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**Hydrogeochemical Assessment of Wadi Abu Al-Qamrah
in Dura city and Methyl tertiary butyl ether (MTBE)
concentration in Hebron District**

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Methyl tertiary butyl ether (MTBE) concentration in Hebron District

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Jerusalem-Palestine

2009/1430

Dedication

To my mother and father who supported me and light up my life since my birth to this date.

To my brothers, sisters,

And to all these people who helped me in this work.

Declaration:

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

Signed.....

(Nazeeh Salameh Mohammad Al-Swiety)

Date:

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Abstract

Wadi Abu Al-Qamrah is an important source of water in Dura city/south of Hebron city.

Forty five dug wells tabbed about 2-100 m³/day from the lower part of Hebron formation. The depth of these dug wells ranges between 2 and 11 m. The dug wells are concentrated in the western part of the Wadi while no wells can be found in the eastern part because Hebron formation ends in this part of the Wadi. Geological, hydrochemical and geophysical investigations were carried during two years of research. Besides that this study included the study of the volatile organic compounds in Hebron District.

MTBE was found in surface runoff with concentrations ranged from 0.2 - 11 ppb, its' rarity in groundwater and soil is caused by a process of evaporation.

The hydrological and hydrogeological study aimed to provide the information on the amount of evaporation rate, the rate of surface runoff, in addition, recharge rate, the average annual rainfall in (1980 – 2008) was 500 mm with annual volume rainfall (1125000 m³), it is also found that the rate of evaporation ranges from 121 mm/month in winter to 186.6 mm/month in summer, and the surface runoff rate is 58,8 mm, (187412 m³) which represents about 20% of the annual rainfall, the recharge rate is 151.7 mm (478500 m³) which represents 30% of the annual rainfall.

The hydrochemical study aimed to provide information about the amount of positive and negative ions, the results of hydrochemical analysis showed that the source of wells water comes from the rainfall mixed with water cesspits, it's also found that the average of EC is 1371 $\mu\text{s}/\text{cm}$. Ions concentration varies from season to another, where most of the ions are more concentrated in summer, except for HCO_3^- , and SO_4^{2-} .

Geophysical survey showed multiple layers in the study area consisting of clay, limestone, marl, and Dolomite with different thickness and depth along the Wadi, the survey also showed that the aquifer found from 2.5 to 11 m below the surface in the west of the Wadi, and from 3 to 4 m below the surface in the east of the Wadi.

المخلص

دراسة تقييمية ايهيدروجيوكيميايية وادي ابو القمره في مدينه دورا ودراسة تركيز

ميثل ثالثي بوتيل ايثرفي محافظه الخليل

يعتبر وادي ابو القمره مصدر مهم للمياه في مدينه دورا / جنوب مدينه الخليل، يحتوي الوادي على 45 بئر يتراوح انتاج هذه الابار ما معدله 2-100م³ / يوم من الطبقة السفليه لتكوين الخليل، يبلغ عمق هذه الابار من 2م الى 11 م وتتركز معظم هذه الابار في الجزء الغربي من الوادي وتنعدم في الجزء الشرقي من الوادي بسبب انتهاء تكوين الخليل من هذا الجزء وظهور تكوين يطا على السطح . كما تضمنت دراسة احد انواع المركبات العضويه المتطايره (MTBE) في منطقه الخليل.

وجد تركيز MTBE في المياه السطحيه في منطقه الخليل بتركيز تراوح من 0.2- 11 PPb بتركيز قليله جدا في التربه والمياه الجوفيه وذلك بسبب ارتفاع درجة الحراره مما ادى الى تطاير هذه الماده.

هدفت دراسة الهيدروجيولوجيا لآبار المنطقه الى توفير معلومات حول معدل التبخر و معدل الجريان السطحي والتغذيه، وجد معدل سقوط الامطار السنوي 500 ملم في الفتره ما بين عامي 1980 - 2008 بحجم 1125000م³، تراوح معدل التبخر من 121 ملم/شهر في فصل الشتاء الى 186.6 في شهر الصيف، وبمعدل جريان سطحي و تغذيه 57.8 ملم، و 151.7 ملم على التوالي.

من خلال التحليل الهيدروكيمياي تبين ان مصدر مياه الابار ناتج عن اختلاط مياه الامطار مع مياه الحفر الامتصاصيه، و ان معدل الموصلية الكهربائيه 1371 ميكروسمنز/سم، كما ان تراكيز الايونات تختلف من فصل الى اخر حيث يكون تركيز معظم هذه الايونات في فصل الصيف اكثر منه في فصل الشتاء باستثناء HCO_3^- و SO_4^{2-} .

اظهر نتائج المسح الجيوفيزيائي ان المنطقه تتكون من طبقات عدة، تراب، حجر جيرى، مارل و دلومايت مختلفه في السمك والعمق على طول الوادي، وان الطبقة الحامله للماء تواجدت على عمق 2.5 م الى 11 م من الجهة الغربيه للوادي و من 3 الى 4 م من الجهة الشرقيه للوادي من سطح التربه.

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List of Symbols

%	Percent.
μS	Micro siemens
Arij	Applied Research Institute-Jerusalem
Aug	August.
Aver	Average.
avP	average annual precipitation.
BTEX	Benzene, toluene, ethyl benzene, xylene
Ca^{2+}	Calcium (ion).
Cl^-	Chloride (ion).
cm^2	Square centimeter.
Ec	Electrical conductivity.
Fig.	Figure.
HCl	Hydrchloric acid.
HCO_3^{-1}	Bicarbonate (ion).
K^+	Potassium (ion).
Km^2	Square kilometer.
L	Liter (volume).
m	Meter.
Mar	March.
masl	Meter above sea level.
Max.	Maximum.
MCM	Million cubic meter.
meq	Milliequivalent.
mg	Milligram
Mg^{2+}	Magnesium (ion).
ml	Millilitre (volume).
MTBE	Methyl tertiary-butyl ether
Na^+	Sodium (ion).
$^{\circ}\text{C}$	Degree centigrade (Celsius scale)
Oct	October.
pH	Acidity value.
Q	the average annual run off (mm/yr).
SAR	sodium adsorption ratio
SI	saturation index
SO_4^{-2}	Sulfate (ion).
T	Tritium.
Tem	Temperature.
VOCs	Volatile organic compounds
yr	Year.

Chapter one

Introduction

Groundwater is one of our most valuable drinking water resources. It is also very important to many agricultural areas. The pollution of the water causes problems to human and other living organisms and environment (Kuran and Sojak, 1996), the major sources of water pollution can be classified as municipal, industrial, and agricultural, the physical and chemical parameters of groundwater play a significant role in classifying and assessing water quality.

1.1 Objectives

The main objective is to investigate the hydrogeological and hydrochemical characteristics of the dug wells along Wadi Abu Al-Qamrah in Dura city.

Further objective is to investigate the Methyl tertiary butyl ether (MTBE) in surface runoff during winter flooding, in the shallow groundwater and in soil of AlAroub, Hebron, and Dura cities.

Specific objectives

- 1- To evaluate the groundwater quality and its chemical characteristics.
- 2- To estimate the recharge volume of the catchment's area.
- 3- To determine the concentration of Methyl tertiary-butyl ether (MTBE) in surface and groundwater.
- 4- To investigate the lithological formation by using geophysical method.

1.2 Hypothesis

The main hypothesis is: that additional water could be abstracted from the shallow aquifer. The thickness of aquifer decreases to the east of the Wadi

It is expected to found MTBE by products in surface runoff, groundwater, and in soil.

1.3 Research Problem

Wadi abu Al-Qamrh contains many wells; these wells are used mostly in agriculture and rarely in domestic purposes, the discharge of these wells are not enough to cover the needs of the agriculture purposes. Besides that the fertilizers and pesticides are widely used which leads to the leakage of these material into the shallow aquifer system, that causes salinization of groundwater (Singh et al., 1995; Oenema et al., 1998). So when these wells' water is used again for irrigation, the salinity of the soil increases.

1.4 Literature review

Volatile organic compounds (VOCs) are considered as volatiles and insoluble or slightly soluble in water. The boiling point less than 200°C (Bianchi et al., 1991) the molecular masses range between 16 and 250 g/mol. Some of these compounds are mutagens, and carcinogens (Bianchi et al., 1991). VOCs are a group of organic compounds can found in gasoline, paints, paint thinners, and solvents used for dry cleaning and metal degreasing.

VOCs cause serious groundwater pollution in many sites in industrial countries (Lerner et al., 1993). Gasoline and other substances containing VOCs that can find their way into the groundwater through point sources such as leaking storage tanks or direct spills. These Compounds also can enter the groundwater from nonpoint sources such as storm water surface runoff in developed areas such as roads and parking lots. Some airborne contain VOCs compounds and can mix with rainfall, and may recharge in to the aquifers as a nonpoint source of contamination.

The first significant studies concerning the risk of groundwater pollution by these contaminants were realized by Schwille (1988), who developed conceptual models and conducted physical experiments in both the saturated and unsaturated zones with chlorinated solvents. VOCs have high vapor pressures that potentially allow a rapid development of contaminated areas due to vapor transport. The extent of the vapor contaminated area is influenced by the properties of the pollutant and the porous medium, the temperature, the water content, the partitioning of the compound into the liquid and vapor phases, and its sorption on soil particles (Falta et al., 1989; Hippelein and Mclachlan, 2000).

Methyl tertiary-butyl ether (MTBE) is one these VOCs and one of the most frequently detected volatile organic compounds in groundwater which is used as oxygenated compound in gasoline.

The MTBE is a compound that has been widely used as an octane enhancer and gasoline oxygenate over the past twenty years. In the 1980's MTBE and other chemicals containing oxygen (particularly alcohols and ethers) were discovered to reduce carbon monoxide emissions from vehicles. MTBE is added to gasoline in concentrations up to 15% by volume to replace lead compounds (Mitani et al., 2002). MTBE is the prim oxygenate used in gasoline because it is the least expensive and in greatest supply. It is promoted as a gasoline blending component due to its high octane rating, low cost of production, ability to readily mix with other gasoline components, ease in distribution through existing pipelines, distillation temperature depression, and beneficial dilution effect on undesirable components of aromatics, sulfur, olefin and benzene.

MTBE in surface and groundwater can originate from point and nonpoint sources. Possible point sources of MTBE include leaking gas tanks, pipelines, landfill sites, dumps, spills, industry, underground injection, and refueling facilities. Leaking underground storage tanks are a major source of contamination (Fig.1.1), (U.S. EPA, 1994).

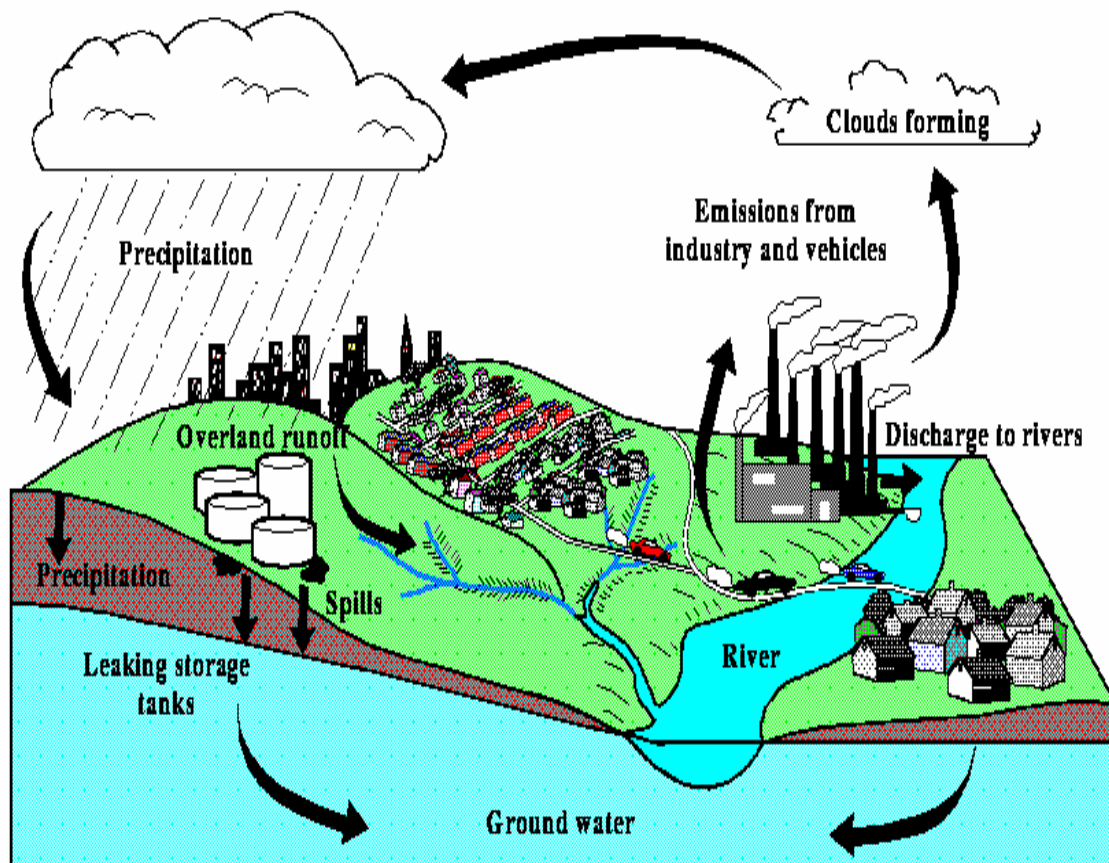


Fig.1.1: point and nonpoint source of MTBE in groundwater (USGS)

MTBE contaminating groundwater, its high solubility led to the spread of MTBE in aquifers as a consequence of gasoline leaks and spills (Stefan et al., 2000). MTBE migrates faster and farther than benzene (C_6H_6), toluene (C_7H_8), ethyl benzene (C_8H_{10}) and xylene (C_8H_{10}) (BTEX) in groundwater (Davidson and Creek, 2000). MTBE migrates rapidly through the soil column. If MTBE is released into soil above groundwater (vadose zone), it tends to move faster than benzene through the soil pore spaces, whether they are filled with air or water vapor: When compared to benzene, MTBE partitions strongly from the gas phase to the water phase. MTBE tends to stay in the liquid phase because of its relatively low Henry's constant of 0.022 at 25°C, as opposed to benzene, which moves more readily from the water to the vapor phase because of its higher Henry's constant of 0.22 at 25°C (Squillace et al., 1998). MTBE poses a particularly difficult environmental problem because of its resulting from its molecule structure of an ether bond and a tertiary carbon group and high water solubility and low sorption onto soils. These unique properties allow it to move quickly and easily through the water column with minimal retardation and also make it difficult to be removed.

The wide usage of MTBE increases opportunities for it to leak into the environment through gasoline underground storage tank leakages, recreational watercraft operations, and accidental spills. It has been reported that approximately 250,000 of the 385,000 confirmed leaking underground storage tank releases in USA involve MTBE (Kane et al., 2001).

MTBE has been commonly found to migrate ahead of the gasoline components such as BTEXs at a gasoline spill site. The reasons are that MTBE has a high mobility and it is less subject to biodegradation during transport (Fiorenza and Rifai, 2003).

In the air, MTBE tends to enter atmospheric water through precipitation (Fig.1.2) in areas where the atmospheric concentration of MTBE is locally high, as near parking garages and gasoline stations, MTBE could occur in measurable quantities in groundwater and storm water in the immediate vicinity (Squillace et al., 1997).

MTBE can be found in surface waters due either to a direct release, fallout from precipitation, discharge from contaminated groundwater, storm water runoff, or emissions from motorized watercraft. Watercraft emissions are the primary source of MTBE in lakes and reservoirs. Volatilization at the air-water boundary is the major mechanism of MTBE loss from lakes and reservoirs (Fiorenza and Rifai, 2003).

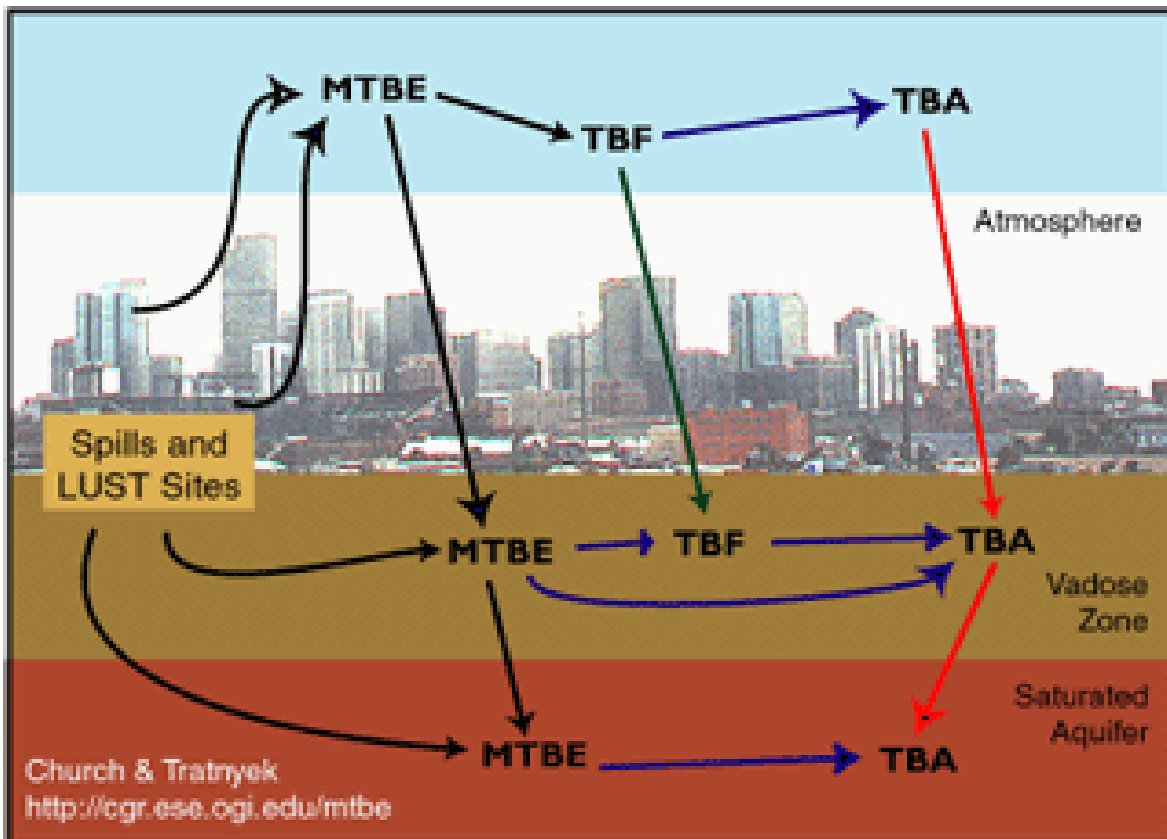


Fig.1.2: movement of MTBE in the environment (Church et al., 1999)

1.4.1. Properties of methyl tertiary-butyl ether (MTBE)

MTBE ($C_5H_{12}O$) is a synthetic chemical without natural sources; MTBE is produced from the chemical reaction of methanol and isobutylene. It is a clear liquid with low viscosity that is flammable and has an offensive odor. Chemically, MTBE is an ether based molecule containing 18% by weight oxygen with physical characteristics akin to other common gasoline constituents such as BTEX (benzene (C_6H_6), toluene (C_7H_8), ethyl benzene (C_8H_{10}) and xylene (C_8H_{10})).

MTBE has a high solubility and a low Henry's constant. Its water solubility is about 50,000 mg/L at 25 °C and its dimensionless Henry's constant ranges from 2.16×10^{-2} to 1.23×10^{-1} and has n-octanol/water partition coefficient log Kow (1.20) (Table.1.1) (Squillace et al., 1997). When considering the partitioning of MTBE between the water phase and soils or subsurface solids. It prefers to be in the water phase as well. MTBE has been found resistant to natural degradation due to the presence of the t-butyl group within its structure (Mitani et al., 2002). MTBE has a strong odor similar to diethyl ether, which was used as a general anesthetic for surgeries on humans and other mammals. It is

detectable by humans at very low concentrations in air and water 53 parts per billion (ppb) in air and as low as 20 to 40 ppb in water (U.S. EPA Drinking Water Advisory. 1997).

Table.1.1: Physical and chemical properties MTBE

Chemical Formula	C ₅ H ₁₂ O
Chemical structure	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{O}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} $
Molecular weight (g/mol)	88.15
Boiling point °C	55.2
Vapor density at 1 atm; 10 °C	3.80
Specific gravity at 25 °C (g/ml)	0.744
Water solubility a (mg/L)	50,000
Vapor pressure a (mm Hg) at 25°C	245-276
Density at 20 °C (g/mL)	0.7404
Henry's Law constant atm-m ³ /mol at 25°C	0.022
Log K _{OW}	1.20

1.4.2. Degradation of MTBE

MTBE degrades rather rapidly in the atmosphere. The primary degradation product is tertiary-butyl format (TBF) (Fig.1.2); half-lives of MTBE in the atmosphere can be as short as 3 days.

Research into MTBE degradation in soil and groundwater is under extensive investigation at the present time. Evidence to date indicates that MTBE degrades much slower than the BTEX compounds, and, therefore, may travel further and persist longer in groundwater plumes. The primary reaction product is tertiary-butyl alcohol (TBA) (Fig.1.2), which is another constituent of gasoline commonly found in conjunction with MTBE. Furthermore, MTBE is a persistent substance in soil and ground water, although degradation of MTBE has been either under aerobic condition or anaerobic condition, the degradation rate has showed to be very slow (Schmidt et al., 2004). The data allow computation results in a half-life for MTBE of at least 2 years in most natural groundwater systems.

1.4.3. Health effects of MTBE

Most of the research on the effect of MTBE on human health has been focused on the effects of inhalation where the exposure to MTBE has the potential to produce effects associated with central nervous system depression (headaches, dizziness, nausea, and disorientation) MTBE is classified as a possible human carcinogen by the EPA as a result of inhalation cancer tests, but no quantitative estimate of its cancer potency has been determined by EPA because of the limitations of the available data (U.S. EPA, 2000).

When MTBE enters the human body via either inhalation or absorption through the skin, it may metabolize into two compounds (tertiary butyl alcohol and formaldehyde) that are carcinogenic in animals and are classified by the EPA as probable human carcinogens.

1.5 Source of MTBE in the study area

Palestine, like other developing countries, depends on oil as the main source of energy, whenever energy consumption is increasing rapidly. This reflects upon population growth, as well as the level of development in all aspects of life. Transportation facilities are the largest energy consumer sector in Palestine reaching approximately 60% of the total energy use in Palestine (ARIJ, 1996).

There are approximately 131 legal gasoline stations in the West Bank, and many other non countable gasoline stations. The geographical distributions of these stations are demonstrated in (Table.1.2) and (Fig.1.3).

From an environmental perspective, practices in these gas stations are threatening the environment. Oil storage tanks and the used motor oil at these stations are threatening the air, and the surface drainage system water resources in the area. Private cars and other vehicles in the West Bank are increased by 12% and 6% respectively (ICBS, 1995).

Between 1975 and 1996, the number of vehicles increased ten times from about 12,964 in 1975 to 133,386 in 1996. These vehicles are the major source of air pollution. In 1996 the Applied Research Institute-Jerusalem has conducted a survey for air pollution produced from the vehicles in the Jerusalem-Ramallah Road shows that the annual number of vehicles pass through this road is estimated at 8,486,504 vehicles, where the result showed that the VOCs are the second pollution of the air after CO (Table.1.3). Similar results were obtained from estimating the emissions from private cars at different districts in the West Bank. The same study also conducted a survey for 64 gas stations in Bethlehem, Ramallah, Hebron and Jenin districts. The results showed that operating practices inside the gas

stations give little consideration to the safety of natural environment, for example, the underground storage tanks are not monitored or checked for leakage, and above ground tanks often have small leaks that are not repaired. Up to 2007, no gasoline station has double liner tanks or sensors for monitoring to any leakage. Moreover, many gas stations are located in shops in residential areas where fuel tanks are located inside the building which threatens the safety and the health of residents (ICBS, 1995).

Table 1.2: Distribution of gas station in west bank (Aliewi, 2006)

District name	No. of station
Bethlehem	8
Hebron	33
Jenin	18
Jericho	8
Jerusalem	18
Nablus	12
Qalqilya	5
Ramallah	19
Salfeet	1
Tulkarem	9
Total	131

Table.1.3: Estimated annual air pollutants emitted due transportation flow in the Jerusalem-Ramallah Road (ARIJ, 1996)

Emission	Estimated annual quantity of pollutants emitted to air (Tons)		
	To Ramallah	To Jerusalem	Total
CO	1019	967	1986
SOx	73	69	142
NOx	84	74	158
VOC	124	117	241
Lead (Pb)	4.7	4.5	9.2

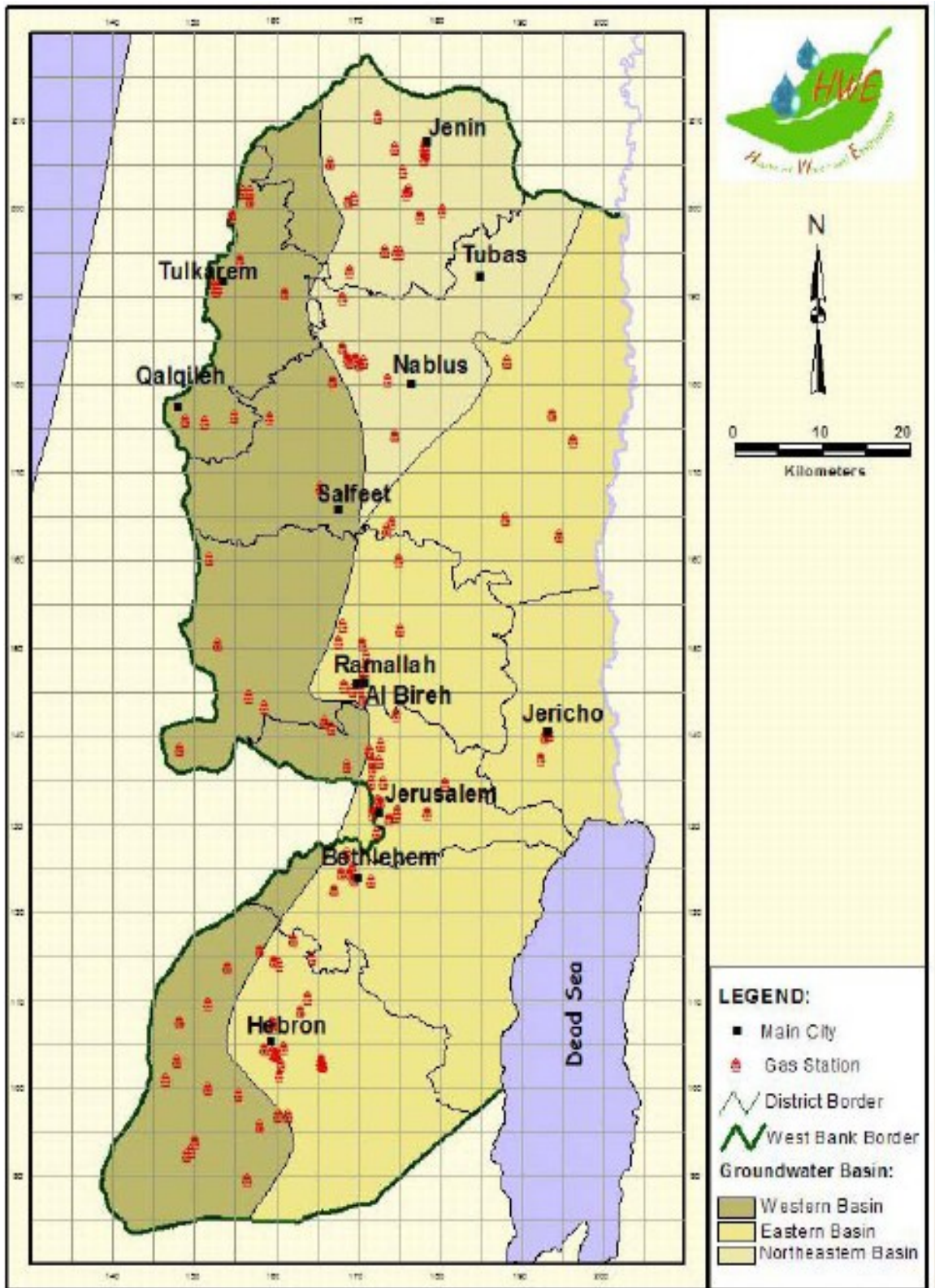


Fig.1.3: Locations of Gas stations in the stations in the West Bank (After Aliewi, 2006)

1.6 Geophysical investigation

Geoelectrical resistivity techniques are popular and successful geophysical exploration for study groundwater conditions in the world. The resistivity method was used to solve more problems of groundwater in the types alluvium, karstic and another hard formation aquifer as an inexpensive and useful method. Some uses of this method in groundwater are: determination of depth, thickness and boundary of an aquifer (Zohdy, 1969),

The resistivity ρ_a of rocks and minerals displays a wide range. For example, graphite has a resistivity of the order of 10^{-6} as ohm-m, whereas 'some dry quartzite rocks have resistivities of more than 10^{12} ohm-m (Parasnis, 1962) (Fig.1.4). The resistivity of material depends on many factors such as groundwater, salinity, saturation, aquifer lithology and porosity (Lashkaripour and Nakhaei, 2001)

Many of arrays are used to to determine the subsurface resistivity distribution, one of these array is Wenner-Schlumberger array which is moderately sensitive to both horizontal and vertical structures (Loke, 1999), Vertical electrical sounding (VES) method is used to determine the resistivity variation with depth. Single VES should only be applied in areas, where the ground is assumed to be horizontal layered with very little lateral variation, (Ernstson & Kirsch 2006).

The resistivity measurements are normally made by injecting current into the ground through two current electrodes; A and B (Fig.1.5), and measuring the resulting voltage difference at two potential electrodes; M and N. From the current (I) and voltage (V) values, an apparent resistivity (ρ_a) values is calculated using the equation (1)

$$\rho_a = KV/I \quad (1)$$

Where k is geometric factor

Resistivity meters normally give a resistance value, $R = V/I$ so in practice the apparent resistivity value is calculated by

$$\rho_a = kR$$

The resistivity value calculated is not the true resistivity of the subsurface, but an apparent value, which is the resistivity of a homogeneous ground, which will give the same voltage, and current values for the same electrode arrangement. The relationship between the apparent resistivity and the true resistivity is a complex relationship.

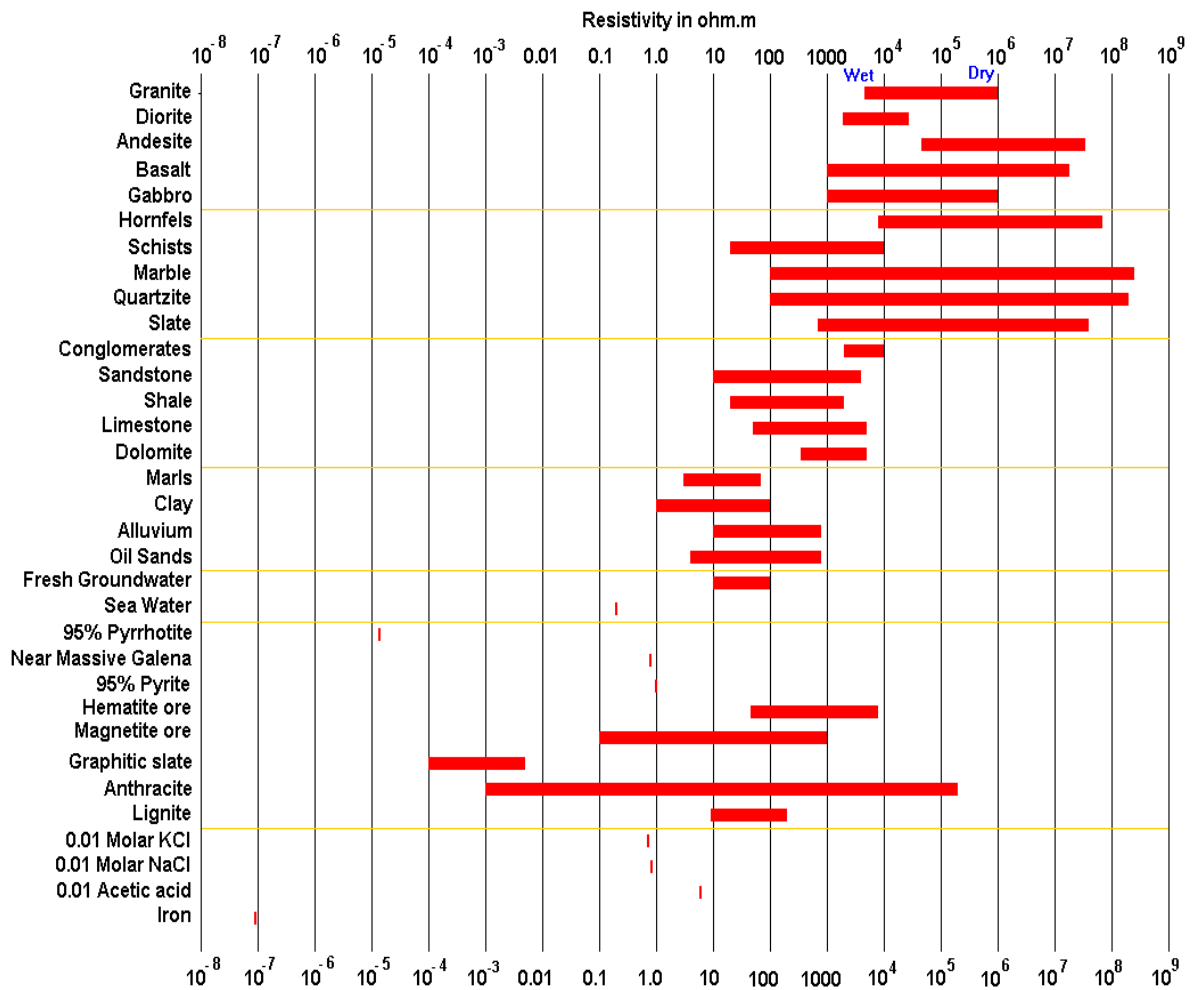


Figure 1.4. The resistivity of rocks, soils and minerals (after Loke, 1997)

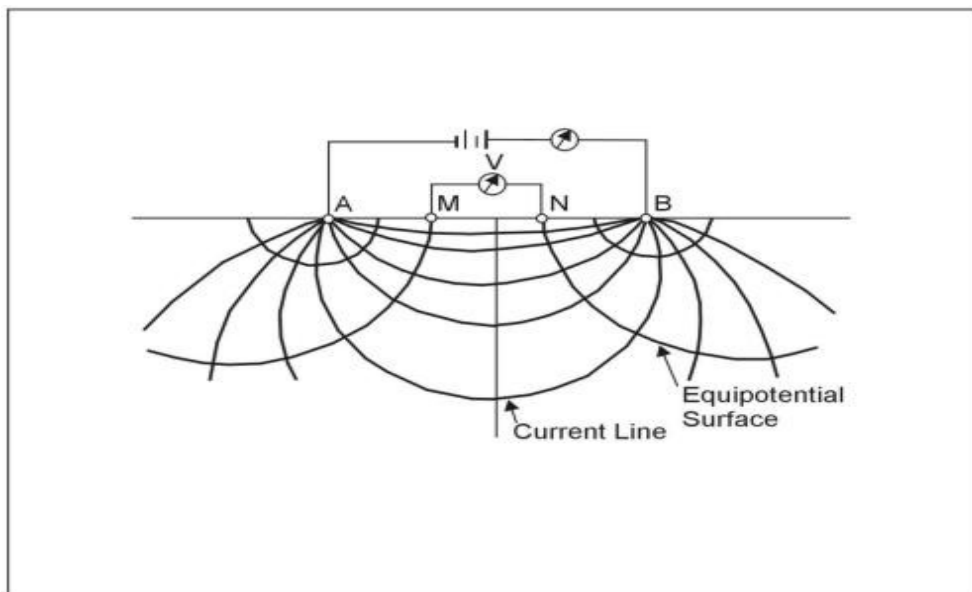


Figure 1.5: Wenner-Schlumberger array

1.7. Previous Studies

A study of PHG-Palestinian Hydrology Group (2005), found the discharging of spring and dug wells in Hebron district from Eocene Alluvial aquifer or from local perched aquifer of Albian lower Cenomanian aquifer and upper Cenomanian-Turonian aquifer. They found that the mean annual precipitation, infiltration and the runoff is 390.7 MCM, 105.5 MCM and 15.8 MCM respectively. 2.1Mill.m³ from the runoff is coming out through spring and wells, and 103.4 MCM infiltrations to the deeper groundwater aquifers. Water type is normal earth alkaline water with prevailing bicarbonate and mainly chloride or sulfate. Most of the springs and dug wells are oversaturated with respect to dolomite.

Nassar (2005) in his M.sc thesis evaluated the hydrological, hydrogeological, isotopical and hydrochemical of the spring in Hebron district. The study showed the runoff, recharge and the average annual rainfall with 16.4 MCM, 141.01 mm/hr and 487.2 mm respectively. The water type in the area is earth alkaline water with increased portions of alkalis with prevailing bicarbonate. From the Durov diagram showed that 48.8 % of the spring indicates water exhibiting dissolution or mixing with wastewater.

Qannam (1997) in his M.sc thesis, studied the water quality of groundwater resources in Bethlehem-Hebron region. He found that the area classified into five type of water, normal earth alkaline water with prevailing bicarbonate, earth alkaline water with bicarbonate and chloride, earth alkaline water with increased portion of alkalis and prevailing bicarbonate and chloride, and alkaline water with prevailing chloride. The chemical and physical analysis for the drink water according to WHO showed that all water samples are below the accepted standards, except 1.4 % of the sample have high concentration for nitrate. Most of the water samples were found to be oversaturated with respect to calcite, aragonite, dolomite, and chalcedony, while unsaturated with respect to gypsum and magnetite mineral phases. the water of all the springs and wells is good for irrigation.

Qannam (2003) in a PhD thesis studied. This thesis contains the results of hydrological, hydrogeological, geomorphological and hydrochemical. He calculated the annual precipitation wadi Al-Arroub area to be equal to 38.14 Mill.m³. Also he found the values of the average pan coefficient, potential evapotranspiration, runoff and actual evapotranspiration to be 0.72, 1108mm/yr, 6.44Mill.m³/yr and 8.87Mill.m³ respectively, also nine type of VOC analyzed in the study area, 14 samples were collected, 7 samples

from the springs and dug wells, 6 are soil water samples, and one sample from the waste water conduit, the analysis result of VOC presented in (Table.1.4) and (Table.1.5).

Matthew and Bruce (1996) presented the results of regional assessment of 60 volatile organic compounds (VOCs) in groundwater; they collected samples from six areas within the Lower Susquehanna River Basin from 118 wells ranging from 30 to 226 feet deep.

MTBE was detected in 16 of the 118 wells and was the most commonly detected compound with concentrations ranged from (0.11 to 51) $\mu\text{g/L}$. Chloroform was the second most commonly detected compound.

Klinger et al., (2002) studied the occurrence of MTBE in groundwater in Germany. Within this survey they examined 170 wells, which are used as groundwater monitoring points or which are foreseen for drinking water extraction in emergency cases or for irrigation purposes. In rural areas MTBE was found only in 9% of all samples in concentrations above the limit of determination (LOD) of 0.05 $\mu\text{g/L}$. In urban areas MTBE was detected in 49% of all wells under investigation and the median concentration was calculated to 0.17 $\mu\text{g/L}$. In one case a maximum MTBE concentration of almost 700 $\mu\text{g/L}$ was detected.

Peckenham (2002) conducted a study on the occurrence and distributions of the fuel oxygenate MTBE in glacial sand and gravel aquifer in southern Maine. Ninety samples were collected from 31 different wells in the Windham aquifer, in North Windham Germany, Maine, for analysis of MTBE between July 1998 and August 2001. MTBE was detected in 42 percent of the samples and 52 percent of the individual wells sampled. In addition, 92 percent of wells with detectable concentrations of MTBE were in an area of the aquifer designated as a "high yielding" aquifer. Land uses were found to be associated with MTBE detection rates in the wells in the study area. The overall median concentration in wells with detectable MTBE was (1.85) $\mu\text{g/L}$. The mean concentration has risen from 0.5 $\mu\text{g/L}$ in April 1998 to 6.3 $\mu\text{g/L}$ in August 2001.

Moran et al., (2002) studied the occurrence of MTBE and other gasoline hydrocarbons in three surveys of water quality conducted by the U.S. Geological Survey-one national-scale survey of ground water, one national-scale survey of source water from ground water, and one regional-scale survey of drinking water from ground water. The overall detection

frequency of MTBE in all three surveys was similar to the detection frequencies of some other volatile organic compounds that have much longer production and use histories in the United States. The detection frequency of MTBE was higher in drinking water and lower in source water and ground water. However, when the data for ground water and source water were limited to the same geographic extent as drinking-water data, the detection frequencies of MTBE were comparable to the detection frequency of MTBE in drinking water. In all three surveys, the detection frequency of any gasoline hydrocarbon was less than the detection frequency of MTBE. No concentration of MTBE in source water exceeded limit of U.S. Environmental Protection Agency's Drinking-Water Advisory of 20 $\mu\text{g/L}$, one concentration of MTBE in ground water exceeded 20 $\mu\text{g/L}$, and 0.9 percent of drinking-water samples exceeded 20 $\mu\text{g/L}$.

Table 1.4: The results of the analysis for the VOC's of the soil water samples and waste water. (Qunnam.2003)

VOC's	Detection limit	Above the conduit			Below the conduit			Birkat Eid	Waste water
		30 cm	60 cm	90 cm	30 cm	60	90		
Limonene	0.9	100	78	<0.85	<0.85	0.9	58	<0.85	40
Toluene	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.7
Styrene	0.25	0.25	0.25	0.25	0.25	0.25	0.25	3.2	<0.25
Trichloroethylene	0.2	0.2	0.2	0.2	0.2	0.2	0.2	3.5	<0.2
O-dichlorobenzene	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	14	35
Dimethyl disulfide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	10
Dimethylsulfide	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.55
Diethylsulfide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1

Table 1.5: The volatile organic chemicals content of the springs and dug wells sampled from Wadi Al Arroub drainage basin, (Qunnam.2003)

VOC's	Detection limit	Eth-Tharwa	Haj-Hamid-1	Ed-Dilbi	Kuweisiba	Birkat Eid	Arroub	Birkat Eid	Waste water
Limonene	0.9	< 0.85	< 0.85	<	< 0.85	< 0.85	< 0.85	< 0.85	40
Toluene	0.1	< 0.1	< 0.1	1.51	0.19	37.54	0.31	< 0.1	1.7
Styrene	0.25	< 0.25	< 0.25	<	< 0.25	< 0.25	< 0.25	3.2	< 0.25
Trichloroethylene	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	3.5	< 0.2
O-dichlorobenzene	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	14	35
Dimethyl disulfide	0.1	< 0.1	< 0.1	1.50	0.19	37.54	0.31	< 0.1	10
Dimethylsulfide	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.55
Diethylsulfide	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1
Methylene chloride	0.04	< 0.04	< 0.04	<	< 0.04	0.89	1.24	< 0.04	< 0.04

1.8 Methodology:

1.8.1. Sampling for MTBE

Water samples were collected in 40 ml glass vials. Before collecting the samples the vials were cleaned very well by water and detergents, then rinse with hydrochloric acid solution and distilled water for several times.

To study the concentration of MTBE, three types of samples were collected from three different places. Surface run off from Dura and Hebron city with different distances from gas stations, groundwater samples from Hebron District and from groundwater and soil which lies on different distances with different depths from various gas stations, (Fig 1.6), Samples were taken from surface water and groundwater to measure the concentration of MTBE in these samples in one hand and to appoint the sources of the polluted material on the other hand. Groundwater samples were collected by pumps. These pumps were operated for a few minutes before collecting the sample from the well to make sure the sample has been taken from the exact source of water. Each vial was washed by the same water of the sample before collection. Then it was fully filled without air bubbles pass through the sample. After that it was tightly closed with Teflon septa. Three bottles were filled from each sample. Lastly all samples were stored in the cold box at 4 °C until arrival at the laboratory (Bianchi et al., 1991).

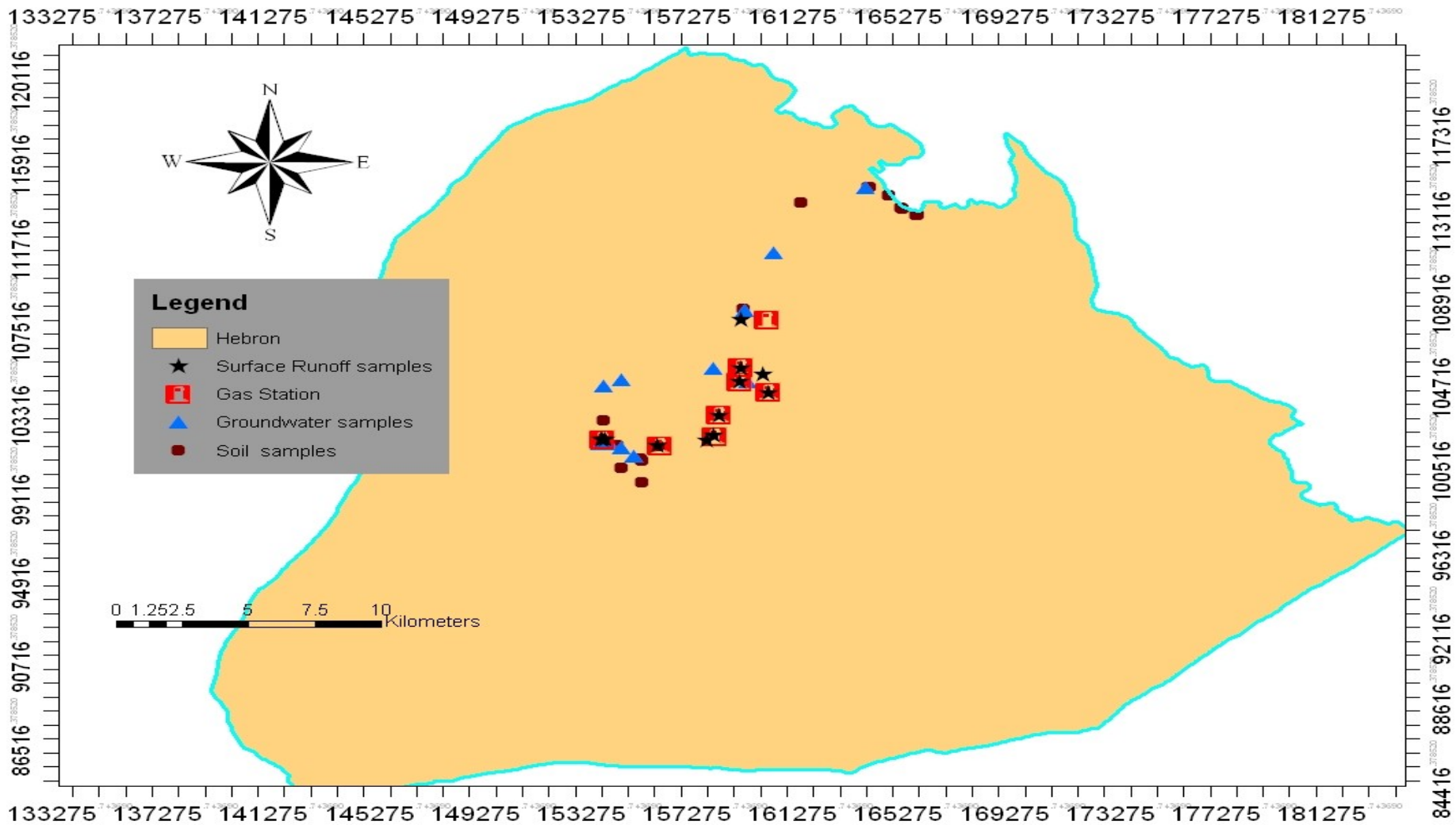


Fig.1.6: Location of MTBE Samples

1.8.2. Estimation of the surface runoff

Goldschmidt formula was used to estimate the surface runoff in Wadi Abu Al-Qamrah.

According to the following equation:

$$Q = 0.237 * (P-252)$$

Where:

Q: is the average annual runoff

P: is the average annual rainfall.

Both Q and P are in mm/yr.

1.8.3. Estimation of the Recharge

Guttman and Zuckerman (1998) developed a modification of the Goldschmid and Jacob formula was used to estimate the recharge of wells in Wadi Abu Al-Qamrah. According to the following equation:

$$R = 0.534 * (avP - 216) \quad \text{Rainfall } 300 - 650 \text{ mm}$$

Where:

$$R = \text{recharge (mm)}. \quad avP = \text{average annual rainfall (mm)}.$$

1.8.4. Estimation of Evaporation

Evaporation depends in many factors such as temperature, wind speed, sunshine, and humidity, which is strong in summer as a result of high temperature.

Evaporation was estimated by Penman equation, which is manly depending on temperature, wind speed, relative humidity.

According to the following equation:

$$E = \frac{\Delta \cdot (K + L) + \gamma \cdot \lambda_v \cdot \rho_w \cdot K_E \cdot v_a \cdot \{e_a^* - e_a\}}{\lambda_v \cdot \rho_w \cdot \{\Delta + \gamma\}}$$

Where:

E = evaporation rate in units of depth per time

Δ = slope of the saturation vapor pressure vs. temperature relationship at T_a

K = short wave radiation net input

L = longwave radiation net input

γ = psychrometric constant $\approx 0.066 \text{ kPa } ^\circ\text{C}^{-1}$

λ_v = latent heat of vaporization = 2.45 MJ kg^{-1}

ρ_w = density of water = 1000 kg m^{-3}

K_E = mass transfer coefficient

v_a = velocity of air

e_a^* = saturation vapor pressure at atm. temp.

e_a = water vapor pressure in atm.

1.8.5. Sampling for Hydrochemical analysis

Before collecting the water samples, we visited the study area, municipality of Dura, farmers and Dura meteorological station to collect information about the study area.

The Global positioning system (GPS) is used to measure the coordinates (X,Y) and elevations of the wells (Appendix.1.1), Geographic information system (GIS software) were used to maps the wells in the study area and identified the coordinates the wells on maps (Fig.1.7).

The groundwater table was identified for 24 wells, after that, 14 samples were collected twice from the study area in November 2007, and the second time was in April 2008. Two bottles for each sample were collected in polyethylene bottle (2L), one for major cations and anions analysis and the second bottle for heavy metals analysis.

Each bottle was rinsed three times before filled, groundwater samples were collected by pumps. The pumps should be operated for a few minutes before collecting the sample from the well to make sure the sample has been taken from the exact source of water, each bottle filled completely. All samples placed in a cold box at 4°C until arrival at the laboratory.

The temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) should be measure in the field by multi 340i meter. (Table .1.6)

1.8.6. Geophysics profile

Wenner-Schlumberger array by Vertical Electrical Soundings (VES) method was used to apply to determine the thicknesses and the true electrical resistivities of the successive layers below each VES site by using Earth Resistivity Meter, this technique is standard to determine the depths of the subsurface rock boundaries and their electrical resistivities.

Two profiles survey was conducted along the Wadi, the first locates in the west and the second east, within the Palestinian coordinates $X = 153334 - 153327$ m, $Y = 101378 - 151315$ m, and elevation of 825 m a.s.l, and $X = 154836 - 154806$ m, $Y = 100623 - 100563$ m, and elevation of 780 m a.s.l, respectively from north to south, two station was conducted in each profile with long 300 m as shown in Fig 1.7. The data analyzed by using IPI2WIN v.2.0 software program which gives an accurate image of the subsurface that can be obtained through the inversion of the pseudo-section (Smith and Vozoff, 1984, Griffiths and Barker, 1993, and Loke and Barker, 1996).

1.8.7. Laboratory work

MTBE

In this study, samples were analyzed to measure the concentration of MTBE. This compound were analyzed by gas chromatography; which uses several techniques for the analysis of volatile organic compound in water that can be subdivided into several groups according to extraction agent: direct aqueous injection, headspace analysis, solid -phase micro extraction, and purge and trap (Torsten, 2003). Headspace analysis is one of the most common techniques used for the isolation of VOCs from water samples is extraction into the gaseous phase, is suitable for compounds that show sufficiently high air-water partitioning (quantified by the Henry's Law constant) (Torsten, 2003) Headspace analysis effective release from the liquid phase (especially aqueous) is possible for volatile, semi-volatile, non-polar or weakly polar compounds. Several methods for EPA used to analyses of oxygenates compound e.g., (8015, 8020, and 8260) but the most common method for the analyses is 8260 because it will give good results for concentration for MTBE and other oxygenated compound.

Hydrochemical

The major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and major anions (Cl^- , SO_4^{2-} , NO_3^- , HCO_3^-) analysis of water samples were conducted at the environmental laboratory of Department of Earth and Environmental Sciences of AL-Quds university (Table .1.6)

Table (1.6): Analytical methods used in the determination of the various parameters.

Parameter	Method of analysis
Temperature, EC, and pH – values.	Multi 340i meter.
Ca^{2+} , Mg^{2+}	Flame photometer.
Na^+ , K^+	Flame photometer.
SO_4^{2-}	Spectrophotometer ($\lambda = 220 \text{ nm}$).
NO_3^-	UV-spectrophotometer method ($\lambda = 220 \text{ nm}$).
Cl^-	Titration with AgNO_3 using potassium chromate as indicator
HCO_3^-	Titration with HCl using bromocresol green and phenolphthalein indicators.
Cu , Mn , Pb , Cd , Sr , Ni and Ba	Atomic Spectrophotometry

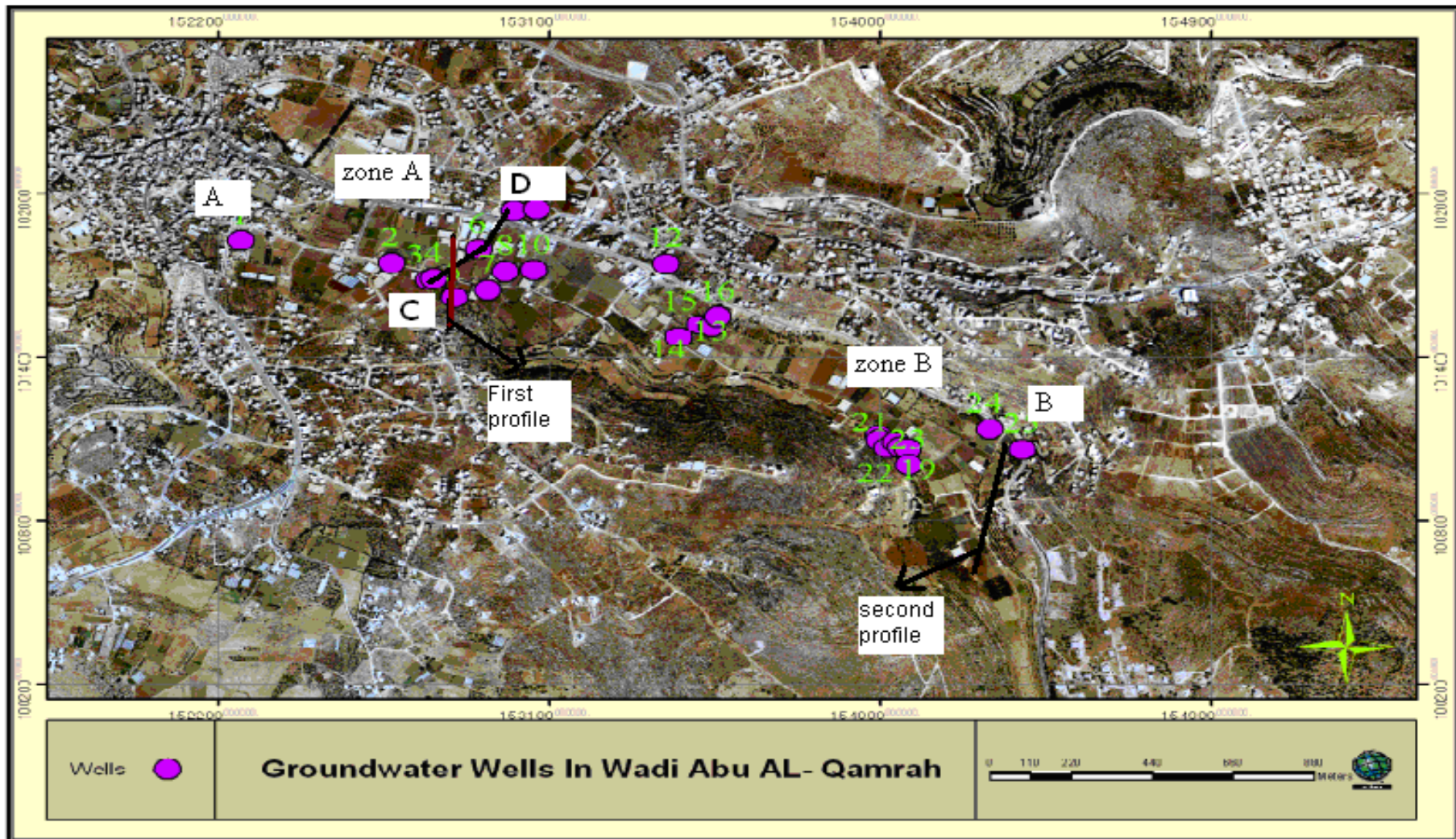


Fig 1.7: dug wells and contour lines in wadi abu Al- Qamrah

Chapter Two

Study Area

2.1 Location of the study area

Dura is located about 9 Km on the south-west of Hebron city. It lies according to the Palestinian grid X= 150000-156200 m, Y= 1096000-1101800 m, with an elevation ranges between (800 - 915) m above sea level. According to Palestinian Center Bureau of Statistics, 1997 the population is about 27000 inhabitants. It covers an area of 15224 dunums (Municipality of Dura, 2008). Dura consists of many villages such as Bait Awwa, Deir Samit, Khursa and other small villages. The city contains many small enterprises such as brick factories, stones backsaw, detergent factory, in addition to few fuel stations and car washing stations.

The Study area lies in wadi Abu al-Qamrah in Dura city (Figure, 2.1) Palestinian grid X= 152800-155400 m, Y= 100600-101550 m, with an elevation range from (800 - 840) m above sea level. In the wadi, they are 45 dug groundwater wells with a depth range from 2 to 10 m. The rate of water abstraction differs from one well to another and from season to another (2 -100) m³/day. The wadi is surrounded by mountains which form the surface recharge area (3 km²). The total area of the wadi floor is about 0.705 km², and considers to be used for agricultural activities in which different crops and vegetables are planted throughout the year.

The Average annual rainfall ranges between 450 - 500 mm (Dura meteorological station, 2008).The soils of the study area is Brown Rendzinas and Pale Rendzinas. the depth of this soil ranges between 0.5 meter at the mountainous areas and 2 meters at the bottom of the wadi. (Fig.2.2). with the infiltration rate ranges between 5 – 26 mm/h (Fig.2.3), the infiltration rat in the study area varies from season to another which is 20% in the dry season to 30% in the wet season (Gvirtzman, 1994). Parent materials are mostly hard to soft limestone and marl. The pH of the soil is mainly nutral to slightly basic (7.5- 8.0), (Palestinian Hydrology Group, 2004).

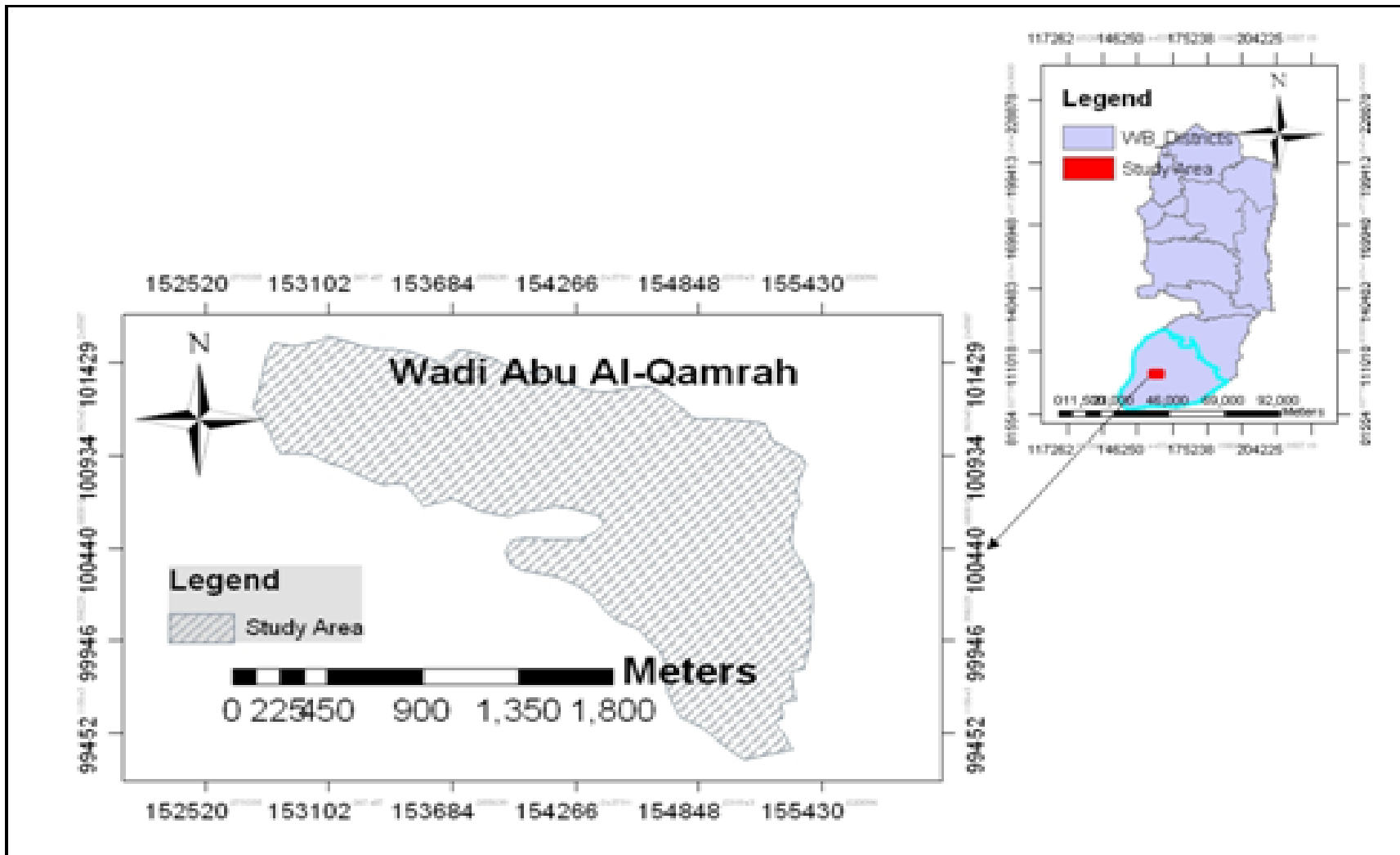


Figure 2.1: Wadi Abu Al-Qamrah study area

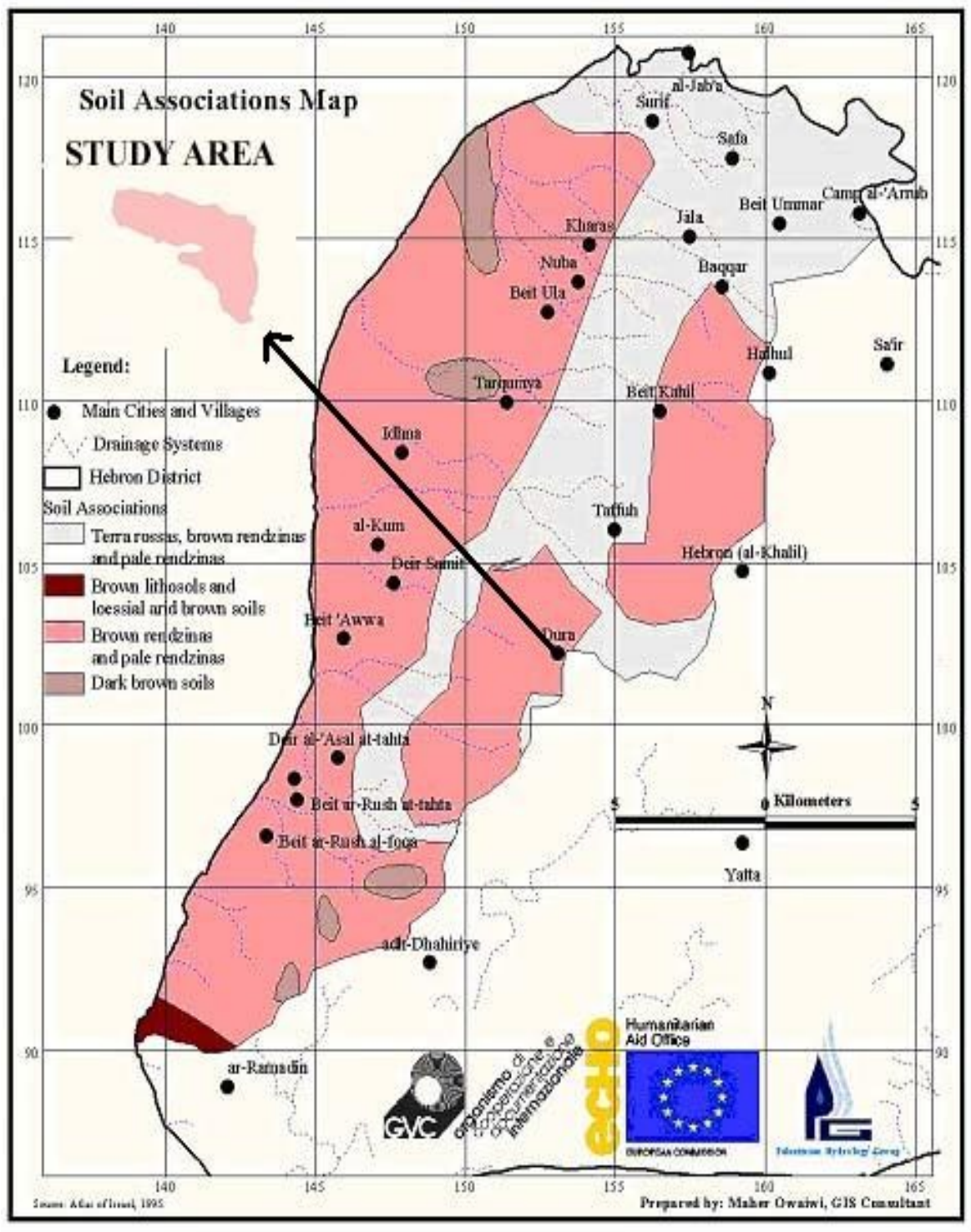


Fig. 2.2: Soil Association of Hebron District (Palestinian Hydrology Group, 2004)

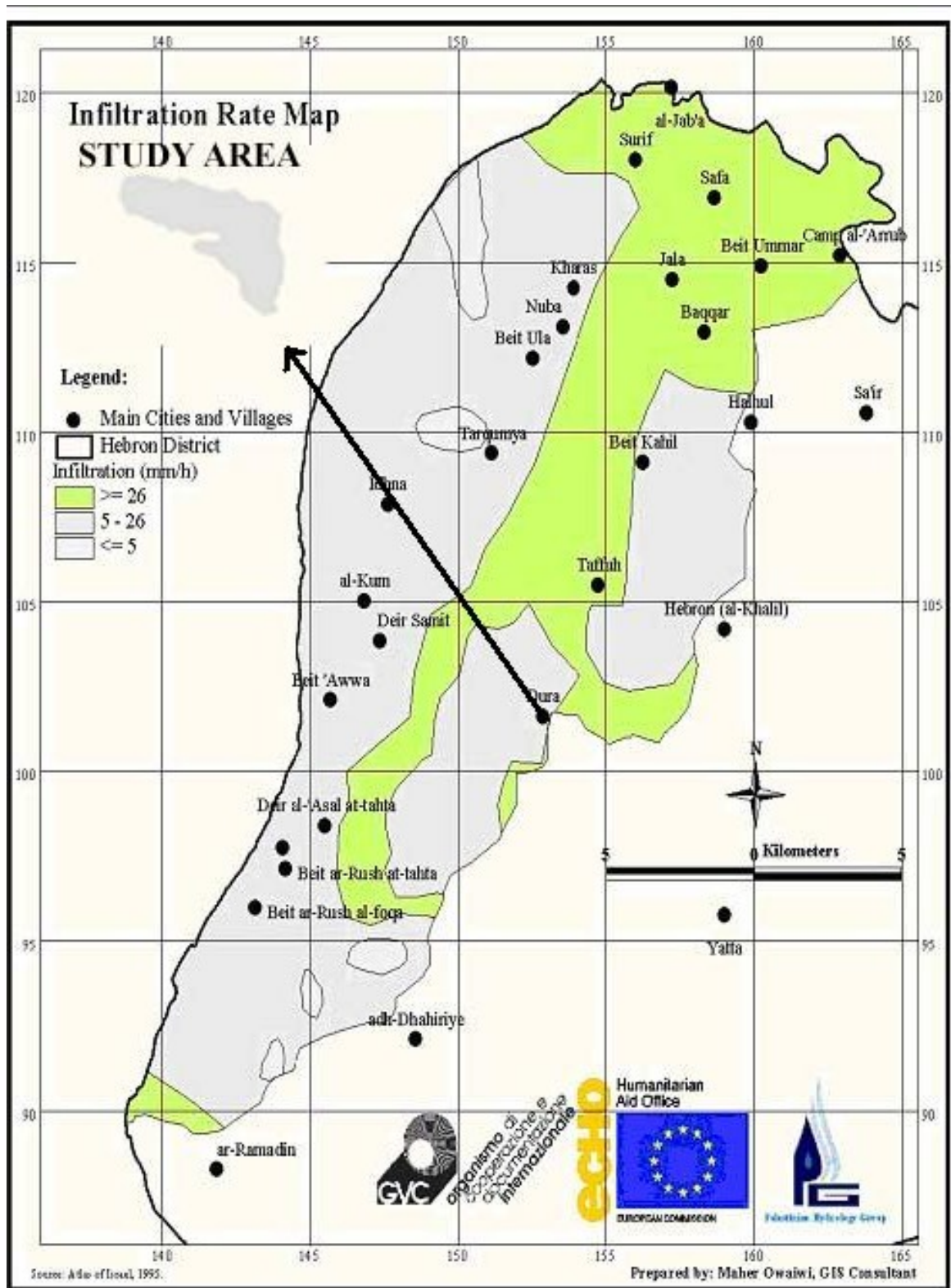


Fig. 2.3: Infiltration Rate Map of Each Soil Type (modified after Palestinian Hydrology Group, 2004)

Dura is a city of Hebron district; it is influenced by the Mediterranean climate with hot, dry summer and mild rainy winters. The study area is a mountainous region. So the temperatures are mild in summer which ranges from 10 – 26 °C and from 7 – 11 °C in winter, (Fig.2.4).

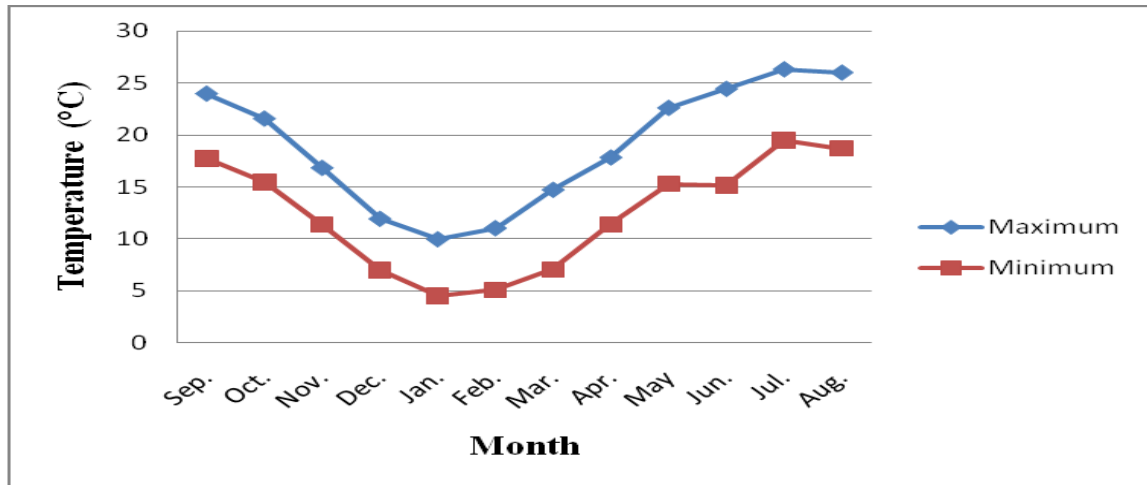


Fig 2.4: Average monthly Minimum & Maximum Temperature (°C) in the Hebron district from (1970-2007).

The annual mean relative humidity ranges from 60 – 70 %. The relative humidity is variable from mid-day to night which reaches 40 % in mid-day to 80 – 100 % in night, and from month to another, the minimum relative humidity is 48.25 % in May and the maximum relative humidity is 74.19 % in January (Fig.2.5), (Hebron climatic station, 2004; Kessler, 1994).

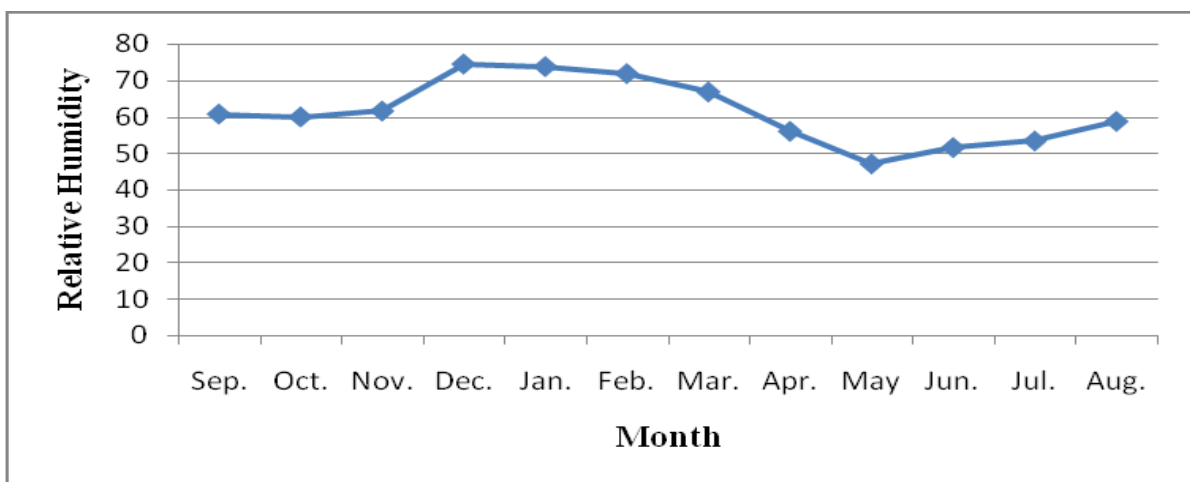


Fig 2.5: Average monthly mean relative humidity (%) in the Hebron district from (1970-2004).

2.2 Water sources in the Dura

There are about 50 shallow dug groundwater wells, with an average depth of 6 meters. These wells scatter in several valleys such as Wadi Abu Al-Qamrah (study area), and Wadi Kanar.

The main purposes of these wells are to use it in agriculture, and few of them are used for domestic purposes. Many of the wells are contaminated by human activities, due to the presence of waste water cesspits. Drinking water comes from several sources, including water net, dug wells, and rainwater.

The Palestinian Water Authority worked to supply the city with additional water from the area of the Tkua'a which provides the city with additional 800 m³/day. In addition to these sources, most of houses have to collect rain water and store it in cistern under the ground.

2.3 Geology of the study area

2.3.1. Yatta Formation

This formation founded in many areas on lateral Jerusalem anticline and in the Dead Sea declivity, and it's located in the east of study area (Fig.2.6). It consists of yellowish-gray chalk marl, limestone, dolomite of the Upper of Cenomanian. Fine crystalline calcite inters bedded chalk, limestone in the lower part (Lower Cenomanian). This formation is an aquiclude because the most consists of this formation is marl (Table.2.1). (Rofe and Raffety, 1963)

2.3.2. Hebron Formation

This formation is large distributed in the mountains of Jerusalem and Hebron. The lower and middle part of this formation consists of thin hard gray dolomitic limestone with silicification, which is consists of one third lower formation. The upper part of this formation consists of hard karistified gray dolomitic limestone. This formation is a good aquifer resulting from high secondary porosity which is produced from the jointed and caristification. The thickness of this formation ranges from 60 to 170 m (Table.2.1).(Rofe and Raffety,1963).

2.4 Aquifer system for the area

2.4.1. Lower cenomanian Aquifer system

This aquifer composed of four formations: kobar, Lower Biet Kahil, Upper Biet Kahil and Yatta. This formation composed of dolomite, limestone, marly and chalky limestone (Table.2.1) (Rofe & Roffety, 1963).

2.4.2. Upper Cenomanian-Turonian aquifer

This aquifer composed of three formation; Hebron, Bethlehem, and Jerusalem. This aquifer system is mainly composed of limestone, chalky limestone, and dolomite (Table.2.1).

Table 2.1: hydrogeology formation at the study area (Rofe and Raffety, 1963)

Geologic Age	Geologic Formation (Palestinian)	Geologic Formation (Israeli)	Dominated Lithology	Thickness (meters)	Aqui-type
Upper Middle Cenomanian	Hebron	Aminadav	Dolomite	20 - 120	Aquifer
Lower Middle Cenomanian	Yatta	Moza	Marl	50 - 130	Aquiclude
		Beit Meir	Limestone, Dolomite		Aquifer

Chapter Three

The Result

3.1 MTBE in Hebron and Dura City

The concentration of MTBE in surface runoff ranges between 0.2 ppb in the sample that was collected from the area that comes before AL-Tahreer gas station to 11 ppb in the sample that was collected from the area that come inside Dura gas station (Table.3.1). As a result, the concentration of MTBE in the area of the gas station is higher than it in the other areas, which emphasize that most of the MTBE comes from gas stations, as a result the concentration of MTBE decreases when we move away from gas station (Fig.3.1), which agree with hypothesis (1). The concentration of MTBE in soil and shallow groundwater samples is very rare because these samples were collected in hot days and MTBE is a volatile organic compound in which the physical properties depend on temperature (Table.1.1). Second, all the wells where the samples were collected are opened and exposed to air.

Tale 3.1: The concentration of MTBE in surface runoff

Name	Concentration (ppb)
Inside Dura gas station	11.0
After Dura gas station	2.8
Before Dura gas station	0.4
Aljanoob gas station	1.0
AL-Tahreer gas station	3.8
Before AL-Tahreer gas station	0.2
Bab Alzaw'i	3.3
Near Hebron Municipality	3.3
Al-Ansar gas station	2.9
Zaid Al-Ahle'a gas station	2.0
Alsalam gas station	9.5
Albass'a gas station	8.7

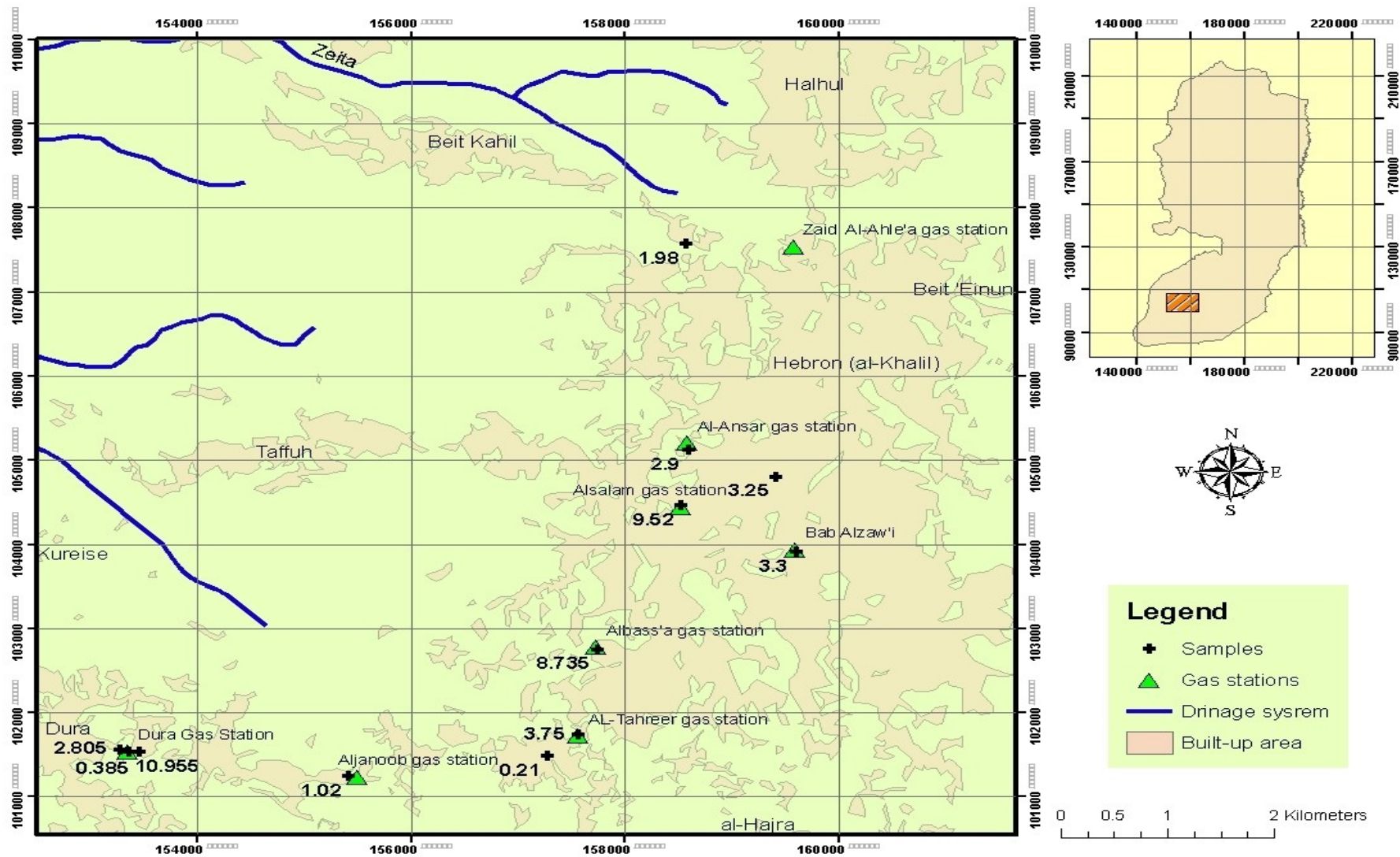


Fig 3.1: Location of gas station and MTBE concentration

3.2. The Results of Hydro-geochemistry

3.2.1. Rainfall

The rainfall in the study area varies from year to year, which is the mean annual rainfall 500 mm/yr from the period of 1980 to 2008, in this period the maximum rainfall recorded in wet year 1991-1992 with 1056.9 mm/yr, and the minimum rainfall recorded in dry year 1998-1999 with 230.2 mm/yr (Dura meteorological station, 2008). The rainfall drops from mid-October to May, about 75% of raining falls from December to February and 25% falls in the rest of the months (Fig.3.2).

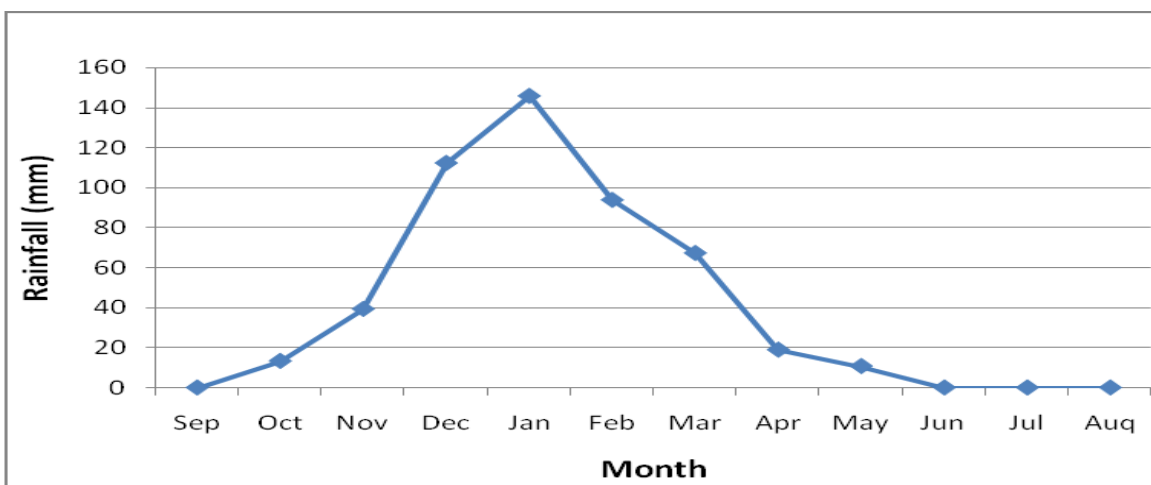


Fig 3.2: Monthly mean rainfall (mm/month) in the Dura city from (1980-2008)

3.2.2. Estimation of Evaporation

According to Penmen formula the mean daily evaporation varies from 4 mm/day in January to 6.22 mm/day in July. The average monthly evaporation is 186.6 mm/month in the summer and 121 mm/month in the winter (Fig.3.3).

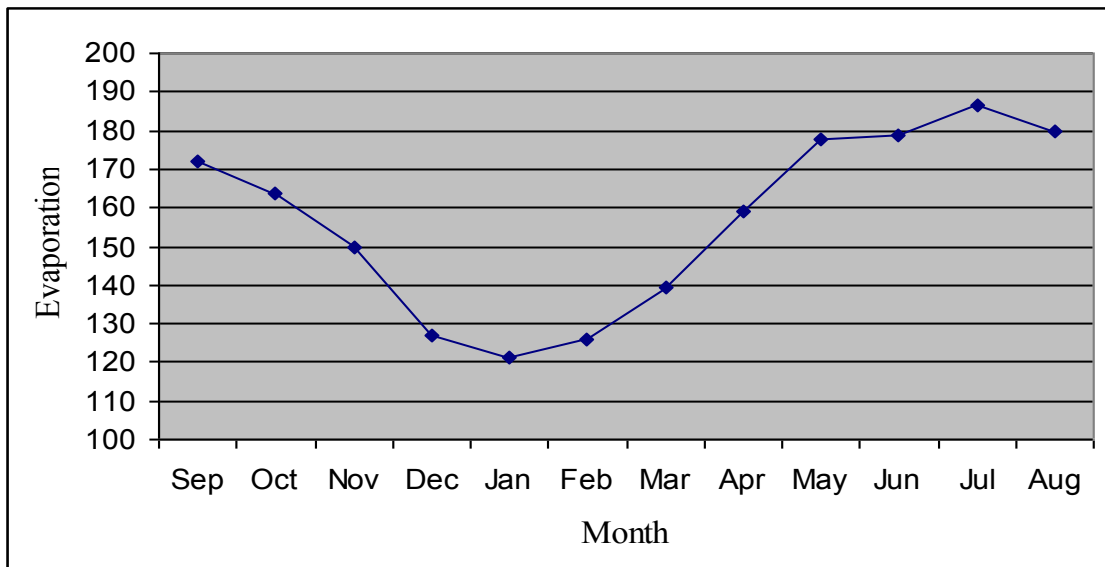


Fig 3.3: Monthly evaporation in the study area, from (1970-2007).

3.2.3. Estimation of the surface runoff:

When applied the Goldschmidt formula it gives an average surface runoff 58.776 mm/yr with total volume 187412 m³ from the precipitation. According to this formula (Arad and Michaeli 1967) the average annual runoff of soil surfaces of low hydraulic conductivity could lead that may reach 20 % of the annual precipitation.

3.2.4. Recharge

When applying Goldschmidt and Jacobs developed formula, it gives an average annual recharge 151.7 mm/yr, which presented 30% of the average annual rainfall with total volume 478500 m³/yr.

The main recharge in the study area from the surrounding mountains with catchment area 2.250 Km², the annual volume rainfall is 1125000 m³ distributions between surface runoff, evaporation, infiltration...al,

Discharges differ from one well to another and from season to another which is range between (2-100) m³/day.

3.2.5. Water Table of the study area

The topography of the study area is hilly, covered with 1 - 3 meter of soil in the wadi. The elevation of the wadi floor in the west is 839 m a.s.l and decreases to 798 m a.s.l in the east side.

As a result of measuring the groundwater table for 24 wells, the level of groundwater table was found to be located at a depth of 7.5 m in the west and decreases to 0.4 m below the surface in the east (Fig.3.4) so the level of water table of groundwater is located from 831.5 m a.s.l in the west to 797.6 m a.s.l in the east. Water holding formation is the upper part of Hebron formation which consists of dolomite limestone.

Figure 3.5 shows that: from the groundwater contour maps the groundwater moves from west to east along the wadi.

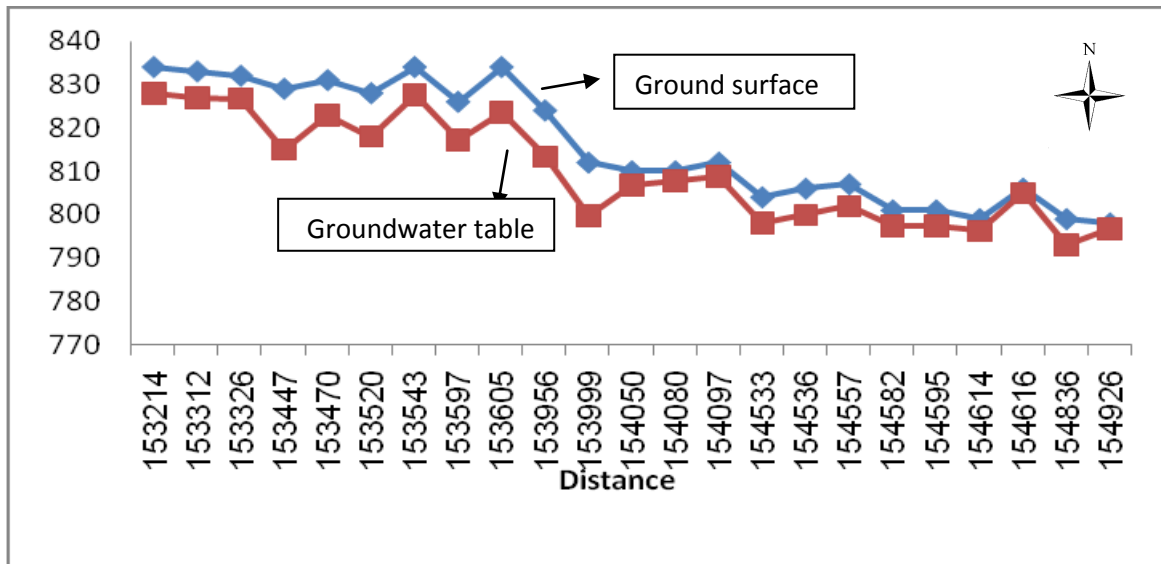


Fig.3.4: Ground surface and groundwater table along the wadi from A-B see Figure 1.7

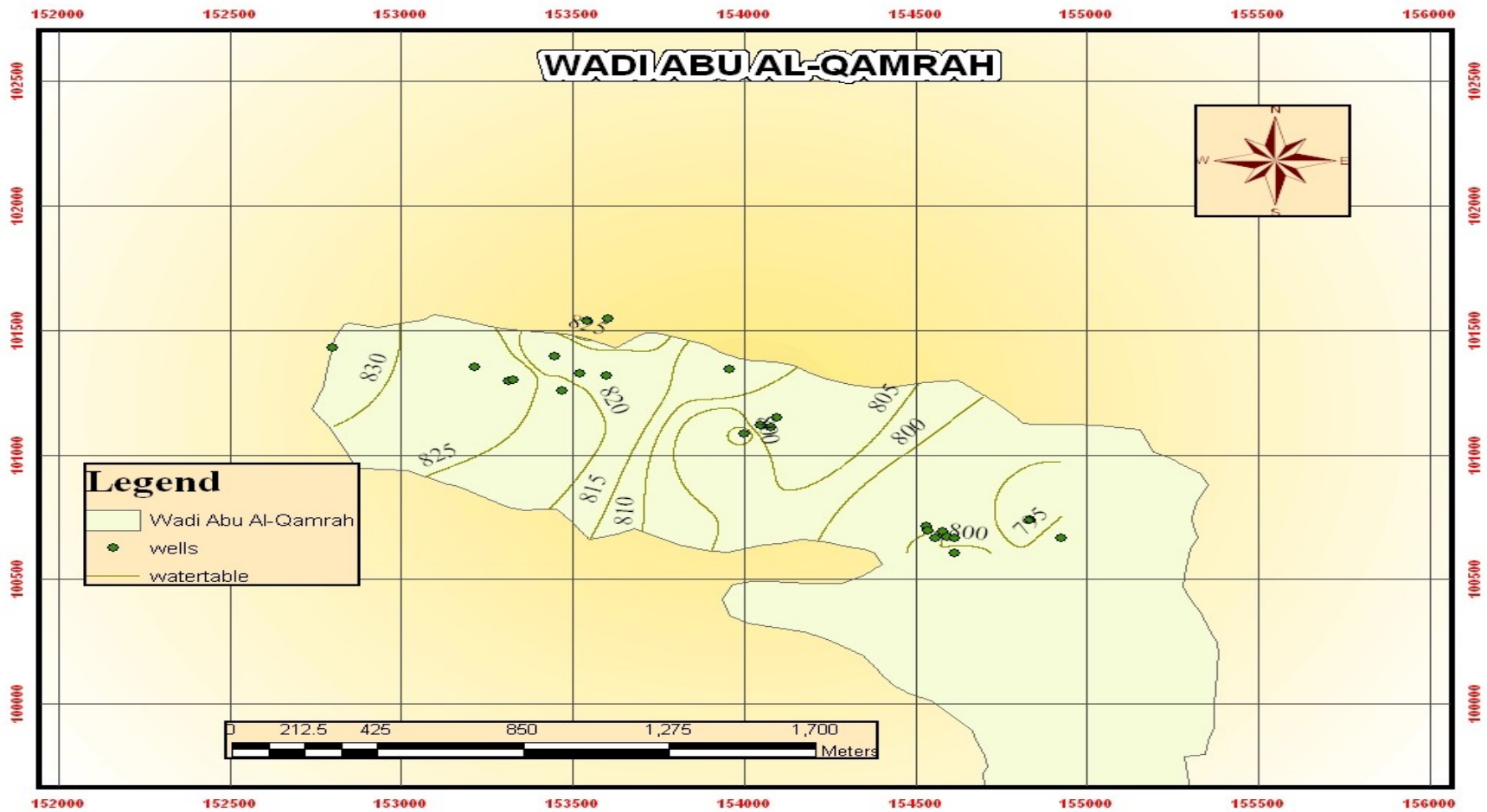


Fig.3.5: Groundwater contour in Wadi Abu Al-Qamrah (2007/2008)

The aquifer direction of the recharge area around the Wadi is directed from south to north, so the southern area is considered as the recharge area (Fig.3.6).

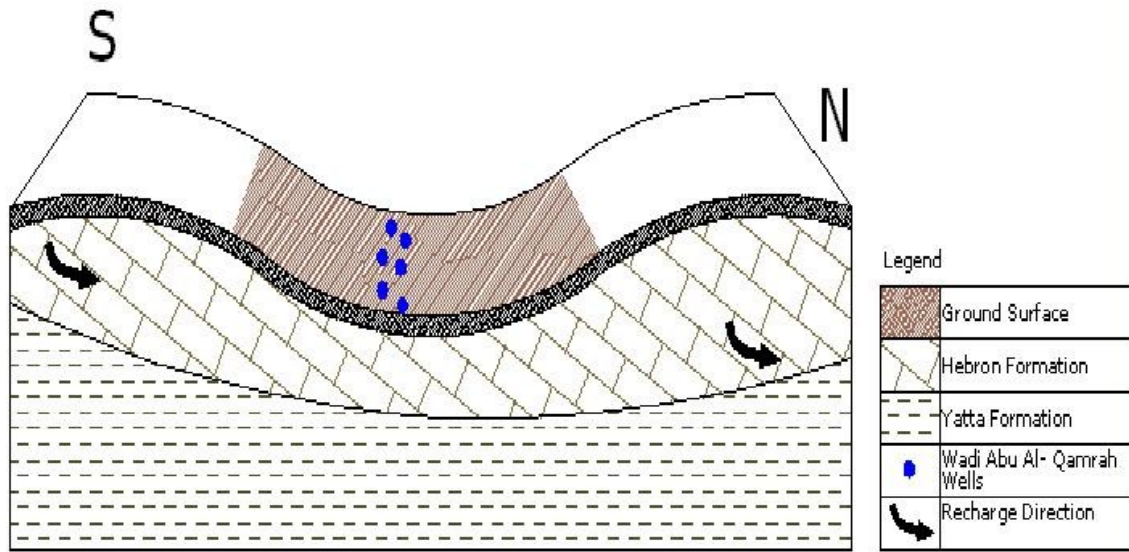


Fig.3.6: Cross section in Wadi Abu Al-Qamrah

Figure (3.7) shows that the aquifer layer decreases from west to east, in which its thickness is about 11 m in the western side.

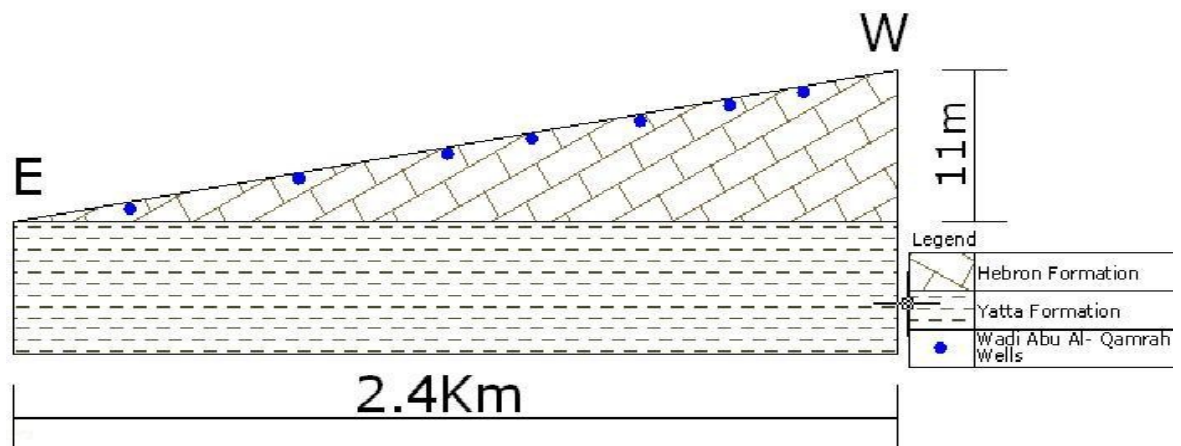


Fig.3.7: the layer of Wadi Abu Al-Qamrah

3.2. 6. Electrical conductivity

Electrical conductivity (EC) is proportional to the quantity of dissolved ion present in solution. EC is expressed in unit of microsiemens/cm ($\mu\text{s}/\text{cm}$).

The values of water samples range from 748 $\mu\text{s}/\text{cm}$ in Waleed Amer well and rise up to 2630 $\mu\text{s}/\text{cm}$ in Issa Shaheen well, with an average of 1636 $\mu\text{s}/\text{cm}$. (Table, 3.2), (Fig.3.8),

Figure 3.8 shows that the EC value in the summer sample is slightly higher than it in winter sample, with range 730 $\mu\text{s}/\text{cm}$ to 2570 $\mu\text{s}/\text{cm}$ with average 1829 $\mu\text{s}/\text{cm}$ in summer (Appendix.1.4). This difference is related to the continuous recharge in winter which decreases the EC, on the other hand; the opposite happens in summer.

The EC value is the same in summer and winter (decreases from west to east) (Fig.3.8). It decreases from west to east because the west part of the study area is located near the building up areas and human activities (Fig, 3.9).

This is due to the long contact time between water and rock and pollutants sources which increase along the wadi; the influence of the recharge with the flow direction of the groundwater makes dilution for the pollution toward the east.

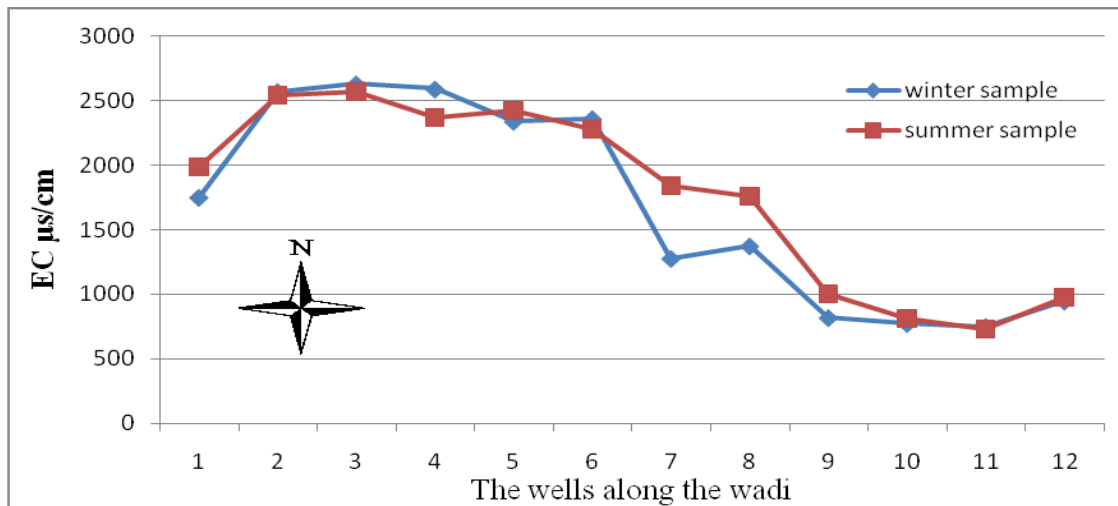


Fig.3.8: Electrical conductivity in $\mu\text{s}/\text{cm}$ versus distance in winter and summer

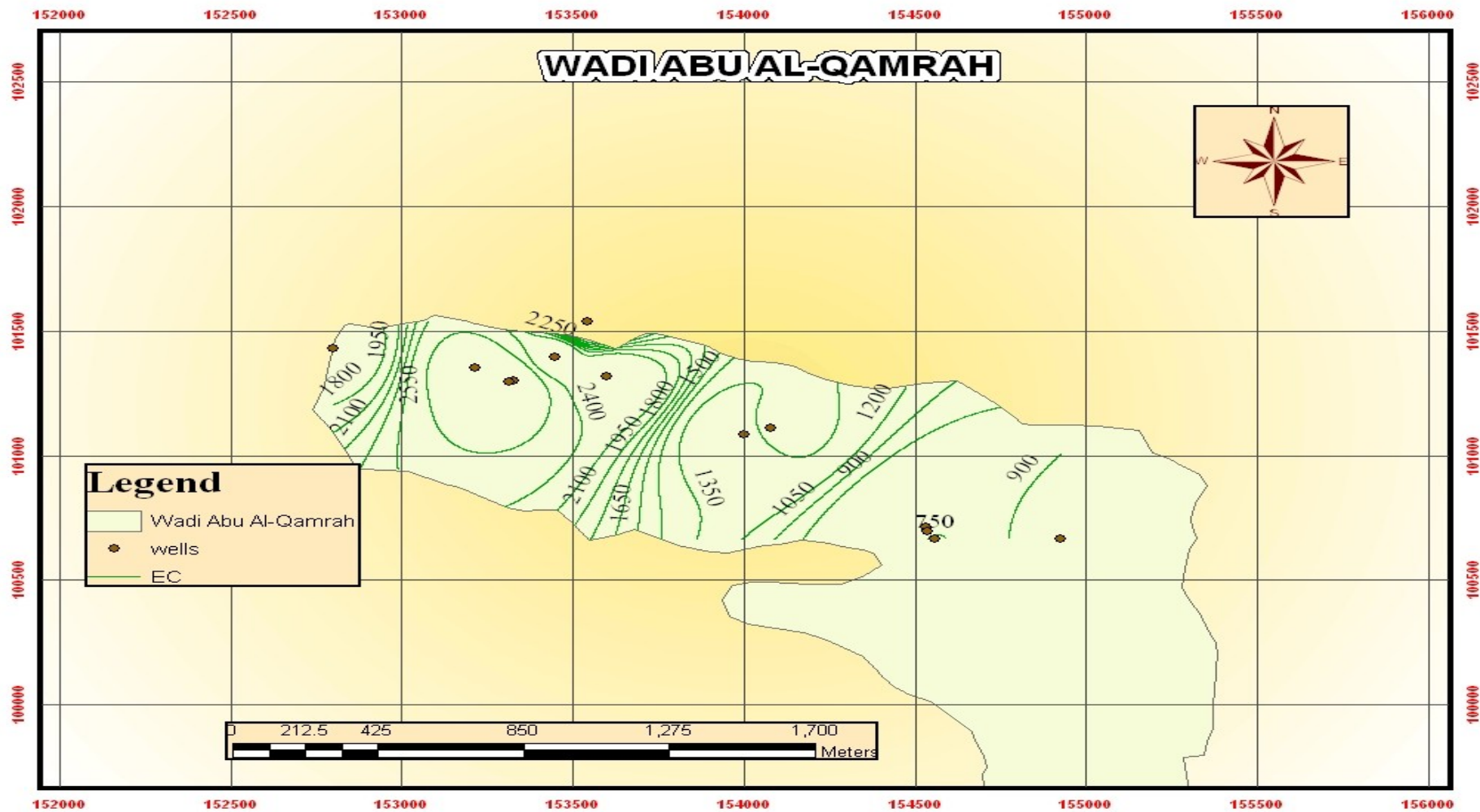


Figure.3.9 : EC contour map in Wadi Abu Al-Qamrah (2007/2008)

3.2.7. Major Cations

The chemical analysis shows high diversity in chemical characteristics (Appendix 1.2), where the highest variation in cation values for K^+ that range between 0.45 mg/l to 146.02 mg/l with average 29.195 mg/l this divers related to the absorption by plant or ion exchange, Ca^{2+} concentration range between 77.46 mg/l to 199.08 mg/l with average 118.34 mg/l, the dissolution of carbonate rock in aquifer is the source of Ca^{2+} in groundwater. The concentration of Mg^{2+} detected from 32.79 mg/l to 76.7 mg/l with average 45.93 mg/l coming from dissolution of dolomite in Hebron aquifer. The concentration of Na^+ range from 29 mg/l to 146.02 mg/l with average 78.31 mg/l (Table.3.2), because the source of Na^+ comes from reversing ion exchange with clay mineral.

3.2.8. Major Anions

The highest variation in the concentration of anion for HCO_3^- ranges between 297.05 mg/l and 756.4 mg/l with average 390.5 mg/l, this diver refers to the dissolution of carbonate rock. The Cl^- concentration is 53.2 mg/l in the Nihad Al-swiety and A'hed Qazaz wells (Appendix 1.2), from fig.3.10; the highest concentration is measured in Akram AL-Shareef well with 301.3 mg/l which is located between Dodeen well and Shaheen well. Beside that, the groundwater table of Al-Shareef well is lower than the groundwater table of Dodeen and Shaheen well with chloride concentration of 88.6 mg/l and 287.1 mg/l respectively, indicates that the groundwater moves to the centre of the Wadi, and this cause a washing of chloride toward the centar of the Wadi in Al-Shareef well, (Fig.3.11), (Fig.3.12).

In general the Cl^- concentration decrease from west to east along the wadi flow direction, (Fig.3.11), only in Dodeen well where Cl^- concentration is low because it's located outside the wadi.

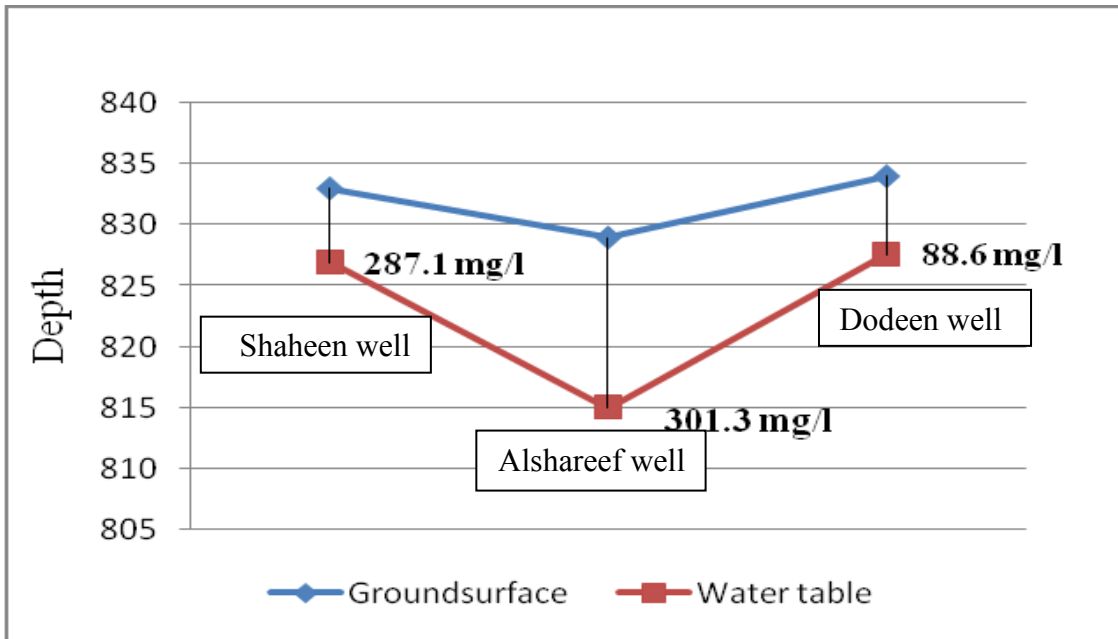


Fig 3.10: N-S cross section for Wadi Abu Al-Qamrah of groundwater table level from C-D see figure 1.7.

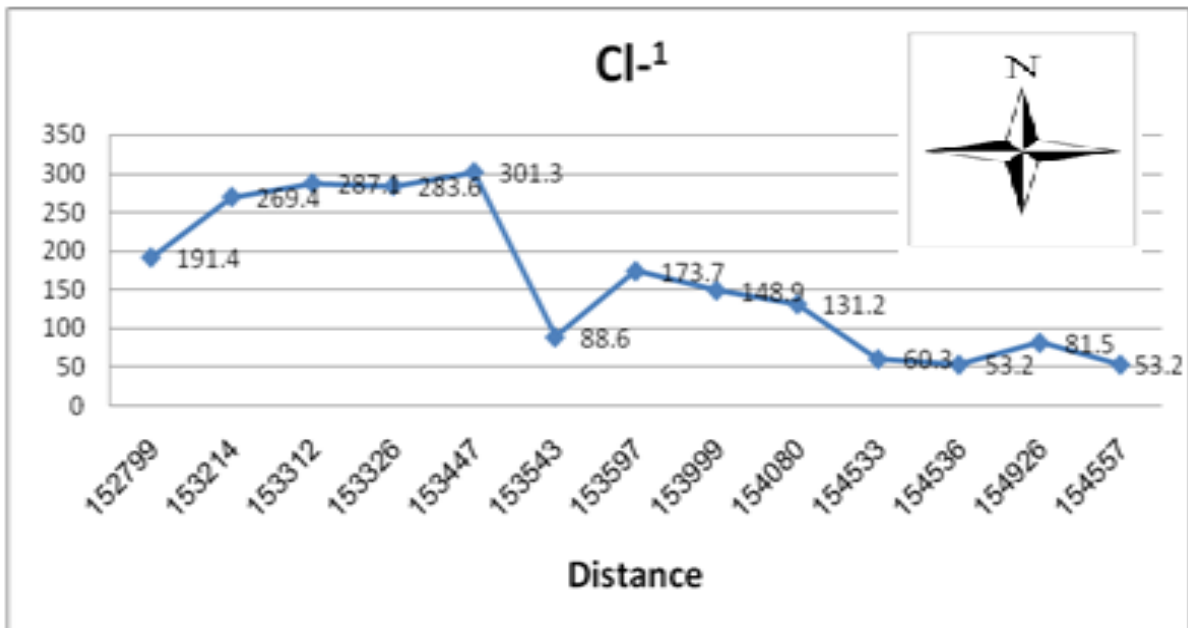


Fig.3.11: Chloride concentration in groundwater wells during winter 2007/2008

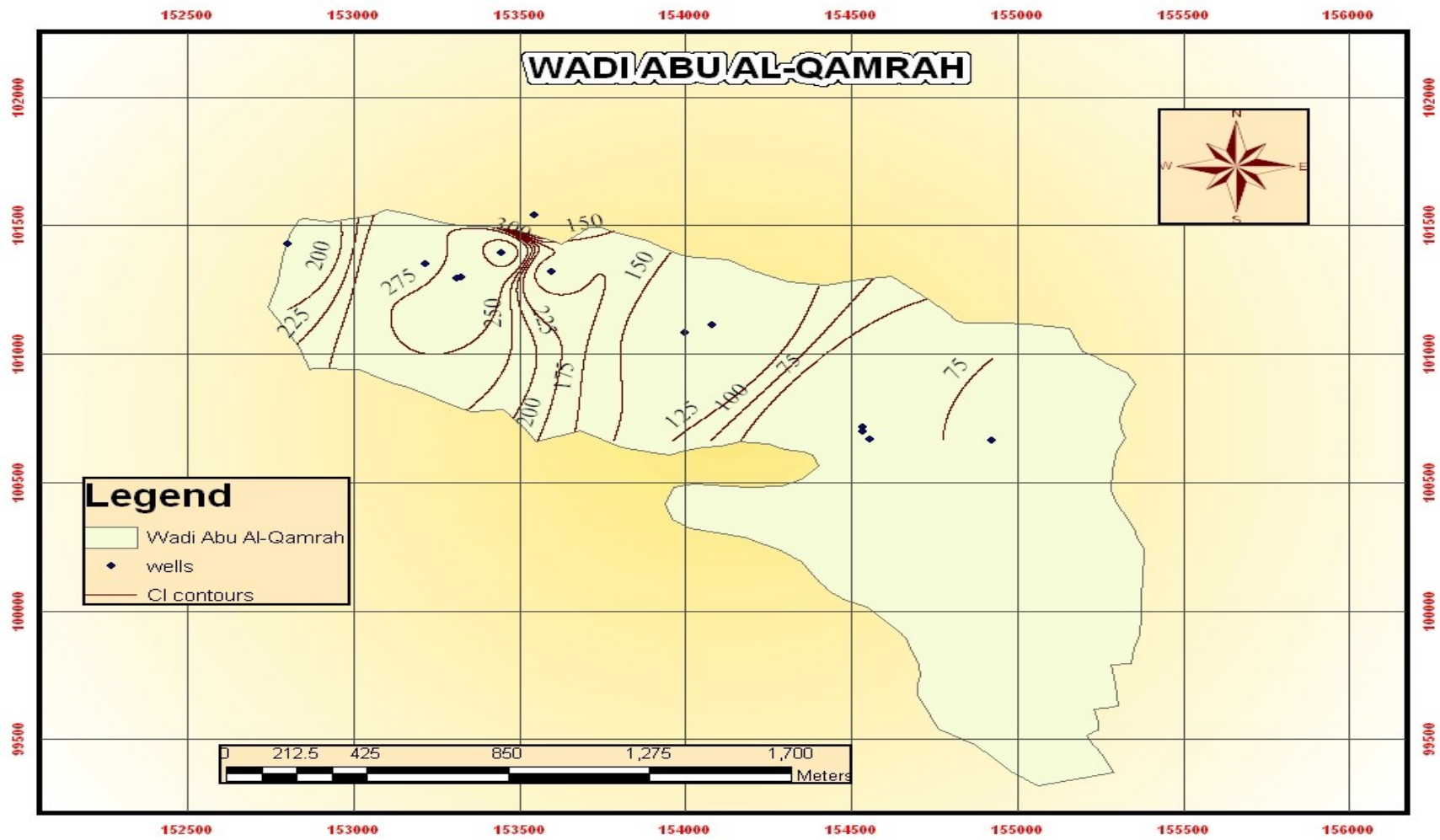


Fig.3.12: CI- contour map in Wadi Abu Al-Qamrah (2007/2008)

The concentration of SO_4^{-2} ranges between 50 mg/l and 200 mg/l with average 90 mg/l coming from dissolution of sulfate forming minerals. The NO_3^- concentration is 17.7 mg/l to 122.8 mg/l with average 74.75 mg/l (Table. 3.2), the mixing with sewage is the source of NO_3^- .

3.2.9. Trace Element

These elements occurs in groundwater in very low concentration of less than 1 mg/l (Chowdhury et al., 2005), which come from rock weathering, geochemical processes, and anthropogenic activities such as agricultural activities from fertilizer and pesticide.

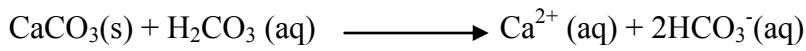
Trace elements were detected in groundwater with different concentrations where strontium has the highest concentration trace element in groundwater with range from 132.2 ppb to 490 ppb, most of strontium compounds are water soluble, so it moves through the environment fairly easily (Lenntech, 2006), the dissolutions of aragonite, strontianite (SrCO_3), and celestite (SrSO_4) are the main sources of strontium in groundwater. Barium concentration ranges from 29.44 ppb to 129.21 ppb, barium comes to groundwater from naturally weathering rocks and dissolution of barite. Ni and Cu are found in groundwater with low concentrations with average 6.34 ppb and 5.72 ppb respectively, Mn, Cd, Pb are found in very low concentrations <5 ppb except in Marzoqa and Shaheen wells with concentrations of 11.21ppb and 34.21ppb for Mn (Appendix 1.3).

3.3 Seasonal variation in water quality

The concentration of ions changes from season to another because of the difference in hydrology and winter precipitation.

In the most of samples, the major cations and anions that are measured in summer is higher than winter samples (Fig.3.13),(Appendix 1.4), except K^+ , SO_4^{-2} and HCO_3^- that they are with average 29.7 mg/l, 42.5 mg/l and 130.79 mg/l respectively. The concentration of K^+ decreases in summer which is related to the absorption by plant or ion exchange process. SO_4^{-2} and HCO_3^- increase in winter due to the dissolution of sulfate forming mineral and carbonate rock during infiltration processes. The high temperature in summer decreases

gases dissolve, so it effects the concentration of SO_4^{-2} and HCO_3^- . The following equation clears the equilibrium reaction when calcium carbonate (CaCO_3) is dissolved in water:



The average concentration of Cl^- and Na^+ is 169.09 mg/l, 107.95 mg/l respectively, so the increasing occurs by mixing the groundwater in aquifer by waste water, and agricultural activities, where the rainfall percentage is about 60% from the annul rainfall, so the dilution is low. The increasing of Ca^{+2} and Mg^{+2} in summer season with average concentration 185.7 mg/l , 51.4 mg/l respectively related to dissolution of carbonate and dolomite in Hebron formation. The increasing of NO_3^- with average 416.25 mg/l is related to decaying of plants or nitrogen oxidation and from waste water mixing.

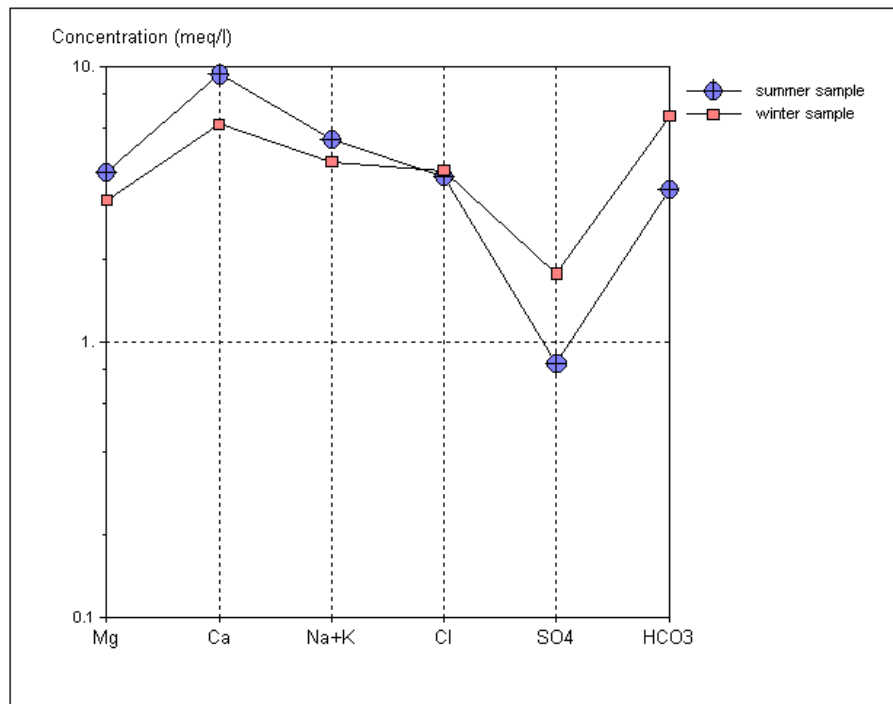


Figure 3.13: Schoeller diagram plot for the samples collected in winter and summer (2007/2008).

Table 3.2: Descriptive statistics of chemical and physical parameters of dug wells in wadi abu Al-Qamrah.

Variable	Min	Max	Mean	St	no
pH	6.81	7.76	7.22	0.29	14
EC	748	2630.00	1603.86	742.36	14
TDS	720	2050.00	1254.44	474.57	14
Ca ⁺²	77.46	199.08	128.65	45.84	14
Mg ⁺²	32.79	76.70	50.82	15.66	14
Na ⁺	29	165.30	91.39	54.44	14
K ⁺	0.45	146.02	48.80	54.36	14
Cl ⁻	53.175	301.25	157.51	94.28	14
HCO ₃ ⁻	297.05	756.40	450.32	153.65	14
SO ₄ ⁻²	50	200.00	108.93	55.71	14
NO ₃ ⁻	17.7	122.80	73.16	30.97	14
PO ₄ ⁻³	0.01	1.24	0.40	0.48	14
Ni	2.29	17.86	6.34	4.23	14
Cu	1	19.94	5.38	5.10	14
Sr	132.2	626.00	312.61	154.51	14
Ba	29.44	129.21	77.26	34.10	14
Mn	<5	34.21	7.71	7.78	14
Pb	<1	3.84	1.25	0.79	14

3.4 Piper Diagram

Piper diagram are a combination anion and cation triangles that lie on a common base line provide an overview of the chemical composition of multiple sample.

In a piper diagram (Fig, 3.14), water type of Wadi Abu Al-Qamrah divided in to four types. Most of samples are earth alkaline water with increased portion of alkalis and with prevailing sulfate and chloride. The second type is normal earth alkaline water with prevailing bicarbonate and sulfate or chloride.

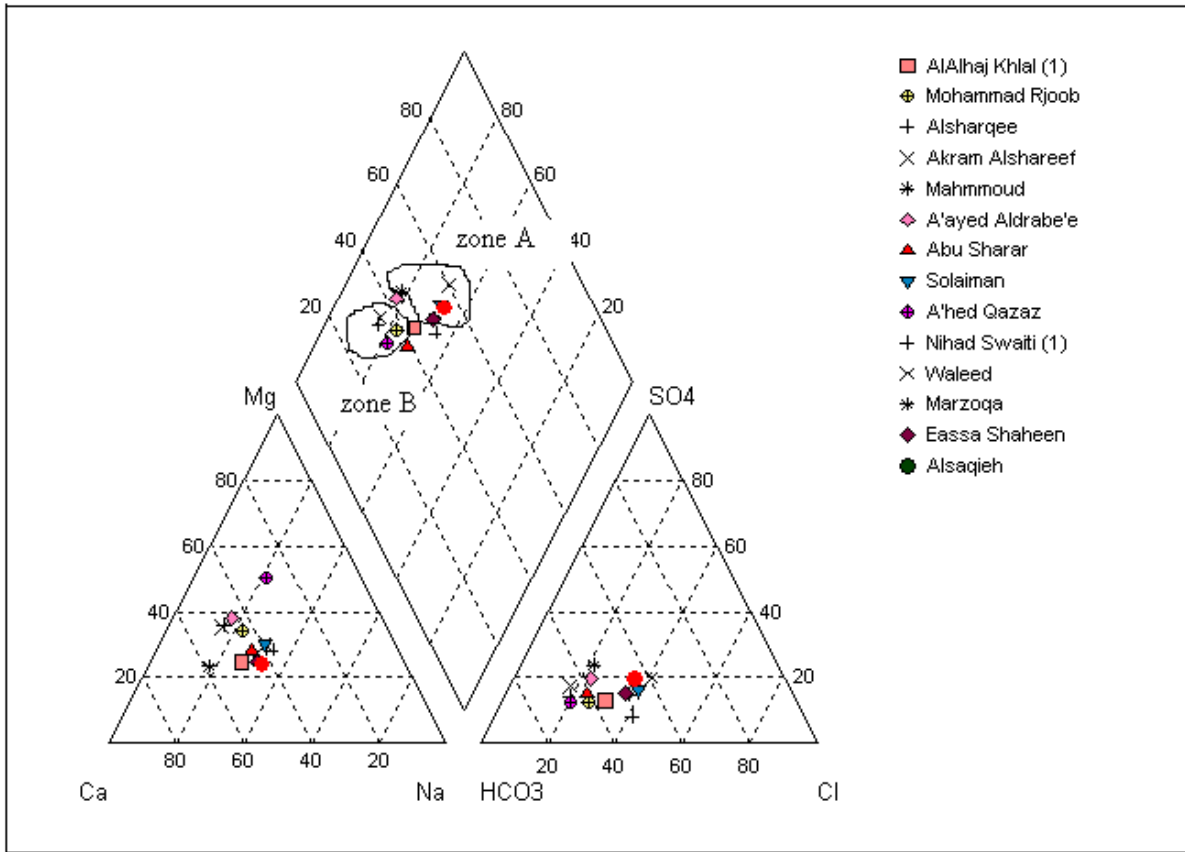


Fig 3.14: Piper diagram for the sample in wadi abu al-Qamrah (2007/2008)

According to this diversity groundwater which could be divided in to two zone.

Zone A

This zone is located in the west part of the study area see figure (1.7) in which the average depth of well is 9 m and water column ranges between 0.3 m to 4.70 m. The production of these wells range between 20 m³/day to 100 m³/day. The physical and chemical composition of this zone is presented in (Table, 3.3). There is no variation in pH which range between 6.81 and 7.22, while there are high variation in EC and TDS, and it range from 1100 μS/cm to 2630 μS/cm, 1056 mg/l to 2050 mg/l respectively. The minimum value of pH and TDS tend to Mahmmod Dodeen because it's located outside the wadi. The highest value in cations is Ca⁺² with concentration range from 135.33 mg/l to 199.08 mg/l. The lowest value tend to Mg⁺² with the mean value 63.02 mg/l, the highest value in anions is HCO₃⁻ with range from 378.30 mg/l to 756.4 mg/l and the lowest value is PO₄⁻³ with range from 0.03 mg/l to 1.24 mg/l, (Table, 3.3). The production of water and the pollution in zone

A are more than it in zone B, and this due to the location of zone A that comes near building up areas and human activates.

Table 3.3: Descriptive statistics of the physical and chemical parameter of wadi abu al-Qamrah in zone A

Variable	Min	Max	Mean	St	no
pH	6.81	7.22	6.97	0.17	6
EC	1100.00	2630.00	2265.00	583.74	6
TDS	1056.00	2050.00	1619.87	407.56	6
Ca	135.33	199.08	174.83	23.27	6
Mg	32.79	76.70	63.02	15.41	6
Na	47.81	165.30	136.21	45.22	6
K	6.78	146.02	93.18	53.55	6
Cl	88.63	301.25	233.96	84.65	6
HCO3	378.30	756.40	588.37	137.68	6
SO4	130.00	200.00	165.83	28.88	6
NO3	17.70	102.20	65.13	37.06	6
PO4	0.03	1.24	0.62	0.58	6
Ni	3.32	10.69	7.23	2.77	6
Cu	1.00	19.94	6.87	6.70	6
Sr	213.10	626.00	438.05	134.37	6
Ba	57.93	129.21	105.31	24.96	6
Mn	5.00	3421.04	761.50	1377.11	6
pb	1.00	1.00	1.00	0.00	6

The water type of this zone is earth alkaline water with increasing portion of alkalis with prevailing bicarbonate, and normal earth alkaline water with bicarbonate and sulphate or chloride in Mahmmod Dodeen (Fig, 3.14) and (Fig, 3.15).

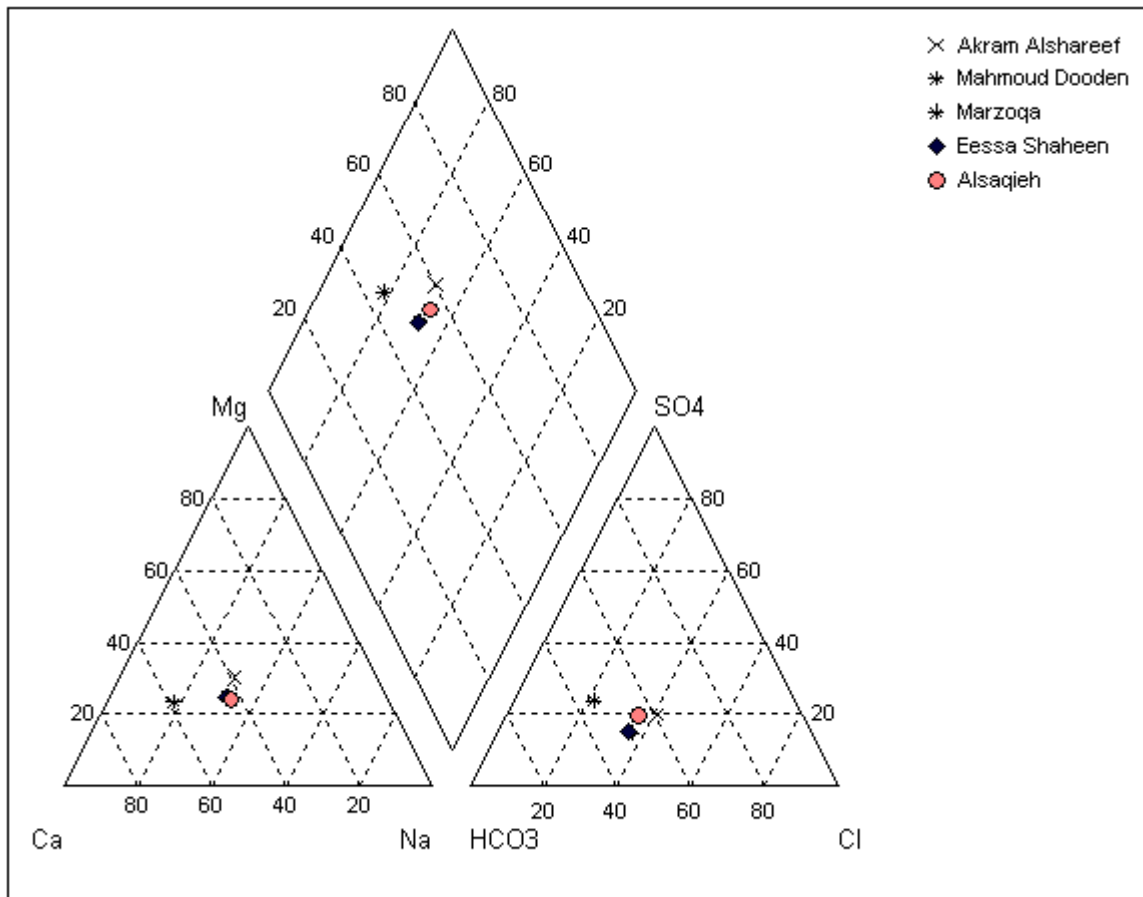


Fig. 3.15: Piper diagram for the sample from zone A (2007/2008)

Zone B

This zone is located in the east part of the study area see figure (1.7), represents four wells (Mohammad Rjoob, A'hed Qazaz, Nihad Sweity (1), Waleed Amro), the dug wells are located in the versants of the mountains of both sides of the wadi in a north south line. The EC of this zone range from 748 $\mu\text{S}/\text{cm}$ to 945 $\mu\text{S}/\text{cm}$. The highest value in cation is Ca^{+2} with range from 77.46 mg/l to 85.42 mg/l but the highest value in anions is HCO_3^- with range from 311.2 mg/l to 335.6 mg/l,(Table.3.4).

The Cl^- , NO_3^- concentration in Mohammed Rjoob well, which is located in the versant of the northern mountain from the Wadi are higher than the values of those well located in the southern side. The reason for this well located in building up area.

Table 3.4: Descriptive statistics of the physical and chemical parameter of wadi abu Al-Qamrah in zone B

Variable	Min	Max	Mean	St	no
pH	7.34	7.76	7.52	0.18	4
EC	748.00	945.00	820.25	87.97	4
TDS	720.00	908.00	788.00	84.35	4
Ca	77.46	85.42	81.05	3.75	4
Mg	34.49	39.75	36.77	2.43	4
Na	29.00	48.54	34.46	9.40	4
K	0.45	3.15	1.37	1.21	4
Cl	53.18	81.54	62.04	13.42	4
HCO3	311.20	335.60	327.98	11.55	4
SO4	50.00	70.00	56.25	9.25	4
NO3	49.70	90.90	68.08	17.15	4
PO4	0.01	0.05	0.03	0.02	4
Ni	2.44	6.04	4.04	1.81	4
Cu	1.78	5.69	3.09	1.77	4
Sr	132.20	161.90	144.78	12.77	4
Ba	29.44	50.87	36.09	9.99	4
Mn	5.00	5.00	5.00	0.00	4
pb	1.00	3.84	1.71	1.42	4

On piper diagram, the water type of Nihad Sweity, A'hed Qazaz, Waleed Amro wells plot in the area are normal earth alkaline water with prevailing bicarbonate. Rjoob well plot of earth alkaline water with increased portion of alkalis and with prevailing bicarbonate (Fig.3.16).

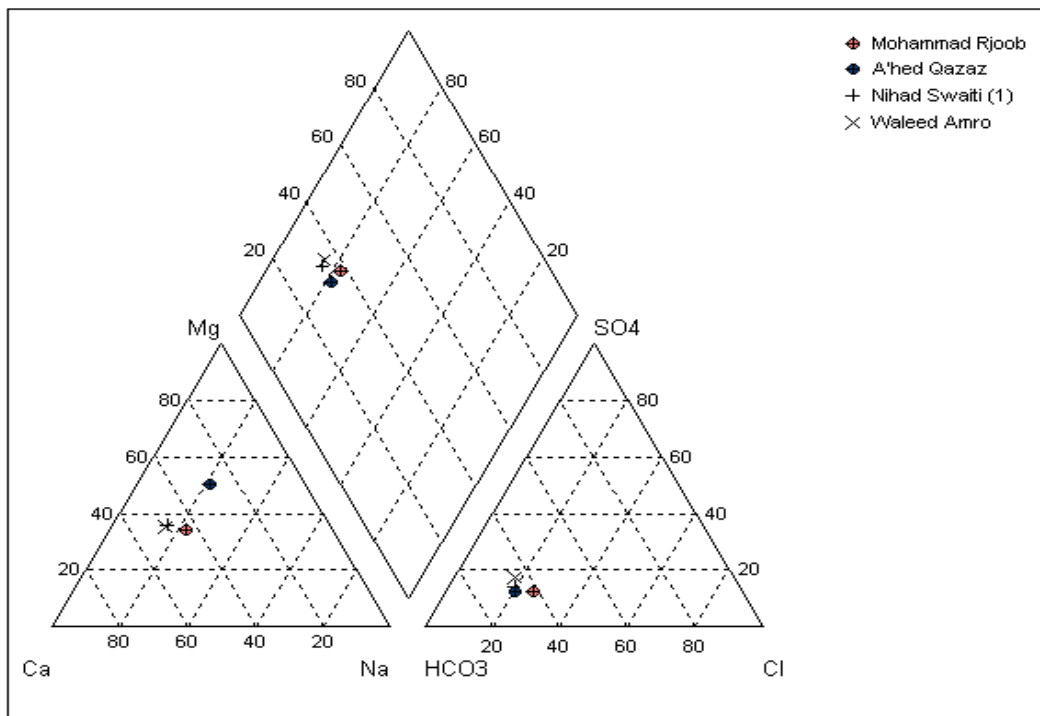
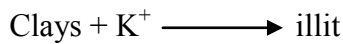


Fig. 3.16: Piper diagram for the sample from zone B (2007/2008)

3.5 Ratio between Ions

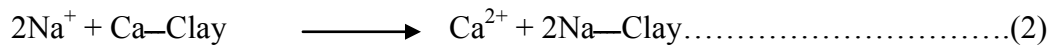
3.5.1. Sodium and potassium

Results of the analysis showed that K^+ concentration in water samples from well 0.86 mg/l in Waleed Amro to 146.02 mg/l in Alsaqieh. The Na^+ concentrations range of 29 mg/l in Waleed Amro to 165.3 mg/l in Eessa Shaheen and Alsaqieh. In all the samples $Na^+ > K^+$ (Table.3.5). The relative low K^+ concentration could be related to the absorption of K^+ by clay minerals which are the mineralogical composition of Yatta formation.



3.5.2. Sodium and Chloride

If $Na^+ > Cl^-$ indicate that Na source other than halites such as clay minerals, when $Na^+ = Cl^-$ indicate halite dissolution, when $Na^+ < Cl^-$ then the source of Na^+ from reverse ion exchange or from the absorption by clay minerals. Part of Na^+ / Cl^- ratio in the groundwater samples are around 1 suggesting that halite was the primary source of Na^+ and Cl^- (Table.3.5), the other results are <1 meaning that the proportion of Cl^- in the water is more than the ratio of Na^+ ($Cl^- > Na^+$), so the source of Na^+ from reverse ion exchange or absorption by clay minerals equation (2), (Table.3.5) (Hounslow, 1995)



3.5.3. Calcium and Sulfate

If $SO_4^{2-} > Ca^{+2}$, then calcium has been removed from the solution. When $Ca^{+2} = SO_4^{2-}$ indicates gypsum, when $Ca^{+2} > SO_4^{2-}$, indicating that the source of Ca^{2+} other than gypsum, such as calcite/dolomite. The Ca^{2+} and SO_4^{2-} concentration are ranges between 77.5 – 199.1 mg/l and between 50 – 200 mg/l respectively (Table.3.5). The average ratio for Ca^{2+}/SO_4^{2-} is > 1 , indicating that the source of Ca^{2+} is calcite/dolomite. (Hounslow, 1995)

3.5.4. Calcium and Magnesium

The analysis result for Ca^{2+} and Mg^{+2} are ranges from 77.5 – 199.1 mg/l and 32.8 – 69.5 mg/l respectively (Table.3.5). The Ca^{+2}/Mg^{+2} ratios in all sample > 1 with average 2.55, indicates that the aquifer is calcite (Hounslow, 1995).

Table 3.5: The ratio between the chemical compositions

no	Name of wells	Na ⁺ /Cl ⁻	Na ⁺ /K ⁺	Ca ²⁺ /SO ₄ ²⁻	Ca ²⁺ /Mg ²⁺
1	Alhaj Khlal (1)	0.93	7.51	3.96	1.92
2	Mohammad Rjoob	0.92	26.13	3.75	1.25
3	Alsharqee	0.97	3.51	5.43	1.30
4	Akram Alshareef	0.76	3.65	1.93	1.26
5	Mahmmoud	0.83	11.96	2.50	2.48
6	A'ayed Aldrabe'e	0.91	33.80	2.70	1.15
7	Abu Sharar	1.17	3.04	2.95	1.54
8	Solaiman	0.80	3.24	2.38	1.27
9	A'hed Qazaz	0.77	113.80	4.10	1.36
10	Nihad Swaiti (1)	0.87	51.04	3.58	1.32
11	Waleed	0.84	57.18	2.69	1.36
12	Marzoqa	0.87	1.97	2.93	1.72
13	Eassa Shaheen	0.89	2.21	2.90	1.73
14	Alsaqieh	0.95	1.92	2.24	1.74

3.6 Hard water

Hardness in water is defined as the presence of multivalent [cations](#). Hardness in water can cause water to form scales and a resistance to soap. It can also be defined as water that doesn't produce lather with soap solutions, but produces white precipitate

Hard water usually consists of [calcium](#) (Ca²⁺), [magnesium](#) (Mg²⁺) [ions](#), and possibly other dissolved compounds such as [bicarbonates](#) and [sulphates](#). Calcium usually enters the water as either calcium carbonate (CaCO₃), in the form of [limestone](#) and [chalk](#), or calcium sulphate (CaSO₄), in the form of other mineral deposits. The predominant source of magnesium is [dolomite](#) (CaMg(CO₃)₂). Total hardness is expressed as CaCO₃ in mg/L, which could be calculated using the equation below (Todd, 1980):

$$\text{Total hardness (CaCO}_3 \text{ mg/L)} = 2.497 \text{ Ca}^{+2} + 4.115 \text{ Mg}^{+2}$$

The concentrations of the cations are in mg/L.

Sawyer and McCarty (1967) classified the water hardness into soft, moderately hard, hard, and very hard waters (Table.3.6).

Table 3.6: Sawyer and McCarty (1967) classification of water, based on hardness.

Hardness	Water type
0-75	Soft
75-150	Moderately hard
150-300	Hard
>300	Very hard

All groundwater wells in Wadi Abu Al-Qamrah samples are very hard water according to classification of Sawyer and McCarty (1967),(Table.3.7), with range from 337.8 mg/l to 744.5 mg/l and average 530.4 mg/l, referring that to geological composition of the study area and the source of Na⁺ and Mg²⁺.

3.6.1. Type of Hardness

Temporary hardness

Temporary hardness is caused by a combination of calcium ions and bicarbonate ions in the water. It can be removed by boiling the water or by the addition of [lime \(calcium hydroxide\)](#), most of groundwater wells are temporary hardness that is related to the geological formation of the study area (Table.3.7).

Permanent hardness

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulfates and/or chlorides, only Solaiman Amro well is permanent hardness because the most of water in the well is rainfall water (Table.3.7). Despite the name, permanent hardness can be removed using a [water softener](#) or ion exchange column.

Table 3.7: The temporary and permanent hardness in Wadi Abu Al-Qamrah.

Sample Name	TH mg/l	Temporary	Permanent
Alsharqee	496.5	330.5	166.0
Alsaqieh	729.6	465.1	264.5
Eessa Shaheen	760.2	435.1	325.1
Marzoqa	744.0	435.6	308.4
A'ayed Aldrabe'e	496.9	285.0	211.9
Akram Alshareef	716.2	405.1	311.1
Mahmmmod Dooden	472.5	310.0	162.5
Abu Sharar	730.5	360.0	370.5
Solaiman Amro	373.4	19.0	354.4
Alhaj Khlal (1)	467.2	340.1	127.1
A'hed Qazaz	368.2	275.1	93.1
Nihad Swaiti (1)	337.7	255.0	82.7
Waleed Amro	337.5	270.0	67.5
Mohammad RjooB	370.6	275.1	95.5

3.7 Water Quality for Agricultural Purposes

Water quality is very important for plant where is water with high salinity is toxic to plants and poses a salinity hazard. High concentrations of salt in the soil can result in a "physiological" drought condition. That is, even though the field appears to have plenty of moisture, the plants wilt because the roots are unable to absorb the water. Water quality can be evaluated by the TDS (total dissolved solids) or the EC (electric conductivity), sodium adsorption ratio and soluble percentage.

3.7.1. Sodium adsorption ratio (SAR)

SAR is a ratio of the sodium to the combination of calcium and magnesium. The concentration of Na^+ in the source water is an important factor in the evaluation of irrigation water suitability because Na^+ strongly influences water infiltration and soil aeration. High irrigation water with Na^+ tends to reduce soil aeration, a critical tree and shrub survival parameter, by causing clays and organic matter to disperse. This dispersal reduces soil structure and clogs soil pores, thereby reducing soil aeration and water infiltration. This condition is exacerbated on soils low in Ca^{+2} and magnesium Mg^{2+} , SAR is a mathematical relationship, set out in Equation.

$$SAR = \frac{[Na^+]}{\sqrt{\frac{1}{2}([Ca^{2+}] + [Mg^{2+}])}}$$

Where Na^+ , Ca^{+2} , and Mg^{+2} are expressed in milliequivalents per liter (meq/l)

Wilcox (1955) classified the water irrigation in to four types, (Table.3.8). According to this classification all groundwater wells have low sodium hazard with an average SAR 1.4 meq/l, (Table.3.10). Therefore can be used for irrigation with low hazard on soil structure.

Table 3.8: Irrigation water classification, based on SAR values (Wilcox, 1955)

SAR	Water Class	Comments
<10	S1	Low sodium: can be used for irrigation on almost all soils with little danger.
10 – 18	S2	Medium sodium: can cause an appreciable sodium hazard, fine-textured soils having high cation exchange capacity under low loading conditions. It can be used on course-textured soil with good permeability.
18 – 26	S3	High sodium: may produce harmful levels of exchangeable sodium in most soils.
>26	S4	Very high sodium: unsatisfactory for irrigation purposes, except for waters with low and medium salinity.

3.7.2. Total Dissolved Solids And Electrical Conductivity:

Dissolved solids are an important indicator of the suitability of water for irrigation; Dissolved solids in irrigation water may adversely affect plants directly by the development of high osmotic conditions in the soil solution and by the presence of phytotoxins. Richard (1954) classified irrigation water according to EC and TDS in four groups (Table. 3.9).

Table 3.9: Grouping of irrigation water, based on EC and TDS. (Richard, 1954).

TDS (mg/L)	EC (μ S/cm)	Water Class	Remarks
<200	<250	C1	Low salinity: can be used for irrigation with most crops on most soils.
200 – 250	250 – 750	C2	Medium salinity: can be used to irrigate plants with moderate salt tolerance if moderate amount of leaching occurs.
500 – 1500	750 – 2250	C3	High salinity: can't be used on soils with restricted drainage. Can be used to irrigate plants with high salt tolerance.
1500 - 3000	2250 - 5000	C4	Very high salinity: not suitable for irrigation under ordinary conditions. It can be used for irrigation occasionally under very special circumstances.

Based on the EC-SAR relation (Table.3.10), the water of this group can be classified into two classes, low sodium- high salinity hazard (SI-C3), the another wells classified to low sodium- very high salinity (SI-C4). But range between high salinity hazard represented to, Alsharqee, Alhaj Khlal (1), A'hed Qazaz, Nihad Swaiti (1), Waleed Amro, Mohammad Rjoob Mahmmod Dodeen, Solaiman Amro, A'ayed Aldrabe'e to very high salinity in other wells.

Table 3.10: The results for determining water quality for irrigation.

Sample Name	SAR	EC
Alsharqee	2.34	1750
Alsaqieh	2.66	2570
Eessa Shaheen	2.61	2630
Marzoqa	2.55	2590
A'ayed Aldrabe'e	0.94	1184
Akram Alshareef	2.41	2340
Mahmmod Dodeen	0.96	1100
Abu Sharar	2.11	2360
Solaiman Amro	1.74	1276
Alhaj Khlal (1)	1.59	1373
A'hed Qazaz	0.68	817
Nihad Swaiti (1)	0.71	771
Waleed Amro	0.69	748
Mohammad Rjoob	1.1	945

3.8 Saturation Indices

This method used to describe the equilibrium between the water and the mineral phases of the aquifer materials are to tendency of water for precipitation or dissolution.

SI was computed by using Aquchem software program based on the following equation:

$$SI = \log (K_{IAP} / K_{SP}).$$

Where:-

SI: is the saturation index of the particular mineral.

K_{IAP} : is the ion activity product and,

K_{SP} : is the solubility product.

The importance of the saturation indices is to show the possible dissolution/precipitation processes during the water-rock interaction.

- a) SI value = 0: The water is in equilibrium with respect to the particular mineral.
- b) SI value >0 : The water is over saturated with respect to that mineral, and thus tends towards its precipitation.
- c) SI value <0 : The water is under saturated with respect to that mineral and tends toward its dissolution.

Fig.3.17, Fig.3.18 and Table.3.11 shows that the water of dug wells of wadi Abu al-Qamrah are saturated with respect to the calcite and dolomite that refers to the geological formation of the study area which is consist of dolomite and calcite, except of Solaiman Amro well are unsaturated with respect to calcite and dolomite because the most of water in the well is rainfall water (Table.3.11).

Table 3.11: Saturation indices of dug well of wadi abu al-Qamrah.

ID	Well	Calcite-SI	Dolomite-SI
1	Alsharqee	0.35	0.72
2	Marzoqa	0.19	0.27
3	A'ayed Aldrabe'e	0.06	0.19
4	Mohammad Rjoob	0.66	1.36
5	Alhaj Khlal (1)	0.43	0.71
6	Nihad Swaiti (1)	0.42	0.85
7	Waleed Amro	0.23	0.45
8	A'hed Qazaz	0.36	0.72
9	Mahmmod Dodeen	0.25	0.23
10	Akram Alshareef	0.47	0.97
11	Eessa Shaheen	0.23	0.37
12	Abu-Sharar	0.23	0.4
13	Solaiman Amro	-0.71	-1.41
14	Alsaqieh	0.18	0.25

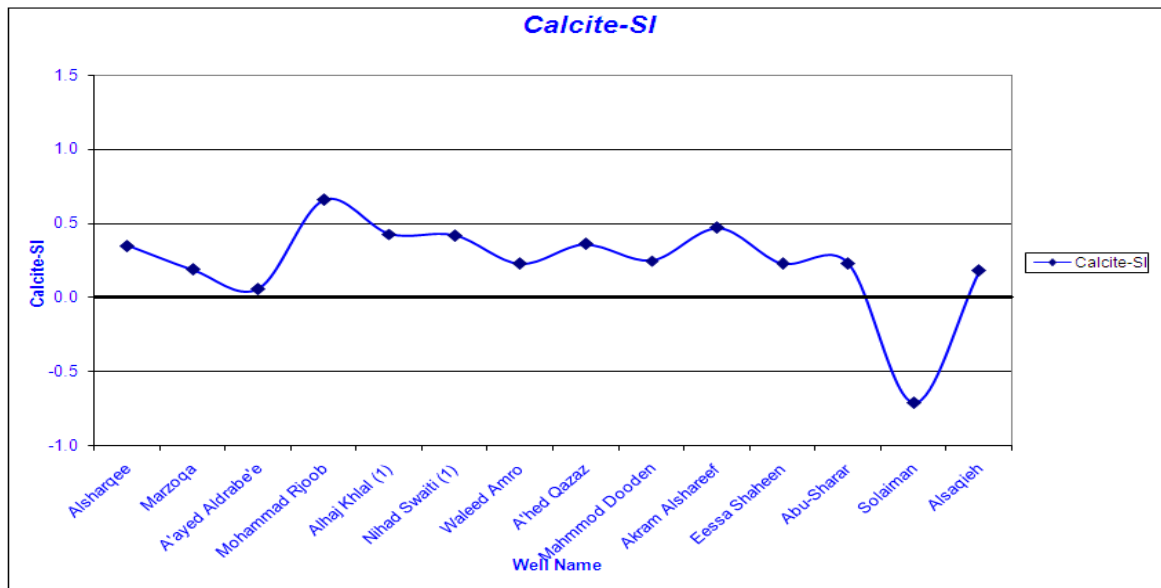


Figure 3.17: Saturation indices of dug well of wadi abu al-Qamrah for calcite.

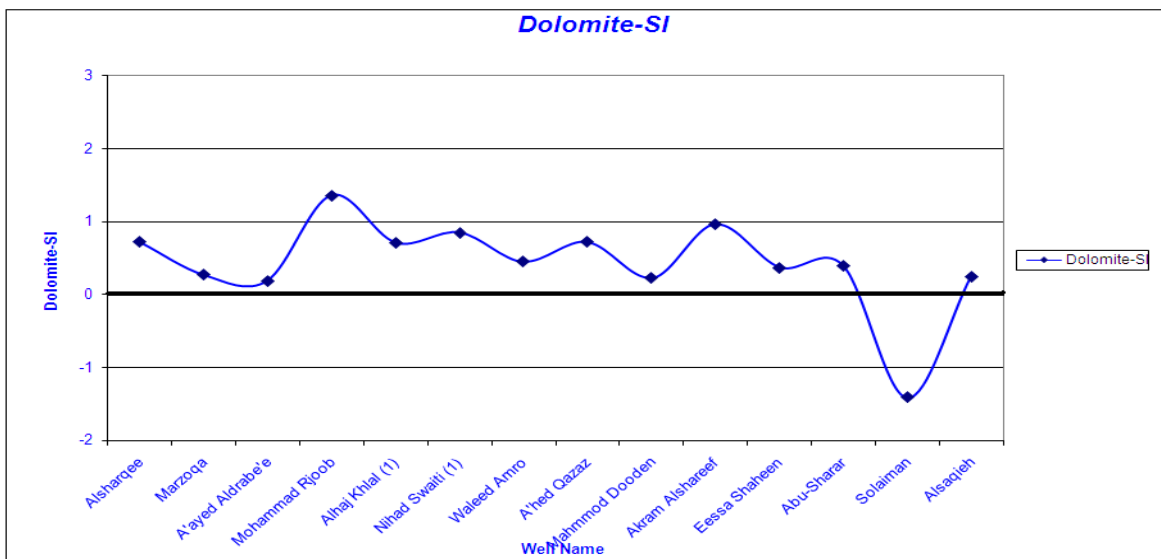


Figure 3.18: Saturation indices of dug well of wadi abu al-Qamrah for dolomite.

3.9 Durov Diagram

The Durov diagram is an alternative to the piper diagram which is used to display the possible geochemical process for determine the water genesis (Lloyd and Heathcoat,1985). The Durov diagram plots the major ions as percentages of (meq) in two base triangles. The total cations and the total anions are set equal to 100 %.

Lloyd and Heathcoat (1985) interpretation the nine square field as the following (Fig.3.19):

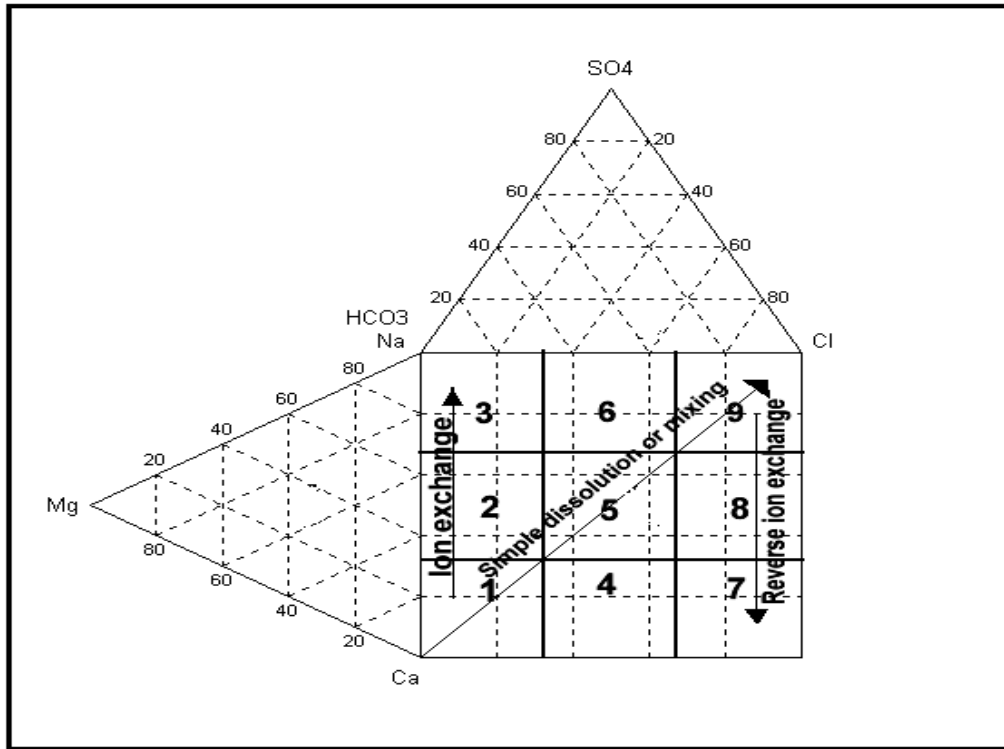


Figure 3.19: Durov plot with water types classification according to Lloyd and Heathcoat (1985)

Field symbol	Field description
1	HCO_3^{-1} and Ca^{+2} dominant , frequently indicates recharging waters in limestone, sandstone, and other aquifers.
2	this water type is dominated by Ca^{+2} and HCO_3^{-1} ions, association with dolomite. If Na^{+1} is significant, an important ion exchange is presumed.
3	HCO_3^{-1} and Na^{+1} are dominated , indicates ion – exchanged water, although the generation of CO_2 at depth can produce HCO_3^{-1} where Na^{+1} is dominant under certain circumstances .
4	SO_4^{-2} is dominant , or anions discriminate and Ca^{+2} dominant, Ca^{+2} and SO_4^{-2} dominant, frequently indicates a recharge water in lava and a gypsyferous deposits, otherwise a mixed
5	No dominant an ion or cation indicates water exhibiting dissolution or mixing.
6	SO_4^{-2} dominant or disicriminant and Na^{+1} dominant; is a water type that is not frequently encountered and indicates probable mixing influence.
7	Cl^{-1} and Na^{+1} dominant is frequently encountered unless cement pollution is present. Otherwise the water may result from reverse ion exchange of Na-Cl waters.
8	Cl^{-1} dominant anion and Na^{+} dominant cation, indicate that the groundwaters be related to reverse ion exchange of Na-Cl waters.
9	Cl^{-1} and Na^{+} dominant frequently indicate end-point waters.

Most of water samples in Wadi abu al-Qamrah plot in field (5), except Nihad and A'hed well are plot in field (2), in the Durov diagram all water samples plot along the mixing-dissolution line (Fig.3.20), which indicates that the water of this area is mixing with wastewater or agriculture return flow and from the dominant with Ca-Mg-HCO₃ as a result of simple dissolution of limestone and dolomite.

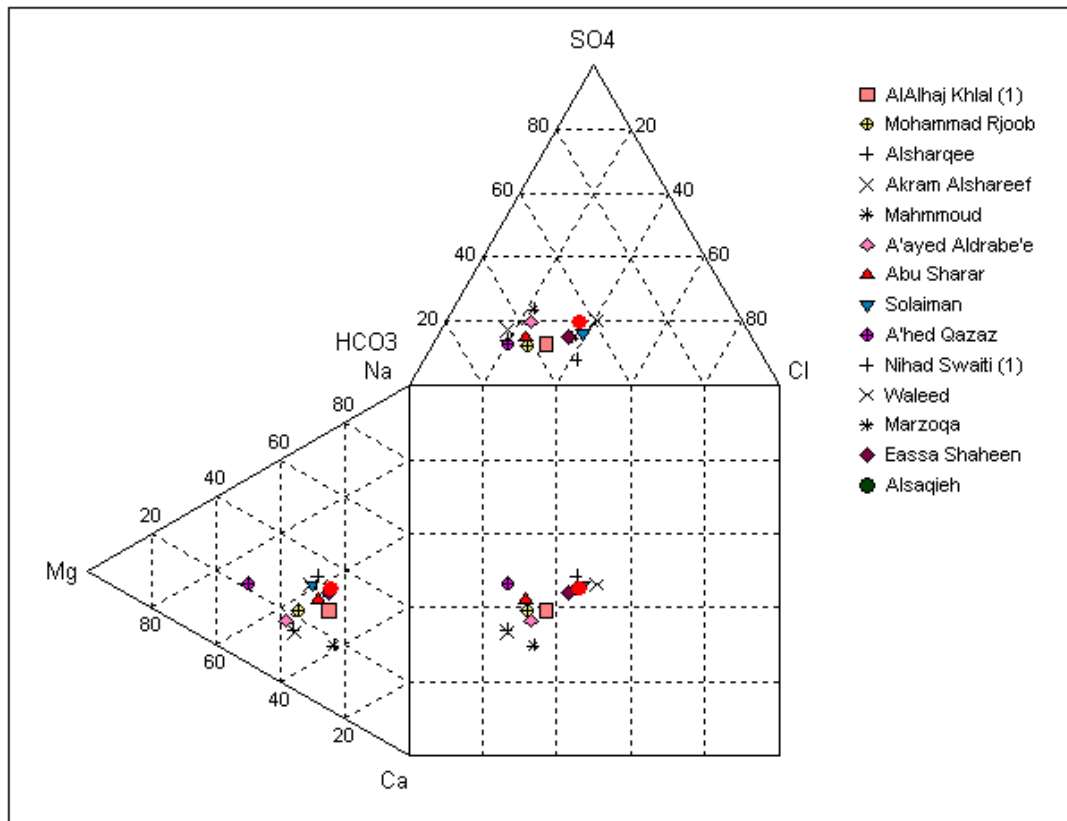


Fig 3.20: Durov diagram for the sample in wadi abu al-Qamrah

3.10 Statistical analyses

3.10.1. The water parameters interrelationships

There are an interrelationships between the different analyzed parametars , a linear correlation was performed, according to the correlation coefficient , the interrelationships between the different parameters were classified into three class.

Class (I) (very high significant relationship): This class includes all the parameters that have correlation coefficient >0.90, (Table, 3.12)

Table.3.12: very high significant relationship between parameters

Parameters	correlation coefficient
Na ⁺ mg/l versus EC μS/cm	0.987
Na ⁺ mg/l versus Cl ⁻ mg/l	0.975
Cl ⁻ mg/l versus EC μS/cm	0.952
Ca ⁺² mg/l versus EC μS/cm	0.944
Ca ⁺² mg/l versus HCO ₃ ⁻ mg/l	0.926
K ⁺ mg/l versus Cl ⁻ mg/l	0.918
Mg ⁺² mg/l versus EC μS/cm	0.912
Na ⁺ mg/l versus TDS mg/l	0.910

Class (II) (High significant relationship): This class includes all the variables that have correlation coefficient between 0.9 and 0.80 (Table, 3.13).

Table.3.13: High significant relationship between parameters

Parameters	correlation coefficient
Ca ⁺² mg/l versus Na ⁺ mg/l	0.898
EC μS/cm versus TDS mg/l	0.887
Na ⁺ mg/l versus Mg ⁺² mg/l	0.878
SO ₄ ⁻² mg/l versus EC μS/cm	0.839
Ca ⁺² mg/l versus Mg ⁺² mg/l	0.827
Mg ⁺² mg/l versus HCO ₃ ⁻ mg/l	0.813

Class (III) (good relationship): This class includes all the parameters that have correlation coefficient between 0.8 and 0.7 (Table, 3.14).

Table.3.14: good relationship between parameters

Parameters	correlation coefficient
Mg ⁺² mg/l versus SO ₄ ⁻² mg/l	0.797
Na ⁺ mg/l versus SO ₄ ⁻² mg/l	0.793
K ⁺ mg/l versus PO ₄ ⁻³ mg/l	0.787
K ⁺ mg/l versus SO ₄ ⁻² mg/l	0.7

Class (IV) (medium relationship): This class includes all the parameters that have correlation coefficient between 0.7 and 0.6 (Table, 3.15).

Table.3.15: medium relationship between parameters

Parameters	correlation coefficient
Na ⁺ mg/l versus PO ₄ ⁻³ mg/l	0.695

3.11 Geophysical results

3.11.1. The first Profile

This profile is extended from north to south, two stations were taken in this profile with 60m between each station, in order to satisfy overlapping of the vertical electrical sounding, the results are drawn and modeled as in Fig (3.21)

The evaluation of these data depends on the resistivity of rocks, soils and minerals shown in Fig (3.21). The expected lithology corresponding to resistivity could be classified as shown in table (3.16).

According to Pseudo cross section (Fig.3.21) and from the geoelectrical results the lithology of the first station can be divided into five layers (Table.3.16).

The first layer covers the upper northern surface, it is composed from clay, with resistivity ranges between (55 - 80 Ω), and thickness of about 1.5 m, which makes it aquiclude for water. and the second layer with weathering limestone with resistivity (35-50 Ω), it is

located at two depth the first at 1.5-2.3 m below the surface with thickens 0.8 m and from 11- 22 m with thickens 11 m, which makes it aquifer for water, the third layer is limestone with resistivity ranges between (13-27 Ω), it is located between 2.5 - 11 m below the surface with thickens 8.5 m, from the resistivity it was clear that this layer is aquifer. That is proved by the two wells Eessa Shaheen and Marzoqa which penetrate this layer on a depth at 6.1 and 5.3 m respectively and water table 3.6 m, 3.3 m below the surface. These three layers are related to Hebron formation, this formation is a good aquifer resulting from high secondary porosity. Yatta formation is below this Hebron formation, it consists of yellowish-gray chalk marl with resistivity ranges between (35-80 Ω) it is located between 23 – 60 m below the surface; this formation is aquiclude for water. The last layer is weathering Dolomite or Dolomite inter-bedded with marl with resistivity ranges between (170-290 Ω) located between 63 – 100 m below the surface, this layer may be semi aquifer because the marl inter bedded with dolomite.

According to Pseudo cross section (Fig.3.21) and from the geoelectrical results; the lithology of the second station can be divided into six layers (Table.3.16).

The first layer covers the upper southern surface, it is composed from soil, with resistivity ranges between (150 - 290 Ω), and thickness about 2 m from south decreasing gradually to the north, which is aquiclude for water, under this layer it's expected to be weathering limestone with resistivity ranges between (35 - 80 Ω), it is located between 2- 3 m and 8 – 14 m below the surface, it's extended from south to north nearly the same depth with the first station. Limestone layer is located between 3 – 8 m below the surface with resistivity ranges between (20 - 27 Ω), the same depth with the first station, this layer expected to be aquifer where Eessa Shaheen and Marzoqa wells are located about 20 m to the north from the station with depth at 6.1 and 5.3 m respectively. Weathering Marl or Limestone inter - bedded with marl, and marl layer are located below limestone layer with resistivity ranges between (60 - 80 Ω), (< 13 Ω) respectively, with depth 15 – 40 m and 40 – 70 m respectively below the surface, decreasing gradually from south to north, this layer is expected to be aquiclude because it contains marl. The last layer is weathering dolomite with resistivity ranges between (170 - 290 Ω) and with depth 70 – 100 m below the surface, this layer is expected to be aquifer.

3.11.2. Second Profile

The second profile composes of two stations, according to Pseudo cross section (Fig .3.22) and Table (3.17). The composition of the first and second station are the same with slightly different in depth of layer (Fig.3.22), (Table.3.17),

The first station covers the upper northern surface and the second one covers the upper southern surface, they are composed from soil, with resistivity ranges between (60 - 180 Ω) and (70 – 80 Ω) respectively, the lower resistivity of the second station refer to the rainwater, in which this profile was measured after two rainy days. The thickness of this layer is about 3 m in the north that decreases to 1.7 m in the south which is aquiclude for water, Limestone layer with resistivity ranges between (45 - 60 Ω), it's located at 3 -4 m and from 14 – 18 m below the surface in the first station with thickness 1 m, 4 m, and from 1.7 – 2.2 m and 25 – 30 m in second station, this layer is aquifer for water, where is the north of this profile there is a well at depth 5 m, but the discharge of this well is low which is referred to the thickness of aquifer. Marl layer is found between the limestone layers at depth between 5 – 13 m with thickness about 8 m in the north, increasing gradually to the south with thickness ranges between 2.3 – 24 m, (Fig.3.22), (Table.3.13). Dolomite interbedded with marl is located at 19 – 50 m below the surface with resistivity ranges between (70 - 90 Ω), this layer is expected to be semi aquifer, that refers to the marl which is inter bedded with dolomite. Dolomite layer is located between 50 – 140 m with resistivity ranges between (125 - 190 Ω), this layer is expected to be aquifer for water.

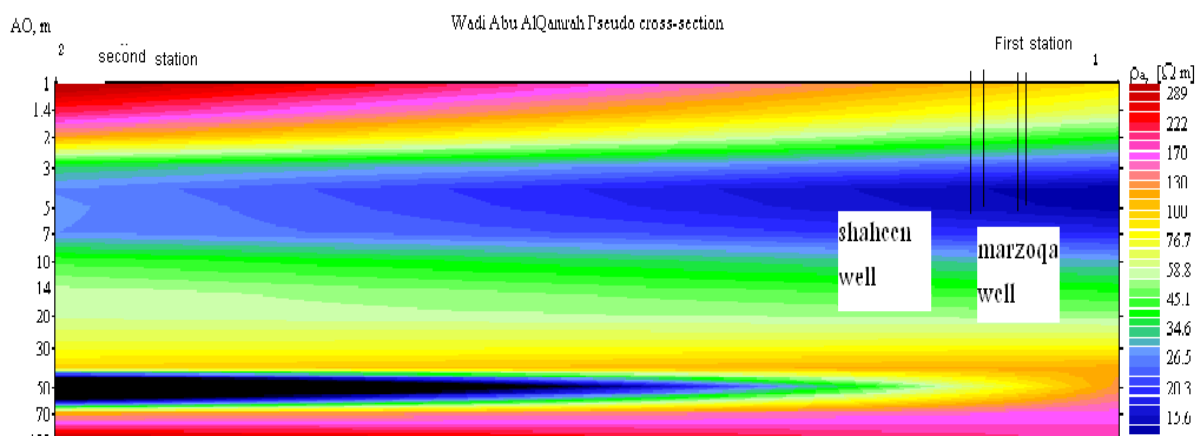


Figure 3.21: Pseudo cross section for the first profile

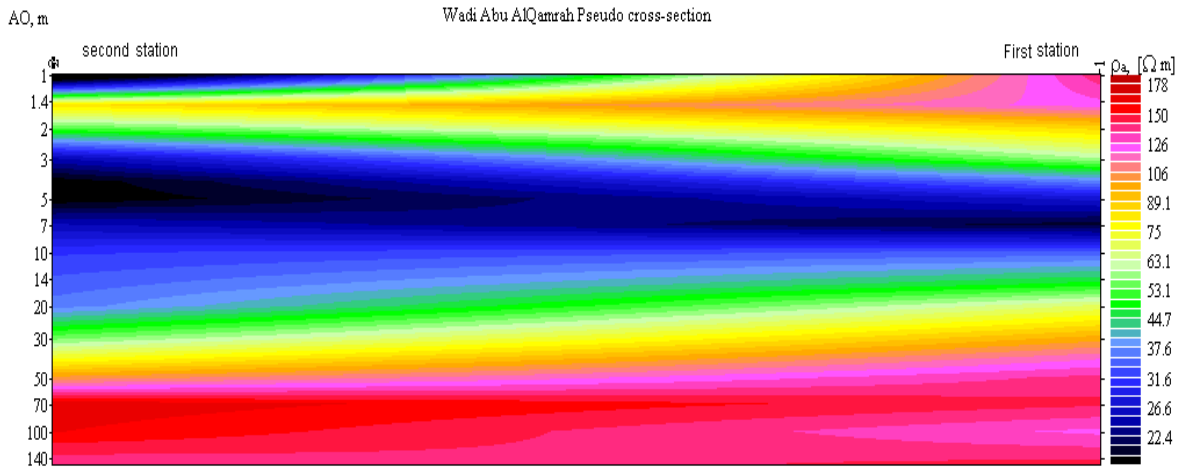


Figure 3.22: Pseudo cross section for the second profile

Table 3.16: Measuring Points along the first profile with resistivity, depth and expected Lithology

Points Id	Resistivity (Ohm-meter)	Depth (m)	Lithology	Potential use For water
1	55 - 80	0 - 1.5	soil	dry
	35 - 50	1.5 - 2.3	Weathering Limestone	dry
	13 - 27	2.5 - 11	Limestone	wet
	35 - 50	11 - 22	Weathering Limestone	dry
	35 - 80	23 - 62	Marl	dry
	170 - 290	63 - 100	Weathering Dolomite	dry
2	150 - 290	0 - 2	Soil	dry
	35 - 80		Weathering Limestone	dry
	20 - 27	3 - 8	Limestone	wet
	35 - 80	8 - 14	Weathering Limestone	dry
	60 - 80	15 - 40	Weathering Marl or Limestone inter-bedded with marl	dry
	< 13	40 - 70	Marl	dry
	170 - 290	70 - 100	Weathering Dolomite	dry

Table 3.17: Measuring Points along the second profile with resistivity, depth and expected Lithology

Points Id	Resistivity (Ohm-meter)	Depth (m)	Lithology	Potential use For water
1	60 - 180	0 – 3	Soil	dry
	45 - 60	3 – 4	Limestone	wet
	10 - 30	5 - 13	Marl	dry
	45 - 60	13 - 18	Limestone	dry
	70 - 90	19 - 50	Dolomite inter-bedded with marl	dry
	125 - 180	50 - 140	Dolomite	dry
2	70 – 80	0 – 1.7	Soil	dry
	45 - 55	1.7 – 2.2	Limestone	dry
	10 - 40	2.3 - 24	Marl	dry
	45 - 55	25 - 30	Limestone	dry
	75 - 85	35 - 50	Dolomite inter-bedded with marl	dry
	120 - 180	50 - 140	Dolomite	dry

Chapter Four

4.1 Conclusion

The MTBE concentration appeared only in surface run off with concentration ranges between 0.2 ppb to 11 ppb. It didn't appear in groundwater and soil because of evaporation and contact with atmosphere as well as MTBE doesn't exist in Wadi Abu Al-Qamrah wells because the gas station doesn't exist in their recharge area.

Dug wells in the study area that are found to be discharging from Hebron formation come from Upper Cenomanian-Turonian Aquifer which mainly composed of limestone and dolomite.

Evaporation rate varies from 4 mm/day in January to 6.22 mm/day in July. The average monthly evaporation is 186.6 mm/month in the summer and 121 mm/month in the winter.

The annual average of rainfall is 500 mm, through calculations the annual average of surface runoff and recharge is 58.8 mm (11.75 % of the precipitation), 151 mm (30.3 % of the precipitation) respectively, the annual volume of precipitation in the study area is 1.125 MCM.

The average concentration of EC and TDS is 1373 $\mu\text{s}/\text{cm}$, 1058 mg/l which is 57.1 % from the wells > 1000 mg/l; the increasing for TDS comes from agricultural activities and mixing with sewage in aquifer.

The major chemical composition of the wells shows that Na^+ , Mg^{2+} , and SO_4^{2-} are acceptable limits for drinking water with average concentration 79.12 mg/l, 39.75 mg/l, and 85 mg/l respectively, most of the wells are within unacceptable limits for drinking water for Ca^{2+} , K^+ , Cl^- , NO_3^- , and HCO_3^{2-} with average 123.6 mg/l, 40.52 mg/l, 148.84 mg/l, 68.5 mg/l and 402.7 mg/l respectively.

On a Durov diagram most of the sample plot along the mixing dissolution line for 85.7 % of the sample, affected by ion exchange of Na^+ with Ca^{2+} for 14.3 % of the sample.

According to Wilcox, 1955 all groundwater wells have low sodium with an average SAR 1.4 meq/l so can used for irrigation with low hazard on soil structure, groundwater are high salinity with average EC $\mu\text{s}/\text{cm}$. 93 % of the samples are saturated with respect to the calcite and dolomite, and 7 % of the samples are unsaturated with calcite and dolomite.

The result of geophysics shows different resistivity values due to type of bedrock in two profiles that are ranged between (13 – 290 Ω) and (10 – 180 Ω) in the first and second profile respectively. According to Pseudo cross section shows that the lithology of the Wadi consists of several layers in different depth with different thickness, the aquifer thickness decreases towards the east in the Wadi, This explains why the discharge of wells in the east are few.

4.2 Recommendations

The groundwater of the wadi is used for irrigation and domestic purposes, the salinity is very high and the quality of water is within the acceptable limit for drinking water. So the following is recommended:

- 1- Reduce the use of chemical fertilizers and replace it by natural ones.
- 2- Make net for cesspit to dispose of sewage to prevent mixing with groundwater.
- 3- Reduce the discharge of groundwater to keep balance between recharge and discharge to prevent the mixing process.
- 4- Build ponds to collect surface runoff from streams during winter months.

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Appendix

Appendix 1.1: coordination of wells in Wadi Abu Al-Qamrah

no	Name	X	Y	contours line	G.W.a.s.l
1	Alsharqee well's	152799	101429	839	831.5
2	Alsaqieh	153214	101352	834	828
3	Eessa Shaheen	153312	101295	833	826.9
4	Marzoqa	153326	101300	832	826.7
5	Akram Alshareef	153447	101396	829	815
6	Jado'a Al-namora (1)	153470	101257	831	822.9
7	Jado'a Al-namora (2)	153520	101325	828	818
8	Mahmmod Dooden	153543	101539	834	827.6
9	Abu-Sharar	153597	101319	826	817.3
10	Nemer Dooden	153605	101545	834	823.6
11	Al-daraweesh	153956	101344	824	813.4
12	Solaiman Amro	153999	101084	812	799.8
13	Alhaj Khlal (2)	154050	101119	810	806.9
14	Alhaj Khlal (1)	154080	101111	810	807.8
15	Alwad well's	154097	101150	812	808.9
16	A'hed Qazaz	154533	100714	804	798
17	Nihad Swaiti (1)	154536	100696	806	800
18	Waleed Amro	154557	100667	807	802
19	Mousa Eqtaet	154582	100690	801	797.4
20	Salem Eqtaet	154595	100669	801	797.5
21	Majed Swaiti	154614	100666	799	796.2
22	Nihad Swaiti (2)	154616	100606	805	803
23	Abd Allah Owdeh Rjoob	154836	100738	799	793
24	Mohammad Rjoob	154926	100663	798	797.6

Appendix 1.2: the chemical analysis of the groundwater samples in Wadi Abu Al-Qamrah in winter season

Sample Name	Date	pH	EC	TDS	Salinity	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	PO ₄ ³⁻
	d/m/y		μS/cm	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Alhaj Khlal (1)	8/12/2007	7.29	1373	974.3	0.5	123.6	38.6	79.12	17.87	0.0	131.2	414.9	75	50	0.95
Mohammad Rjoob	8/12/2007	7.76	945	908	0.2	82.9	39.8	48.54	3.15	0.05	81.5	335.6	53	90.9	0.02
Alsharqee well's	8/12/2007	7.27	1750	1683	0.7	113.1	52.1	119.72	57.85	0.02	191.4	402.7	50	81	0.47
Akram Alshareef	8/12/2007	7.22	2340	2000	1.1	160.6	76.7	147.97	68.75	0.02	301.3	494.3	200	100	0.03
Mahmmod Dodeen	8/12/2007	7.11	1100	1056	0.3	135.3	32.8	47.81	6.78	0.05	88.6	378.3	130	102.2	0.16
A'ayed Aldrabe'e	8/12/2007	7.05	1184	1138	0.4	107.0	55.9	48.04	2.41	0.01	81.8	347.8	95	107.3	0.02
Abu-Sharar	8/12/2007	6.96	2360	1208.7	0.4	178.2	69.5	131.2	73.28	0.02	173.7	756.4	145	90.1	0.11
Solaiman Amro	8/12/2007	7.51	1276	895.6	0.4	84.2	39.7	77.5	40.52	0.01	148.9	297.1	85	122.8	0.28
A'hed Qazaz	8/12/2007	7.43	817	784	0.2	85.4	37.7	30.2	0.45	0.02	60.3	335.6	50	68.5	0.01
Nihad Swaity (1)	8/12/2007	7.56	771	740	0.1	77.5	35.1	30.1	1	0.01	53.2	311.2	52	63.2	0.05
Waleed Amro	8/12/2007	7.34	748	720	0.1	78.4	34.5	29	0.86	0.01	53.2	329.5	70	49.7	0.02
Marzoqa	8/12/2007	6.83	2590	1687.6	1.2	189.4	66.0	159.7	137.36	0.01	283.6	646.7	155	49.9	1.23
Eessa Shaheen	8/12/2007	6.87	2630	1716.9	1.2	199.1	68.9	165.3	126.88	0.01	287.1	687.0	165	17.7	0.97
Alsaqieh	8/12/2007	6.81	2570	2050	1.2	186.4	64.3	165.3	146.02	0.1	269.4	567.5	200	30.9	1.24

Appendix 1.3: the trace element analysis of the groundwater samples in wadi abu al-Qamrah

Sample Name	Date	Mn	Ni	Cu	Sr	Cd	Ba	Pb
	d/m/y	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Alhaj Khlal (1)	8/12/2007	<5	5.64	3.17	224.30	<1	66.19	<1
Mohammad Rjoob	8/12/2007	<5	6.04	2.66	161.90	<1	50.87	<1
Alsharqee well's	8/12/2007	<5	17.86	12.64	343.50	<1	80.88	1.41
Akram Alshareef	8/12/2007	<5	7.73	19.94	626	ND	101.26	<1
Mahmmod Dodeen	8/12/2007	11.48	3.32	4.40	213.1	ND	57.93	ND
A'ayed Aldrabe'e	8/12/2007	<1	2.29	2.25	342.2	ND	84.61	<1
Abu-Sharar	8/12/2007	<5	4.71	4.10	490.3	ND	110.42	<1
Solaiman Amro	8/12/2007	<5	3.41	3.65	259.1	ND	73.79	<1
A'hed Qazaz	8/12/2007	<5	5.11	5.69	132.2	ND	29.44	3.84
Nihad Swaiti (1)	8/12/2007	<5	2.44	1.78	146.2	ND	33.36	<1
Waleed Amro	8/12/2007	<5	2.58	2.23	138.8	ND	30.68	<1
Marzoqa	8/12/2007	1121.46	9.29	4.55	427.60	ND	118.20	<1
Eessa Shaheen	8/12/2007	3421.04	7.62	<1	463.00	ND	129.21	<1
Alsaqieh	8/12/2007	<5	10.69	7.24	408.30	ND	114.82	<1

Appendix 1.4: the chemical analysis of the groundwater samples in wadi abu al-Qamrah in summer season

Sample name	pH	EC	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	NO ₃
		μS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Alsharqee	7.05	1989	192.4	95.5	108	80.316	141.8	615.82	120	127.5
Alsaqieh	6.42	2540	192.82	23.6	170.1	131.1	260.69	251.2	4.00	584.5
Eessa Shaheen	7.42	2570	224.22	33.32	148.1	52.8	214.013	310.5	34.00	597
Marzoqa	6.96	2370	200.4	51.2	106	98.226	248.15	46.9854	135	535
Akram Alshareef	7.17	2420	324.8	112	195.6	88.866	302.74	45.154	190	1667.5
Abu Sharar	7.25	2280	196.58	49.66	168.4	115.1	283.6	492.7	24.00	557
Alhaj Khlal (1)	7.11	1759	168.3	60.8	68.8	10.476	73.67	36.612	105	1312.3
A'hed Qazaz	7.43	1006	121.06	32.34	25.32	1.9	89.81	212.8	9.00	287
Nihad Swaiti (1)	7.43	814	111	54.8	79.2	4.44	71.87	36.612	40	415
Waleed Amro	8.12	730	154.48	41.1	140.3	2.7	332.6	315.4	42.00	245
Mohammad Rjoob	7.78	980	104.2	51.6	6.4	6.542	92.17	32.9508	45	232.5

