate and high, respectively. Such water, when used for irrigation will lead to cation exchange and Na⁺ is adsorbed on clay minerals while calcium (Ca²⁺) and magnesium (Mg²⁺) are released to the liquid phase. The salinity hazard is regarded as medium to high and special management for salinity control is required. Thus, the water quality for irrigation is low, providing the necessary drainage to avoid the build-up of toxic salt concentrations

- **Owoyemi et al (2006)**; examines the hydro-chemical facies of groundwater present in the Deltaic Plain Sands aquifer of Warri and its immediate environs, 60 water samples were collected from wells and analyzed for various parameters including pH, total dissolved solids (TDS), K, Na, Ca, Mg, Cl, HCO₃ and SO₄. The data obtained were subjected to R-mode factor analysis. Three factors were extracted. Factor 1 includes K, Na, Cl, and EC and reflects the signature of saline water incursion resulting from seepages into the aquifer of water from the tide-influenced River Warri. Factor 2 has high loading values of Mg, Ca, HCO₃ and pH and represents the processes of natural rainwater recharge and water-soil/rock interaction. Factor 3 includes SO₄ and can be related to the dissolution of sulphides from interstratified peat within the geological formation heavy vehicular activity and the petroleum refining process in the town. His research demonstrates the effectiveness of factor analysis in evaluating hydro-chemical processes in coastal land industrial areas.
- The water quality for the Palestinian wells in the West Bank was analyzed by **PWA (2001)**. The water quality has been considered for only two major parameters: chloride and nitrate concentrations. There is chloride data of 363 wells available and nitrate concentration for 365 wells. It was found that 96 wells exceed the WHO standards for drinking water where none of which is domestic concerning the nitrate concentration, whereas most of these wells locate in the Eastern Basin (Jericho area). As for the nitrate analyses, about 97 wells have concentrations exceeding the WHO standards for drinking water, 13 of which are domestic wells. The maximum nitrate concentration in the domestic wells was measured at 112 mg/l in the Tulkarm area tapping the Cenomanian-Turonian aquifer.

- **Abed and Wishahi (1999)**; carried out a comprehensive field study on the geology of Palestine. This field study includes an assessment of water resources, geologic formation of Palestine, groundwater basins, water uses, and many other disciplines. This study also assessed the quality of drinking water in Palestine. Nitrate contamination of groundwater is caused by infiltration of fertilizers and raw sewage, and elevated concentrations are found throughout the West Bank.
- A detailed study by **Marei and Haddad (1996)**; found nitrate levels above the WHO standard for drinking water (i.e. > 50 mg/l) in up to one-third of the sampled wells in the Jordan Valley, Nablus, Jenin, and Tulkarm districts.
- **Qannam (1997)**; studied, classified, and evaluated the water of the wells in the southern part of the West Bank, south of Jerusalem, for both drinking and irrigation purposes and highlighted the main environmental water-related issues. The study showed that most of the wells have low sodium, potassium, chloride, sulphate, and nitrate concentrations, and thus are suitable for both drinking and irrigation purposes.

Our research will focus in studying the chemical composition of rainwater samples and groundwater samples abstracted from Deep Aquifer System, from different positions in North Eastern Basin (NEB), and make an interpretation for changes between them, in order to determine the main reactions happened in underground, and causes these changes.

Chapter Four

Methodology

4.1 Rainwater Sampling

Samples of rainwater were collected in Abu-Dis weather station by using porcelain sampler container to collect rainwater sample and measure rain amount by using mechanical precipitation recorder .For physical and chemical analysis pH meter by WTW Company, EC meter from the same company, spectrophotometer (HACH type DR 2010) and atomic absorption spectrometer (Perkinelmer. A .Analysis 200) were used. Figure 10,11,12,13,14.



Figure 10: pH meter

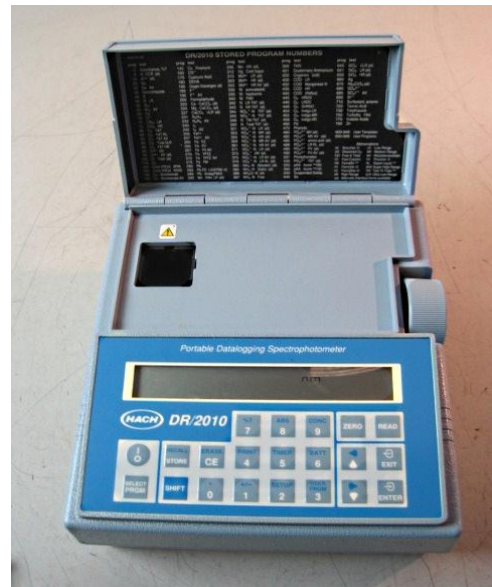


Figure 11: Spectrophotometer



Figure 12: Atomic absorption spectrometer



Figure13: Porcelain sampler container



Figure14: Mechanical precipitation recorder

4.2 Groundwater Sampling

Seventeen groundwater samples were collected from the deep groundwater boreholes that are tapping water from the Upper Aquifer system. Table 1 list information about these wells and Figure 15 show the wells site. Physical characteristics of water such as pH, EC and temperature were measured immediately in the field. Chemical analysis for cations and anions concentration were carried out at Al-Quds University-Lab and analyzed by using standard methods (APHA, 1995). Calcium (Ca) and Magnesium (Mg) were determined titrimetrically using standard EDTA(Ethylene diamine tetra acetic acid) . Chloride (Cl) was determined by standard AgNO_3 titration. Bicarbonate (HCO_3) by titration with HCl. Sodium (Na) and Potassium (K) by flame photometry. Sulphate (SO_4) and Nitrate (NO_3) were determined by spectrophotometer (Table 2). The quantity controls of the measurements consisted of duplicate samples. (Krishnaraj, 2011)

Table 1: Wells used to collect groundwater samples in study area

Well Name	Location	Well code	Elevation (m)	Depth(m)
Tubas well	Tubas	18-18/017	223	150
Beit Aeba	Nablus	16-18/005	330	595
Abu Arab	Jenin	17-20/052J	245	923
Qabatia	Jenin	17-20/014Q	260	62
Al Far'a	Nablus	18-18/038	90	413
Sabastya	Nablus	-	-	-
Hewara	Nablus	17-17/003	510	525
Araba	Jenin	17-20/051A	300	370
Roujeb	Nablus	17-17/001	500	585
Sanor	Jenin	16-19/012	293	466
Al Bathan	Nablus	18-18/037	210	748
Tamoun	Jenin	18-18/040	260	400
Deir Sharaf	Nablus	16-18/003A	272	670
Yamoun	Jenin	17-21/035	123	425
Caferet	Jenin	-	-	600
Maythaloun	Jenin	17-19/008	360	1301
AL-Sa'da	Jenin	-	-	899

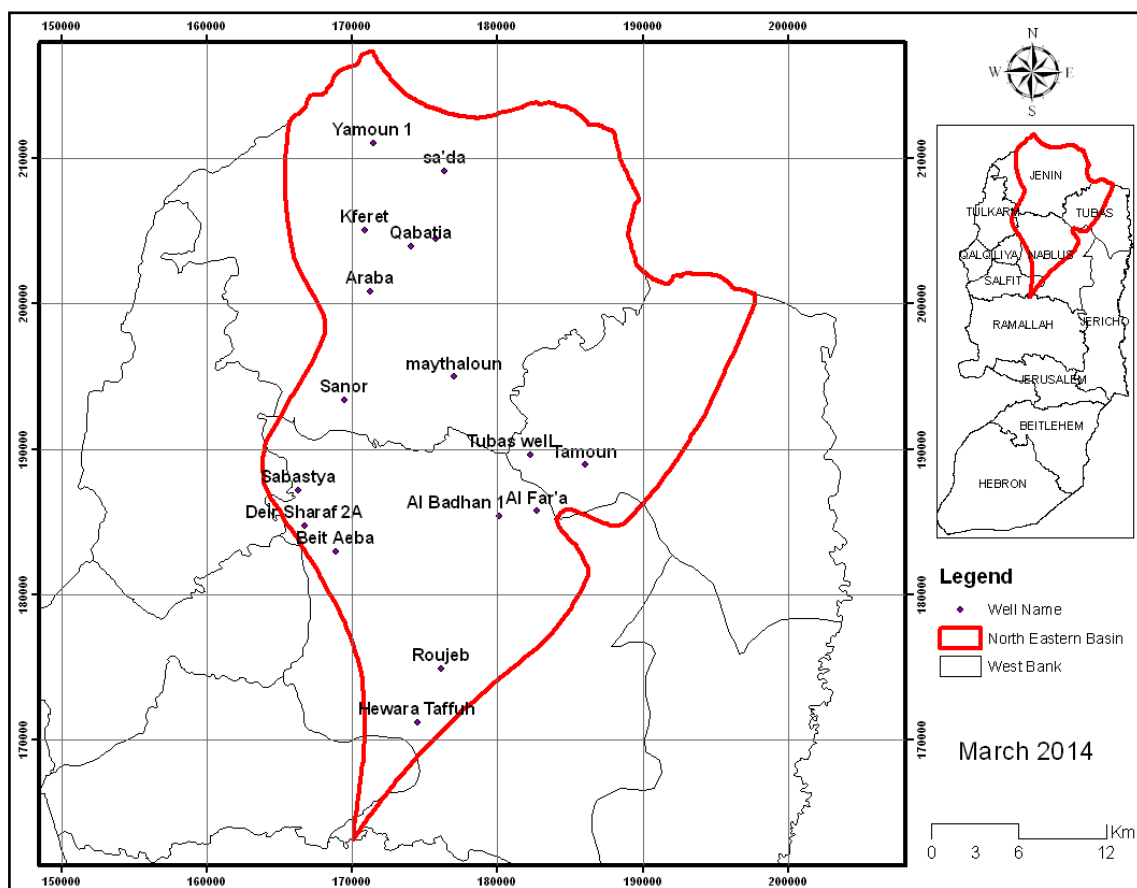


Figure15: Groundwater sampling sites.

Table2: Methods used for physical and chemical analysis for groundwater samples.

Parameter	Method
PH	pH meter
EC	EC meter
Ca ²⁺ , Mg ²⁺	Titration (using standard EDTA)
Na ⁺ , K ⁺	Flame photometry
NO ₃ ⁻ , SO ₄ ²⁻	Spectrophotometer
Cl ⁻	Titration (Potassium chromate K ₂ CrO ₄ used as indicator & AgNO ₃ used as titrant)
HCO ₃ ⁻	Titration (mixed orange used as indicator & HCl used as titrant)

4.3 Geological Cross Sections

In order to understand the changes in water chemistry from the recharge sites to the discharge zones, new geological cross sections were constructed. Lithological boreholes data from the Palestinian Water Authority (PWA) and from published geological map were used to understand the changes in geology and consequently the water chemistry.

4.4 Type of Water

Piper's diagram (1944) has been used to determine the hydrochemical facies of water, which are a function of lithology, solution kinetics and flow pattern of groundwater through the aquifer, and provide insight into the geochemical evolution of groundwater (Rina,2012).

4.5 Saturation Index

The changes in saturation state has been used to distinguish different stages of hydrochemical evolution and to identify which geochemical reactions are important in controlling water chemistry (Koetsiers and Walraevens, 2006).

To evaluate the degree of equilibrium between water and the respective mineral, the saturation index (SI) of minerals was calculated by PHREEQC in Aqua Chem program, using the following equation (Garrels and Mackenzie, 1967):

$$SI = \log (IAP / K_t)$$

Where, SI is saturation index of a mineral, IAP is ion activity product of the dissociated mineral,

K_t = equilibrium solubility at mineral temperature.

SI<0 indicates that the groundwater is under-saturated with respect to a particular mineral.

SI>0 reflects whether the groundwater is oversaturated with respect to a particular mineral (Rina, 2012).

Chapter Five

Results and Discussion:

5.1 Physical and Chemical Analysis for Rainwater

One hundred sixteen (116) rainwater samples have been analyzed hydrochemically for the period between November 2007 and April 2013.

Table 3, listed number of sample, arithmetic average, standard deviation maximum and minimum value of physical and chemical parameters that is related to the rainwater samples collected during the period 2007-2013.

Table 3: Physical and chemical parameters of rainwater samples collected during the period (2007-2013), ion concentration measure in (mg/L)

Parameter	number of sample	arithmetic average	standard deviation	Maximum value	Minimum value
pH	104	7.14	0.54	8.81	5.67
EC ($\mu\text{S}/\text{cm}$)	105	122.61	98.01	637.00	32.00
Ca^{+2}	102	10.96	8.79	43.00	0.68
Mg^{+2}	98	1.69	1.71	7.30	0.04
K^{+}	95	2.63	2.33	11.47	0.08
Na^{+}	99	8.94	9.70	37.40	0.09
NH_4^{+}	31	1.79	1.32	6.50	0.03
Cl^{-}	71	22.42	15.88	78.00	3.60
HCO_3^{-}	64	38.0	18.6	97.20	12.20
SO_4^{-2}	87	8.51	7.13	32.00	0.00
NO_3^{-}	76	10.28	6.61	39.20	1.75
Br^{-}	47	0.77	0.71	2.60	0.017

5.1.1 pH value

Figure 16 represent pH value for 104 sample of rainwater, (7-7.4) interval represent the highest percent with 41%. Also 88% of samples range between 6.5 and 7.9, which is in the range of neutral water, because pH value of rainwater affected by the atmospheric dust, which is rich in carbonate dust. 2% of sample lie within the acidic range, but it still light acidic with pH (5.5-5.9) and 4% in basic range also still light basic with PH (8-8.9). The explanation of these results that in this area there was no factories emitting gases or products have an acidic or alkaline impact on the atmosphere. These results similar to Qabajeh, 2008; Herut, 2000 and Al-Khashman, 2009 results, table 4.

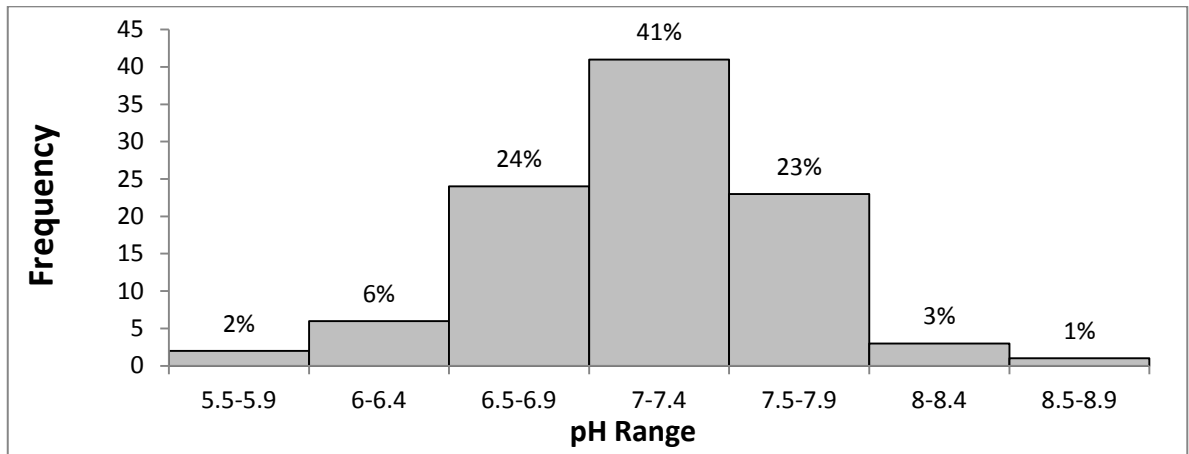


Figure 16: Histogram of pH value of rainwater sample during the period of (2007-2013)

5.1.2 Electrical Conductivity (EC) value

The average value of EC is 122.61 $\mu\text{S}/\text{cm}$, with maximum value 637 $\mu\text{S}/\text{cm}$ that is record in first rain event in 14 January 2012, which mean after long dry event, and minimum value 32 $\mu\text{S}/\text{cm}$, which record after long rainy days, and 86.6 % of samples range between 32 and 200 $\mu\text{S}/\text{cm}$, figure 17.

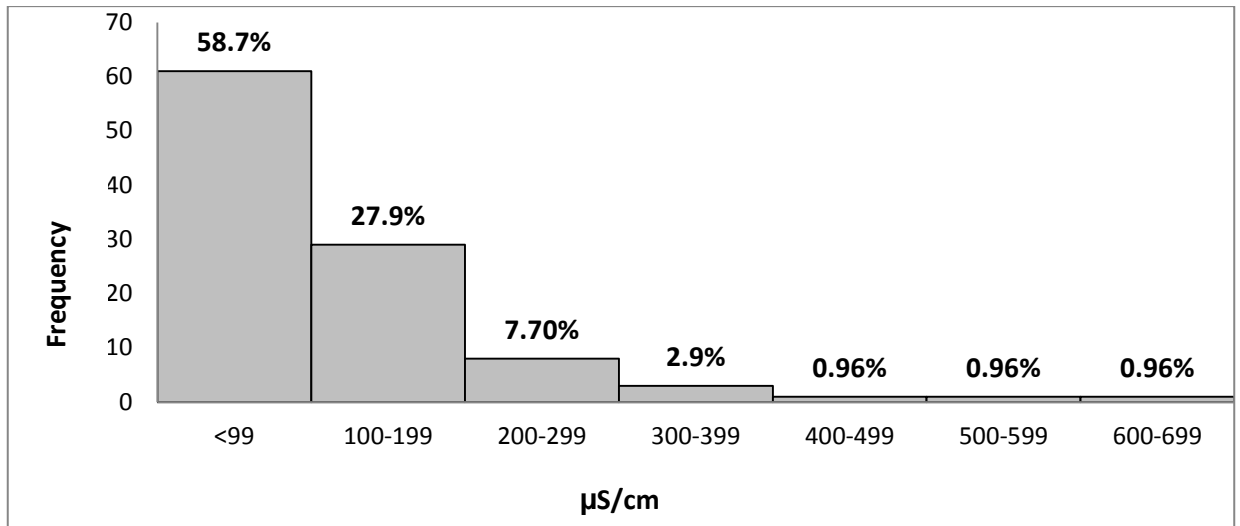


Figure17: Histogram of EC value of rainwater sample during the period of (2007-2013)

In figure 18 , have two types of value for EC , type A represent high value of EC result from long dry events where large amount of dust will accumulate in the first rain events and result of high EC value such as 637 , 514 , 411 , 344 , 321 , 293 , and type B which represent samples during middle of hydrological year with normal amount of accumulate dust and these value range between (32-200) μS/cm.

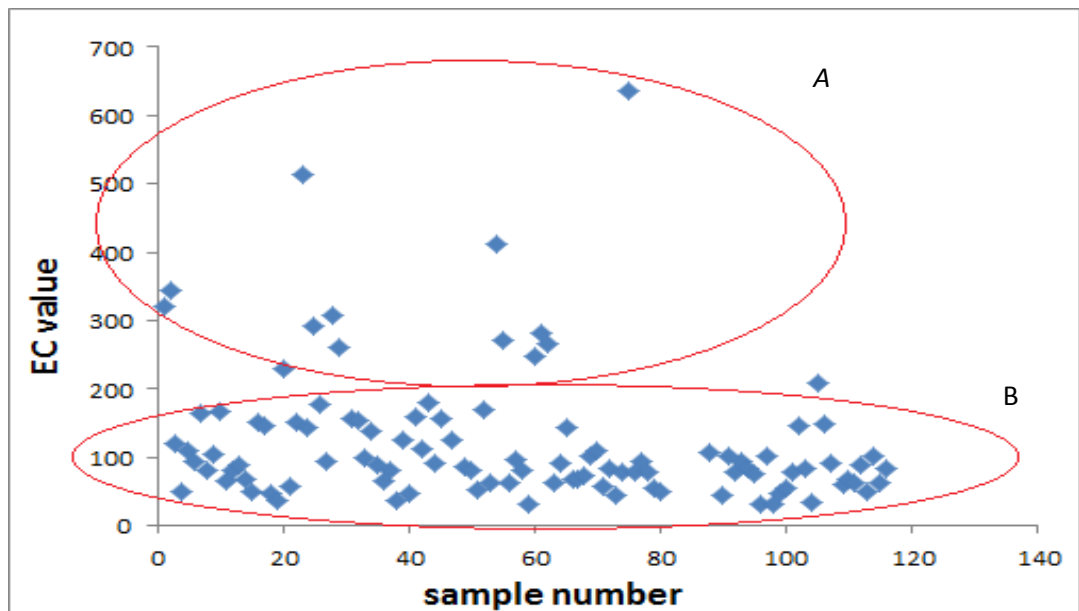


Figure 18: Plot of EC for rainwater sample for the period of (2007-2013) from Abu-Dis Weather Station.

5.1.3 Ions Contribution of Rainwater

The average abundance of various ionic species in mg/L, were $\text{Ca}^{+2} > \text{Na}^+ > \text{Mg}^{+2} > \text{NH}_4^+ > \text{K}^+$ for cations (figure 19 A), where for anions was $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{-2}$ (figure 19 B), the mean concentration of HCO_3^- was 38 mg/L, mainly contributing to anions 40 %. Calcium has the highest concentration 10.96mg/L among cations with a contribution of 44 %. High Percentage of Ca^{+2} and HCO_3^- was mainly due to the influence of the crustal dust in the area that rich in carbonate minerals. The contribution of other ions were as the following , Chloride (38 %) , Sodium, Magnesium ,sulfate and nitrate (31% , 11% ,11 % , 10% respectively) makes a relatively moderate contribution. The percentage of Ammonium and Potassium (8% and 6% respectively) are relatively small.

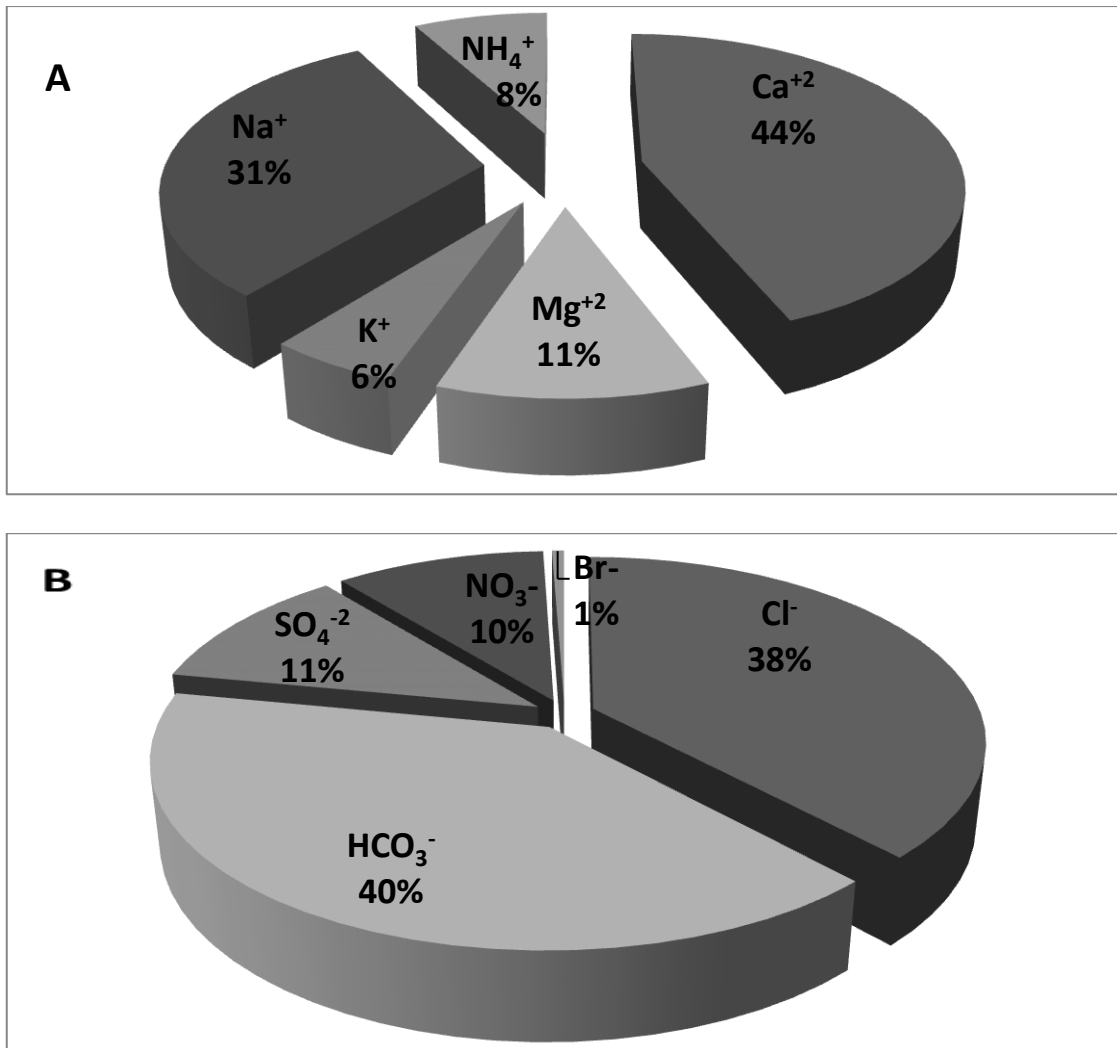


Figure 19: Contribution of ions in rainwater in period (2007-2013)

A - Contribution for cation ,

B - Contribution for anion

5.2 Comparison of Chemical Composition of Rainwater:

Table 4, present the average of chemical composition of rainwater in Abu-Dis station during the period (2007-2013) and chemical composition of rainwater obtain from other place in the world.

In this study the ions contribution were $\text{Ca}^{+2} > \text{Na}^+ > \text{Mg}^{+2} > \text{NH}_4^+ > \text{K}^+$ for cations and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{-2} > \text{NO}_3^- > \text{Br}^-$ for anions. When compare this chemical composition of rainwater in Abu-Dis with other studies done for chemical composition of rainwater in West Bank and Israel, there was similar .Qabajeh .R (2008) studied rainwater composition in Abu-Dis and found the order $\text{Ca}^{+2} > \text{Na}^+ > \text{Mg}^{+2} > \text{K}^+ > \text{NH}_4^+$ for cations and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{-2} > \text{NO}_3^-$ for anions, which mean that Ca^{+2} and HCO_3^- ions were dominated as in this study.

Herut.B(2000), who is found that ion contribution in southern part in Israel (Negev) was $\text{Ca}^{+2} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{+2}$ and for anion $\text{HCO}_3^- > \text{SO}_4^{-2} > \text{Cl}^- > \text{NO}_3^-$ also for Judea Mt both Ca^{+2} and HCO_3^- are dominated, but in Northern Coastal Plain Na^+ and Cl^- are dominant due to nearest to the sea since it is located on Mediterranean sea.

In Hifa which was studied by Mamane.Y (1995), he found the order $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+$ for cation and $\text{Cl}^- > \text{SO}_4^{-2} > \text{HCO}_3^- > \text{NO}_3^-$ for anions, and in Ashdod which was studied by Asaf (2005) the order was $\text{Na}^+ > \text{Ca}^{+2} > \text{K}^+ > \text{Mg}^{+2} > \text{NH}_4^+$ and $\text{Cl}^- > \text{SO}_4^{-2} > \text{HCO}_3^- > \text{NO}_3^-$. Na^+ and Cl^- ions were dominate in both study because Hifa and Ashdod are costal area and located on Mediterranean Sea.

Al-Khashman (2009) , studied the chemical composition of rainwater in Ghore EI-Safi area western side of Jordan nearby the Dead Sea and found the abundance of ions was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{-2}$. Also study the chemical composition of rainwater in Eshidiya area in south Jordan in 2005 and found the major ions are Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{-2} and Cl^- .He suggest that the rainwater chemistry is strongly influenced by local dusts which contain a large fraction of calcite and dolomite.

In Abu-Dis and its near places will found the same composition because rainwater composition will affected by the surrounding conditions , so the high percentage of Ca^{2+} and HCO_3^- is mainly due to dissolution of carbonate from limestone CaCO_3 ,dolomite $\text{CaMg}(\text{HCO}_3)_2$ and gypsum CaSO_4 from the terrestrial system and prevailing in

atmospheric dust derived from the Negev ,Sinai, and incursion of Saharan dust. (Qabajeh, 2008; Herut, 2000; Asaf, 2005; Al-Momani, 1997) where NH_4^+ result from NH_3 and the main source of these is fertilizer application, barns and biomass burning. (Al-Momani, 1997; Al-Khashman, 2009), Na^+ , Cl^- and Mg^{2+} from sea salts spray (Al-Khashman, 2009).

Table 4: Comparison of chemical composition of rainwater of Abu-Dis in period (2007-2013) with the chemical composition of rainwater in other site in the world

Site	Abu-Dis West Bank	Abu-Dis West Bank	Judea Mt Israel	Negev Southern Israel	Northern Coastal Plain Israel	Hifa Israel	Ghore El-Safi Jordan
Periods	2007-2013	2001-2007	1981-1990	1981-1990	1981-1990	1981-1990	2006-2007
pH	7.14	7.10	6.74	7.46	6.07	5.3	6.91
EC(μ S/cm)	122.61	159.78	-	-	-	-	-
Ca ⁺² (mg/L)	10.96	16.2	8.96	39.92	5.36	4.56	3.3
Mg ⁺²	1.69	5.28	1.338	3.498	2.23	1.43	1.12
K ⁺	2.63	1.17	0.663	4.173	1.14	0.75	3.33
Na ⁺	8.94	10.58	5.17	13.17	16.28	6.9	3.00
NH ₄ ⁺	1.79	1.08	-	-	-	0.31	-
Cl ⁻	22.42	25.2	9.195	32.58	29.46	11.26	5.05
HCO ₃ ⁻	38.0	39.65	21.96	71.18	7.08	-	8.15
SO ₄ ⁻²	8.51	11.52	7.82	44.06	10.22	8.98	5.39
NO ₃ ⁻	10.28	7.44	4.433	7.44	3.38	0.96	0.41
Reference	This study	Qabajeh.R 2008	Herut et al 2000	Herut et al 2000	Herut et al 2000	Mamane et al 1994	Al-Khashman 2009

5.3 Physical and Chemical Analysis for Groundwater

The Physical and chemical analysis of groundwater samples of North Eastern Basin where listed in table 5.

5.3.1 PH value

From table 5 , the PH value of the sixteen samples were range from (6.85-7.51) , which means it is a good water, neutral and not acidic or basic, except for one sample (Maythaloun) which has PH equal to 8.46 , which is mean alkaline water.

5.3.2 Electrical Conductivity (EC)

From table 5 ,the value of EC for fourteen sample from seventeen were range between 566 to 986 $\mu\text{S}/\text{cm}$, the low EC value indicate for young groundwater with low residence time and minimum rock-water interaction (Krishnaraj,2012) , and these value were increase in the study area from south to north along the pathway of water, figure20.

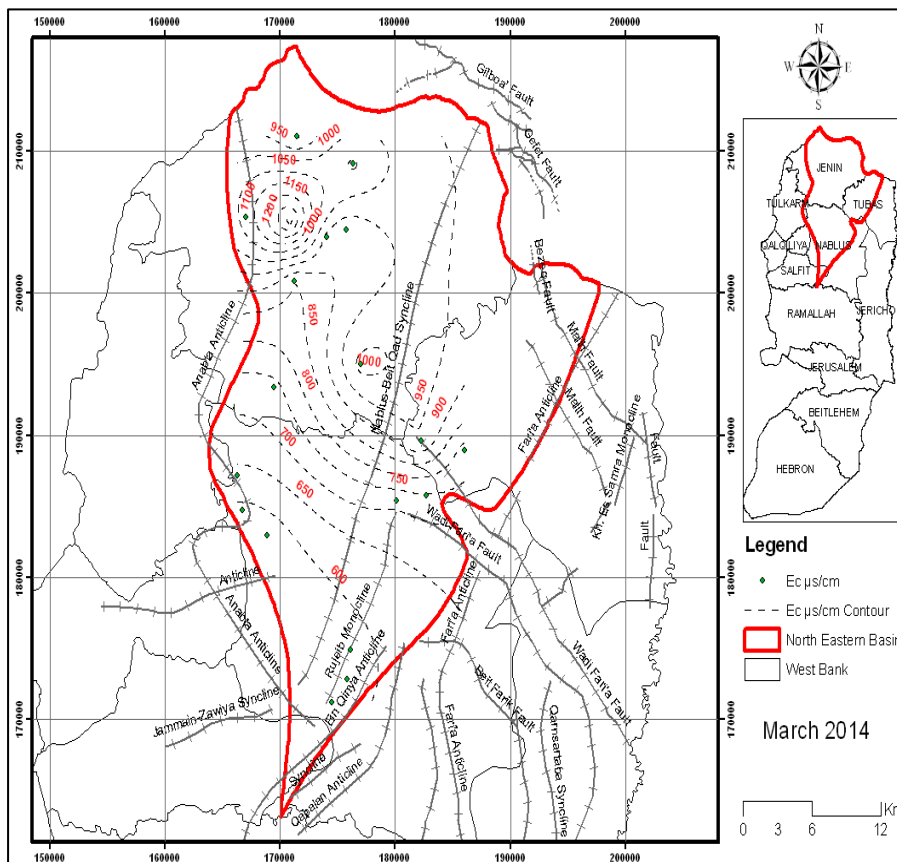


Figure 20: Contour map for EC in study area.

In addition, we have three high value ($EC > 1000$) and these wells are Caferet, Maythaloun and Al-Sa'da with EC 1381, 1050 and 1089 $\mu\text{S}/\text{cm}$ respectively. The explain of this result that these wells extracted water from the Upper aquifer but with exception of Maythaloun, the other two wells is locate close to the western boundary of the basin and water level close the current Mediterranean sea level, this could be possible reason for high EC value and increase it to more than 1000 $\mu\text{S}/\text{cm}$.

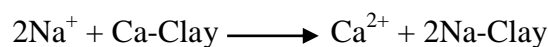
Table 5: Analysis of groundwater samples collected in March 2014

Well Name	pH	EC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻
		μS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Tubas well	7.13	986	112.2	48.6	32.1	9.98	0.71	118.2	284.8	36	22.1
Beit Aeba	7.08	566	72.1	14.6	10.6	9.58	0.25	47.3	244.1	9	15.9
Abu Arab	6.85	883	112.2	43.8	26.1	17.68	0.43	70.9	366.1	38	9.7
Qabatia	6.91	898	80.2	38.9	34.2	12.41	0.61	94.5	406.8	34	6.8
Al Far'a	7.22	739	80.2	34.3	20.8	8.36	0.28	70.9	325.4	19	20.8
Sabastya	7.24	641	80.2	24.3	14.8	13.63	0.13	47.3	284.8	11	15.8
Hewara	7.33	588	72.1	24.3	11.5	5.93	0.11	35.5	284.8	11	14.3
Araba	7.01	8.3	80.2	34.0	18.0	11.60	0.55	70.9	366.1	28	15.1
Roujeb	7.51	587	64.1	28.7	14.8	12.01	0.29	70.9	244.1	10	29.8
Sanor	7.23	720	88.2	34.0	16.7	6.34	0.37	35.5	366.1	19	16.7
Al Badhan	7.33	698	96.2	19.4	18.0	8.77	0.22	70.9	305.1	25	15.9
Tamoun	7.37	753	80.2	56.7	19.6	9.98	0.38	106.4	366.1	25	18.8
Deir Sharaf	7.33	581	64.1	44.3	10.3	7.96	0.24	70.9	305.1	14	15.6
Yamoun	7.02	850	72.1	53.2	21.6	16.47	0.36	88.6	366.1	20	19.8
Caferet	7.16	1381	56.1	72.9	53.9	12.01	1.2	159.5	445.4	39	27
Maythaloun	8.46	1050	18.4	48.6	71.8	3.60	5.65	87.2	338	2	4.1
AL-Sa'da	7.2	1089	104.2	116.6	235.3	3.70	0	132.5	1256.3	34	8.3

5.3.3 Concentration of Ions in Groundwater

From table 5, Calcium is the most abundant cation in groundwater, it varies from 56.1 to 112.2 mg/l. Magnesium varies in concentration ranging from 14.6 to 104.2 mg/l. The sources of Calcium and Magnesium in the groundwater are from the minerals like calcite, dolomite, limestone, aragonite and gypsum identified in the rock types of the study area. High concentration of Ca^{2+} and Mg^{2+} in the groundwater attributed to dissolution of calcite, dolomite and limestone. (Hounslow, 1995)

Sodium concentration for major sample ranges from 10.6-53.9 mg/l, the low value is due to reverse softening according to equation:



Except for two sample (Maythaloun and Al-Sa'da), have 71.8 and 235.3 respectively, and this due to ion-exchange process.

Potassium ranges from 3.60 to 17.7 mg/l. Due to the resistance of potassium bearing minerals (Orthoclase, Microcline and Biotite). Potassium is generally lower in groundwater. (Subbarao et al., 1999).

The bicarbonate ion ranges from 244.1 to 1256.3 mg/l, the high value due to exist carbonate rocks in the study area .Chloride in groundwater ranges from 35.5 to 159.5 mg/l. Nitrate ion concentration ranges from 6.8 to 29.8 mg/l , Sulfate concentration ranges from 2 to 39 mg/l. Concentrations of Nitrate and Sulfate are low, which is indicate the absence of pollution from wastewater.

The abundance of the major cations and anions in the groundwater were as the following order: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ respectively.

A comparison of the concentration of ions, we recognize that $\text{Na}^+ > \text{K}^+$, because the potassium is readily removed from solution by plants and clay minerals than sodium . $\text{Ca}^{2+} > \text{Mg}^{2+}$ because the most soluble minerals are sedimentary carbonate , calcite and gypsum , and concentration of Ca^{2+} is more than Mg^{2+} in these rocks . $\text{Ca}^{2+} > \text{SO}_4^{2-}$ because the main source of sulfate is some variety of CaSO_4 such as anhydrite , gypsum or sulfuric acid from pyrite neutralized by carbonate unless Ca^{2+} is removed by precipitation or ion exchange and it is an indicating of Ca^{2+} source other than gypsum such as calcite , dolomite or silicate . $\text{Na}^+ < \text{Cl}^-$, which indicate reverse ion exchange.

5.4 Saturation Indices

By using the saturation index approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy (Deutsch, 1997). The saturation indices were determined using PHREEQC in computer program Aqua Chem (version 3.7.42).

The saturation index (SI) of a given mineral is defined as: $SI = \log_{10} (IAP/K_{SP})$ (Lloyd and Heathcode, 1985)

The IAP represents ion activity product and K_{sp} is the solubility product at a given temperature. ($SI > 0$) indicates that precipitation is thermodynamically favorable in spite of the fact that slow rates of reaction can inhibit precipitation. On the other hand, undersaturation ($SI < 0$) signifies that dissolution is favored.

The summary statistics of saturated indices of some of the common mineral phases presented in Table 6.

Table 6: Saturation Indices for sampling in the study area.

Sample	Phases				
	Anhydrite	Aragonite	Calcite	Dolomite	Gypsum
Tubas well	-2.19	-0.04	0.10	0.19	-1.97
BeitAeba	-2.84	-0.28	-0.14	-0.62	-2.62
Abu Arab	-2.16	-0.21	-0.07	-0.19	-1.94
Qabatia	-2.32	-0.24	-0.10	-0.16	-2.10
Al Far'a	-2.55	-0.01	0.13	0.25	-2.33
Sabastya	-2.75	-0.03	0.11	0.06	-2.53
Hewara	-2.55	-0.10	0.13	0.25	-2.25
Araba	-2.39	-0.18	-0.03	-0.08	-2.17
Roujeb	-2.88	0.08	0.22	0.45	-2.66
Sanor	-2.51	0.09	0.23	0.40	-2.29
Al Bathan	-2.33	0.15	0.30	0.25	-2.11
Tamoun	-2.48	0.16	0.31	0.82	-2.26
Deir Sharaf 2A	-2.77	-0.02	0.12	0.44	-2.55
Yamoun 1	-2.61	-0.22	-0.08	0.06	-2.39
Caferet	-2.48	-0.14	0.01	0.48	-2.26
Maythaloun	-4.15	0.56	0.71	2.20	-3.93
Al-sa'da	-2.44	0.51	0.65	1.72	-2.22

Nearly all of the water samples were saturated or slightly saturated with respect to calcite, dolomite and aragonite and undersaturated with respect to gypsum and anhydrite,

suggesting that these carbonate mineral phases may have influenced the chemical composition of the study area. The results also indicate that the waters are likely to precipitate calcite and dolomite, while they undersaturated with respect to gypsum mineral.

5.5 Hydrogeochemical Facies

The Hydrochemical water type of the groundwater samples from the study area is represent in Piper diagram Figure 21.

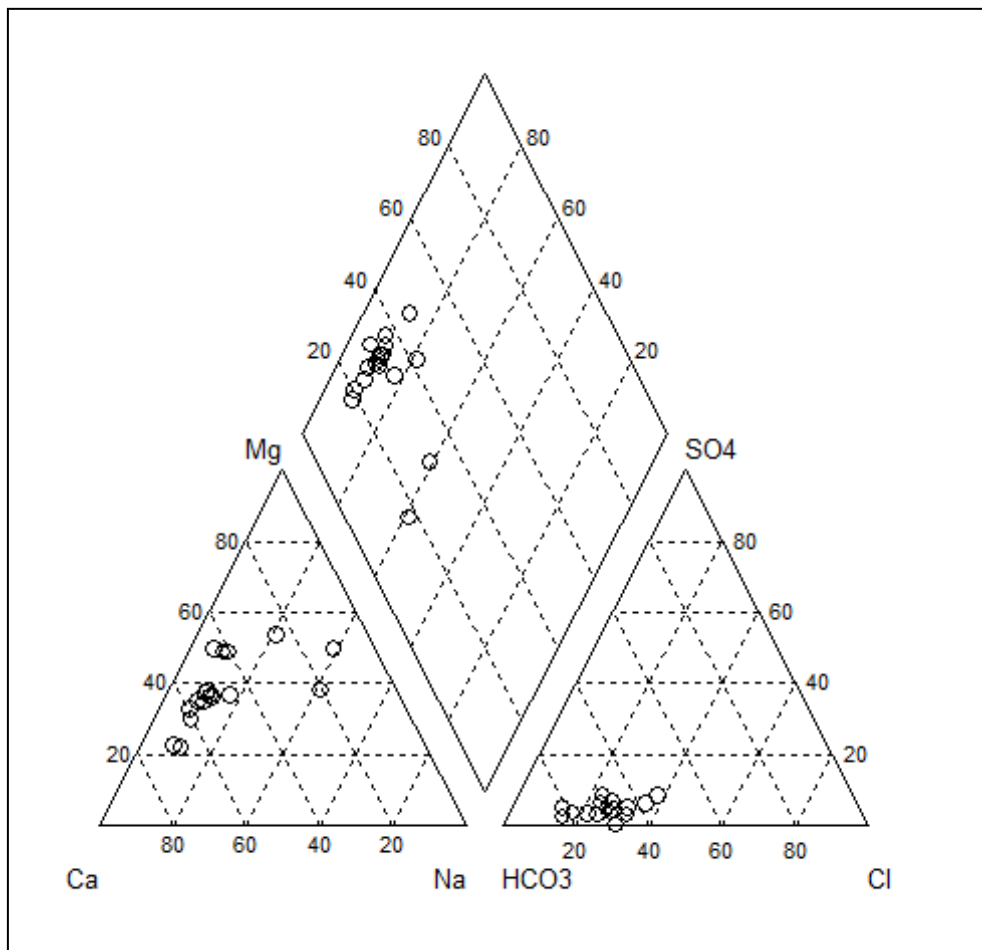


Figure 21: Piper diagram for groundwater in the study area

The groundwater on the diamond diagram shows that nearly all groundwater have a water type Ca-Mg-HCO₃-Cl except Al-Sa'da and Maythaloun wells, which have the type Na-Mg-Ca-HCO₃ and Mg-Na-HCO₃-Cl respectively .This suggests that the groundwater hydrochemistry is controlled by water– rock interaction.

5.6 Source of Ionic Constituents in Groundwater

During rock weathering, Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- and SiO_2 are added to water. The amount of each ion in water is dependent on the rock mineralogy. However, use of major ions chemistry to identify rock mineralogy can be useful but must be applied carefully. Mineral precipitation, ion exchange and evaporation can modify chemical composition. In many cases, the source rock minerals may be deduced from the water composition (Nwankwoala, 2013).

Using ionic ratios in groundwater is possible to indicate the minerals of source rock types (Hounslow, 1995). For this purpose, the concentrations of the various constituents converted to meqL^{-1} to be able to combine the various ions in a chemically meaningful way. In this study, most of the ion ratios have been calculated in table 7.

Ratio of $\text{Ca}^{2+}/(\text{Ca}^{2+} + \text{SO}_4^{2-})$ for all samples is greater than 0.5, figure 22 which means calcium source other than gypsum and from carbonate weathering, so the saturation indices for calcite, dolomite and aragonite is above zero.

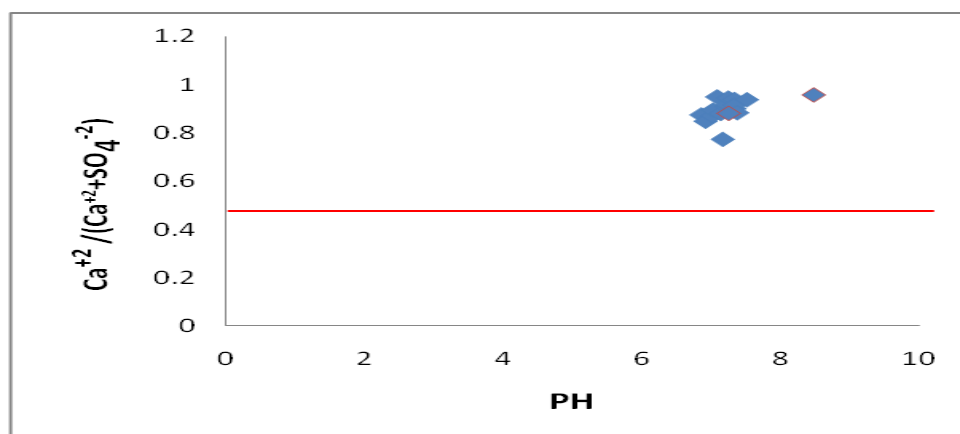
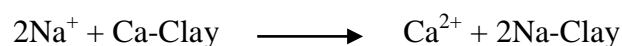


Figure 22: Scatter plot of $\text{Ca}^{+2} / (\text{Ca}^{+2} + \text{SO}_4^{-2})$ VS PH

If the ratio of $\text{Na}^+/\text{Cl}^- < 1$, indicate reverse ion-exchange, because increase Ca^{2+} and decrease Na^+ according to equation :



But if the ratio of $\text{Na}^+/\text{Cl}^- > 1$, indicate ion-exchange, nearly all the samples have molar ratio below 1 except for two samples (Al-Sa'da and Maythaloun) have molar ratio above 1, which indicating of seawater intrusion or remnant of old brine water, figure 23

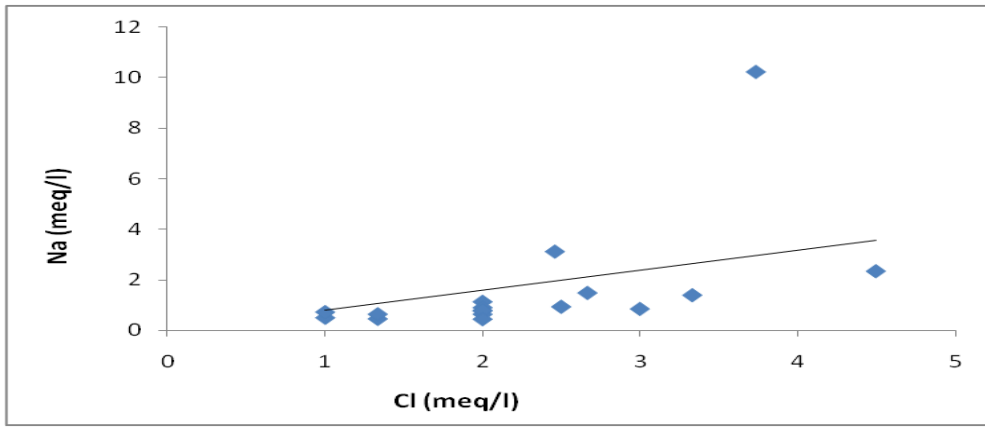


Figure 23: Scatter plot of Na^+ VS Cl^-

The ratio of $\text{Cl}^- / \text{sum of anions}$, for all samples is below than 0.8, figure 24 and this mean there is rock weathering.

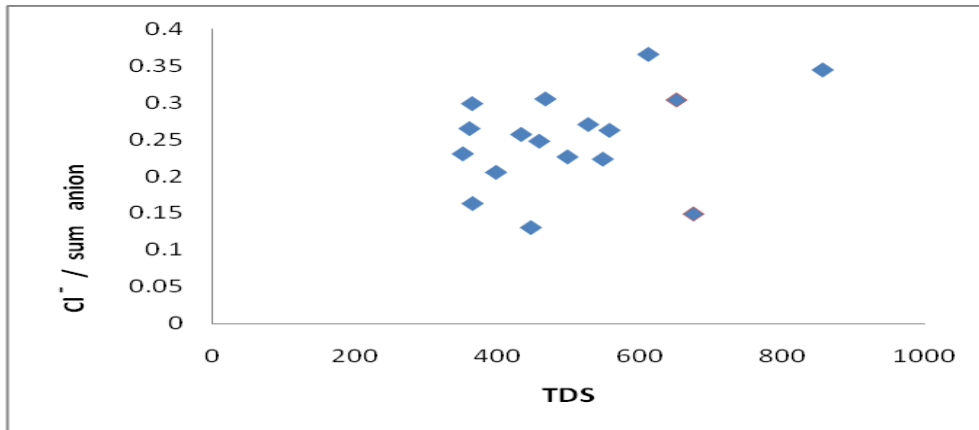


Figure 24: Scatter plot of $\text{Cl}^- / \text{sum of anions}$ VS TDS

If the ratio of $\text{Na}^+ / \text{Cl}^- > 1$ and $\text{SO}_4^{2-} / \text{Ca}^{2+} > 0.05$ suggest salinization due to wastewater infiltration (Rina, 2012), in our case there was no salinization for all sample and there is no pollution and this expected the aquifer is protected with thick chalk unit of Abu-Dis formation.

If the ratio of $\text{Mg}^{2+} / (\text{Mg}^{2+} + \text{Ca}^{2+})$ is greater than 0.5, there is dolomite dissolution or calcite precipitation but if it smaller than 0.5 it is an indication of limestone – dolomite weathering. From table 6 we have six samples above 0.5 and have dolomite dissolution or calcite precipitation and the rest of the samples have limestone – dolomite weathering, figure 25.

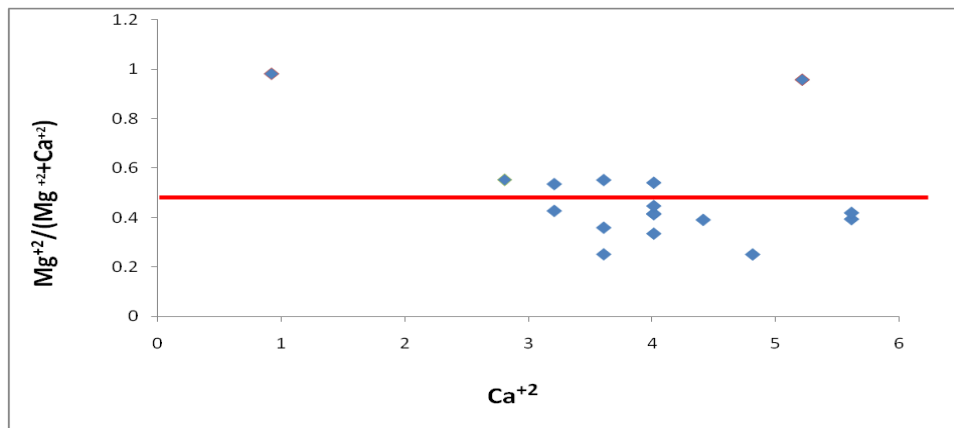


Figure25: Scatter plot of $Mg^{2+}/(Mg^{2+} + Ca^{2+})$ VS Ca^{2+}

Binary plots of $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + SO_4^{-2})$ (Figure 26) were examined to study the relative importance of ion exchange. If Ca^{2+} , Mg^{2+} , SO_4^{-2} and HCO_3^- are derived from a simple dissolution of Calcite, Dolomite and Gypsum, a 1:1 stoichiometry of $(Ca^{2+}+Mg^{2+})$ to $(SO_4^{-2}+HCO_3^-)$ should exist. When ion exchange takes place the points shift right but if reverse ion exchange is the process, it will shift the points to the left (Krishnaraj, 2011). The plot shows that nearly all the groundwater samples are clustered above the 1:1 line representing reverse exchange except for two samples (Al-Sa'da and Maythaloun) clustered below point toward ion exchange. Also when samples fall above the equiline due to excess of $(Ca^{2+} + Mg^{2+})$ over $(SO_4^{-2} + HCO_3^-)$ indicate that these ions have resulted from carbonate weathering, whereas two samples fall below the equiline which indicate silicate weathering (Datta et al, 1996; Rajmohan and Elango, 2004).

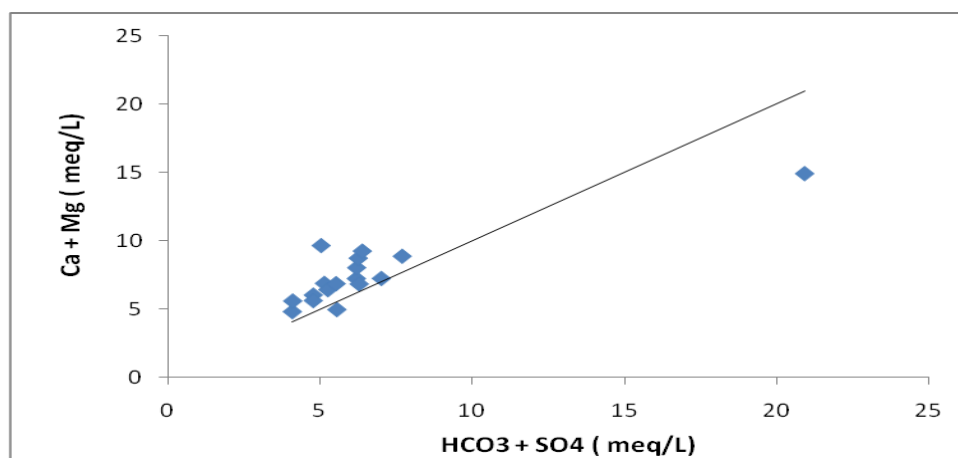


Figure 26: The plot of $(Ca^{+2}+Mg^{+2})$ verses $(HCO_3^- + SO_4^{-2})$

Table 7: Ionic Ratio of the groundwater in the study area

Well Name	$\frac{Na}{Cl}$	$\frac{Na}{Ca}$	$\frac{Mg}{Ca}$	$\frac{Ca}{SO_4}$	$\frac{Ca}{SO_4 + HCO_3}$	$\frac{Cl}{\text{sum of anions}}$	$\frac{Mg}{Mg + Ca}$	$\frac{Ca + Mg}{SO_4}$	$\frac{Ca}{Ca + SO_4}$	$\frac{Ca + Mg}{HCO_3 + SO_4}$	$\frac{Ca + Mg}{HCO_3}$	$\frac{Na + K}{Cl}$
Tubas well	0.419	0.249	0.722	7.480	1.035	0.366	0.419	12.880	0.882	1.783	2.069	0.495
Beit Aeba	0.345	0.127	0.337	19.238	0.861	0.231	0.252	25.718	0.951	1.151	1.205	0.529
Abu Arab	0.568	0.202	0.650	7.086	0.826	0.223	0.394	11.692	0.876	1.362	1.542	0.794
Qabatia	0.558	0.371	0.809	5.658	0.543	0.263	0.447	10.235	0.850	0.983	1.087	0.677
Al Far'a	0.451	0.225	0.713	10.131	0.700	0.248	0.416	17.352	0.910	1.198	1.287	0.559
Sabastya	0.482	0.160	0.505	17.498	0.819	0.206	0.336	26.335	0.946	1.232	1.293	0.744
Hewara	0.502	0.139	0.562	15.731	0.736	0.163	0.360	24.567	0.940	1.150	1.206	0.654
Araba	0.392	0.195	0.707	6.874	0.609	0.227	0.414	11.734	0.873	1.039	1.140	0.540
Roujeb	0.321	0.201	0.746	15.384	0.761	0.299	0.427	26.864	0.939	1.329	1.399	0.475
Sanor	0.727	0.165	0.642	11.141	0.689	0.130	0.391	18.299	0.918	1.132	1.207	0.890
Al Bathan 1	0.392	0.163	0.337	9.235	0.871	0.257	0.252	12.346	0.902	1.164	1.286	0.504

Continue. Table7: Ionic Ratio of the groundwater in the study area

Well Name	$\frac{Na}{Cl}$	$\frac{Na}{Ca}$	$\frac{Mg}{Ca}$	$\frac{Ca}{SO4}$	$\frac{Ca}{SO4 + HCO3}$	$\frac{Cl}{\text{sum of anions}}$	$\frac{Mg}{Mg + Ca}$	$\frac{Ca + Mg}{SO4}$	$\frac{Ca}{Ca + SO4}$	$\frac{Ca + Mg}{HCO3 + SO4}$	$\frac{Ca + Mg}{HCO3}$	$\frac{Na + K}{Cl}$
Tamoun	0.285	0.213	1.178	7.699	0.615	0.305	0.541	16.771	0.885	1.339	1.455	0.370
Deir Sharaf 2A	0.223	0.139	1.152	10.989	0.605	0.265	0.535	23.646	0.917	1.303	1.379	0.325
Yamoun	0.375	0.260	1.230	8.652	0.562	0.271	0.552	19.292	0.896	1.252	1.339	0.544
Caferet	0.521	0.836	2.166	3.452	0.346	0.345	0.684	10.929	0.775	1.094	1.216	0.589
Maythaloun	1.269	3.388	4.395	22.116	0.165	0.303	0.815	119.316	0.957	0.891	0.897	1.307
Al-Sa'da	2.737	1.964	1.866	7.355	0.245	0.148	0.651	21.078	0.880	0.701	0.725	2.763

5.7 Comparison between the Chemical Composition of Rainwater and Groundwater

From table 8, can distinguish the changes in chemical composition starting from rainwater to groundwater and between groundwater along its pathway from south to north along Nablus - Beit Qad syncline which consider as the pathway of water in this basin. Electrical conductivity value increase along the pathway of water due to increase the water-rock interaction.

Concentration of Calcium, Magnesium and bicarbonate increase due to carbonate weathering, Potassium concentration shown a slight change due to resistance of Potassium bearing minerals, Sodium concentration not increase due to reverse softening ,Sulfate and Nitrate concentration remain low because there was no pollution.

Table 8: Comparison between the chemical composition of rainwater and groundwater

Parameter	Rainwater	Hewara	Roujeb	Al-Bathan	Tubas
pH	7.14	7.33	7.15	7.33	7.13
EC ($\mu\text{S}/\text{cm}$)	122.61	588	587	698	986
Ca^{+2}	10.96	72.1	64.1	96.2	112.2
Mg^{+2}	1.69	24.3	28.7	19.4	48.6
K^{+}	2.63	5.93	12.01	8.77	9.98
Na^{+}	8.94	11.5	14.8	18	32.1
Cl^{-}	22.42	35.5	70.9	70.9	118.2
HCO_3^{-}	38.0	284.8	244.1	305.1	284.8
SO_4^{-2}	8.51	11	10	25	36
NO_3^{-}	10.28	14.3	29.8	15.9	22.1

Chapter Six

Conclusion and Recommendation

6.1 Conclusions:

In this study chemical composition of rainwater and groundwater are studied, the main result are summarized in the following points:

For Rainwater:

- The arithmetic average for the pH is 7.14 and for EC is 122.6 $\mu\text{S}/\text{cm}$ and have some high value due to accumulate dust in atmosphere so rise the value of EC to above 200 $\mu\text{S}/\text{cm}$.
- The abundance of the major cations and anions is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$.
- High concentration of Ca^{2+} and HCO_3^- due to affect the atmosphere by the dust which rich by carbonate minerals.
- Low concentration of NO_3^- and SO_4^{2-} is an indication of there is no atmospheric pollution in our study area.

For groundwater:

- pH value range between (6.8 – 7.5) and EC for most samples is below 1000 $\mu\text{S}/\text{cm}$ which is indication of young groundwater with low residence time and minimum water-rock interaction except for two samples have EC value above 1000 $\mu\text{S}/\text{cm}$ because the water level in these wells is close to the current Mediterranean sea level.
- The abundance of the major cations and anions is $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$.
- High concentration of Ca^{2+} and HCO_3^- are resulting from dissolution of carbonate minerals like calcite and dolomite, which identified in rock type of study area.
- Low concentration of NO_3^- and SO_4^{2-} is an indication of there is no pollution from wastewater in our study area.

- Saturation indices show that nearly all the samples saturated with respect to calcite, dolomite and aragonite, which found in rock of study area and undersaturated with respect to gypsum.
- Nearly all samples have a water type Ca-Mg-HCO₃-Cl except for two sample, which have the type Na-Mg-Ca-HCO₃ and Mg-Na-HCO₃-Cl.
- The integration of ionic ratio, hydrochemistry and various conventional graphs show there is carbonate weathering and reverse ion exchange for all sample except in two sample-position have ion exchange process.

6.2 Recommendations.

- Environmental isotopes studies such as ¹⁸O, ²H, ³H and ¹⁴C are needed to identify recharge zones and recharge volume. These data are to integrate within available hydrological model
- Drilling more wells within Faquaa area, which is in the flow direction within Nablus-Beit Qad syncline and the well could not be deep as Maythaloun.
- Not drill deep wells in northwestern part of this basin because the water quality could not be good and the salinity could be high due to presence of saltwater intrusion from Mediterranean Sea.

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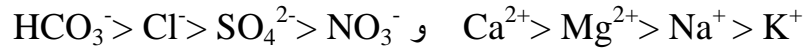
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وبعد تسلل مياه الامطار الى باطن الأرض أصبحت هذه القيم بالنسبة للمياه الجوفية على النحو التالي، الرقم الهيدروجيني pH يتراوح بين (6.8- 7.5) والتدفق الالكتروني EC كان لمعظم العينات اقل من 1000 ميكروسيتمت/سم دلالة على حداثة هذه المياه وقصر زمن بقاءها وتفاعلها مع الصخور المحيطة بها. باستثناء عينتين حيث كانت قيمة التدفق الالكتروني لهما أكبر من 1000 ميكروسيتمت/سم، وبالنسبة لتواجد الايونات الموجبة والسالبة كانت كالتالي:



التركيز المرتفع للكالسيوم والبايكربونات هو بسبب انحلال معادن الكربونات الموجودة في الصخور المتواجدة في المنطقة. في حين ان التركيز المنخفض من النترات والكبريتات دليل على عدم وجود تلوث بالمياه العادمة في منطقة الدراسة.

وتظهر مؤشرات التشبع ان معظم العينات متشعبة بالكالسايت و الدولومايت و الارجوناييت وعدم تشبعها بالجبس، وكانت نوعية المياه لمعظم عينات الدراسة هي Ca-Mg-HCO₃-Cl باستثناء عينتين حيث كانت Mg-Na-HCO₃-Cl و Na-Mg-Ca-HCO₃. كما أوضحت نتائج الرسوم البيانية للنسب بين الايونات بأن المياه تتأثر بعملية التبادل العكسي للأيونات وتجوية الصخور الكربونية باستثناء موقعين بهما تبادل ايوني. وأخيرا فإنني اوصي بإجراء دراسات باستخدام النظائر لتحديد مناطق التغذية وحجم التغذية في المنطقة.

كيمياء مياه الأمطار والمياه الجوفية في الآبار العميقة في الحوض الشمالي الشرقي / الضفة الغربية - فلسطين

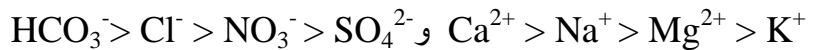
إعداد: سناء "محمد سالم" مصطفى نبروخ.

المشرف: د. عامر مرعي.

الملخص

يعتبر الحوض الشمالي الشرقي من أهم مصادر المياه للفلسطينيين في شمال الضفة الغربية، لذلك فإنه للاستفادة من مصادر هذه المياه وحمايتها على نحو فعال ولتوقع التغيرات التي تحدث فيها فإنه من الضروري فهم الخصائص الهيدروكيميائية للمياه الجوفية، وكيفية تطورها خلال دورتها في الطبيعة. لذلك فإن الهدف الرئيسي لهذه الدراسة هو فهم التغيرات التي تحدث في خصائص المياه بدءاً من مياه الأمطار وانتهاءً بالمياه الجوفية في الآبار العميقة في منطقة الحوض الشمالي الشرقي. هذه الدراسة تبين أن منطقة التغذية بالنسبة للنظام العميق من الآبار تقع على طول الجناح الشرقي والغربي للتحذب الموجود بين الفارعة شرقاً وعنبتا غرباً.

وقد أوضحت نتائج التحليل الكيميائي لمياه الأمطار أن المتوسط الحسابي للرقم الهيدروجيني pH و التدفق الكهربائي EC هو 7.14 و 122.6 ميكروسيتمت/سم على الترتيب و كانت هناك بعض القيم المرتفعة بالنسبة لـ EC حيث تجاوزت 200 ميكروسيمنت/سم ويعزي ذلك إلى أن هذه القيم تم قياسها في أول فترة مطرة، حيث كان هناك العديد من الغبار المتراكم في الغلاف الجوي. وبالنسبة لتواجد الأيونات الموجبة والسالبة كانت على النحو التالي:



التركيز المرتفع للكالسيوم والبايكربونات هو بسبب تأثير الغلاف الجوي بمعادن الكربونات. في حين أن التركيز المنخفض من النترات والكبريتات دليل على عدم وجود تلوث جوي في منطقة الدراسة.