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Faculty of Graduate Studies

**Development of a Quality Monitoring System for
Groundwater in Karst Eastern Aquifer**

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**This Thesis is Submitted in Partial Fulfillment of the Requirements for
the Degree of Master of Environmental Sciences, Faculty of Graduate
Studies, An-Najah National University, Nablus-Palestine.**

2018

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Dedication

This thesis is dedicated with all respect, love and gratitude to:

My dear father and **my lovely mother** who always lightened my life with their love and care, and always encouraged and gave me an endless support, may God bless them.

My beloved sisters (Manal, Sana', Raja' and Wafa').

My beloved brothers (Maen, Munsif, Nader and Mohammed).

My beloved Husband (Shaher).

My Father in Law (Yousef Khamees).

My Friend (Hala Masoud).

For their support, love and encouragement.

Acknowledgment

First and foremost, praise and thanks to Almighty ALLAH for giving me the strength and the patience to complete this thesis.

I would like to express my special thanks and gratitude to my supervisors, **Dr. Anan Jayyousi** and **Dr. Saed Khayat** for their valuable guidance, tips, help, effort, and encouragement throughout this work.

My deepest gratitude, love, and appreciation are also expressed to my beloved **Father, Mother, Sisters, and Brothers** for their valuable support, endless encouragement, and care to complete this thesis.

Thanks are also extended to **Dr. Stefan Geyer** and **Dr. Tino Rodiger**, in Helmholtz Research Centre For Environmental Research-UFZ, Halle, Germany, for their support and help throughout the entire project.

Also thanks are for **Dr. Roland Bol** and **Dr. Andreas Lucke** in Forschungszentrum Julich, Julich, Germany for their support and help in implementing this work. Many thanks are extended to the German Federal Ministry of Education and Research (BMBF), the Palestinian Ministry of Education, the Forschungszentrum Julich (FZ), Julich, Germany and Helmholtz Research Centre For Environmental Research-UFZ, Halle, Germany for funding this project and for providing every facility needed to complete this work in a convenient way.

Finally, I would like to thank everybody who supported me in any respect during the completion of this thesis, meanwhile expressing my apologies for being unable to mention their names.

Reem Odeh

الإقرار

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Development of a Quality Monitoring System for Groundwater in Karst Eastern Aquifer

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List of Abbreviations

EC	Electrical Conductivity.
DOC	Dissolved Organic Carbon.
TC	Total Coliform Bacteria.
WAB	Western Aquifer Basin.
EAB	Eastern Aquifer Basin
a.s.l	Above Mean Sea Level.
GIS	Geographic Information Systems.
PWA	Palestine Water Authority.
TOC	Total Organic Carbon.
TIC	Total Inorganic Carbon.
EDTA	Ethylene Diamine Tetra Acetic Acid.
VSMOW	Vienna Standard Mean Ocean Water.
VSLAP	Vienna Standard Light Antarctic Precipitation Scale.
WHO	World Health Organization.
TDS	Total Dissolved Solids.
LMWL	Local Meteoric Water Line.

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Abstract

This study was conducted to develop a quality monitoring system for groundwater in the karst eastern aquifer in Palestine. This system depends on hydrological, hydro-chemical and hydrobiological monitoring, in addition to the use of stable isotopes of Hydrogen, Oxygen and Nitrogen as tracers for the sources of recharge to the catchment area and the sources of pollutants. Ein Samia well 1, which is part of the auja spring, the biggest spring in the eastern aquifer, was chosen as a case study.

Seasonal rainfall analysis and rain events analysis were conducted to study the evolution of hydrochemistry in response to rainfall events. In general, the pollutants in Ein Samia well 1 could be easily noticed after every rain event with intensity higher than 13 mm within 48 hours.

The water samples collected in the dry period were of Ca-CO₃ type, while the samples in the wet period were of Mg-CO₃ type. The two periods had some sulphate, however in the karst regions carbonate rocks are the

dominant so carbonate water type is the most expected type. In the late hours of rain events, Mg^{2+} showed higher concentration more than Ca^{2+} , Mg^{2+} comes from the dissolution of dolomite which increases with rainfall. While there was more Ca^{2+} in the early hours of rain from the dissolution of calcite.

The sodium ion showed higher concentration more than potassium most of the time, which may be generated from sewage effluent or infiltration of leachate from landfills or industrial sites.

The nitrate reached the highest concentration (83 mg/l) in the rain event of 18-22/1/2018, this concentration exceeds the World Health Organization Standards. Followed by an increase in the orthophosphate concentration. On the other hand, the dissolved organic carbon (DOC) showed late flush out.

Total coliform bacteria were also monitored in this study and it showed high concentrations but relatively late. Further diagnosis for the colonies of bacteria indicated that there are large amounts of E-coli bacteria which is usually found in the sewage water.

Stable isotopes of Hydrogen (Deuterium, 2H) and Oxygen (Oxygen 18, ^{18}O) were used in this study as tracers for the source of the recharge to the aquifer, which is responsible for the release of contaminants that are accumulated in the catchment region. The analysis of the isotopes in this study revealed that the main source of recharge is from precipitation. The

precipitation infiltrates quickly and discharges directly through the spring within few hours.

Stable isotopes of nitrate, ^{15}N and ^{18}O , were analysed to detect the main sources of nitrate in the groundwater. The analysis showed that the main source of nitrate is the sewage water which comes from the unsanitary septic tanks in the study area, in addition to the animal manure that is used as a natural fertilizer in the agricultural activities in the area.

Chapter One

Introduction

1.1 Background

Water is one of the most important elements that life depends on. It covers two third of the earth's surface and it forms 75 percent of human body. But as the human population increases, the demand for water also increases. More shortage in water is expected in the coming decades, because of the increasing impacts of human on water such as population, deterioration of water resources, and different anthropogenic activities (Shadeed, 2008). Groundwater is considered to be the main source of fresh water for domestic and agricultural use in the Mediterranean region (EUWI, 2007). The Mediterranean region with respect to climate change has been identified to be a “hotspot”, which imposes more pressure on the limited water resources (Giorgi, 2006, IPCC,2013).

"Scarcity and misuse of fresh water pose a serious and growing threat to sustainable development and protection of the environment. Human health and welfare, food security, industrial development and the ecosystems on which they depend, are all at risk, unless water and land resources are managed more effectively in the present decade and beyond than they have been in the past" (ICWE, 1992). This quote was the introductory paragraph of the Dublin statement on water and sustainable development. So, it is the responsibility of water resources managers to develop management

strategies and to take every action that can save water in the future from more and more shortage.

Karst regions form almost about 25% of the surface of the earth (Hao., et al, 2006). In semiarid regions, karst groundwater forms a very important source for drinking water. Karst is a word that was derived from the word “kras” from vicinity of Trieste, Italy, and adjacent Slovenia, which means bare, stony ground (Huntoon, 1995). Dissolution is karst’s primary process in developing a distinctive surface topography, a topography characterized by sinkholes, caves, and underground drainage (Bates and Jackson, 1984). A karst Aquifer has been defined by Huntoon (1995), as follows “ *A karst aquifer is an aquifer containing soluble rocks with a permeability structure dominated by interconnected conduits dissolved from the host rock which are organized to facilitate the circulation of fluid in the downgradient direction where in the permeability structure evolved as a consequence of dissolution by the fluid*”. Overexploitation of water from karst aquifers for municipal, agricultural and industrial activities may affect water supply and impairment of water quality. The specific hydraulic and hydrogeologic features of these aquifers make them more vulnerable to contamination from anthropogenic activities (Kačaroğlu, 1999), such as wastewater disposal, sewer leakage and agricultural activities. Karst groundwater is susceptible to pollution because of rapid infiltration and fast pollutants transport within a highly porous conduit system and lack of a protective cover (Schmidt., et al, 2013). So, groundwater in this kind of aquifers needs strategies for protection and monitoring.

Karst Eastern Basin in Palestine presents a good example of this problem, as previous studies for the springs and wells in several regions in the West Bank showed that there is a seasonal washing out process related to rain events which take place annually after the summer dry period. During this period large quantities of organic and chemical pollutants accumulate in the catchment areas which have karstic nature as result of agricultural and anthropogenic activities (Khayat 2006; Khayat 2009; Hillel., et al, 2015). According to the previous studies, the amount of pollutants which reach the groundwater depends on several factors like rainfall intensity, geological formations of the recharge area, ground flow velocity and the closeness of discharge area to the recharge point. All of these factors facilitate a rapid infiltration of water during its passing through the permeable rocks, which finally reach to the ground water. According to previous studies, heavy rain events in a short period of time imposes pressure on the accumulated pollutants in the unsaturated zones of the recharge zone, which leads to wash them out producing a noticeable increase in the quantity of pollutants in the wells and springs. This pollutant peak lasts for several days after the pollutants reach the discharge zone and disappear for the rest of the hydrological year.

Ein Samia was found to be a special case of this problem, as Ein Samia spring is a typical of highly developed karst system with a fast response to precipitation variations because of droughts or heavy rain events (Klinger et al. 2015). The large varieties in industrial and anthropogenic activities that produce different kinds of pollutants, and the small recharge area, in

addition to the highly permeable karstic nature which is characterized by the presence of caves and cracks, are strong factors that cause a fast flow of rain water holding the pollutants from the recharge area to the spring (Figure 1.1).

To study this problem in Ein Samia well 1, a monitoring system for the quality of groundwater was developed. This system depends on measuring several variables on site like electrical conductivity, temperature, water level and on analysis of main anions and cations including nitrate, phosphate, sodium, potassium, calcium and magnesium. The chemical analysis was conducted at Palestine Technical University/Kadoori in Palestine.

In addition to that, isotopic analysis for ^2H , ^{18}O was carried out in Forschungszentrum Juelich, Germany, and ^{15}N of nitrate in Helmholtz Zentrum Umweltforschungs (UFZ), Halle, Germany.

Use of stable isotopes as tracers is a well-known approach that is made all over the world. The stable isotopes of water molecule constituents (^2H , ^{18}O) are ideal tracers for the sources of water and movement (Gat & Gonfiantini, 1981). (Clark & Fritz, 2013) in their book (Environmental isotopes in hydrology) showed that the oxygen and hydrogen undergo changes in the different periods of hydrologic environments, these changes cause isotopic fractionation which give an isotopic “fingerprint” that is related to the geology of the area and the

origin of water. Also the isotopes (^{15}N) and (^{18}O) of nitrate are usually used to indicate the sources of nitrogen (Heaton, 1986).

Nitrate is a main source of pollution for water supplies and it presents a serious threat to human health especially in infants by causing a case called methemoglobinemia or “blue baby” syndrome, which is a blood disorder in which too little oxygen is delivered to the cells, so it is very important to know the source of nitrate as a first step in solving the problem of contamination (Khayat et al. 2006). It reaches high concentrations in many places around the world and may be generated from different sources like for example synthetic fertilizers, atmospheric deposition and sewage manure (Kendall et al. 2008). Usually nitrate from each source has a distinctive isotopic signature, for example values for $\delta^{15}\text{N}_{\text{nitrate}}$ for chemical fertilizers ranges from -4 to +4 ‰ and for human and animal waste from +7 to more than +30‰ (Clark & Fritz, 2013). $\delta^{18}\text{O}_{\text{nitrate}}$ values are for atmospheric deposition more than +25‰, for fertilizers ranges from +18 to +22‰, and for human and animal waste from -10 to +10‰. So, these isotopic signatures are perfect tracers for the origin of water unless any alteration because of a biochemical reaction like denitrification took place.

In this research a monitoring system is developed to detect the hydro-chemical, hydro-biological and hydrological response of groundwater in the study area to anthropogenic activities which may cause pollutants shock in response to a heavy rain event.

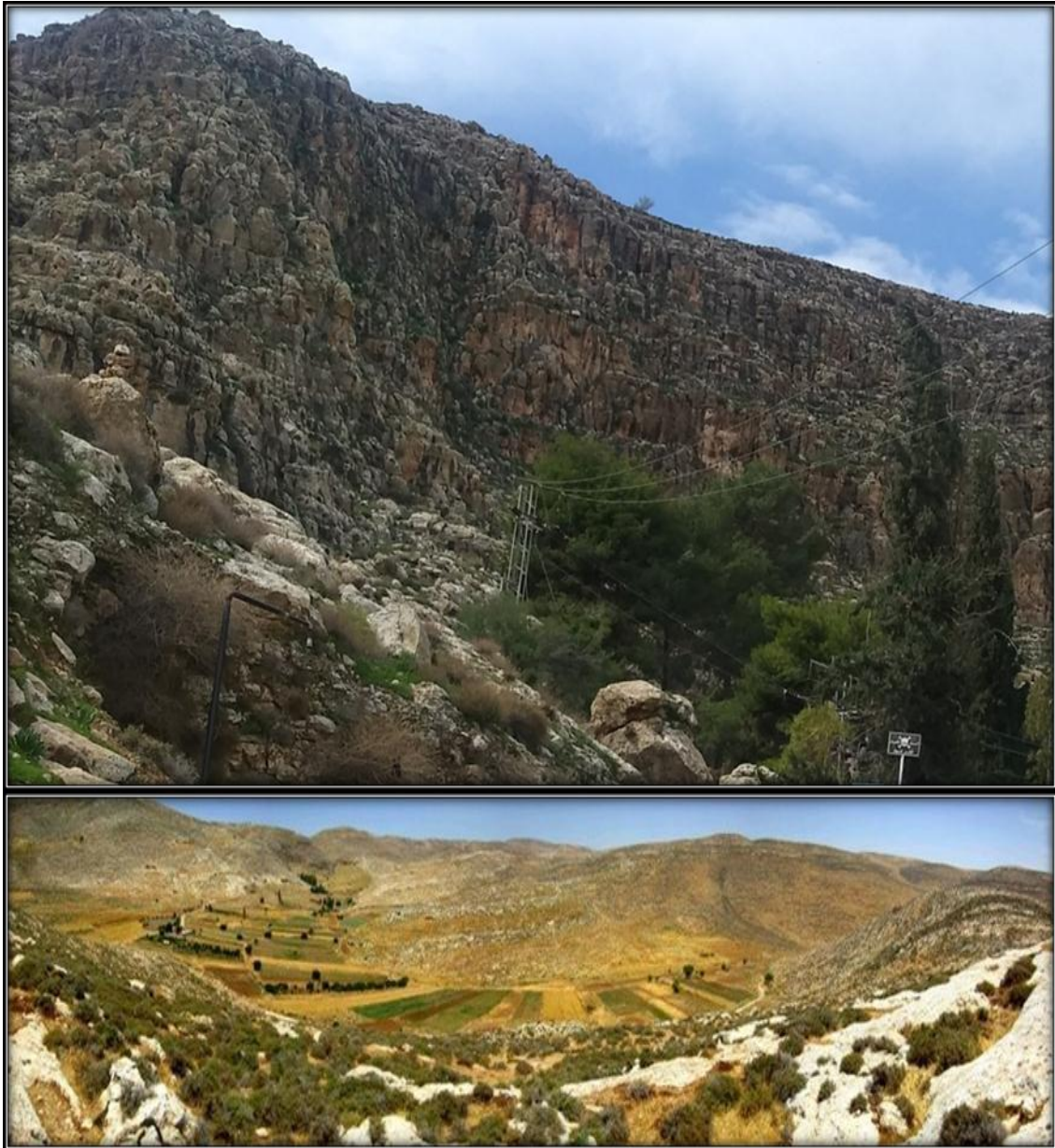


Figure (1.1) Photo of Ein Samia Fault Region, Karstic Permeable Rocks, Photo of the Low Slopes of Recharge Area (used partly in agricultural activities and grazing). * Photo from the UFZ project group (2018).

1.2 Research Objectives

The scientific goal of this research is to develop a simple, workable monitoring and characterization method to give a pre-warning system for temporal polluted drinking water wells. The monitoring method should be easily transferred and used also in other Karst regions.

Within the research period, the aim is to install in one producing well a monitoring equipment which will detect temporal groundwater pollution after rainy events. The monitoring results will show the specific behavior of different water quality parameters in the well.

The study is going to achieve specific objectives as well, they are:

- To give assistance to Jerusalem water Undertaking to maintain the sustainability and continuity of groundwater in Ein Samia well 1 and to guarantee less exposed to washed pollutants from the recharge zones after a heavy rain event.

- Make recommendations to the Water and Environmental Authorities about the kind of pollutants, the sources of different pollutants, possible time of their existence and the reoccurrence of them during the rainy season, suggesting the proper mitigation measures that should be taken to avoid such pollution during these times.

1.3 Research Importance

The benefit of early detection of pollutants in Palestine lies in the savings of costs in the subsequent water treatment and in the assurance of a constant water quality. The costs of preventive measures are generally predictable and often fall on only a limited period, while the cost of failure to act incurred less predictable and generally long-term. In addition to the cost aspect, health aspect is very critical in this manner, as it is well known that high content of organic matter in drinking water might be a reason for

health problems, this is because of using chlorination as a disinfectant for drinking water in these regions. Chlorination in the presence of organic content increases the halogenated hydrocarbons, which they are now known as cancerogenic substances. Also, high nitrate content in drinking water represents a serious health threat, especially for infants as it causes for them a case called methemoglobinemia or “blue baby” syndrome.

1.4 Literature Review

Karst aquifers are considered to be an essential source of drinking water all over the world. Their unique hydrogeological features make them vulnerable to contamination by different kinds of contaminants like chemical, natural or pathogenic contaminants, there are numerous point and non-point sources of such contaminants to ground water, for example agricultural run-off, fertilizers, improperly functioning septic systems, waste-water discharges, unintentional releases of sewage (Mahler et al. 2000).

So many studies and researches have been conducted to identify their vulnerability to contamination, their hydrological and hydro chemical response to rain events, and so different strategies for protection and monitoring were proposed for a sustainable management of such an important source of water.

The Dead sea is known as a semi-arid to arid area, in which the groundwater is a main source for water (Gräbe et al. 2013), increasing population leads to a stress on the aquifer system in the region, so a

sustainable water resource management was needed (Gräbe et al. 2013). A regional groundwater flow model of the eastern and southern mountain Group Aquifer was developed to investigate the groundwater regime in the western Dead Sea drainage basin of Palestine (Gräbe et al. 2013).

Anthropogenic activities have influenced the water quality in many rivers, Lower Jordan valley is an example (Hillel et al. 2015). The temporal variations of its discharge and hydrochemistry have been studied by installing a hydrometric station, samples were analyzed for some ions like (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} , NO_3^- , Br^-) (Hillel et al. 2015). The relation between EC and water level had an inverse trend. High levels of EC and high concentration of measured ions, and flood events which distinguished by inverse relation between EC and discharge could be related to the dissolution of the precipitated ions in the basin (Hillel et al. 2015).

A regional surface water modeling for Wadi Auj east of Hebron was developed to investigate the amount of surface water run off drained to the Dead Sea under different scenarios. The module shows that in the worst scenario, the amount of surface run off was about 250000 m^3/yr . However, the total amount of runoff was compromised about 40% of the total rainfall over the study area, while the total amount of groundwater recharge exceeds 40% at the best scenario, which means that the karst aquifer is highly susceptible in response to rainfall intensity and amount (Khayat et al. 2016).

During the hydrological season (2006\2007), the spatial and chemical composition of the groundwater of the springs along the Wadi Qilt running from Jerusalem- Ramallah mountains toward Jericho plain has been studied. The study showed that many factors had an important role in the chemical composition of spring water, for example the residence time and recharge intensity. Oxidation of organics which came from sewage and garbage have been found to be another factor, as it controls the concentration of dissolved CO₂ and HCO₃⁻ concentration. The study had a good effect on increasing the effective exploitation of freshwater (Khayat et al. 2009).

A monitoring system for groundwater based on using sensors was developed in a study in USA. Groundwater known to be a major water resource for 50% of the population in USA, so a precise monitoring system was needed. The sensors were used to measure the electrical conductivity of water, which is directly related to salinity. Salinity is one of the major parameters needed to be monitored in groundwater. This monitoring system showed that it was practical for water conductivity measurement as it was low cost application and flexible (Parra et al. 2015).

A recent study based on analyzing isotopic constituents of water (Deuterium, Oxygen, Tritium) and hydro chemical analysis for some cations and anions to explain the relations between different sub-aquifers in the Bethlehem-Hebron area (Khayat et al. 2017). The study finds out that studying stable isotopes could be a useful tool for water resources management and for the evaluation of the quality of water for human use in

addition to give a better understanding of aquifer recharge and spring discharge which is important for explaining groundwater hydrodynamics.

In a study of the shallow Pleistocene aquifer in the Jericho area Palestine, the researchers identified the sources of nitrate in the groundwater using $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$. The $\delta^{15}\text{N}_{\text{nitrate}}$ values $>+7$ ‰. Oxygen isotope ratios of nitrate were around +3 to +6 ‰. These results suggest that the source of high concentrations of nitrate is the sewage water or manure (Khayat et al., 2006).

In a study for quantification of wastewater impacts on karst groundwater resources in the western margin of the lower Jordan valley which is a semi-arid environment, chloride mass balance method was used. Chloride was used in this study as an environmental tracer to achieve two major points, first regional groundwater recharge estimation and quantification of anthropogenic impacts, also nitrate was used in this study as an indicator for human activities impacts. The study find out a strong correlation between nitrate and chloride concentrations, as the springs that are generally existed in or near populated areas showed a high level of both nitrate and chloride (Schmidt et al. 2013).

Kacaroglu, Fikret (1999), showed in his paper a good example of karst groundwater pollution problem. Antalya is a city in Turkey, which is located in a travertine area. The city lack to sewer system, and include different industrial activities like food and beverages, textile, leather, paper, plastics and other industries. The International Research and Application

Center for Karst Water Resources, Hacettepe University, Ankara, studied the groundwater pollution problem in the city. They collected seasonal samples from 35 points, from major springs in the area, they analyzed some of water quality variables like temperature(T), electrical conductivity (EC), dissolved oxygen (DO), major cations and anions (Ca, Mg, Na, K, Cl, SO₄) and nitrogen compounds (NO₃, NH₃, NO₂). Some of the measured parameters were as follows: NO₃ (0.2-42.0 mg\L), EC (500-900 μS\cm), PO₄ (0-0.66 mg\L), these results indicate the presence of pollution problem and so protection strategies were suggested (Kačaroğlu, 1999) .

Chapter Two

Study Area

2.1 General Overview

Palestine forms an active part of the African-Syrian rift, which extends for about 6000 km, from east Africa through the Red Sea, Wadi Araba, and the Dead Sea, Jordan Valley to south Turkey. The area of the West Bank has shaped by two major tectonic events, they are; the Syrian Arc System folded up at the end of the Cretaceous Period and the Red Sea-Aqaba fault which formed the Dead Sea from the Miocene (Krenkel, 1924; Rofe& Raffety, 1963 and Andrew, 2000).

The Afro-Arabian tectonic plate remained relatively stable from Precambrian to the early Cretaceous. The Cretaceous period began with extensional faulting and volcanism over part of the Levant countries and eastern Mediterranean, and terminated in compression, inversion, folding and faulting processes, expressed in Palestine by the anticlines of the Syrian Arc (Krenkel, 1924) and fault structures, distinguished by lateral thickness variations of the sedimentary section between nil and a few hundred meters. The formation of the Syrian Arc, manifested in the reactivation of the pre-existing faults, resulted in the inversion of the late Paleozoic-Turonian lows and highs (Flexer et al. 1989).

Two stages of movement took place between the African and Arabian plates from the late Eocene to Pliocene (Girdler, 1983). The first stage separated the Arabian Shield from the great African Shield in form of an

extensional rift system, and thus initiated the opening of the Red Sea. The second stage was caused by Ocean spreading in the Gulf of Aden (Quennell, 1956; Gass, 1979; Bayer et al. 1988). It creates a northward movement of the Arabian plate along a left lateral transform fault along Aqaba- Dead Sea- Jordan Valley, now called Dead Sea-Jordan Rift system.

The Jordan Rift, the Jerusalem (Judean) Anticline, and Nablus Syncline dominate the structure of the West Bank, where Jerusalem Anticline expresses both Surif (Hebron) and Ein Qiniya Anticlines.

Figure (2.1) illustrates the general geological and structural setting of the West Bank.

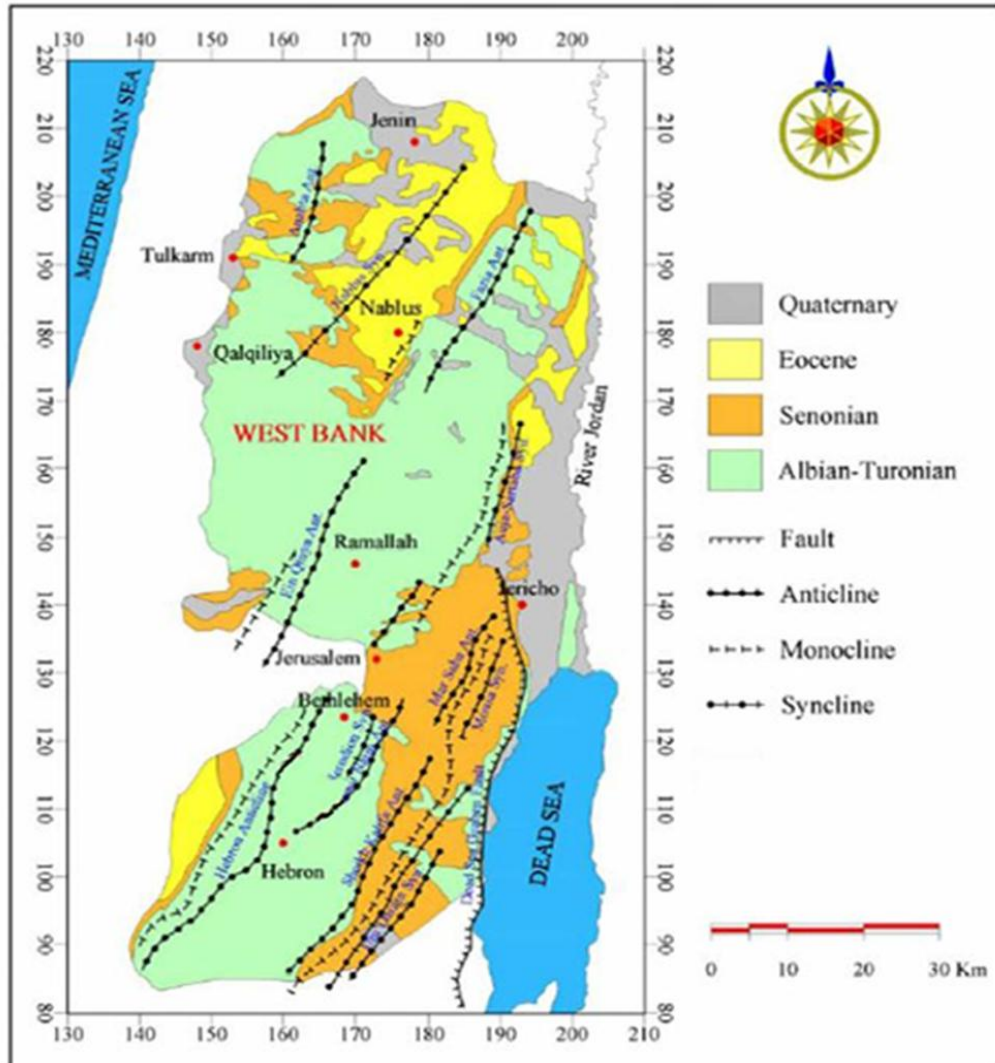


Figure (2.1): General Geological and Structural Map of the West Bank (modified after Rofe& Raffety, 1963).

In West Bank, there are three main groundwater basins: The Eastern, North-eastern and Western Basins, Figure (2.2). The Western Basin (WB) is considered to be the largest one in terms of area, storage capacity and sustainable yield. Most of WB water is fresh water and can be used as drinking water.

The Eastern Basin (EB) overlays the eastern side of the West Bank. This aquifer extends from the Ramallah-Hebron Anticline to the west and to the Jordan Rift Fault to the east (Froukh, 2002). In the south; it stretches to the area beyond the southern Hebron hills, whereas the eastern border is the Jordan Valley. It consists of two layers, Upper and Lower aquifer layers which separated by a less permeable layer, in addition the valley aquifer in the Jordan valley is considered as an important source of water within this aquifer. The Upper aquifer is Cenomanian to Turonian age, it is mostly unconfined layer while the Lower aquifer is confined in most of the West Bank.

The Cenomanian to Turonian Upper aquifer is built- up of tertiary and cretaceous rocks which are mainly made of limestone, dolomite, chalk and marl with bands of chert (Qannam, 2000).

The Upper aquifer consists of the Jerusalem, Hebron and Upper Bethlehem Formations with a thickness varying between 170 m in the Jericho area and 200 m in the Jerusalem area (Khayat et al. 2009). The region is considered to be karstic, this is characterized by limestones and other soluble rocks at or near the surface that have been modified by corrosive solution of limestone.

This Upper aquifer is hydrogeologically separated from the Lower one by an impermeable layer of marls and chinks of the Lower Bethlehem Formation acting as an aquitard (Khayat et al. 2009).

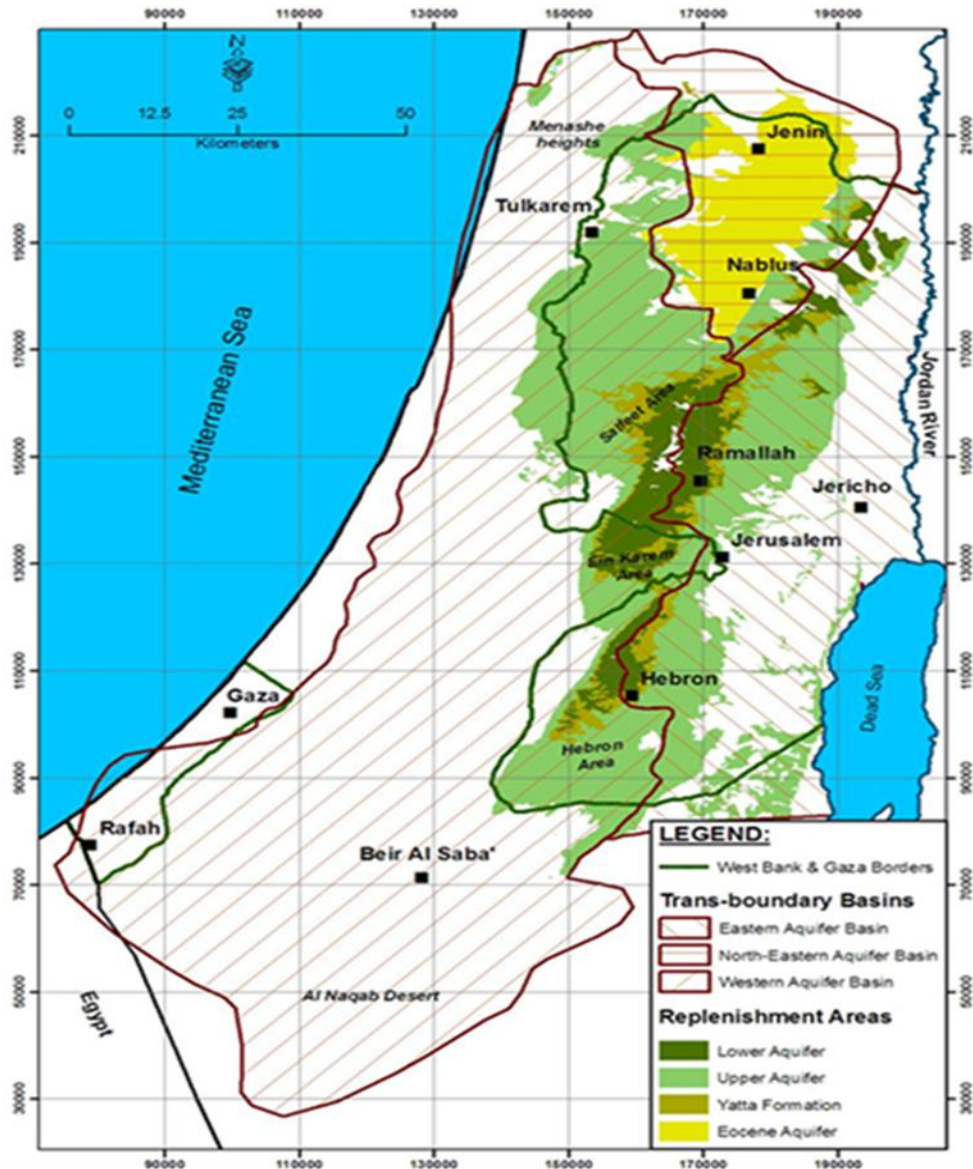


Figure (2.2): Location Map of the Three Trans-Boundary Basins. (Modified after Abusaada,2011).

Ein Samia is located in the northeast of Ramallah district near Kufur Malek village. Ein Samia well field is part of auja spring the biggest spring in the eastern basin. Ein Samia well field consists of six wells. The average production capacity for this field is ranging between 550-600 m³/hr (5.7 million m³/year), it supplies Ramallah district with drinking water (Rimmer, 2011). The geologic nature of Ein Samia recharge area is

basically in its upper part composed of Jerusalem formation with Turonian-Upper Cenomanian age (figure 2.2), make the area more vulnerable to the pollutants in addition to the ability of passing large amounts of rain water through the karstic caves and cracks.

Ein Samia well 1 is the chosen well in this study, the groundwater level in this well is 500 m above sea level, which represents the upper aquifer, Ein Samia well 1 was drilled in the year 1964 with an average production capacity of 100 m³/hr, the depth of this well is 60 m, the well pumps from the upper mountain group aquifer (Rimmer, 2011).

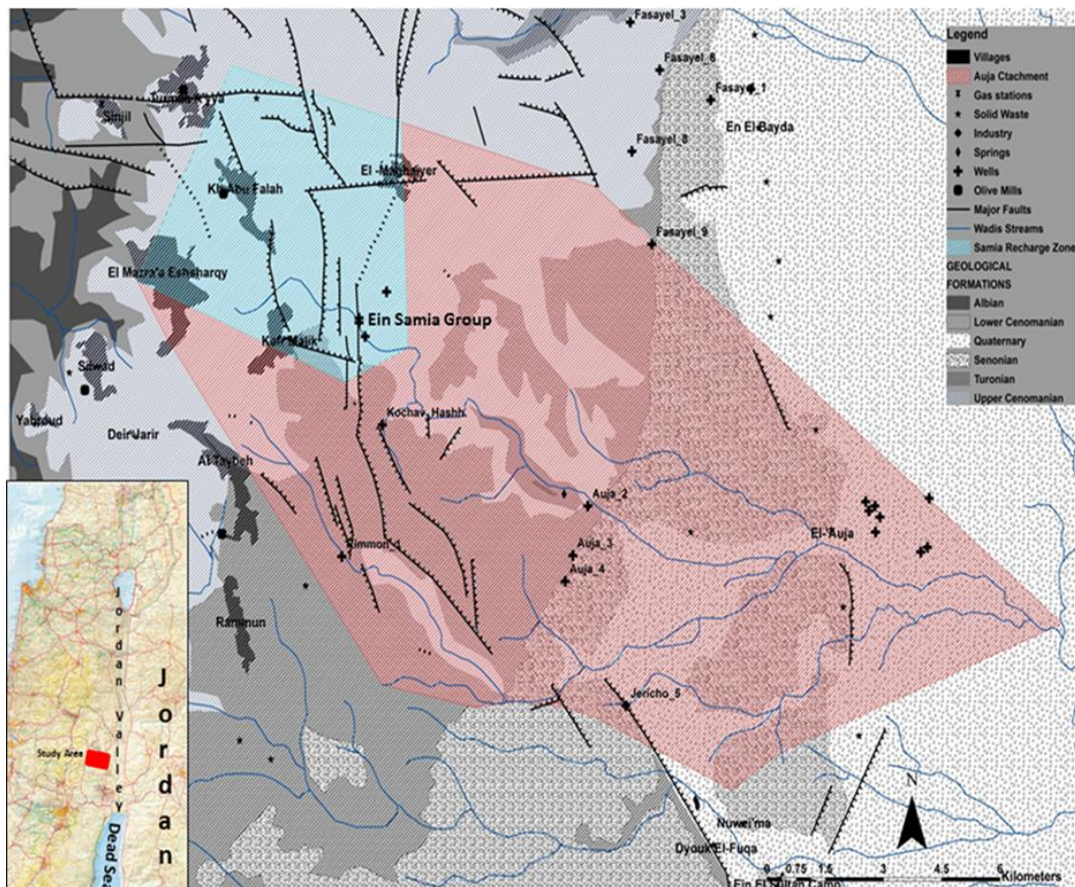


Figure (2.3): Geologic Map of the Area and Catchment Areas Including the Activities in Recharge Area. * GIS Map by Dr. Saed Khayat, 2018.

Figure (2.4). Illustrates the cross section of the study area, it shows the recharge area of Ein Samia well 1 which has a depth of 500 m Above Mean Sea Level (a.s.l.).

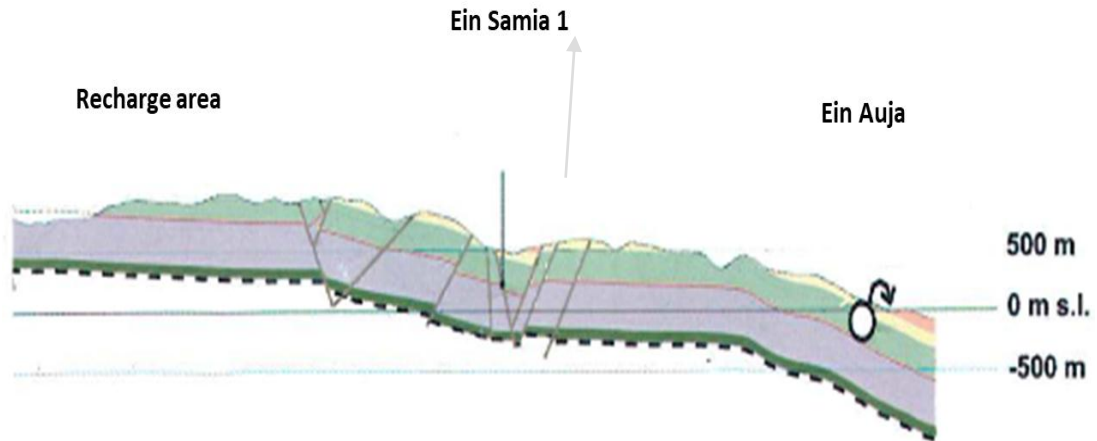


Figure (2.4). Cross Section of the Recharge Area Ein Samia well 1. By UFZ project group, 2018.

2.2 Hydrogeology and Climate

Karst is formed where the fractures and joints are enlarged by dissolution to form conduits and caves. The groundwater in the aquifer is stored in these fractures and joint. Then the water flows through these fractures and the flow could be fast through the fractures which are increasingly enlarged by dissolution.

The Eastern Aquifer is discrete from the western aquifer by a groundwater divide along the axis of the mountain. Comparing with the western basin, the upper and lower aquifers of the eastern basin are not as good as the western basin. The recharge to the aquifers is lower and the characteristics

of the aquifer like permeability and storage are not so convenient (SUSMAQ, 2002).

The Eastern Aquifer Basin lies wholly in the West Bank. The basin has an area of 3100Km² (abusaada, 2011). The water flow is in the direction of eastward toward the Jordan river and the dead sea (Qannam & Merkel, 2002). In particular the basin is drained by many springs in the West Bank with a small amount discharges to the Jordan river and dead sea and almost nothing leaks to the occupied part of Palestine. The recharge area of this basin covers more than 2200 km² and has a storage area of more than 2000 km² (Gvirtzman, 1994). The EAB is mainly recharged by rainfall, the long term annual average recharge is estimated at 125 - 197 Mm³/yr (SUSMAQ, 2004).

While Palestinians in the West Bank use 39 to 48% of the water from this aquifer, Israeli settlers use up to 60% (Fadel et al. 2001).

The Upper and Lower aquifers are joined by faults and groundwater flows from the Upper to the Lower aquifer. The Upper and Lower aquifers are cut off by a large fault in the Jordan valley. Because of this fault the groundwater forced to discharge as springs or leak into the shallow valley aquifer (Qannam,2000).

The Upper aquifer of the eastern basin outcrops along Wadi Qilt, Wadi Nueima, and Wadi Auja of the eastern slopes draining to the Jericho–Auja area close to the Western Boundary Fault (Khayat et al. 2009). Individual strong storm events control the recharge of the mountain aquifer.

According to ARIJ (1997), almost 95% of the annual rainfall occurs between December and March and more than 65% in the 3 months between December and February. The dry period extends from May to end of September. During the winter months the precipitation ranges from 5 to 100 mm in each storm event.

The climate in this area is in general a Mediterranean climate, with a long dry summer and mild, short rainy winter. The average rainfall recorded in the area is 694 mm, with minimum value of 307 mm and maximum value of 1591 mm (Al-Rimmawi et al. 2010).

2.3 Lithology

Generally, the outcrops of rocks in an area is controlled by the folding of rocks in this area. The outcrops in the west bank are mainly carbonate sediments and rocks of Tertiary and Cretaceous ages (khayat, 2005).

In many parts of the West Bank and along the axes of the main anticlines, the younger Senonian and Eocene rocks have been corroded leaving the older Cenomanian and Turonian rocks bared across these parts (Froukh, 2002).

The older rocks cannot be seen at the surface but they are identified from the boreholes (Qannam & Merkel, 2002). These oldest exposed rocks belong to the Albian, covered by younger strata of the cenomanian, Turonian, Senonian and Eocene, exposed on both flanks of the anticlinal axis in the West Bank. However, the youngest formations of the

Pleistocene-Holocene age are found in the Jordan Valley and the shorelines of the Dead Sea (Qannam,2000).

In the West Bank, the Cretaceous and the Tertiary rocks are basically made of limestone, dolomite, chalk and marl. The two main regional aquifers in the West Bank are the Cenomanian-Turonian aquifer (Upper) in the Jerusalem, Bethlehem and Hebron formations and the Albian aquifer (Lower) are built up of Tertiary and Cretaceous rocks. The main aquiclude in the West Bank, which is the Yattah Formation separates the two aquifers (Guttman, 2000).

The exposed rocks of the west bank are (Khayat, 2005), (Rofe and Raffety, 1965):

1. Albian - Lower Cretaceous formations comprising the regional West Bank groundwater system (Beit Kahil, Yatta formations). The thickness of the groundwater system in this area ranges from 500-970 meters .
2. Upper Cretaceous formations comprising the regional West Bank groundwater system (Hebron, Bethlehem and Jerusalem formations). The thickness of the groundwater system in this area ranges from 190-490 meters.
3. Senonian age rocks (Abu Dis formation) are composed mainly of chalks and marls. The thickness ranges between 0-450m.
4. Pleistocene to Eocene rocks overlay the Senonian rocks in the Northern and Northeastern area of the West Bank, the rocks are composed mainly of

limestone, chalky limestone, chalks, marls, and siltstone, which are of limited extent and thickness.

5. Unconsolidated, Quaternary alluvial sediments overlie the major rock formations.

In the Eastern Basin most of the outcrops are Cretaceous rocks of Cenomanian, Turonian, and Senonian age. These outcrops represent the major recharge area of the aquifer as they are located in the high rainfall area.

The lithology in this aquifer is characterized by karstified limestone and dolomite along with marl and clay specially near the bottom (Qannam, 2000), (Guttman, 2006). The general stratigraphy of the West Bank and the Israeli and the Palestinian names of the different geological formations in the West Bank as well as their lithology, thickness and aquifer potentiality are described and illustrated in Table 2.1.

Table 2.1: Generalized stratigraphic column of the West Bank (modified after Guttman, 2000; and Qannam, 2000)

Geological Time Scale				Group		Formation		Lithology	Thickness (m)	Hydrostratigraphy			
Era	System	Epoch	Palestinian	Israeli	Palestinian	Israeli							
CENOZOIC	Quaternary	Holocene	Recent		Kurkar	Alluvium	Alluvium	Marl, alluvium, gravel	Variable	Aquifer			
						Gravel	River gravel			Aquifer			
		Pleistocene		Lisan		Dead Sea	Lisan	Lisan	Thinly laminated marl with gypsum bands	200+			
	Tertiary	Neogene	Pliocene-Miocene	Beida	Jenin Sub Series	Saqia	Beida	Bit Nir and Ziglag	conglomerate	0-200	Aquifer		
		Paleogene	Eocene	Belqa		Avidat	Reef nummulitic limestone	Zor'a	Reef limestone, bedded limestone, chalk with limestone undifferentiated	100-500	Aquifer in limestone and aquiclude in chalk		
	Paleocene		Mount Scopus			Nummulitic limestone	Taqiya	Marl, chalk and clay	Aquiclude				
MESOZOIC	Senonian	Mastrichtian				Khan Al Ahmar and Zerqa	Ghareb	Yellowish chalk		Aquiclude			
		Campanian				Anman and Abu Dis	Mishash	Chalk with back chert		Aquiclude			
		Santonian					Menuha	Chalk		Aquiclude			
		Turonian				Ajlun	Judea	Jerusalem		Bina	Limestone and dolomite (karstic).	90-120	Aquifer
		Cenomanian					Bethlehem	Weradim		Hard gray porous dolomite	90-100	Aquifer	
								Kfar Shaul		Chalky limestone, chalk and marl	30-40	Aquitard	
	Cretaceous	Albian			Hebron	Aminadav	Karstic limestone and dolomite	110-140	Aquifer				
					Yatta	Moza	Marl, clay and marly limestone	10-20	Aquiclude				
					Beit Meir	Limestone, chalky limestone and dolomite	120-140	Aquifer					
						Limestone inter-bedded with marl		Aquiclude					
				Upper Beit Kahil	Kesalon	Limestone inter-bedded with marl	30-50	Aquifer					
					Soreq	Dolomite inter-bedded with marl	110-170	Aquifer					
				Lower Beit Kahil	Giva't Yearim	Limestone, dolomite	20-70	Aquifer					
					Kefira	Limestone, dolomite and marly limestone	120-180	Aquifer					
				Kurnub		Kobar	Qatana	Marl and clay	50	Aquitard			
							Ein Qinyia	Marl and marly limestone	60-70	Aquitard			
			Aptian		Kurnub	Tammun	Caly and marl	80-150	Aquitard				
						Ein Al Asad	Limestone		Aquifer				
		Neocomian			Nabi Said	Limestone		Aquifer					
					Ramali	Hatira	Sandstone	150	Aquifer				
Jurassic	Callovia-Bajocian		Zerqa	'Arad	Upper Malih	Upper Malih	Marl interbedded with chalky limestone	190	Aquitard				
					Lower Malih	Lower Malih	Dolomitic limestone, jointed and karstic	55	Aquifer				

2.4 Land Use and Human Activities

Ein Samia is located in the northeast of Ramallah district near Kufur Malek village. As shown in figure (2.3) Ein Samia region is surrounded by Palestinian small villages, they are Kufur Malek, Mazra'a e-Sharkiya, Khirbat Abu Falah and Turmos Ayya and Israeli settlements called Shilo and Shvut Rahel. There are different anthropogenic activities in the area which are direct sources of pollutants that affect the ground water quality, like agriculture, unsanitary septic tanks, landfills, waste from industrial activities. The Palestinian communities' area lack of the infrastructure for the sewage networks, and depend mainly on septic tanks, which lack the least conditions of sanitary and healthy environment. In addition, the amount of sewage water drains directly from Shilo settlement and other villages to the Wadis' areas. Moreover, a considerable amount of waste water and other wastes drain from some of the quarries that are located within the recharge area. Another important potential source for the pollution is the landfills found in Turmusayya – Abu falah region, the landfills' leachate reaches the ground layers through the cracks and faults.



Figure (2.5): Aerial Map of the Recharge Area, Identifying the Anthropogenic and Industrial Activities which Affect the Appearance of Pollutants in the Spring (Dr Saed Khayat, 2018).

Chapter Three

Methodology

3.1 Collecting Data

To collect database for the study, first an instrument (Diver) has been installed to measure water level, electrical conductivity (EC) and temperature. EC reflects the presence of soluble pollutants in water and it depends on the change of temperature. As the temperature of a solution increases, the viscosity decreases and so the movement of the ions increases, also the increase of temperature may cause an increase in the number of ions because of the dissociation of molecules and the temperature depends on all of these factors, so an increase in the temperature will cause an increase in the conductivity (Barron & Ashton, 2005). These instruments measure these parameters in situ every hour and send them through a modem to a server, so to ease its monitoring. Second a tipping bucket rain gauge was installed in Ramallah to measure rainfall amounts and to get rainfall measurements for the rain events of season 2017-2018. And then information about the activities that take place in the recharge area, their nature and place, has been collected, in addition to the possible pollutants which may directly affect water during the recharge process. And by using GIS and aerial maps (Figure 2.3), geologic maps were constructed, and catchment area was defined.

3.2 Sampling

Samples were collected with the help of an employee at the Palestine Water Authority (PWA) and stored in plastic bottles in the refrigerator and label every bottle with the exact time and date of sampling. The samples were repeatedly taken after each rain event or after noticing a change in the EC reading. The samples were filtered immediately when they received in the lab using cellulose Whatman filter paper. The filtration is carried out to test the water for total coliform bacteria later and is also important for the test of Dissolved Organic Carbon (DOC). Then the pH was measured for each sample using Hanna pH meters. The samples were kept in the refrigerator all the time of testing them.

3.3 Hydro-chemical Analysis

The samples were tested in Palestine Technical university, Kadoree, Palestine, for several chemical variables which are considered as indicators for the flush-out effect and so for the contamination of groundwater resource. Total dissolved organic carbon (DOC) was measured using TOC analyzer instrument, the instrument measures both the total organic carbon (TOC) and the total inorganic carbon (TIC), the difference between TOC and TIC equals the total dissolved organic carbon (DOC).

The main anions including nitrate, sulfate and phosphate were measured using HACH spectrophotometer by using a specific reagent added to the measured sample. The sodium and potassium cations were analyzed using flame photometer. Chloride ion was analyzed by titration with silver nitrate

using potassium chromate indicator. Calcium and magnesium were analyzed by titration with EDTA (ethylene diamine tetra acetic acid) using Ero-chrome Black T indicator, in the titration with EDTA we performed two titrations, the first titration is to calculate the total hardness which equals to the sum of Ca and Mg concentrations, and the second titration done by adding drops of sodium hydroxide to precipitate the Mg and left the Ca so in this part of titration we calculate the concentration of Ca.

In addition to the previous analysis the samples were tested for total coliform bacteria using filter membrane method, first the samples were filtered immediately as we received them at the lab, then we use the filter paper to isolate the total coliform bacteria on a petri dish and incubate the petri dishes in the oven at 37C° for 24-48 hours to let the colonies grow, after this time we counted the colonies of bacteria figure (3.1) and then the growing bacteria was immediately isolated and tested for E-coli bacteria using a specific media called MacConkey.

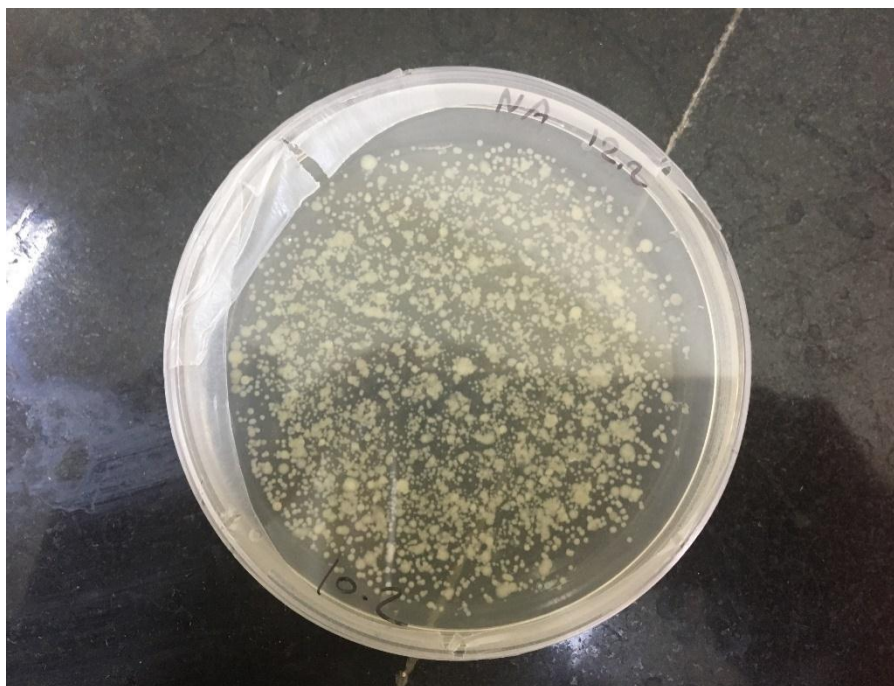


Figure 3.1: Total Coliform Bacteria Colonies after Incubation for 24 hours.

3.4 Stable Isotope Analysis

Isotopes of an element have the same number of protons but a different number of neutrons. Elements have predominant isotopes and less abundant isotopes.

The term stable isotopes simply refer to isotopes that are no radioactive forms of an element.

Stable isotopes are measured as the ratio compared with the most abundant isotope of a given element. Isotope ratios are quantified as δ values in which

$$\delta = [(R_{\text{SAMPLE}} - R_{\text{STANDARD}}) / R_{\text{STANDARD}}] \quad (1)$$

R is defined as D/H for δ D values, $^{18}\text{O}/^{16}\text{O}$ for δ ^{18}O and $^{15}\text{N}/^{14}\text{N}$ for δ N. These δ values are proportional in nature and they reflect the positive or negative deviation from the reference standard material for each element,

as each element has its own reference standard (Clarck and Fritz, 2013). δ values are expressed as the parts per thousand or permil (‰). For the stable isotopes of H and O the standard used in this study is Vienna Standard Mean Ocean Water (VSMOW).

Positive δ values mean “enriched ” or “heavy ”, while a negative δ values are said to be “depleted ” or “light ”.

In the element cycle in nature, there are several steps that can alter the stable isotope composition in different chemical compounds. This kind of changes, called fractionation, happen as a result of physical and chemical reactions.

Isotopic effects in a chemical reaction tend to hold the same signature of the starting material. This means that the same compound could have different isotopic composition depending on the starting material. So, stable isotopes supply a very beneficial tool in recognizing the sources of groundwater pollution (khayat et al, 2017).

In this study, the stable isotopes analysis will help in indicating the sources of groundwater in the recharge area, if there is a source for recharge other than direct rainfall, and if there is water from far recharge catchments. Also, it will indicate how much is the recharge area close to recharge source.

In addition to chemical analysis, samples were taken to study the stable isotopes ^2H , ^{18}O of water in Forschungszentrum Juelich, Germany.

Stable oxygen and hydrogen isotope analyses of water samples were performed by cavity ring-down spectroscopy (L2130-I, Picarro Inc., Santa Clara, CA, USA). About 0.8 μl of filtered water was injected into the vaporizer, converted to water vapor and transported into the cavity with synthetic air as carrier gas. Water samples were measured in replicate together with internal laboratory standards calibrated against international isotopic reference materials (Brand et al. 2014). The isotopic compositions are expressed as δ -values in per mil (‰) as follows in the equation:

$$\delta = (R_{\text{sample}} / R_{\text{standard}} - 1) * 1000$$

With R_{sample} and R_{standard} as isotope ratios ($^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$) of sample and standard, respectively. Isotope values of oxygen and hydrogen are reported normalized to the Vienna Standard Mean Ocean Water (VSMOW)- Vienna Standard Light Antarctic Precipitation (VSLAP) scale. Analytical precision as determined from internal standards was better than ± 0.05 ‰ for $\delta^{18}\text{O}$ and 0.1 ‰ for $\delta^2\text{H}$.

And ^{15}N , ^{18}O isotopes of nitrate at Helmholtz Zentrum Umweltforschungs (UFZ), Halle, Germany. The method used for the analysis of ^{15}N and ^{16}O of nitrate was described by (Sigman et al. 2001), (Casciotti et al. 2002) and it is based on the isotopic analysis of nitrous oxide (N_2O), which is produced from nitrate by using a denitrifying bacteria which lack to N_2O -reductase

activity. In this method, both ^{15}N and ^{18}O isotopes are accessible. The denitrification pathway is as follows:

Reduction of nitrate to nitrite, then to nitric oxide, then to nitrous oxide and dinitrogen.



Both *Pseudomonas chlororaphis* (ATCC# 43928, deposited by J. M. Tiedje) and *Pseudomonas aureofaciens* (ATCC# 13985, recently reclassified as a strain of *P. chlororaphis*), both strains could be used for the isotopic measurement as they lack the nitrous oxide reductase activity.

The first step is to prepare the bacterial working culture, the culture medium for this bacterium is tryptic soy broth amended with KNO_3 , NH_4Cl and KH_2PO_4 . Then the bacteria with the medium is incubated for 7-16 days at room temperature with regular shaking, after incubation 3-fold concentration of the culture is centrifuged, and then vented with nitrogen gas for 2 hours. 2 ml of concentrated culture is poured in each sample vial and tightly closed with septum, the sample vials flushed with He for 15 minutes, then 2 ml of the sample solution is injected into the vial and incubated for 2-3 days at room temperature. At the end of incubation period a 0.5 ml of 10N of NaOH solution is injected into the sample vial to kill the bacteria and so stop the reaction. The sample headspace N_2O is carried by He-flow (50 ml/min) to a cold trap. Then the N_2O is flushed out of the cold trap to the mass spectrophotometer (conflow-IRMS) by He-flow (5 ml/min). Calibration and normalization of the results to the AIR and

VSMOW (Vienna Standard Mean Ocean Water) scale by reference materials that are treated as samples, is done. The analytical precision of this method is as follows:

$$^{15}\text{N} : \delta ^{15}\text{N} : \pm 0.2 \text{ ‰} \quad ^{18}\text{O} : \delta ^{18}\text{O} : \pm 0.5 \text{ ‰}.$$

The overall research methodology is illustrated in Figure 3.2. And Table 3.1 shows the measured parameters in this research and illustrate the method of analysis for each parameter.

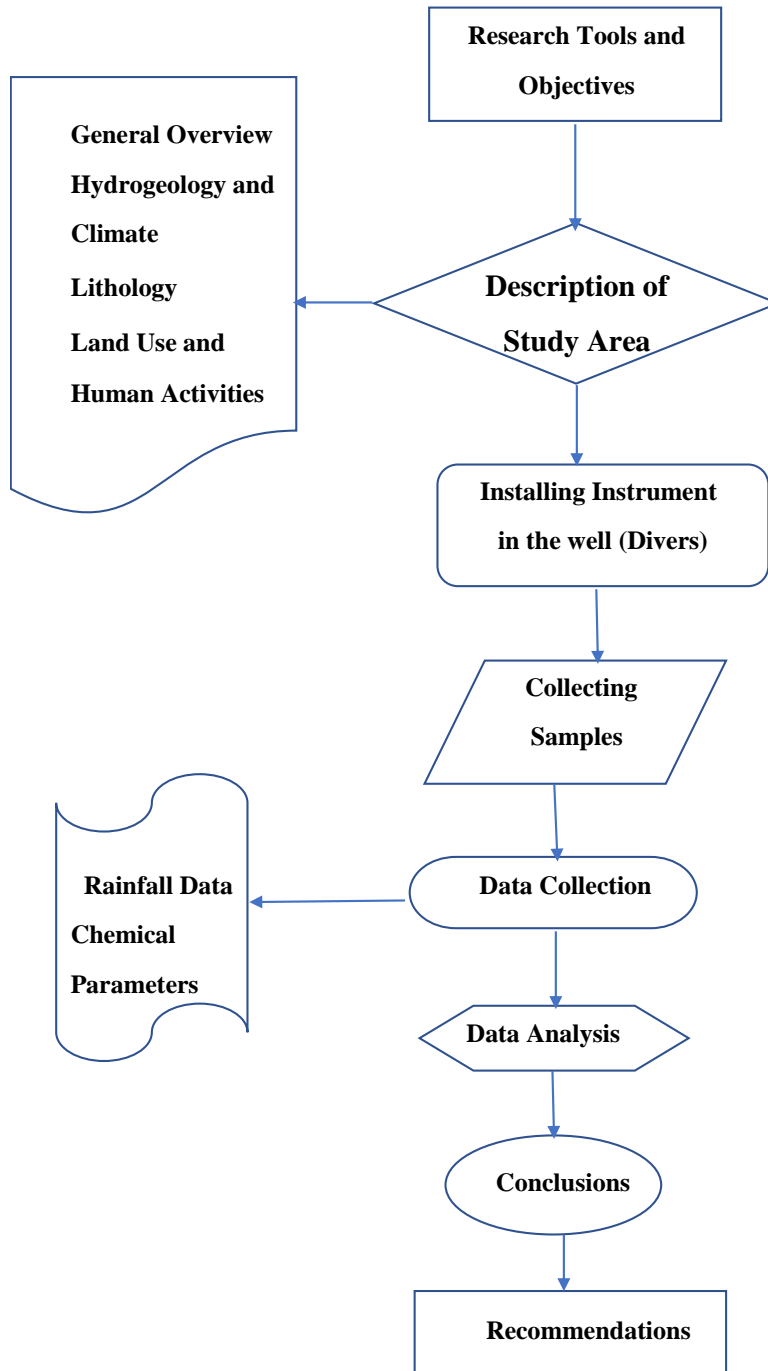


Figure 3.2: Overall Methodology

Table 3.1: Measured Parameters and Methods of Analysis.

Parameter	Method of analysis
Temperature, EC, water level	Field meter (Divers)
Ca ²⁺	Titration with Na ₂ -EDTA using Eriochrome black-T indicator with adding NaOH
Total Hardness (Ca ²⁺ and Mg ²⁺)	Titration with Na ₂ -EDTA using Eriochrome black-T indicator
Na ⁺ and K ⁺	Flame Photometer
SO ₄ ²⁻	Spectrophotometer ($\lambda=220$ nm)
Cl ⁻	Titration with AgNO ₃ using potassium chromate indicator
NO ₃ ⁻	UV-Spectrophotometric method ($\lambda=500$ nm)
DOC	TOC analyser instrument
PO ₄ ³⁻	Spectrophotometer ($\lambda=700$ nm)
Fecal Coliform, E-coli	Filter membrane method, MacConkey specific media

Chapter Four

Results and Discussion

4.1 Evolution of Hydrochemistry in Response to Rainfall

The phenomena of pollutants' washing out or what is called "Flush out effect" in response to the pressure of heavy rain, is a well-known phenomenon which repeatedly happens annually after rain event with a certain intensity in the permeable karstic aquifers of the upper ground aquifer. According to previous studies, this phenomenon almost happens under the effect of water pressure of a heavy rain event once a year (Khayat et al. 2009).

In Ein Samia well 1, the noticeable thing is that the flush out happens in every time after each rain event, but this usually takes place after the unsaturated recharge zone becomes enough saturated. As the seasonal rainfall analysis of the 2017-2018 rainfall season showed that there was not flush out in the first four rain events figure (4.1). The electrical conductivity (EC) was the indicator of the flush out of the pollutants, because the (EC) reflects the presence of such soluble pollutants. The pollutants began to appear after the rain event of 5.1.2018, while the first shock in EC was noticed with a value of 643 μS as shown in figure (4.1), and after this date many flush out processes happened in response to rain events. This shock in EC value was accompanied by an increase in the monitored chemical parameters as will be shown later.

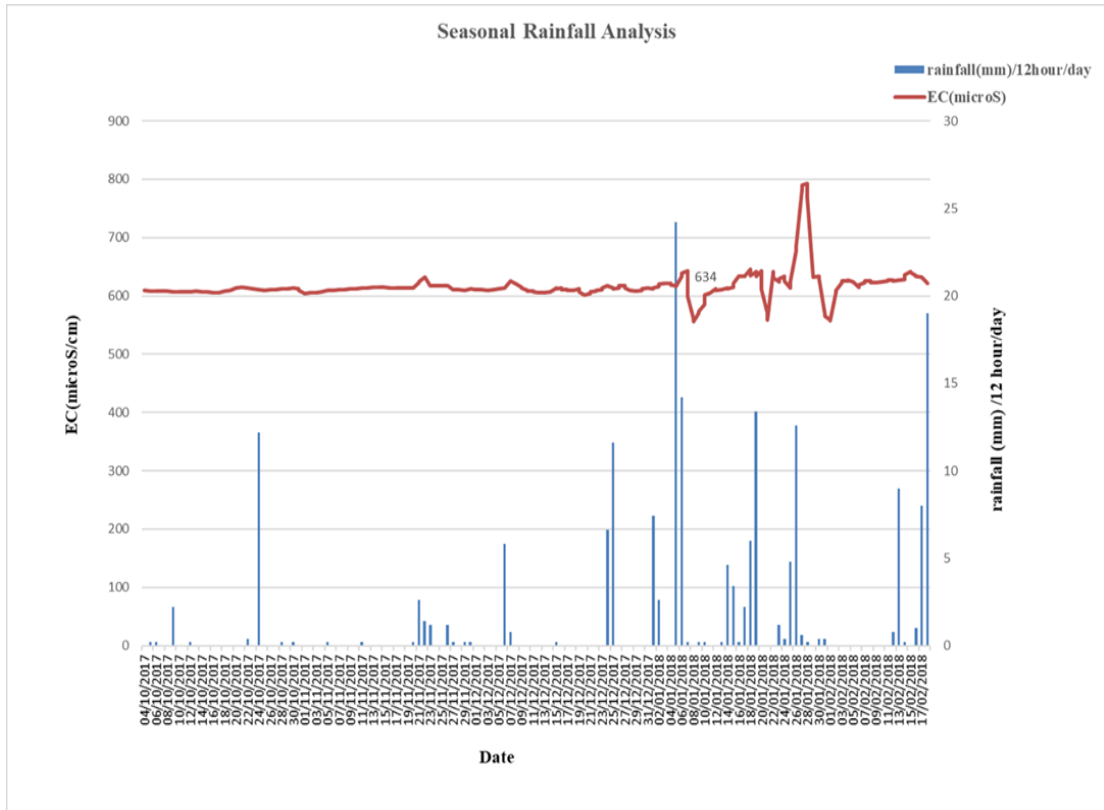


Figure (4.1): Seasonal Rainfall Analysis, Winter Season (2017-2018).

In general, the pollutants in Ein Samia well 1 could be easily noticed after every rain event with intensity higher 13 mm within 48 hours even with eyes because of the yellow-reddish sample colors.

In the analysis of the rain event of 05-07 January 2018, 40 mm rainfall intensity within 24 hours caused the first shock or flush-out of the pollutants with a value of 640 $\mu\text{S}/\text{cm}$ for the EC as shown in figure (4.2).

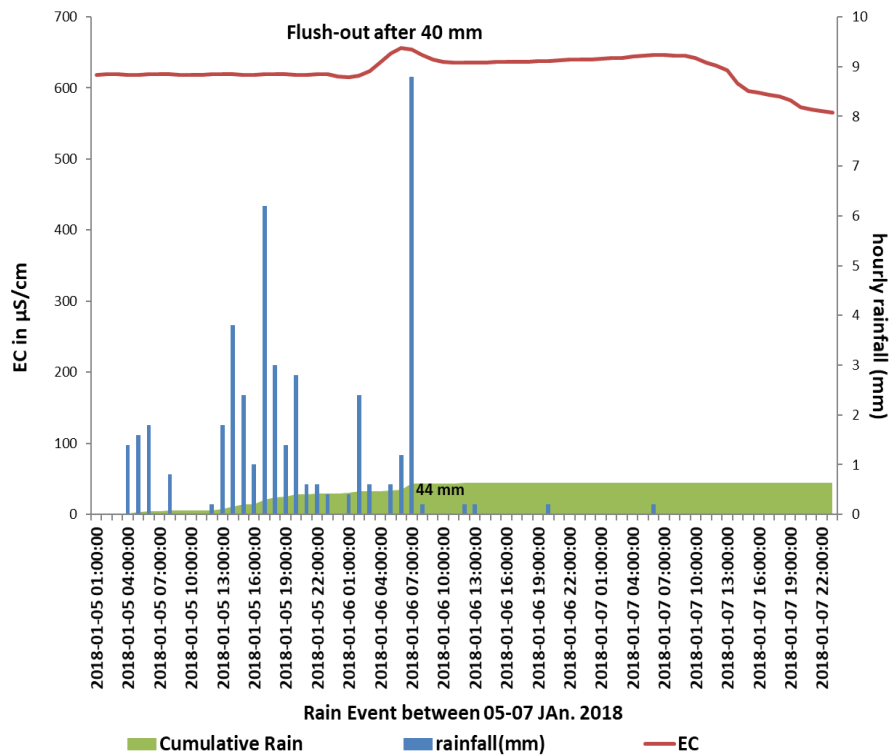


Figure (4.2): Rain Event Analysis of 05-07- January- 2018.

The figure shows continuous heavy rainfall in one day (5.1), with different intensities and irregular distribution during the day, as we can notice that each hour has a different intensity of rain. Also, in the day after (6.1), the rain was unequally distributed during the day but with a high intensity (8.5mm) in one hour (7:00 am). During these two days, there was not any noticeable change in the electrical conductivity (EC), with almost a constant value (\square 600 μ S).

It is clear that the first shock required accumulative rainfall intensity (40 mm) in a duration of one day of continuous rainfall, where the accumulated pollutants from the dry summer period washed out. This could be attributed to that at the beginning of the season the heavy rainfall goes

directly to the unsaturated zone and after a certain intensity the flush out take place.

Further rain event analysis of other rain events showed other flush out processes, which indicates that the sources of pollutants are continuously producing these pollutants. In the analysis of the rain event of 16.1-28.1.2018, two flush-out events were noticed figure (4.3).

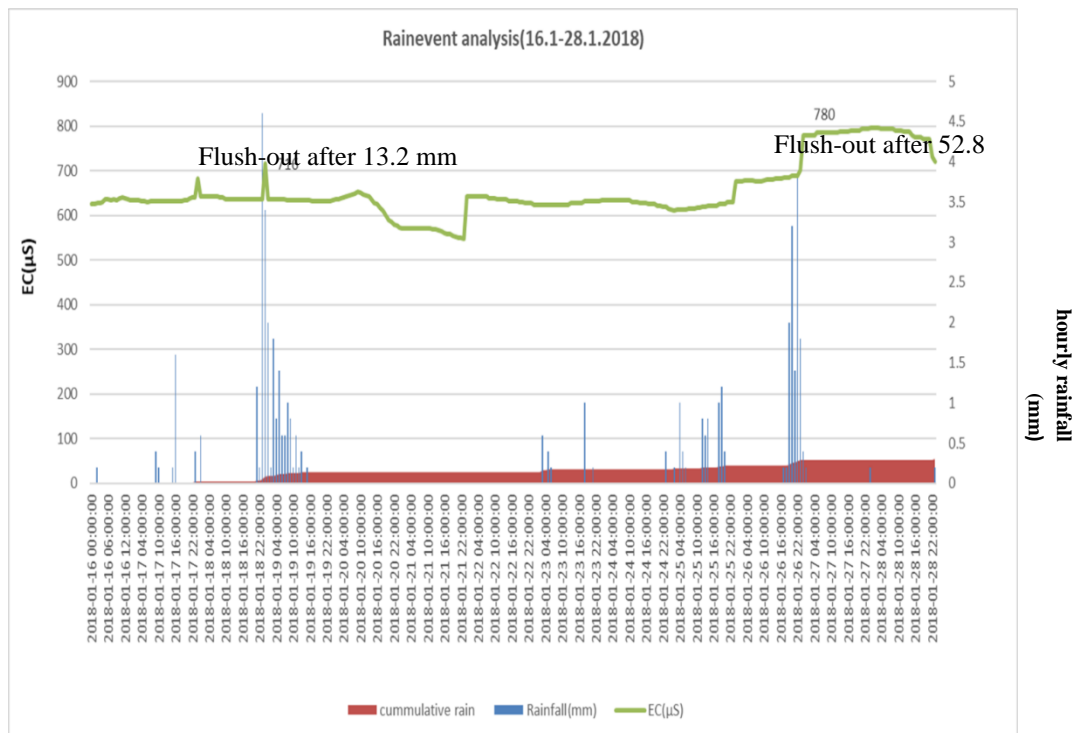


Figure (4.3) Rain Event Analysis (16-28- January- 2018).

In the first rain event (16-18.1) the rainfall was not intensive with unequal distribution along hours of the two days, however in (18.1) at 22:00 pm there was an intensive shot of rain with an intensity of 4.5 mm. A shock in the EC (716 μ S) was noticed after three days with accumulative rain of 13.2 mm. In this rain event, the shock required a lower intensity to take place from the one which occurred in the rain event of (5-7.1), this is due to

that the unsaturated recharge zone is now saturated and a lower rainfall intensity could cause a flush out. In the period from 23-26.1 the rainfall was noncontinuous, irregularly distributed with different intensities, while in 26.1 in 7 hours there was heavy rain which as a result caused a new flush out. This flush out happened after accumulative rain of 52.8 mm within 48 hours. Table 4.1 summarizes the results of the monitoring system.

Table 4.1. Summarized Results of the Monitoring System

Date	EC ($\mu\text{S}/\text{cm}$)	Accumulative Rainfall Intensity (mm)	Rainfall Duration (hr)
5/1/2018	634	40	24
18/1/2018	716	13.2	24
25-26/1/2018	780	52.8	48

4.1.1 Hydro-chemical Response to Anthropogenic Activities

Different chemical parameters were monitored in response to rainfall events Table (1.1). It was noticed that as there was a shock in EC, there was also an increase in other monitored parameters. Nitrate (NO_3^-), Orthophosphate, dissolved organic carbon (DOC) were monitored in this research. According to the results shown in figure (4,4), nitrate had high increase in the rain event of 5-10/1/2018 with concentration around 60 mg/l, and according to World Health Organization (WHO, WHO website) drinking water with more than 50 mg/l nitrate is not safe for human use. The nitrate reached the highest concentration (83 mg/l) in the rain event of 18-22/1/2018. Nitrate increase followed by orthophosphate flush out (4.4.E). Orthophosphate is known as reactive phosphate, which are main constituents in fertilizers used for agriculture. Orthophosphate is produced from natural sources like natural decomposition of rocks and minerals,

stormwater runoff and atmospheric deposition. But it also produced from man-made sources like partially treated and untreated sewage and application of some lawn fertilizers. This emphasizes that the main source of pollution of nitrate and orthophosphate is the same which is the sewage wastewater.

The dissolved organic carbon (DOC) (4.4.D) concentration show a late flush out peak, this is because the organic carbon and nitrogen may convert to nitrate at the beginning of the season through an oxidation process in the unsaturated zone of the soil, also this kind of substances usually adhered to the soil granules which makes it difficult to be washed out in the first rain events. However, the presence of nitrate and DOC with this high concentration at the same time could be attributed to applying the organic manure, which is usually used in October after the first rain event to fertilize olive trees and continue to increase in the ground water after rain events during rainy season.

The noticeable thing is that the flush out processes followed by decrease in the electrical conductivity (EC) for a while after rain stop, then it increases again after the next rain event, this indicates the continuity of pollutants from the different activities in the area.

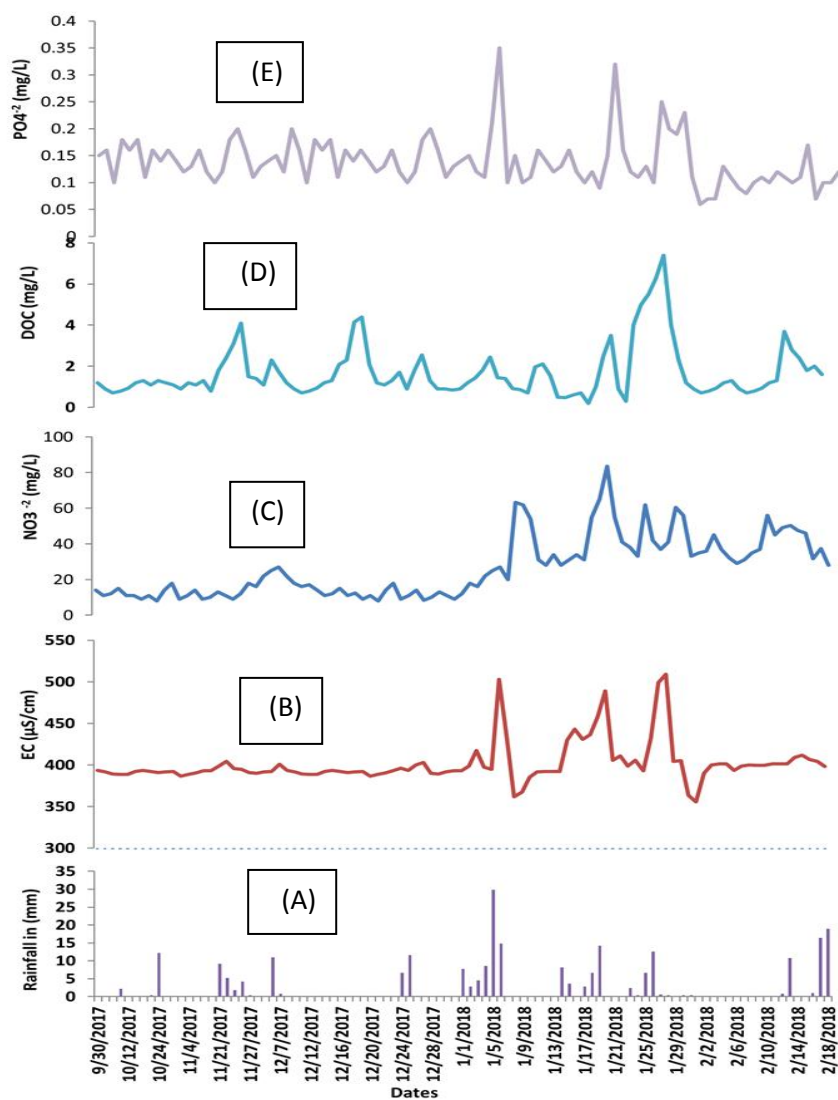


Figure (4.4): Relation Between Daily Rainfall(mm) (A), EC (B), nitrate (C), DOC (D) and phosphates (E).

Table (4.2) Hydro-chemical Data in mg/l of Ein Samia Well 1in the Season (2017-2018).

Date	EC(MicroS)	EC (mS)	TDS	Rainfall in mm	TOC (mg/L)	pH	Total Coliform	Mg(mg/L)	Ca(mg/L)	Na(mg/L)	K(mg/L)	Cl(mg/L)	TIC(mg/L)	SO4(mg/L)	NO3(mg/L)	PO4(mg/L)
30/09/2017	615	0.615	393.6	0	1.2	7.8	26	26	214	20	0.9	45	42.2	9	14	0.15
01/10/2017	612	0.612	391.68	0	0.9	7.7	28	23	231	20.2	0.8	38	44.1	7	11	0.16
06/10/2017	608	0.608	389.12	0	0.7	7.9	24	25	254	19.3	0.78	33	45.8	8	12	0.1
09/10/2017	607	0.607	388.48	2.2	0.8	7.5	26	23	218	18.23	0.8	38	43.5	9	15	0.18
12/10/2017	607	0.607	388.48	0.2	0.93	7.6	21	24	222	18.1	0.8	34	45.74	7	11	0.16
20/10/2017	613	0.613	392.32	0	1.2	7.8	23	31	242	1.84	0.81	38	46.3	7	11	0.18
21/10/2017	615	0.615	393.6	0.2	1.3	7.6	21	25	248	18.3	0.79	36	45.2	8	9	0.11
22/10/2017	613	0.613	392.32	0.4	1.1	7.8	24	28	260	18.2	0.8	34	44.7	7	11	0.16
24/10/2017	611	0.611	391.04	12.2	1.3	8	26	26	254	17	0.88	35	42.1	8	8	0.14
28/10/2017	612	0.612	391.68	0.2	1.2	8.08	25	30	214	17.5	0.85	37	40.8	9	14	0.16
30/10/2017	613	0.613	392.32	0	1.1	8	24	24	222	18.3	0.83	44	43.1	8	18	0.14
01/11/2017	604	0.604	386.56	0	0.9	7.9	23	26	242	17.2	0.82	35	44.2	7	9	0.12
04/11/2017	607	0.607	388.48	0	1.2	7.9	21	28	248	18.9	0.88	36	43.5	7	11	0.13
05/11/2017	610	0.61	390.4	0	1.1	7.8	24	25	260	19.5	0.9	34	45	7	14	0.16
11/11/2017	614	0.614	392.96	0	1.3	7.6	26	23	254	20	0.9	35	43.2	8	9	0.12
20/11/2017	614	0.614	392.96	0.2	0.8	7.8	21	26	214	20.2	0.8	36	45.74	9	10	0.1
21/11/2017	623	0.623	398.72	9.2	1.8	7.7	22	30	214	19.3	0.7	34	46.3	8	13	0.12
22/11/2017	632	0.632	404.48	5.2	2.4	7.8	21	24	231	18.23	0.9	35	45.2	8	11	0.18
23/11/2017	618	0.618	395.52	1.8	3.1	7.9	24	26	254	18.1	0.8	37	44.7	7	9	0.2
26/11/2017	617	0.617	394.88	4.2	4.1	8	26	28	218	17	0.8	44	42.1	8	12	0.16
27/11/2017	611	0.611	391.04	0.4	1.5	8.1	25	25	222	17.5	0.8	46	40.8	7	18	0.11
29/11/2017	609	0.609	389.76	0.2	1.4	7.9	24	23	231	18.3	0.81	38	43.1	9	16	0.13
30/11/2017	612	0.612	391.68	0.2	1.1	7.8	23	22	242	17.2	0.79	34	44.2	8	22	0.14
06/12/2017	613	0.613	392.32	11	2.3	7.7	21	25	234	18.9	0.8	38	43.5	9	25	0.15
07/12/2017	626	0.626	400.64	0.8	1.7	7.8	24	31	243	19.5	0.88	36	45	8	27	0.12
09/12/2017	615	0.615	393.6	0	1.2	7.8	34	26	231	17	0.9	34	43.1	7	22	0.35
10/12/2017	612	0.612	391.68	0	0.9	7.7	51	23	255	17.5	0.8	36	44.2	6	18	0.16
11/12/2017	608	0.608	389.12	0	0.7	7.9	31	25	214	18.3	0.7	34	43.5	6	16	0.1
12/12/2017	607	0.607	388.48	0	0.8	7.5	21	23	231	17.2	0.9	35	45	8	17	0.18
13/12/2017	607	0.607	388.48	0	0.93	7.6	36	24	254	18.9	0.8	37	43.2	9	14	0.16
14/12/2017	613	0.613	392.32	0	1.2	7.8	38	31	218	19.5	0.9	44	42.2	7	11	0.18
15/12/2017	615	0.615	393.6	0	1.3	7.6	27	25	222	20	0.8	46	44.1	8	12	0.11
16/12/2017	613	0.613	392.32	0	2.1	7.8	29	28	242	20.2	0.78	51	45.8	9	15	0.16
17/12/2017	611	0.611	391.04	0	2.3	8	31	26	248	19.3	0.8	52	43.5	7	11	0.14
18/12/2017	612	0.612	391.68	0	4.14	8.08	26	30	260	18.23	0.8	70.9	45.74	7	12.404	0.16
19/12/2017	613	0.613	392.32	0	4.4	8	28	24	254	18.1	0.81	61	46.3	8	9	0.14
20/12/2017	604	0.604	386.56	0	2.1	7.9	24	26	214	1.84	0.79	45	45.2	7	11	0.12
21/12/2017	607	0.607	388.48	0	1.2	7.9	26	28	224	18.3	0.8	38	44.7	8	8	0.13
22/12/2017	610	0.61	390.4	0	1.1	7.8	21	25	243	18.2	0.88	33	42.1	9	14	0.16
23/12/2017	614	0.614	392.96	0	1.3	7.6	23	23	252	18.5	0.85	38	40.8	8	18	0.12
24/12/2017	619	0.619	396.16	6.6	1.7	7.8	21	21	254	18.2	0.83	34	43.6	7	9	0.1
25/12/2017	615	0.615	393.6	11.6	0.9	7.7	24	20	261	18.4	0.82	38	41.7	7	11	0.12
26/12/2017	625	0.625	400	0	1.8	7.8	26	22	258	18.3	0.88	37	45.8	7	14	0.18
27/12/2017	630	0.63	403.2	0	2.55	7.9	25	20	260	18.23	0.9	35.45	47.05	8	8.417	0.2
28/12/2017	609	0.609	389.76	0	1.3	8	24	26	243	18.5	0.91	35	48.6	9	10	0.16
29/12/2017	608	0.608	389.12	0	0.89	8.1	23	24	221	18.4	0.88	37	49.1	8	13	0.11
30/12/2017	612	0.612	391.68	0	0.9	7.9	21	23	231	18.3	0.86	36	46.3	8	11	0.13
31/12/2017	614	0.614	392.96	0	0.84	7.8	24	21	227	18	0.82	37	44.2	7	9	0.14

Table (4.2) Hydro-chemical Data in mg/l of Ein Samia Well 1in the Season of (2017-2018).

Date	EC(MicroS)	EC(mS)	TDS	Rainfall in mm	TOC (mg/L)	pH	Total Coliform	Mg(mg/L)	Ca(mg/L)	Na(mg/L)	K(mg/L)	Cl(mg/L)	TC(mg/L)	SO4(mg/L)	NO3(mg/L)	PO4(mg/L)
01/01/2018	614	0.614	392.96	7.8	0.9	7.7	26	25	234	18.1	0.84	35	42.8	8	12	0.15
02/01/2018	623	0.623	398.72	2.8	1.2	7.8	21	24	224	18.6	0.83	34	44.3	7	18	0.12
03/01/2018	652	0.652	417.28	4.5	1.43	7.9	22	22	246	19.1	0.86	39	43.4	9	16	0.11
04/01/2018	621	0.621	397.44	8.6	1.81	7.8	31	21	241	18.7	0.82	36	45.2	8	22	0.21
05/01/2018	617	0.617	394.88	29.8	2.45	7.7	360	20	250	18.23	0.9	53	47.5	9	25	0.35
06/01/2018	786	0.786	503.04	14.8	1.44	7.6	1120	44	237	20.1	1.03	106	48.7	8	27	0.1
07/01/2018	680	0.68	435.2	0.2	1.41	7.6	1400	30	235	20.1	1.1	71	49.8	10	20	0.15
08/01/2018	565	0.565	361.6	0.2	0.91	6.68	115	50	200	21.1	1.9	76	45.12	12	63.36	0.1
09/01/2018	574	0.574	367.36	0.2	0.87	6.7	60	20	210	22	1.6	81	45.97	10	61.92	0.11
10/01/2018	602	0.602	385.28	0.2	0.71	6.7	48	24	234	19.8	1.1	42	45	12	54	0.16
11/01/2018	612	0.612	391.68	0	1.97	6.8	42	23	231	19.7	1.3	38	43.5	11	31	0.14
12/01/2018	613	0.613	392.32	0.2	2.11	7	56	25	241	19.6	0.93	71	44	13	28	0.12
13/01/2018	613	0.613	392.32	0.2	1.55	7.1	57	22	224	19.5	0.97	65	41.2	12	34	0.13
14/01/2018	613	0.613	392.32	8.2	0.5	7.4	66	21	218	20.2	0.96	68	43.1	10	28	0.16
15/01/2018	672	0.672	430.08	3.6	0.47	7.1	67	25	209	20.4	0.84	69	42.5	8	31	0.12
16/01/2018	692	0.692	442.88	0.2	0.6	6.8	78	26	211	21.2	0.75	71	44.8	9	34	0.1
17/01/2018	673	0.673	430.72	2.8	0.7	6.9	54	35	201	21.4	0.77	71	45.2	9	31	0.12
18/01/2018	682	0.682	436.48	6.6	0.2	6.8	50	100	180	21.7	0.79	71	46.81	7	54.72	0.09
19/01/2018	716	0.716	458.24	14.2	1	6.8	1150	90	165	19.9	0.81	57	47	11	65	0.15
20/01/2018	764	0.764	488.96	0	2.5	6.76	430	50	200	19.7	0.85	61	48	12	83.5	0.32
21/01/2018	634	0.634	405.76	0	3.5	6.9	400	25	215	20.1	0.91	47	49	12	55	0.16
22/01/2018	642	0.642	410.88	0	0.9	6.8	215	24	224	20.4	0.93	71	49.8	12	41	0.12
23/01/2018	623	0.623	398.72	2.4	0.3	6.7	114	26	218	20.2	0.92	71	46.7	11	38	0.11
24/01/2018	634	0.634	405.76	0.4	4	6.8	254	31	205	20.1	0.87	85	47.1	9	33	0.13
25/01/2018	614	0.614	392.96	6.6	5	6.9	500	50	200	19.9	0.88	106	46.79	11	61.92	0.1
26/01/2018	675	0.675	432	12.6	5.5	6.88	940	20	250	19.7	0.83	71	3	9	42	0.25
27/01/2018	780	0.78	499.2	0.6	6.3	6.9	412	23	254	19.9	0.85	71	48.5	11	37	0.2
28/01/2018	795	0.795	508.8	0.4	7.4	6.8	265	21	261	19.5	0.88	76	44.3	10	41	0.19
29/01/2018	632	0.632	404.48	0	4	6.9	1300	85	160	20	0.9	81	43.5	12	60.4	0.23
30/01/2018	633	0.633	405.12	0.4	2.3	6.8	312	70	194	20.2	0.89	42	43.8	11	56	0.11
31/01/2018	568	0.568	363.52	0.4	1.2	7.5	250	20	270	19.3	0.76	38	51.74	6	33	0.06
01/02/2018	556	0.556	355.84	0	0.9		245	30	260	18.23	0.85	44	52.62	8	35	0.07
02/02/2018	609	0.609	389.76	0	0.7	7.4	225	20	270	18.5	0.83	49	47.72	11	36	0.07
03/02/2018	625	0.625	400	0	0.8	7.3	300	20	240	18.4	0.9	53	45.52	9	45	0.13
04/02/2018	627	0.627	401.28	0	0.93	7.4	350	30	250	18.73	0.88	55	45.61	7	37	0.11
05/02/2018	627	0.627	401.28	0	1.2	7.6	290	20	230	18.2	0.88	62	45.42	8	32	0.09
06/02/2018	615	0.615	393.6	0	1.3	7.3	270	25	225	18.5	0.9	71	46.12	7	29	0.08
07/02/2018	623	0.623	398.72	0	0.9	7.5	380	40	245	18.6	0.92	76	46.2	9	31	0.1
08/02/2018	625	0.625	400	0	0.7	7.4	490	35	220	18.4	0.91	81	46.43	10	35	0.11
09/02/2018	624	0.624	399.36	0	0.8	7.6	950	30	235	18.3	0.94	77	47.1	8	37	0.1
10/02/2018	624	0.624	399.36	0	0.93	7.4	1500	70	230	18.23	0.93	75	48.12	9	56	0.12
11/02/2018	627	0.627	401.28	0	1.2	7.3	900	25	250	18.5	0.88	68	48.25	9	45	0.11
12/02/2018	627	0.627	401.28	0.8	1.3	7.5	750	30	240	18.8	0.87	69	48.31	11	49	0.1
13/02/2018	627	0.627	401.28	10.8	3.7	7.7	800	20	260	19	0.85	71	48.67	9	50.4	0.11
14/02/2018	639	0.639	408.96	0.2	2.8	7.6	1600	30	250	18.9	0.82	78	52.66	10	47.5	0.17
15/02/2018	643	0.643	411.52	0	2.4	7.5	750	20	280	18.8	0.88	76	58.7	9	46	0.07
16/02/2018	635	0.635	406.4	1	1.8	7.6	520	140	150	18.6	0.9	79	72.49	8	31.7	0.1
17/02/2018	632	0.632	404.48	16.4	2	7.8	1100	100	180	19.1	0.91	83	52.41	9	37.4	0.1
18/02/2018	622	0.622	398.08	19	1.6	7.7	850	80	170	18.7	0.88	85	51.32	8	28	0.12

4.1.2 Hydro-Biological Response to Anthropogenic Activities

Total coliform bacteria were one of the parameters that monitored in this study. The presence of total coliform bacteria in ground water was relatively late, where the highest peak of total coliform colonies raised after the rain event of 5.1.2018 figure (4.5), and the color of water samples that were collected after this event was yellow.

When the samples, which taken after the rain event of 26.1.2018, were filtered, a microbial mat was captured on the filter paper figure (4.6). Microbial mat is yellow mucous secretions, excreted by bacteria and fungi under anaerobic conditions. This layer of mat forms a biofilm, when the bacteria excrete a polymeric material outside the cell wall called “extra cellular polymeric substance”, these biofilms are slimy films of bacteria that adhere to the surface of septic tanks, then with a heavy rain event, the pollutants move through the cracks of septic tanks to the karstic layers and flush out the chemical and bacterial pollutants as well.

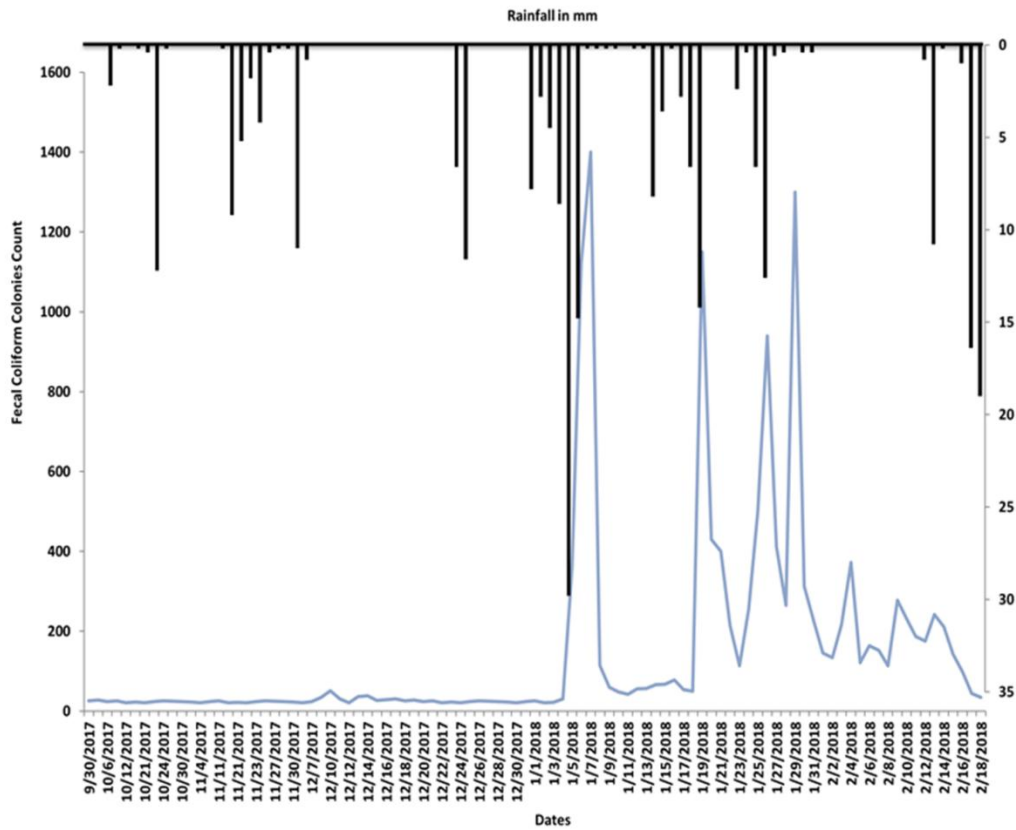


Figure (4.5): Relation Between Daily Rainfall (mm) and Total Coliform Bacteria Colonies of the Samples.

Samples from the total coliform colonies was tested and analyzed in the lab, it was found that it is gram-negative bacteria, motile and has a rod shape. Then a specified media called “MacConkey agar” was used for further testing, this test approves that there are large amounts of E-coli bacteria which is usually found in sewage water, and it may include pathogenic strains which live in the human intestine figure (4.7).



Figure (4.6): Biofilms of Total Coliform Bacteria, Microbial Mat.

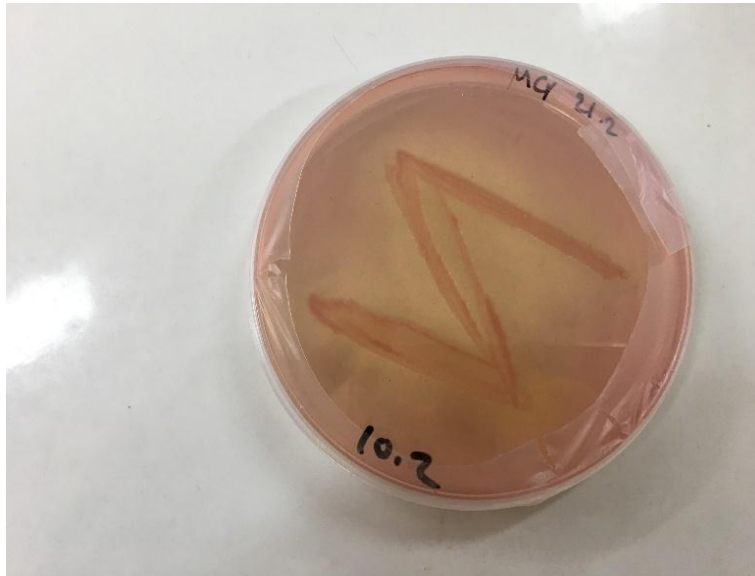


Figure (4.7): E-coli Bacteria Growth on MacConkey Agar.

4.1.3 Water Type Evolution with Successive Rain Events

Classification of water samples supplies a basis for grouping these samples with similar characteristics.

Using Grapher 10 software, the results of the samples were plotted on piper diagram figure (4.8), and the data represents two different periods, the dry period of the season and the wet period.

Samples in the dry period are mostly of the type of Ca-CO₃, or sometimes they have equilibrium between Ca and Mg.

The figure shows that in the wet period, the samples are of Mg-CO₃ type, as we can see the dissolution of more Mg and carbonate in wet period, this is because of the change in aquifer dynamics.

In the two periods, the water types have some sulfate, but in the karst regions carbonate rocks are the dominant, so carbonate water type is the most expected in such areas.

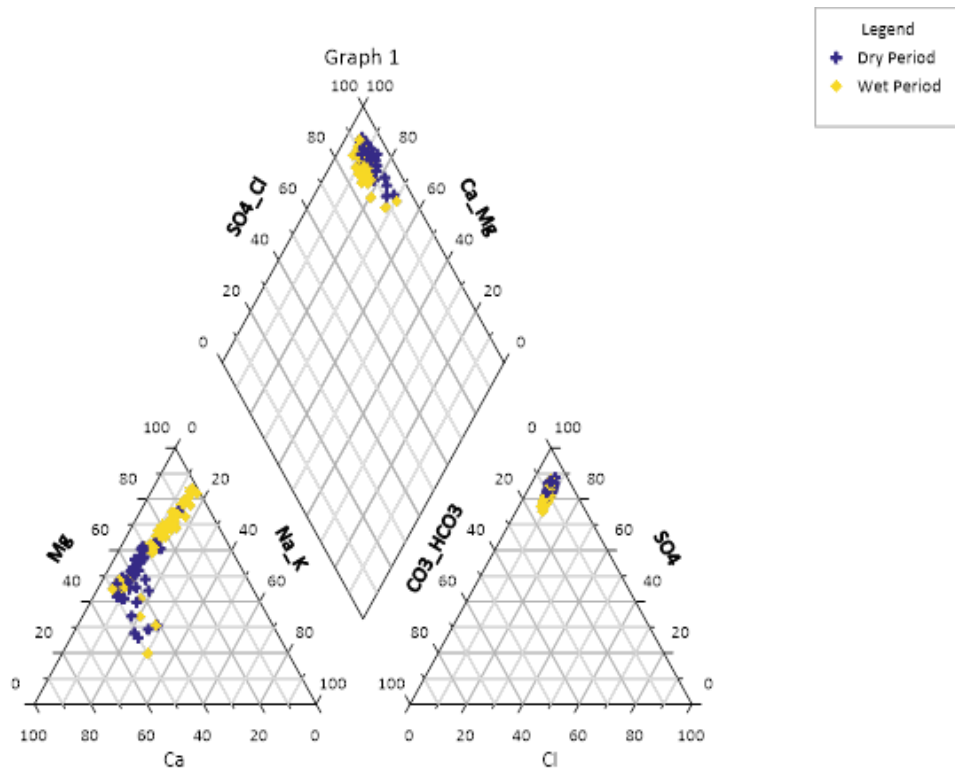


Figure (4.8): Piper Diagram

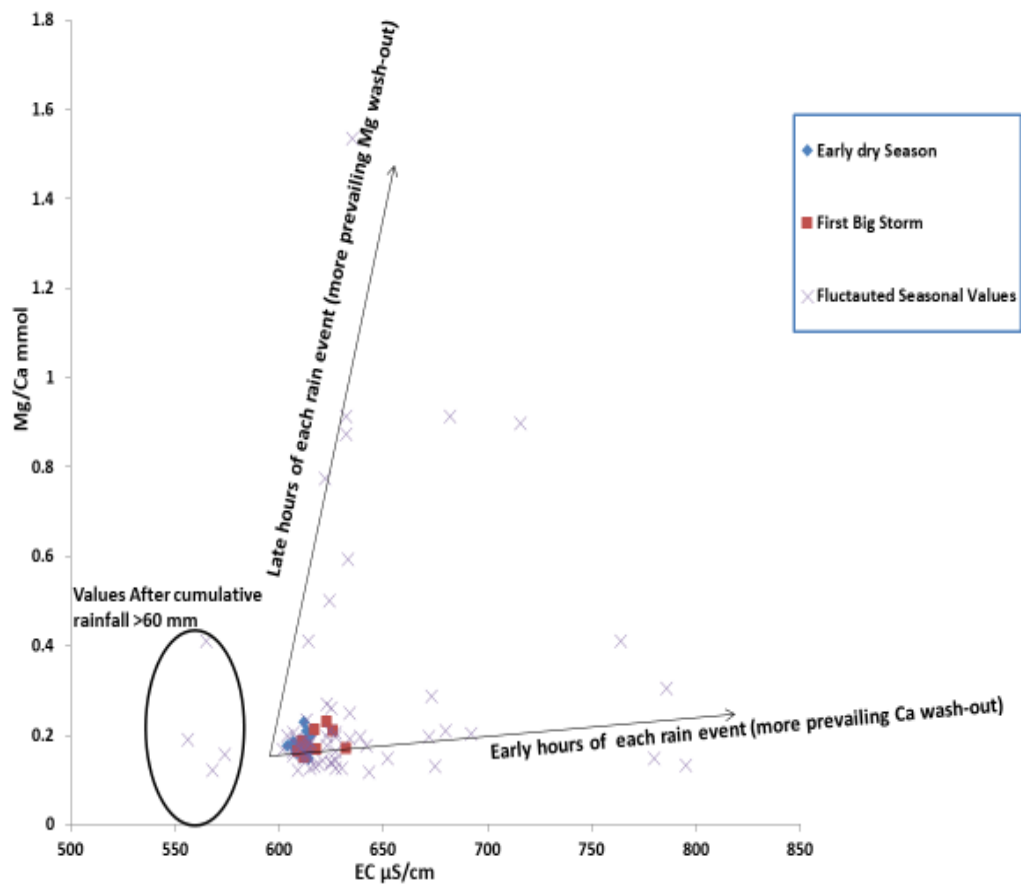
4.2 Geogenic Hydro-chemical Evolution in Response to Hydrological Situation

The behavior of Mg and Ca that could be produced from dolomite and calcite, as the samples originate from a karst limestone aquifer, was studied during the season.

Different from Ca, Mg shows higher concentrations in the late hours of each rain event figure (4.9). Mg comes from the dissolution of dolomite which increases with more rainfall. While in the early hours of each rainfall and in the dry period, there was more Ca wash out, because of the dissolution of calcite.

Dissolution of dolomite ($\text{Mg Ca} (\text{CO}_3)_2$) is slower than dissolution of calcite, so the calcite is precipitated while the dolomite is dissolved (Milanovic, 1981). The decrease in Mg/Ca molar ratio after accumulative rainfall more than 60 mm indicate mixing of water in the aquifer by the new recharge water.

Generally, Ca and Mg concentrations mainly rely on the residence of water in the aquifer which is affected by the volume and mechanism of recharge and the distance from recharge area.



Early hours of each rain event (more prevailing Ca wash-out)

Figure (4.9): Cross Plot of Mg/Ca Molar Ratio versus EC (μS)

Na and K behavior also was studied during the season figure (4.10). In the late hours of rainfall events K shows higher concentration than Na, this could be explained by a reverse softening process between these two cations as they have same valence, which means an ion exchange between Na and K on soil cation exchange sites or sediments in response to change in aquifer dynamics with rain events. While the sodium ion showed higher concentration most of the time, which may be generate from sewage effluent or infiltration of leachate from landfills or industrial sites.

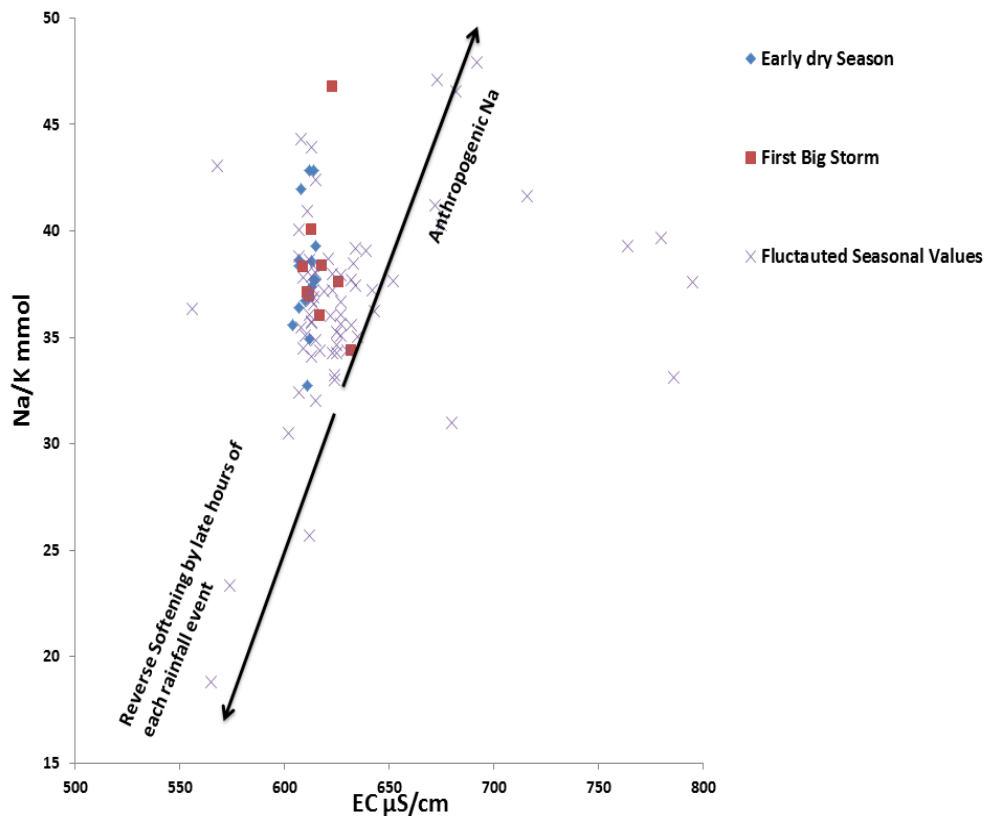


Figure (4.10): Cross Plot of Na/K Molar Ratio versus EC (μS).

4.3 Deuterium and Oxygen Isotopes

Hydrogen has two stable isotopes, ^1H and ^2H (Deuterium) and one radioactive isotope, ^3H (Tritium); oxygen has three stable isotopes ^{16}O , ^{17}O and ^{18}O . Oxygen and Hydrogen present in many forms in the earth's geosphere, biosphere and hydrosphere. Oxygen and Hydrogen combine to compose water, this makes their isotopic composition a strong tracer for the hydrosphere. Stable isotopes in water (^{18}O and ^1H) are influenced mainly by meteorological processes that give a distinctive fingerprint of their origin (Clark and Fritz, 2013). The isotopes O and H are fractionated by different hydrologic processes such as evaporation, rainout, snow, among various freshwater reservoirs. In the evaporation process for example, the lighter isotopes, ^{16}O and ^1H are removed and the remaining water is now enriched with the heavier isotopes. Because of this fractionation process, water evolve a unique isotopic structure that can give an evidence of their source or the processes that formed them.

Models of oxygen/hydrogen isotopic fractionation have been constructed and refined along the last 50 years. Craig (1961) explained that ^{18}O and ^2H behave in a predicted manner and that they correlate on a global scale, and he developed a global meteoric water line that describes the relation between ^{18}O and ^2H by the equation:

$$\delta ^2\text{H} = 8 \delta ^{18}\text{O} + 10\text{‰ SMOW} \quad (2)$$

But this equation represents a global observation, so to represent the local situation, a local meteoric water line (LMWL) was developed by the UFZ

isotopic hydrogeology department in cooperation with Al-Quds University, by analyzing of surface water samples from the recharge area of Jerusalem-Ramallah mountains (Khayat, 2005), LMWL is represented by the equation:

$$\delta ^2\text{H} = 8 \delta ^{18}\text{O} + 19.5 \text{‰ SMOW} \quad (3)$$

In this study the stable isotopes of oxygen and hydrogen for the collected samples Table 2, were analyzed at Forschungszentrum Juelich, Germany.

The data shows that all the groundwater is from meteoric origin, which is infiltrate quickly and discharge through the spring within few hours.

At the beginning of the season, the groundwater shows relatively slight enrichment, which might reflect few months stored water in the saturated zone of recharge area.

However, as the rainfall events continue along the season, the isotope signatures tend to be more negatively, in a depleted trend toward the end of the season Figure (4.11).

Table (4.3) Stable Isotope Analysis of (^{18}O , ^2H) of Different Samples in Season (2017-2018).

Date	$\delta^{18}\text{O}$ vs. VSMOW	$\delta^2\text{H}$ vs. VSMOW
18\12\2017	-5,68	-24,8
27\12\2017	-5,53	-24,3
5\1\2018	-5,80	-25,2
5\1\2018	-5,84	-25,1
6\1\2018	-5,70	-24,1
6\1\2018	-5,68	-24,5
6\1\2018	-5,87	-25,4
7\1\2018	-5,82	-24,4
7\1\2018	-5,89	-25,1
8\1\2018	-5,98	-26,8
9\1\2018	-6,19	-28,2
18\1\2018	-5,86	-24,8
19\1\2018	-5,82	-24,4
19\1\2018	-5,90	-24,9
20\1\2018	-5,82	-24,1
20\1\2018	-5,85	-24,3
21\1\2018	-5,47	-21,9
21\1\2018	-5,72	-22,6
25\1\2018	-5,85	-24,2
26\1\2018	-5,82	-24,3
29\1\2018	-6,20	-26,3
29\1\2018	-6,22	-26,3
29\1\2018	-5,88	-23,9
30\1\2018	-5,87	-24,1
31\1\2018	-5,85	-25,5
2\2\2018	-5,89	-24,4
3\2\2018	-5,99	-25,7
10\2\2018	-5,79	-24,5
13\2\2018	-5,89	-25,1
14\2\2018	-6,08	-26,7
15\2\2018	-6,10	-27,4
16\2\2018	-6,02	-26,5
17\2\2018	-5,88	-25,0

Table (4.4) Nitrate Concentrations, $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$ for Groundwater Samples with Highest Nitrate Concentrations.

Date	NO ₃ - (mg/l)	N-15 / NO ₃ -> AIR	O-18 / NO ₃ -> VSMOW
8\1\2018	63.36	10.00	2.70
9\1\2018	61.92	10.60	7.50
19\1\2018	69.12	10.10	1.90
19\1\2018	60.48	10.40	3.90
20\1\2018	83.52	10.40	3.50
20\1\2018	67.68	9.60	2.90
21\1\2018	54.72	8.60	3.20
21\1\2018	56.16	8.50	3.60
25\1\2018	61.92	8.20	1.10
29\1\2018	63.36	6.90	1.90
29\1\2018	60.48	7.70	4.20
29\1\2018	59	7.70	5.30
30\1\2018	48	7.00	-0.90
10\2\2018	56	7.70	-2.90
13\2\2018	50.4	8.20	1.80

The $\delta^{15}\text{N}_{\text{nitrate}}$ values ranged from + 6.90 to + 10.40 ‰. Oxygen isotope values of nitrate ranged from - 2.90 to +7.50 ‰.

There are different sources in the environment for the nitrate, including fertilizers, sewage, manure, atmospheric deposition and soil organic nitrification. Nitrate produced from each one of these sources has a distinct isotopic signature. $\delta^{15}\text{N}_{\text{nitrate}}$ values for human and animal waste has a wide range between + 7 and more than + 30‰, for soil nitrate range from less than - 10 to + 4‰, and from - 4 to + 4‰ for chemical fertilizers. While $\delta^{18}\text{O}_{\text{nitrate}}$ values for human and animal waste and soil nitrate range from - 10 to +10‰, for chemical fertilizers range from + 18 to + 22 ‰, and for atmospheric deposition is > + 25 Figure (4.12) (Fritz and Clark, 1997).

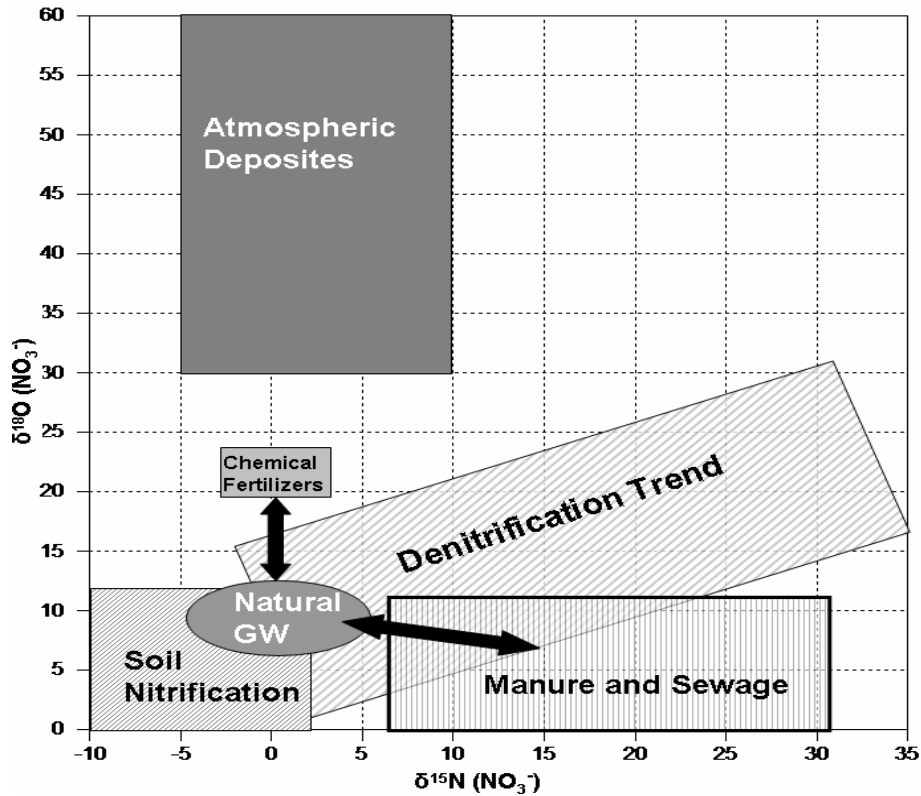


Figure (4.12): $\delta^{15}\text{N}_{\text{nitrate}}$ vs. $\delta^{18}\text{O}_{\text{nitrate}}$, Isotopic Composition of Major Nitrate Sources (Clark, 1997)

So, the isotopic composition of nitrate comprises a beneficial tracer for characterizing its sources, as long as, no change of the isotopic ratios because of biogeochemical reactions, like denitrification has occurred.

The data shown in Table (4.2) and plotted in Figure (4.13) for the groundwater samples suggest that sewage and manure as a major source for the high concentrations of nitrate, with $\delta^{15}\text{N}_{\text{nitrate}}$ ranged from + 6.90 to + 10.40 ‰ and $\delta^{18}\text{O}_{\text{nitrate}}$ ranged from - 2.90 to 7.50 ‰.

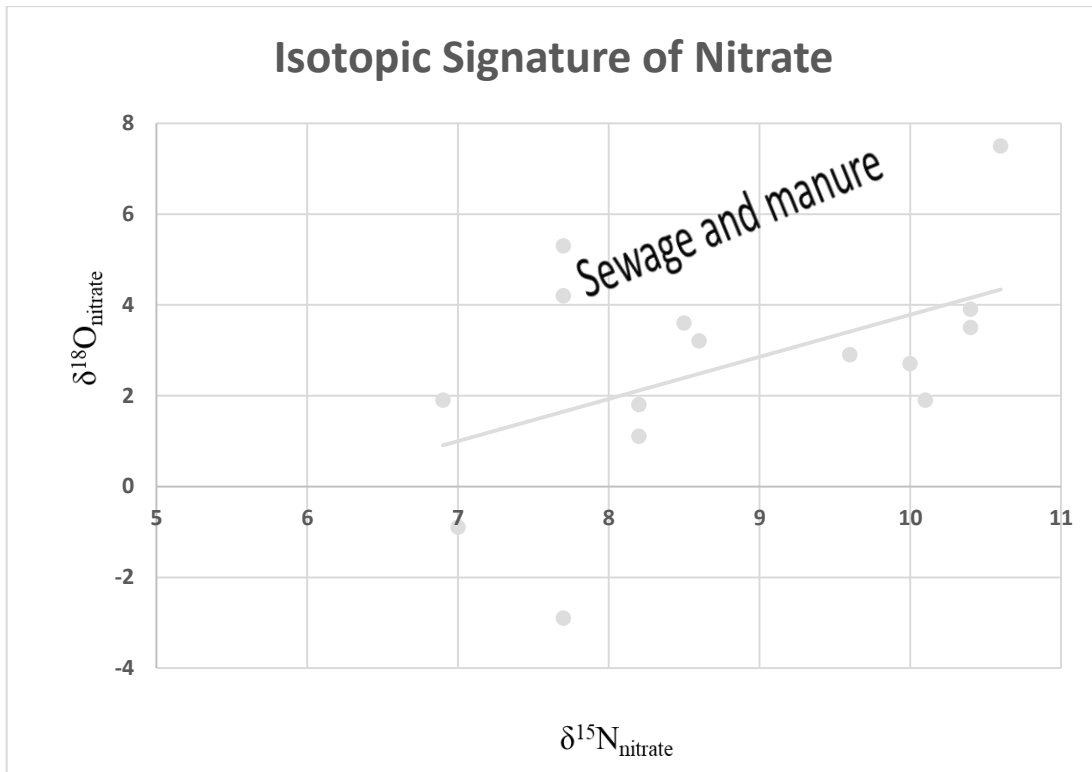


Figure (4.13): Nitrate Isotopic Signature, $\delta^{15}\text{N}_{\text{nitrate}}$ vs. $\delta^{18}\text{O}_{\text{nitrate}}$.

Sewage contains high amounts of urea and other organic and inorganic nitrogenous compounds, so it is considered to be a major source of nitrate. Also, manure is a source for nitrate especially in the presence of aerobic conditions as it originates by oxidation process. In the study area the unsanitary septic tanks with no suitable infrastructure for the disposal of waste water, the sewage mixes with rain and discharge to the groundwater and increases the concentration of nitrate. The presence of agricultural activities in the area and using the animal manure as a natural fertilizer plays a major role in increasing the concentration of nitrate in the groundwater.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

Karst evolves from carbonate rocks, such as limestone (composing of the mineral calcite, CaCO_3) and dolomite rocks (consisting of the mineral dolomite, MgCaCO_3).

Karst aquifers represent a vital source of groundwater for the growing population around the world. However, karst groundwater aquifers are highly vulnerable to pollution and anthropogenic amendments, due to the hydrological and hydrogeological properties of the karst areas.

Karstified aquifers are particularly vulnerable to contamination because of focussed infiltration and quick transport of contaminants within a highly porous conduit system, as the residence time of groundwater in these aquifers tend to be shorter in comparison with non-karst aquifers.

The stress on the karst groundwater is increasing in terms of quantity as a result of overexploitation of water resources because of population growth and the increased anthropogenic activities, and in terms of quality due to pollution by several sources like sewage water, fertilizers, industries, landfill leachate etc.

The eastern aquifer basin is one of the three basins (western basin, north-eastern basin and eastern basin) located within the political boundaries of

the west bank, but it is the only one that is fully located within the west bank.

The eastern aquifer is composed of two aquifers, upper and lower mountain aquifers. Comparing with the western basin, the upper and lower aquifers are not so good in the context of recharge and some properties like permeability and storage.

The aquifers are karstic, developed from cretaceous rocks which are mainly made of limestone, dolomite, chalk and marl. Groundwater moves through fractures and caves within the aquifers and can flow rapidly through conduit system, so water moves quickly and directly from the ground surface to the aquifer and then to the springs and wells, also this quick transport could be attributed to the closeness of the discharge point from the recharge point. This quick transport does not allow a natural filtration of water to take place, as a consequence the contaminants move with the water to the springs.

Population growth in the region leads to overexploitation of water resources and so this causes deterioration of water quality. In addition, the groundwater quality is highly affected by the anthropogenic activities like unorganized land use, sewage seepage, overuse of fertilizers, landfills leachate and different industrial activities.

Ein Samia wells represent a main resource of drinking water in Ramallah district and the villages close to them, so suitable mitigation measures should be taken seriously to solve the pollution problem.

The geologic nature in Ein Samia well 1 catchment area, which is part of auaj catchment the biggest spring in the eastern aquifer, is a highly permeable karstic nature, as the response in Ein Samia well 1 was ranging from 24-28 hours, however in the first rain events and because of the dryness of the unsaturated layer, the response was not so clear. Also because of the fault system in Ein Samia region, the rain reaches Ein Samia well 1 without natural filtration which is actually happen to the remaining amount of water which reaches Ein Samia wells (2, 3).

Although the recharge area is small, it is actually expanded in a way that makes it difficult to define the point sources of pollution. The area widens to include Palestinian communities and settlements with all the industrial and anthropogenic activities, and this definitely forms a challenge for constructing a protection zone for this important catchment.

The problem of flush out in the upper groundwater wells is considered to be a general problem, but it takes place after the big rain event for once time as a shock then it disappears after washing out the accumulated pollutants from the summer dry period. But the repetition of flush out in Ein Samia well 1 emphasizes the presence of continuous resources for pollutants, which appear again and again after each rain event, this will affect the sustainability of water resources over a long term.

The isotopic analysis of stable isotopes of hydrogen and oxygen shows that the groundwater in the region is from a meteoric origin. So the precipitation is the responsible for the release of the accumulated contaminants in the

catchment area. Precipitation infiltrates quickly and discharges through the spring within few hours, this doesn't allow the natural filtration of water to take place.

The septic tanks which lack the least conditions of constructing in the recharge area are the main source of sewage pollutants like nitrate and bacteria. Rain water accumulates in these tanks and mix up with the sewage water, then move to the wells as polluted water.

There are many agricultural activities in the region like using organic manure to fertilize lot of donums of olive trees, the chemical bacterial contents of these fertilizers penetrate easily to the well region.

Another important source of pollution is the unorganized landfills in the recharge area, which are spreading over large areas to the west of Ein Samia region. These landfills produce a polluted leachate which could be very dangerous.

Many industrial activities in the area throw up their wastes in the wadis that located to the east of auja aquifer passing Ein Samia. These activities are also sources for pollution as their pollutants accumulate in the summer dry period inside the soil layers and then washed out with repeatedly rain events as explained in the results.

5.2 Recommendations

Karst groundwater needs specific protection and management strategies to protect it as a sustainable source of drinking water. In order to do this:

1- Detailed investigations about the geological, hydrological and hydrogeological features should be carried out, and detailed information about the human activities and potential sources of pollution should be collected.

2- An overall management, control and protection strategies should be developed to maintain these resources of water. For example; developing a groundwater monitoring system, constructing protection zones, developing suitable land use strategies, controlling or eliminating potential sources of pollution and increasing public awareness of the importance and vulnerability of karst aquifers.

Ein Samia recharge area needs more intensive studies because it is a vital, important source of water, the suggested solutions for the pollution problem could be as follow:

1- Constructing a protection zone in cooperation with Palestine Water Authority (PWA).

2- The requirement to work with the stakeholders in the area to close up the unorganized landfills in the recharge area and to be committed to fulfill the conditions of health and safety concerning the deal with produced pollutants.

3- The necessity to work with the stakeholders and the ministry of local government on regular checking for the septic tanks and to construct a good infrastructure for a sanitary sewage network, so to avoid any seepage of sewage water to the recharge area.

4- In addition to the possibility of cooperation with Environmental Quality Authority and PWA to put plans for monitoring the industrial activities in the region, and to adopt a clear strategy for getting rid of the different kinds of wastes, liquid or solid wastes.

5- A protection period in which the pumping should be stopped has to be determined. Stop pumping could be taken when the flush out take place, like in the period of 15.12.2017-15.2.2018, or the periods of heavy rain, or when the presence of pollutants is expected, depending on the intensity and duration of rain fall, which is expected to be 40mm during 24 hours.

References

- **Abed Rabbo, A., Scarpa, D.J., Qannam, Z., Abdul Jaber, Q. and Younger, P. (1999). Springs in the West Bank- water quality and chemistry.**
- **Abusaada, M. (2011). Flow Dynamics and Management Options in a Stressed Carbonate Aquifer System, The Western Aquifer Basin, Palestine.** Göttingen, Germany: Georg-August-University, PhD Thesis.
- **Al-Rimmawi, H., Ghanem, M., & Shalash, I. (2010). Rainfall trends in the district of Ramallah and Al-Bireh, Palestine.**
- **Andrew, I.J. (2000). Geology and geography of Jordan – a tourist’s guide.**
- **Barron, J. J., & Ashton, C. (2005). The effect of temperature on conductivity measurement. *TSP*, 7(73), 1-5.**
- **Bates, R.L., and Jackson, J.A., 1984. Dictionary of Geological Terms 3rd Edition.**
- **Bayer, H.-J., Hotzl, H., Jado, A. R., Roscher, B. & Voggenreiter, W. 1988. Sedimentary and structural evolution of the northwest Arabian Red Sea margin. *Tectonophysics*, 153, 137-152.**
- **Brand, W. A., Coplen, T. B., Vogl, J., Rosner, M., & Prohaska, T. (2014).**

- **Assessment of international reference materials for isotope-ratio analysis** (IUPAC Technical Report). *Pure and Applied Chemistry*, 86(3), 425-467.
- Casciotti, K. L., Sigman, D. M., Hastings, M. G., Böhlke, J., & Hilkert, A. (2002). **Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method**. *Analytical chemistry*, 74(19), 4905-4912.
- Clark, I. D., & Fritz, P. (1997, 2013). **Environmental isotopes in hydrogeology**: CRC press.
- Craig H., (1961): **Isotopic variation in meteoric waters**.
- EUWI, J. M. (2007). **Mediterranean wastewater reuse report: MEDiterranean WasteWater Reuse Working Group (MED WWR WG)**.
- Fenchel, T., Blackburn, H., King, G. M., & Blackburn, T. H. (2012). **Bacterial biogeochemistry: the ecophysiology of mineral cycling**: Academic press.
- Flexer, A., Gilat, A., Hirsch, F., Honigstein, A.S., Rosenfeild, A., and Rueffer, T. (1989). **Late Cretaceous evolution of the Judean Mountains as indicated by ostracods**.
- Froukh, L. (2002). **Groundwater Modelling in Aquifers with highly Karstic and Heterogeneous Characteristics (KHC) in Palestine**.

- Gass, I. G. (1979). **Evolutionary model for the Pan-African crystalline basement. In: Evolution and mineralization of the Arabian-Nubian Shield.** Bulletin of the Institute of Applied Geology, Jeddah, 1, 11-20.
- Gat, J. R., & Gonfiantini, R. (1981). **Stable isotope hydrology. Deuterium and oxygen-18 in the water cycle.**
- Giorgi, F. (2006). **Climate change hot-spots. Geophysical research letters, 33(8).**
- Girdler, R.W. (1983). **Processes of planetary rifting as seen in the rifting and break up of Africa.**
- Gräbe, A., et al.(2013). **"Numerical analysis of the groundwater regime in the western Dead Sea escarpment, Israel+ West Bank."** Environmental earth sciences 69.2.
- Guttman, J. and Zukerman, CH. (2000). **A model of the flow in the Eastern Basin of the Mountains of Judea and Samaria from the Far'ah to the Judean Desert.** Water Planning for Israel, Tel Aviv. (unpublished report).
- Guttman, J. (2006). **Geology and Hydrogeology of the the Jordan Valley.** Multi-lateral project, project 02WT9719 within the framework of the German-Israeli-Jordanian-Palestinian joint research program for the sustainable utilization of the aquifer systems.
- Gvirtzman, H. (1994). **Groundwater allocation in Judea and Samaria** *Studies in Environmental Science* (Vol. 58, pp. 205-218): Elsevier.

- Hao, Y., Yeh, T.-C. J., Hu, C., Wang, Y., & Li, X. (2006). **Karst groundwater management by defining protection zones based on regional geological structures and groundwater flow fields.** *Environmental geology*, 50(3), 415-422.
- Heaton, T. H. (1986). **Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review.** *Chemical Geology*, 59(1), 87-102.
- Hillel N, Geyer S, Licha T, Khayat S, Laronne JB, Siebert C.(2015). ***Water quality and discharge of the Lower Jordan River.*** *Journal of Hydrology*.
- Huntoon, W.P., 1995. **Is it Appropriate to Apply Porous Media Groundwater Circulation Models to Karstic Aquifers? Groundwater Models for Resources Analysis and Management.**
- ICWE. (1992). **The Dublin Statement and report of the conference. International Conference on Water and the Environment: Development issues for the 21st century, (pp.26-31).** Dublin, Ireland.
- IPCC (Intergovernmental Panel on Climate Change), (2013). **Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.**

- Kačaroğlu, F. (1999). **Review of groundwater pollution and protection in karst areas.** *Water, Air, and Soil Pollution*, 113(1-4), 337-356. 1-11
- Kendall, C., Elliott, E. M., & Wankel, S. D. (2008). **Tracing anthropogenic inputs of nitrogen to ecosystems.** *Stable Isotopes in Ecology and Environmental Science*, Second Edition, 375-449.
- Khayat, S. (2005). **Hydrochemistry and Isotope Hydrogeology in the Jericho Area/Palestine.** University of Karlsruhe, Germany. PhD Thesis.
- Khayat, S., Geyer, S., Hötzl, H., Ghanem, M., & Ali, W. (2006). **Identification of nitrate sources in groundwater by $\delta^{15}\text{N}$ nitrate and $\delta^{18}\text{O}$ nitrate isotopes: a study of the shallow Pleistocene aquifer in the Jericho area, Palestine.** *CLEAN–Soil, Air, Water*, 34(1- 2), 27-33.
- Khayat, S., Ghanem, M., Tamimi, A., Haddad, M., Geyer, S., Hötzl, H., . . . Möller, P. (2009). **Hydrochemistry and isotope hydrogeology in the Jericho area/Palestine** *The Water of the Jordan Valley* (pp. 325-348): Springer.
- Khayat, S., Möller, P., Geyer, S., Marei, A., Siebert, C., & Hilo, F. A. (2009). **Hydrochemical variation in the springs water between Jerusalem–Ramallah Mountains and Jericho Fault, Palestine.** *Environmental geology*, 57(8), 1739-1751.

- Khayat S, Marei A, Etir H, Geyer S. (2016). *Quantifying the surface water runoff to the Dead Sea under different climate scenarios. A case study from WadiArogut*. **International Journal of Water**.
- Khayat S, Marei A, Roediger T, Geyer, S. (2017). **Using stable isotopes to delineate the relations between sub-aquifer systems in the eastern slope of Bethlehem-Hebron to the Dead Sea/Palestine**.
- Klinger, Jochen, NicoGoldscheider, and Heinz Hoetzl, eds. (2015). **SMART-IWRM-Sustainable Management of Available Water Resources with Innovative Technologies-Integrated Water Resources Management in the Lower Jordan Rift Valley: Final Report Phase II**. Vol. 7698. KIT Scientific Publishing.
- Krenkel, E. *Geol Rundsch* (1924). **The fractured zones of East Africa**. 14: 209. doi.org/10.1007/BF01810069.
- Lorena Parra, Sandra Sendra , Jaime Lloret , and Ignacio Bosch.(2015). **Development of a Conductivity Sensor for Monitoring Groundwater Resources to Optimize Water Management in Smart City Environments**.
- Mahler, B., Personné, J.-C., Lods, G., & Drogue, C. (2000). *Transport of free and particulate-associated bacteria in karst*. **Journal of hydrology**, 238(3-4), 179-193.

- M. El-Fadel, R. Qubaía, N. El-Hougeiri, Z. Hashisho and D. Jamali. (2001). **The Israeli Palestinian Mountain Aquifer: A Case Study in Ground Water Conflict Resolution**
- Milanovic, P. T. (1981). **Karst hydrogeology. water resources publications.**
- Qannam, Z. (2000). **A hydrological, hydrochemical and environmental study in Wadi Al Arroub drainage basin, south west bank, Palestine.** PhD Thesis.
- Qannam, Z., & Merkel, B. (2002). **Hydrogeology, hydrochemistry and contamination sources in Wadi Al Arroub drainage basin, Palestine.** Freiburger Forschungshefte—selected contribution to applied geology in the Jordan Rift Valley, C, 494, 111-123.
- Quennel, A.M. (1956). **Tectonics of the Dead Sea Rift. Proc. 20th. Int. Geol. Congress. Mexico, Ass. Deserv. Geol. Afrfricanos, 385-403.**
- Rimmer, A. (2011). **Hydrological Survey of Auja Spring.**
- Rofe and Raffety Consulting Eng. (1965). **West Bank hydrology: Nablus district water resources survey, geological and hydrological report.**
- Schmidt, S., Geyer, T., Marei, A., Guttman, J., & Sauter, M. (2013). *Quantification of long-term wastewater impacts on karst groundwater resources in a semi-arid environment by chloride mass balance methods.* **Journal of hydrology, 502, 177-190.**

- Shadeed, S. (2008). **Up to date hydrological modeling in arid and semi-arid catchment, the case of Faria catchment, West Bank, Palestine.** Freiburg, Germany: Universität Freiburg im Breisgau, PhD Thesis.
- Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Böhlke, J. (2001). **A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater.** Analytical chemistry, 73(17), 4145-4153.
- SUSMAQ, (2002,2004). **Sustainable Management of the West Bank and Gaza Aquifers. A brief summary of the hydrogeology of the West Bank.** Management Options Study Working Note.
- [www.who.int/water_sanitation_health/water quality](http://www.who.int/water_sanitation_health/water_quality)

جامعة النجاح الوطنية
كلية الدراسات العليا

تطوير نظام مراقبة لجودة المياه الجوفية في الحوض الجوفي الشرقي

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في علوم البيئة، في كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس - فلسطين.

2018

ب

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الملخص

أجريت هذه الدراسة لتطوير نظام مراقبة لجودة المياه الجوفية في الحوض الجوفي الشرقي في فلسطين. يعتمد هذا النظام على المراقبة الهيدرولوجية، الهيدروكيميائية و الهيدروبيولوجية، إضافة الى استخدام النظائر المستقرة لكل من الهيدروجين والاكسجين و النيتروجين كمقننات لمصادر التغذية والملوثات في مناطق المساقط الأمانية. لقد تم اختيار بئر عين سامية 1 كحالة دراسية، وهو يعد جزءا من نبع العوجة، النبع الأكبر في الحوض الشرقي.

لقد أجري في هذه الدراسة تحليل موسمي للأمطار وللأحداث المطرية وذلك لدراسة تطور الخصائص الهيدروكيميائية استجابة للأحداث المطرية. بشكل عام، فانه من السهل ملاحظة الملوثات في بئر عين سامية 1 بعد كل حدث مطري بكثافة أعلى من 13 ملم خلال 48 ساعة.

عينات المياه الي تم جمعها في الفترة الجافة كانت من نوع كربونات الكالسيوم، بينما العينات التي جمعت في الفترة الرطبة كانت من نوع كربونات المغنيسيوم. على الرغم من ان الصخور الكربونية هي السائدة في المناطق الكارستية وبالتالي فان المياه الكربونية هي النوع الأكثر توقعاً، الا أن المياه في الفترتين الجافة و الرطبة احتوت على بعض الكبريتات.

أظهر المغنسيوم تراكيز اعلى من الكالسيوم في الساعات المتأخرة من الأحداث المطرية، وذلك لأن انحلال الدولميت يزداد بزيادة الأمطار، بينما يزداد انحلال الكالسييت في الساعات الأولى من المطر، وبالتالي يكون تركيز الكالسيوم أعلى حينها.

أظهر أيون الصوديوم تركيز أعلى من البوتاسيوم معظم الوقت، والذي قد ينتج من مياه الصرف الصحي المتدفقة أو تسرب العصارة من مكبات النفايات أو من المواقع الصناعية.

وصل تركيز النترات الى 83 ملغم/لتر وهو الاعلى وذلك في الحدث المطري 18-22/1/2018، وهذا التركيز يفوق مواصفات منظمة الصحة العالمية. وتبع تلك الزيادة، زيادة في تركيز الاورثوفوسفات. من ناحية أخرى، فقد أظهر الكربون العضوي الذائب عملية غسل متأخرة.

في هذه الدراسة أيضا تم مراقبة البكتيريا القولونية الكلية و التي أظهرت تراكيز عالية و لكن في وقت متأخر نسبيا. و قد أظهر تشخيص مستعمرات البكتيريا وجود كميات كبيرة من بكتيريا الايكولاي و التي تتواجد عادة في مياه الصرف الصحي.

استخدمت النظائر المستقرة للهيدروجين (الديتيريوم، H^2) وللأكسجين (أكسجين O^{18}) في هذه الدراسة لمعرفة مصدر التغذية في الحوض، والتي هي مسؤولة عن تحرر الملوثات المتراكمة في منطقة المساقط المائية. وقد تبين أن الهطول المطري هو المصدر الرئيسي للتغذية، والذي ينفذ بشكل سريع ومباشر خلال النبع وفي ساعات قليلة.

للكشف عن مصادر النترات في المياه، تم القيام بتحليل للنظائر المستقرة للنترات (O^{18} ، N^{15}). وقد أظهر هذا التحليل أن المصدر الرئيسي للنترات هو مياه الصرف الصحي والتي تنتج من خزانات الصرف الصحي الغير صحية في منطقة الدراسة، اضافة الى روث الحيوانات المستخدم كسماد طبيعي في النشاطات الزراعية في المناطق الزراعية.