

APPLICATION OF ENVIRONMENTAL ISOTOPES TECHNIQUE IN GROUNDWATER RECHARGE WITHIN MULLUSA CARBONATE AQUIFER-WEST IRAQ

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Abstract:

This paper applies environmental isotope techniques to interpret recharge mechanisms of Mullusa aquifer (East Rutba) and offers an environmental isotope view . Mullusa aquifer is of major importance for the water supply of Rutba region in particular of increasing demand of water resources and sustainability assessment in the future.

The traditional hydro chemical and hydraulic interpretation show same phenomenon of groundwater source and interconnection, which may need advance isotope technique to define the exact actual origin of recharge water, using carbon-14 and tritium dating .

Based on the isotope analysis of deuterium, oxygen-18, tritium, carbon-13 and carbon-14, the recharge of the carbonate aquifer is mainly from direct infiltration of atmospheric water (Rainfalls and / or runoff) originated to Indian low pressure depression through exposure outcrops within Hauran catchments area of (600-740)m.asl due to south and southwest Rutba town . The isotope compositions also show that the groundwater is a mixture of an old groundwater with modern recharge in the areas adjacent to Rutba .

The maximum percentage of modern water (pMC %) is 71% (29% ancient), which was usually found at the intensively infiltration zones of porous media and / or fractured areas (Hauran valley), while the minimum percentage of modern water is 10% (90 % ancient), which was found at discharge zones as fossil water with very poor replenishment mechanism. Also, this research shed light on the paleo-hydrologic setting , that may control the recharge mechanism using ¹⁴C dating for each site . Finally, the important detected result is that Mullusa aquifer in Dhabaa site (pumping station of multi boreholes system) stored ancient fossil water with slow and limited recharge. The reachable transit time of replenishment is of about 29000 years calculated by traditional hydrogeologic technique, which is closed to the value of residence time that detected by ¹⁴C dating (31500 years), so that it is necessary to regulate the production of groundwater according to active plan.

تطبيق تقنية النظائر البيئية في دراسة تغذية المياه الجوفية ضمن خزان ملصا الجيري الجوفي- ضبعة- غرب العراق

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المستخلص:

استخدمت النظائر المستقرة و الإشعاعية المتمثلة بعناصر الديتريوم ، التريتيوم ، الأوكسجين-18 ، الكربون-13 و الكربون-14 في تحديد الوضع الهيدرولوجي القديم لمنطقة الدراسة، بالإضافة إلى تحديد أصل ومصادر تغذية المياه الجوفية وعمرها في خزان ملصا الجوفي شرق الرطبة (موقع الضبعة)، وبالتكامل مع بعض التطبيقات الهيدروليكية و الهيدروكيميائية التقليدية.

استنادا إلى قيم نسب نظائر الديتريوم ($\delta^2\text{H} \%$) ، الأوكسجين-18 ($\delta^{18}\text{O} \%$) و الكربون-13 ($\delta^{13}\text{C} \%$) في المياه الجوفية فقد تبين أن مصدرها من ترشح مياه الأمطار والسيول عبر مقاطع وادي حوران وفروعه غرب و جنوب غرب الرطبة خلال فترات متعددة امتدت بين

فترتي البليستوسين المتأخر و الهولوسين ، ويعود أصلها إلى مياه الأمطار المحمولة بواسطة الغيوم المتكونة من تبخر مياه البحار والمحيطات المفتوحة مباشرة دون المرور بمراحل ثانوية من الدورة الهيدرولوجية (عدم وجود مؤثرات قارية) مثل البحار والبحيرات المغلقة وهي شبيهة بمياه الخط المطري القاري الداخلي بعيدا عن خط الأمطار الساحلي ويرجح أن يكون مصدرها ضمن حدود المنخفض الجوي الهندي (المحيط الهندي) . أوضحت نتائج محتوى التريتيوم ^3H (TU) بأن هنالك نسبة من المياه الجوفية حديثة قدر عمرها (بعد عام 1950) في مواقع أم ارضمة ، مساد الرطبة و ابيلة ، فيما قدر عمر المياه الجوفية في بقية المواقع قبل عام 1950، وقد أكدت نتائج محتوى الكربون- 14 (pMC) ، والتي أثبتت وجود تغذية للمياه الجوفية مصدرها الفترة المطيرة الرابعة (هولوسين-2410BP) قبل الآن (قبل عام 1950) في موقع أم ارضمة، إذ بلغت نسبة المياه الحديثة (pMC) 71% بالإضافة إلى عملية خلط للمياه الجوفية القديمة في موقعي رميلة و مساد الرطبة مصدرها الفترة المطيرة الثالثة (هولوسين-10000BP) قبل الآن، إذ بلغت نسبة المياه الحديثة إلى المياه القديمة حوالي (pMC) 45%. كما بلغت اوطا نسبة للمياه الحديثة في موقع الضبعة و بنسبة (pMC) 10% وهي مياه مصدرها الفترة المطيرة الأولى (بليستوسين-31500BP) قبل الآن. و أخيرا فان أبار محطة الضبعة تنتج من خزان جوفي يحمل مياه قديمة المصدر ولا يتميز بصفات الخزانات الجوفية المتجددة، إذ بلغت فترة عبور المياه الجوفية بين نطاق التغذية و التصريف حوالي 29000 سنة، لذا ينبغي وضع خطة إنتاج فعالة لضمان أطول فترة إنتاج ممكنة للمياه الصالحة لشرب الإنسان قبل تدهور مياهه بسبب الخلط مع مياه خزان الكعرة الجوفي.

INTRODUCTION:

The study area is situated east of Rutba city, located between ($32^{\circ} 45' 30'' - 33^{\circ} 17' 00''$) latitude N and ($40^{\circ} 13' 00'' - 40^{\circ} 43' 00''$) longitude E within the marginal zone between Hamad and high valleys regions with an elevation of (540 – 740) m. asl. Structurally, at the southern limb of subsurface Rutba anticline (Rutba uplift) . Hauran influent valley of intermittent discharges and its tributaries are the major physiographic feature incised multi undulated plateau plains such as (Hartha, Rutba-Mssad and Zor Hauran – Ubaid – Maudod Plateau), which gently sloped northeast wards. Geomorphologically, characterized by Hilly and Badlands areas gradually, elevated in the southern part of the territory, which represents the initiation of tributary drainage basins (Mssad el Rutba , Dhalaa and Dhabaa valleys), (Fig.1).

The climate is classified as continental arid according to the UNEP,1991 classification in (World Environment Day, 2006) , where the long term (1941-2008) mean annual amount of P/ PE is (0.07). At Rutba meteorological station, the mean annual air temperature is 20.1°C , the average long-term precipitation is 107.9 mm/yr, predominantly in Nov. to Apr. and the long term average potential evaporation is 1,636 mm/yr. Ground water pumped from Dhabaa Basin, about 17 kms east of Rutba, is a major source of supply for the city of Rutba and surrounding areas, so that it is necessary to understand the groundwater recharge mechanism for

Dhabaa basin to design a successful remediation strategy and to develop water-management plans involving recharge and pumpage throughout active exploitation plan without aquifers contamination mechanism.

Methodology:

Traditional quantitative and qualitative hydrogeologic techniques are applied in this study supported by environmental isotope techniques which based on measurements of the variations in the environmental isotope compositions of natural water. Groundwater level, were recorded in twenty six bore holes. Also, groundwater samples from twenty six bore holes are analyzed for eleven physio-chemical constituents for each one . In addition , previous available groundwater level records in (37) boreholes are used for comparing hydraulic results , supported by measured isotopes includes ^{18}O , ^2H (D), ^3H (T), (^{13}C) and (^{14}C) in five boreholes (ECSAD , 1983). The isotopes results are expressed with respect to Standard Mean Ocean Water (SMOW) .The results for ^{13}C , ^{18}O and ^2H are expressed as: $\delta\text{‰} = \{ (\delta \text{ sample} / \delta \text{ standard}) - 1 \} * 1000$. The tritium contents of water are expressed as tritium units (TU), where $1\text{ TU} = 1^3\text{H}$ per $3.19 \times 10^{17} \text{ }^1\text{H}$.(Prior to 1952). The ^{14}C contents of water are expressed as pMC (percent measured carbon,%) ,where the ^{14}C contents are referenced to National Bureau of Standards oxalic acid of (12.88) disintegrations per minute per gram of

carbon in the year 1950 which equals to 100 percent. Groundwater is commonly used for drinking water, over 90% of the Rutba potable water resources come from groundwater. It is safe for healthy people in Rutba town. However, information both on recharge mechanisms and the time scales on which modern groundwater renewed is often difficult to obtain. This may lead to mismanagement of water resources, inappropriate strategies to protect the quality of the groundwater and permits to over-utilization of the groundwater. These facts encourage us to use the technique of environmental isotopes in this study, although, the measured isotopes represent previous environment state (during 1980s). A detailed appraisal of ground-water chemistry in particular, isotopic chemistry with spatial distribution is needed for better hydrogeologic interpretation especially in determining the interface of recharge and discharge zones in two-dimensions. However, The data were used to evaluate the source, movement, and age of ground water in saturated hydrogeologic units within Mullusa aquifer.

Hydrogeologic condition:

The hydrogeologic conditions in the study area considered as a main part of regional hydrogeologic settings represented by regional depositional basin of Carboniferous- Triassic sediments, which structurally, controlled by Rutba uplift. According to the properties of the formation sediments, the hydrogeologic system (Hussien, 2009) divided into:

1-Hydrogeologic System of Permo-Carboniferous Sandstones: This system includes multi water bearing horizons of Ga'ara sands & sandstones. The Transmissivity of Ga'ara sandstones ranges between (30-250) m^2/day , where the aquifer is confined & the storage coefficient is in the order of 10^{-4} . The upper contact exists at depths range between 154 -190 m. The average

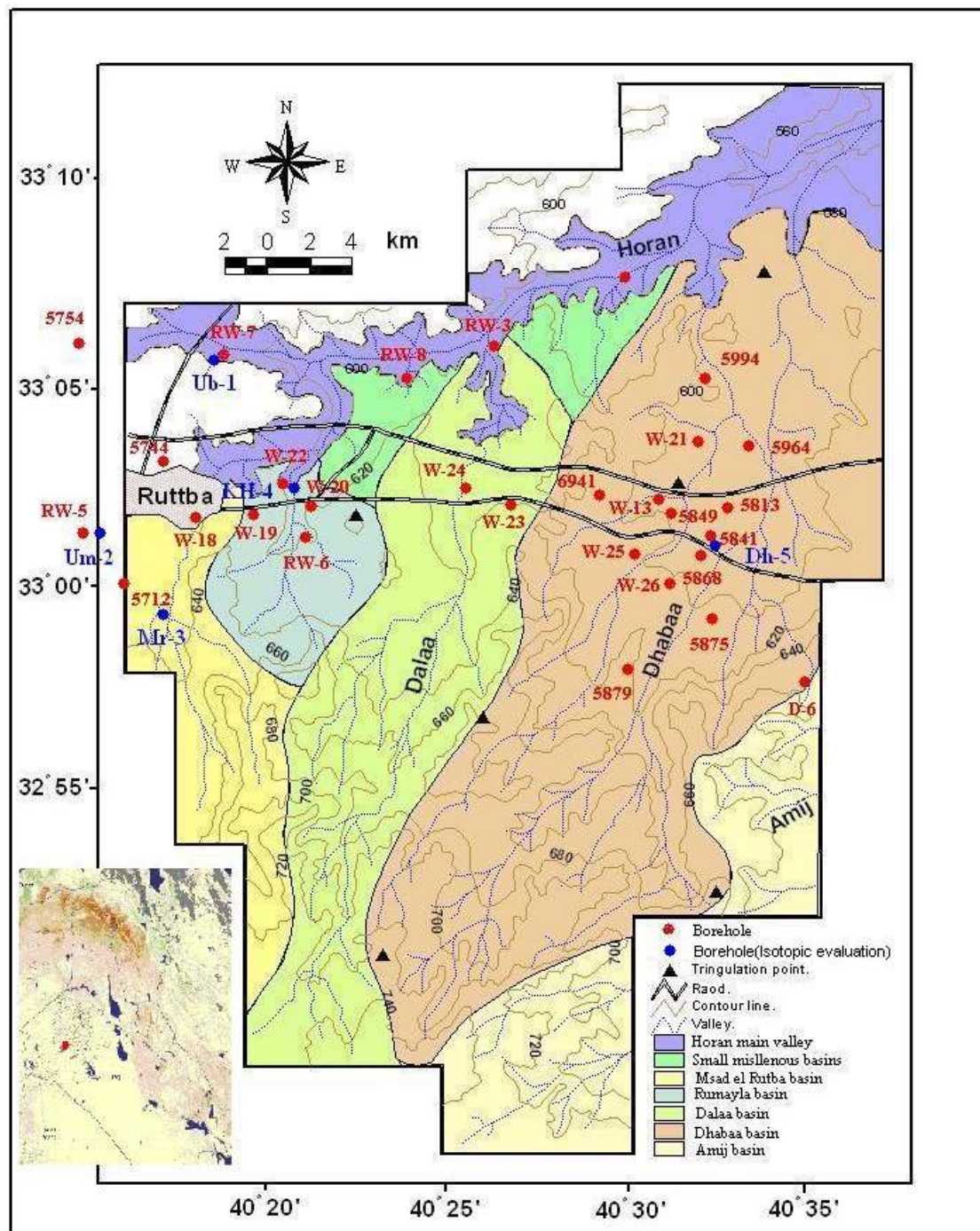
effective productive thickness is 350m from total thickness range between (700-726)m. The specific capacity values of the production wells range between (2.4–72.0) $\text{m}^3/\text{day}/\text{m}$.

2-Hydrogeologic System of Triassic – Carbonates:

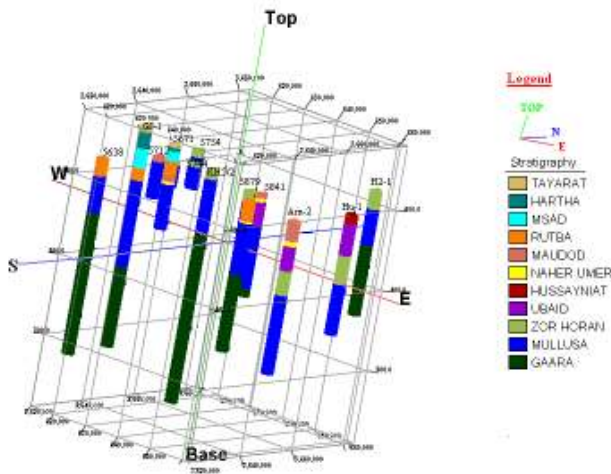
The system includes the water bearing horizons of Mullusa carbonates formation produced water from depth 30 m in the vicinity of Rutba town reaching 200m in Dhabaa Site. The aquifer thickness ranges between (100-120) m. The Transmissivity varies from 1 m^2/day – 161 m^2/day due to the variability of the sedimentological properties and structural characteristics (fractures & joints), where the aquifer is unconfined in the exposed recharge area (where Mullusa carbonate rocks exposures appear only sporadically in Hauran valley), to semi-confined in the discharge area. The storage coefficient is in the order of 10^{-2} - 10^{-4} . The permeability coefficient is of 0.687 m/day ranged between (0.03- 4.4) m/day. The main structural boundaries that affect this hydrogeologic system are Hauran Anticlinorium's structure, and Dhabaa strike slip fault at the east of study area. The fractures connected to these structures belts offer passageways and enlarged storage capacities for groundwater and promote karst evolution as in Dhabaa basin. The specific yield (rejuvenated storage) is of about $7 \times 10^6 \text{ m}^3/\text{year}$. The specific capacity values of the productive wells are ranged between (2.3 -18) $\text{m}^3/\text{day}/\text{m}$.

Hydrogeologic Units:

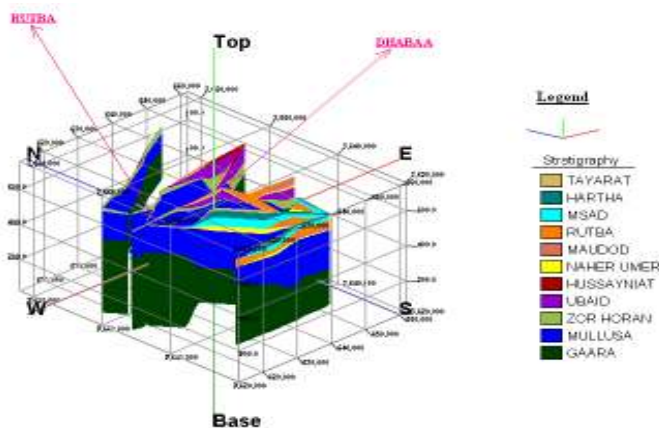
On the basis of available different source boreholes litho- logs (Fig.2), using ROCKWARE program; A three dimension hydrogeologic model achieved, showing the spatial distribution of the two hydrogeologic systems and their hosted geologic formations (Fig.3). This model represents the conceptual framework for current study, especially the extension of the Hydrogeologic Units in X, Y and Z directions.



Fig(1). Location map of the study area .



Fig(2) 3D litho-well logs of the study area .



Fig(3)- 3D Hydrogeological model .

Recharge, Discharge and Ground-Water Movement (Traditional technique):

The ground water flows generally from recharge areas along the base of the Hauran valley and its tributaries, either through Mullusa aquifer, or exposed transitional zones of overlain formations such as Rutba - Msad, Maudod - Naher Umer Formations.

Flow in these intermittent streams is diverted into artificial-recharge basins through man made earthy dams using for surface water harvesting like Hauran , Ubayla and Ghezlan small dams , where it infiltrates and recharges the underlying aquifer.

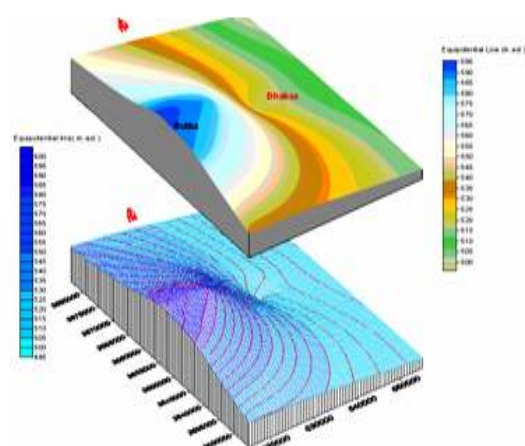
Most ground water discharged as under flow to the adjacent aquifers through permeable materials out of study area. Locally, the ground-water pumpage increased near Dhabaa Fault causing lateral effects on ground-water flow, and the hydraulic gradient increased towards Dhabaa Site which, indicates a downward movement of ground water. The flow behavior regime and the groundwater movement, considering the regional and local structural phenomena, show general pattern of groundwater flow to the E direction, deviated to NE and SE direction reflected groundwater divide along Hauran valley Fig(4) .

A hydrodynamic phenomena was obviously observed in the zone of Dhabaa province where ,the groundwater moves towards this zone from three directions (NW , W , SW) ,this phenomenon shows that the groundwater be in intense discharge increased during last ten years as shown in comparison maps which represent two periods of groundwater level measurements (prior 2000 and 2009). The groundwater seem to be retarded in this zone but actually, the high rate pumpage affect the continuity of groundwater flow through releasing head pressure reflected by low hydraulic gradient during 2009 (0.001-0.005) than hydraulic gradient during 2000 (0.012 - 0.017) in the area followed Dhabaa Site , despite the amount of hydraulic gradients in all study area during 2009 recorded high values ranged between (0.001- 0.017) than the amount of hydraulic gradients during 2000 which ranged between (0.00013-0.0079) . Finally, the mean values of hydraulic gradient within study area is of about 0.0033,which can be used in transit time calculation. In any case ,the groundwater still moves towards east with the regional flow direction Fig (4.b,d).

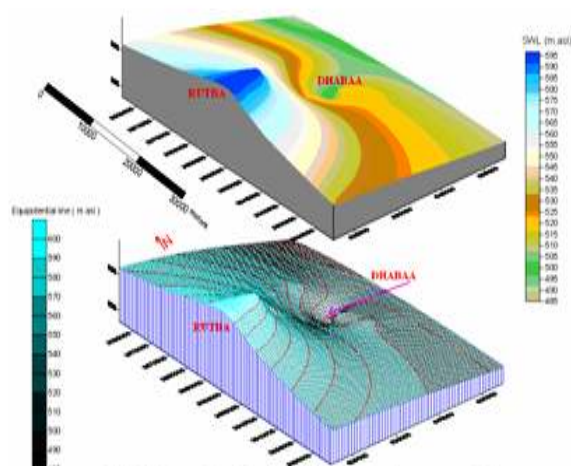
Detailed explanation about the effect of intense exploitation on the groundwater

levels as dewatering mechanism in the area restricted between Rutba and Dhabaa Site is shown in Fig(5.a), and more detailed for Dhabaa Site in Fig(5.b). The abovementioned conclusion pay to more reliable interpretation lead to explain another probable phenomenon may occurs in the future like plume contaminant, we can expect that throughout appearance of hydraulic plumes detected from hydraulic gradient distribution map .

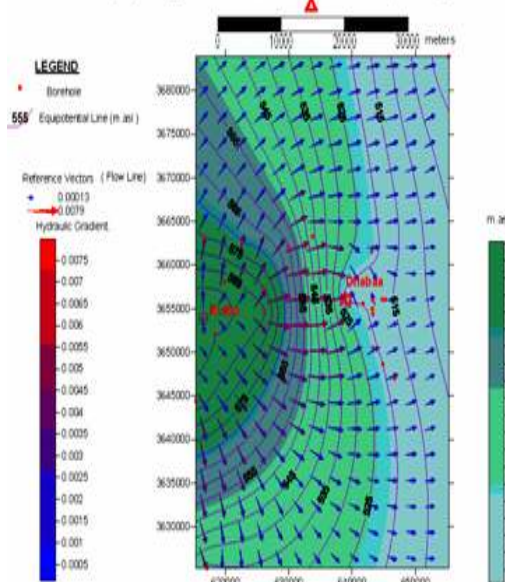
This map developed from a flow net of groundwater movement , using the values of the hydraulic gradient in each Node . In any case the study area divided into two hundred nodes (50 x 40), using the groundwater level measurements of the available bore holes (37) supplemented and integrated by Rock Ware software with computing hydraulic gradient in space of (1 x1) .



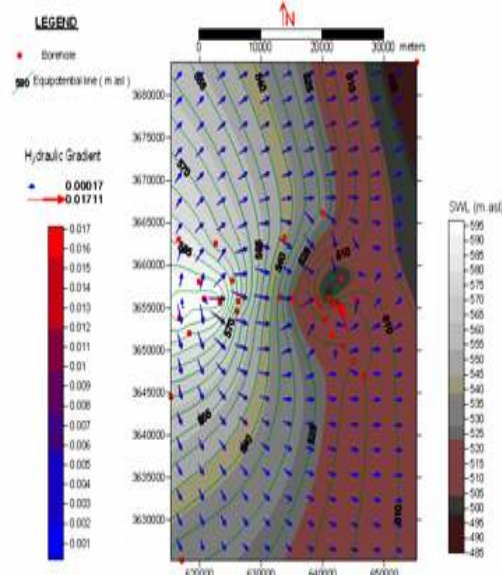
(4.a). 3D groundwater Flow within the study area (prior 2000).



(4.c). 3D Groundwater Flow Model within the study area during 2009.



(4.b). Groundwater Flow within the study area (prior 2000).



(4.d). Groundwater Flow within the study area during 2009.

Fig (4) . Groundwater movement within study area .

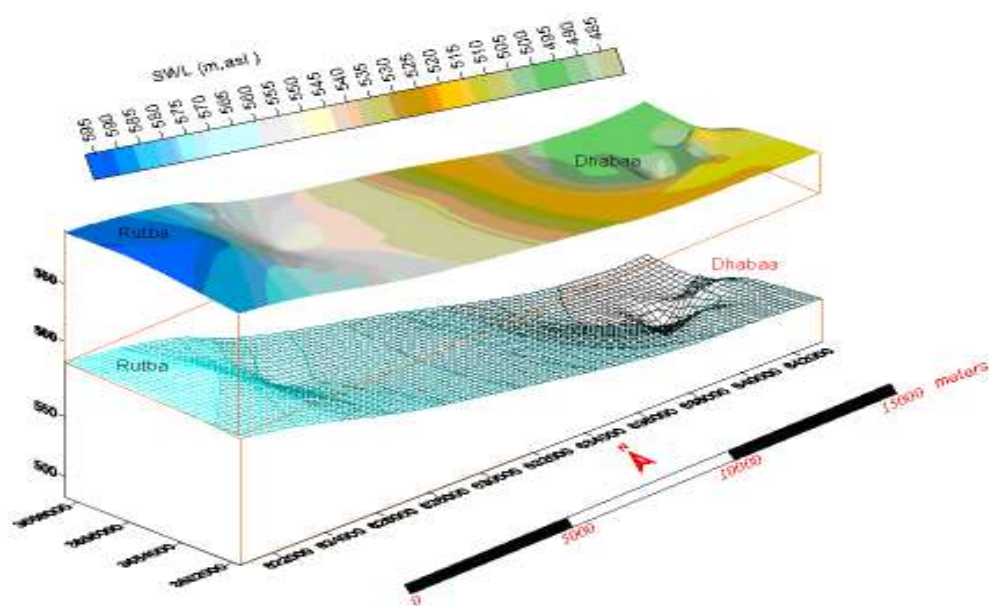


FIG.(5. a) Groundwater Flow (3D) model within Rutba- Dhabaa area.

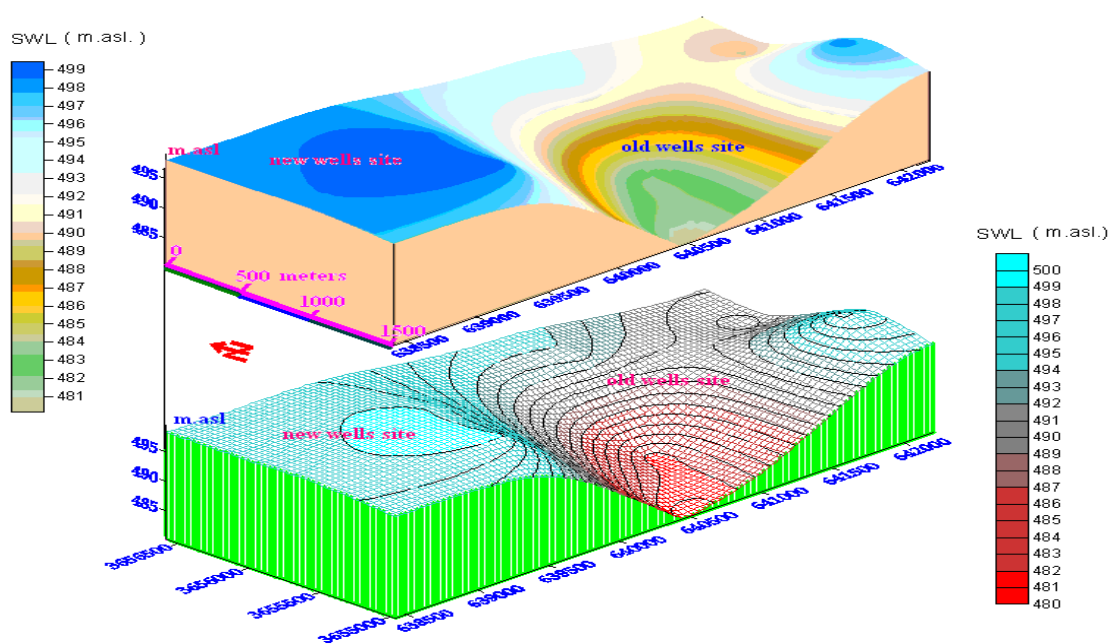


FIG.(5. b) Groundwater Flow (3D) model within Dhabaa Site.

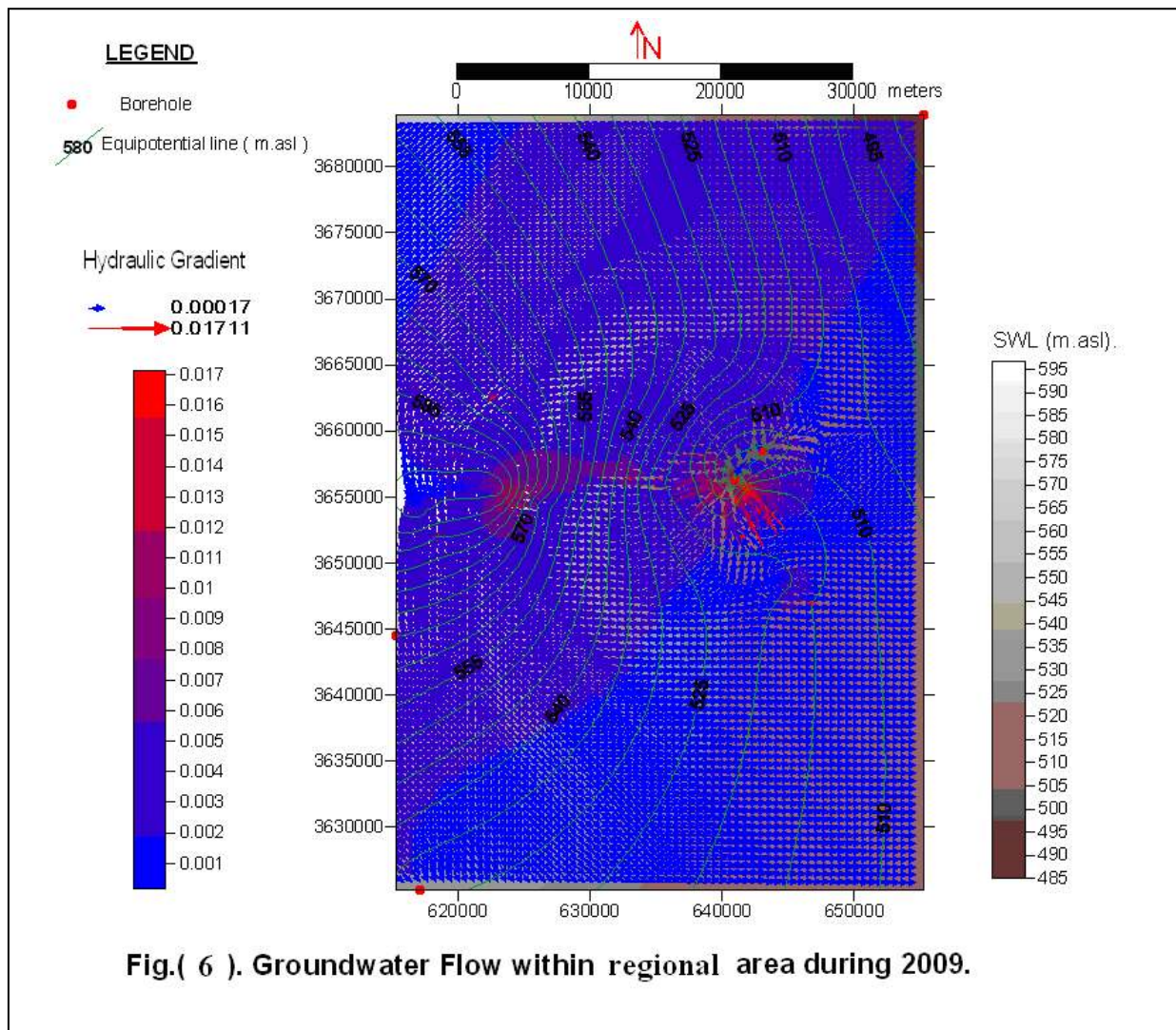
Integrated vector analyses technique shows the output map Fig.(6). The spatial distribution map of hydraulic gradients indicates two obvious phenomena , the first is in Dhabaa Site with a hydraulic gradient ranges between (0.012-0.017) , means 12-17 meters per kilometer represents cone shape dewatering .The second phenomenon occurs (7 km) east of Rutba with a hydraulic gradient ranges between (0.007-0.012) , means 7-12 meters per kilometer represents plume like shape terminated near Dhabaa Site . Hence, another increasing in pumping rate within Dhabaa Site the plume should be connect with the cone of depression and the groundwater quality of (660 ppm) mixed with ground water of (730ppm) and the mixing mechanism is

initiated,then it is difficult to stop it .

The average transit time for groundwater to reach the discharge zone in Dhabaa site initiated from Hauran valley (recharge zone) is calculated from groundwater velocity, which depends on average values of permeability coefficient within Mullusa aquifer (0.687 m/day) and average values of hydraulic gradient (0.0033).

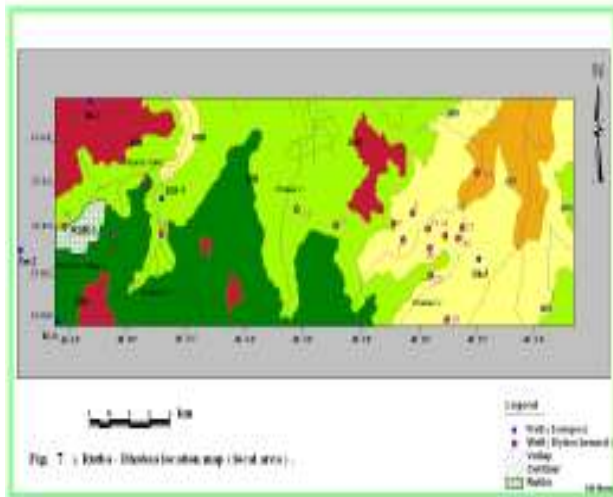
$V=KI$, and $V= L / t$, where, L represents distance of groundwater flow path , t represents transit time .Then;

$t = L / KI = 24000 \text{ m} / (0.678 \times 0.0033)$
m/day = 10586211 days , or 29003 years.



Hydrochemistry of groundwater:

On the basis of chemical analyses of 26 water samples from 26 wells (Fig.7) ; the groundwater classified as fresh water with a concentration of dissolved solids ranged from 610 to 838 mg/L.



In general, dissolved-solids concentration was lower in water samples from recharge areas near Hauran valley and its tributaries in the southern part .

Given the pH values of ground water which range between (7.21-7.9) show slightly alkali reaction, almost the measured alkalinity is present as mainly bicarbonate with low percent of carbonate.

The dissolved-oxygen concentrations in the groundwater ranged between (0.8-5.5) mg/l more than the detection limit of 0.2 mg/L , as a consequence of the low dissolved-oxygen concentrations.

On the basis of major-ion data plotted on the Piper diagram(Piper, 1944) shown in Fig (8), water from wells sampled can be classified as one group, having partial different in the concentrations of chemical compositions.

The major-ion composition of water samples was dominated by alkaline earths elements (calcium and magnesium) with (chloride and bicarbonate) , but no one cation – anion pair exceeds 50 percent . The ground water may have reacted with the matrix of the Mullusa carbonate aquifer, Where the increase in dissolved solids may be the result of the dissolution mechanism .

These data suggest that because of chemical reactions that occur as water moves through an aquifer, chemical data alone are not sufficient to identify the source of water.

Therefore, available isotopic data are used to answer questions about the source of ground water that could not be answered on the basis of groundwater-chemistry data alone.

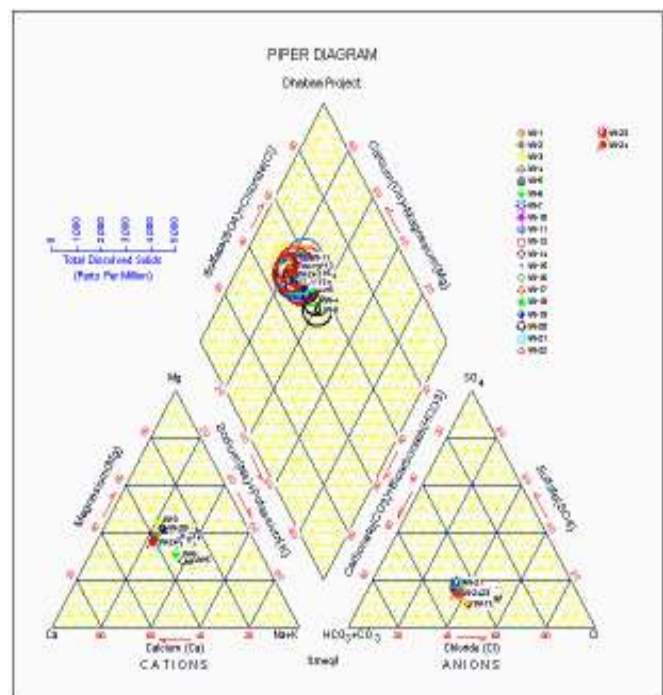


Fig (8) . Chemical analyses of the groundwater plotted on Piper diagram.

ISOTOPIC COMPOSITION OF GROUND WATER :

Isotopes are atoms of the same element, in which the nuclei of the atoms have the same number of protons but different numbers of neutrons. In this study, stable, naturally occurring isotopes of oxygen (oxygen-18) and hydrogen (deuterium) were used to determine the source of ground water.

Naturally occurring radioactive isotopes of hydrogen (tritium) and carbon (carbon-14) were used to determine the age (time since recharge) of the ground water. The presence of tritium was used to identify younger ground water (water recharged after 1952). Carbon-14 data were used to estimate the age of older ground water that did not contain tritium.

Oxygen-18 and Deuterium :

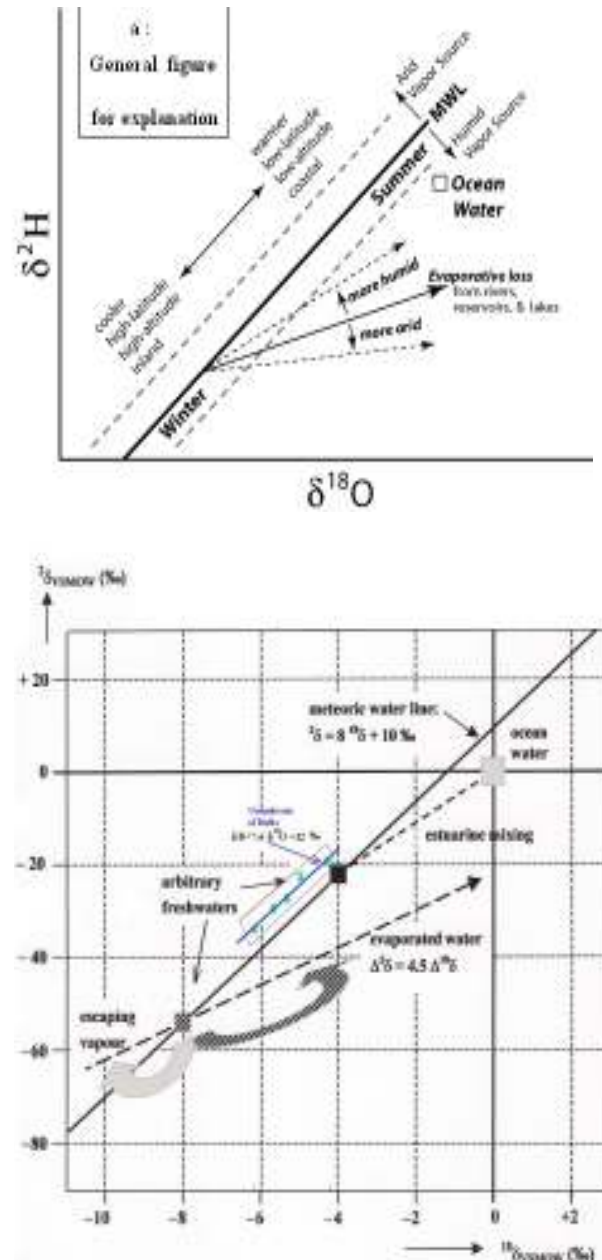
Atoms of oxygen-18 (^{18}O) and deuterium (^2H) have more neutrons and a greater atomic mass (weight) than more common isotopes, oxygen-16 and hydrogen, respectively.

Oxygen-18 and deuterium abundances are expressed as ratios, in delta notation (delta), as per mil (parts per thousand) differences, relative to the standard known as Vienna Standard Mean Ocean Water (VSMOW) (Gonfiantini, 1978).

The value of VSMOW is 0 per mil. of Oxygen-18 (delta ^{18}O) and deuterium (delta D) ratios. The relative to VSMOW can be measured more precisely than absolute abundances, and these ratios are useful in a wide variety of hydrologic studies (International Atomic Energy Agency, 1981). (Mook, 2000).

Most precipitation throughout the world originates from the evaporation of seawater. The oxygen-18 and deuterium composition of precipitation throughout the

world is linearly correlated. This relation is expressed on a graph of delta ^{18}O and delta D as the meteoric water line (Craig, 1961) Fig (9).



Fig(9). Isotopic composition ($\delta^2\text{H}$ & $\delta^{18}\text{O}$) of ground water within Rutba region compared with Global Meteoric Water Line(GMWL,after,Craig,1961).

Over time, the isotopic composition of water vapor in different storms trends to an average value; therefore, the isotopic composition of ground water is determined primarily by local differences in the

temperature of condensation of water vapor, prior to its being recharged in different places and at different times. Water that condenses at cooler temperatures (often associated with higher altitudes, cooler climatic regimes, or higher latitudes) is lighter (more negative) than water that condenses at warmer temperatures (often associated with lower altitudes, warmer climatic regimes, or lower latitudes) Fig. (9.a). In addition, water that has been partly evaporated is enriched by heavier isotopes relative to its original composition. These values plot to the right of the meteoric water line along a line known as the evaporative trend line. As a result, the $\delta^{18}\text{O}$ and δD composition of a water sample can provide a record of the source and evaporative history of the water. The $\delta^{18}\text{O}$ and δD composition of groundwater (ECSAD-1983) ranged from -4.2 to -6.2 per mil, and from -19.9 to -35.12 per mil, respectively. The isotopic composition of groundwater from the wells of the study area as seen in Fig.(9) plots along a local ground-water line about 6.66 per mil above, and parallel to, the meteoric water line represented by the following equation :

$$\delta\text{D} = 7.6 \delta^{18}\text{O} + 12 \text{ (‰) per mil.}$$

which means that the ground-water recharge is mainly derived from the infiltration of rainwater and surface water (stream water flow and sheet runoff). This water usually is not exposed to significant evaporation prior to recharge.

Tritium:

Tritium (^3H) is a naturally occurring radioactive isotope of hydrogen that has a half-life of about 12.4 years. About 800 kg of tritium was released to the atmosphere during 1952-62 (Michel, 1976) as a result of the atmospheric testing of nuclear weapons. Because tritium is part of the water molecule, tritium is not affected by reactions other than radioactive decay, and tritium is an excellent tracer of the movement of water on time scales ranging

from 10 to less than 100 years before present. In this study, the activity of tritium was measured in TU, where, 1TU = 3.19 pC/ liter .

Ground water having tritium activities less than the detection limit of 0.3 pC/L is considered to be water recharged before 1952. Ground water having measurable tritium activity more than 0.3 pC/L is considered to be water recharged after 1952, (Izbicki, et.al, 1997) .While Clark

<0.8 TU Sub modern (prior to 1950s)

0.8 - 4 TU mix of sub modern and modern

5 - 15 TU modern

15 - 30 TU some bomb tritium

>30 TU recharge in the 1960's to 1970's

>50 TU recharge in the 1960's

and Fritz,1997, generalized the follow guidelines for age estimation using tritium activity as TU .(Table-1).

Tab-1:Ageclassification(Clark and Fritz,1997) .

tritium activity Relative age .

Tritium activity in ground water from the wells of study area ranged from (0.2 pC/L, to 65 pC/L). On the basis of tritium data (Table-2), comparing with Clark and Fritz,1997 guideline : the groundwater within Dhabaa and Rumayla locations are sub modern means of age prior 1950s (for mentioned this result is unlimited).

While the groundwater within Ubayla and Emsad el Rutba locations are modern means of age after 1950s (the bore holes are inside tributaries sections of Hauran valley) , finally the groundwater within Um Erdhuma location is recharged in the period of 1960s which is the newest one .These results as explained in Fig(10) ,indicate the followings:

1-The recharge zones are determined exactly in the locations of Um Erdhuma, Ubayla and Emsad el Rutba which represent sites crossed by streams of

intermittent runoff within the basin of Hauran valley , which indicate the result

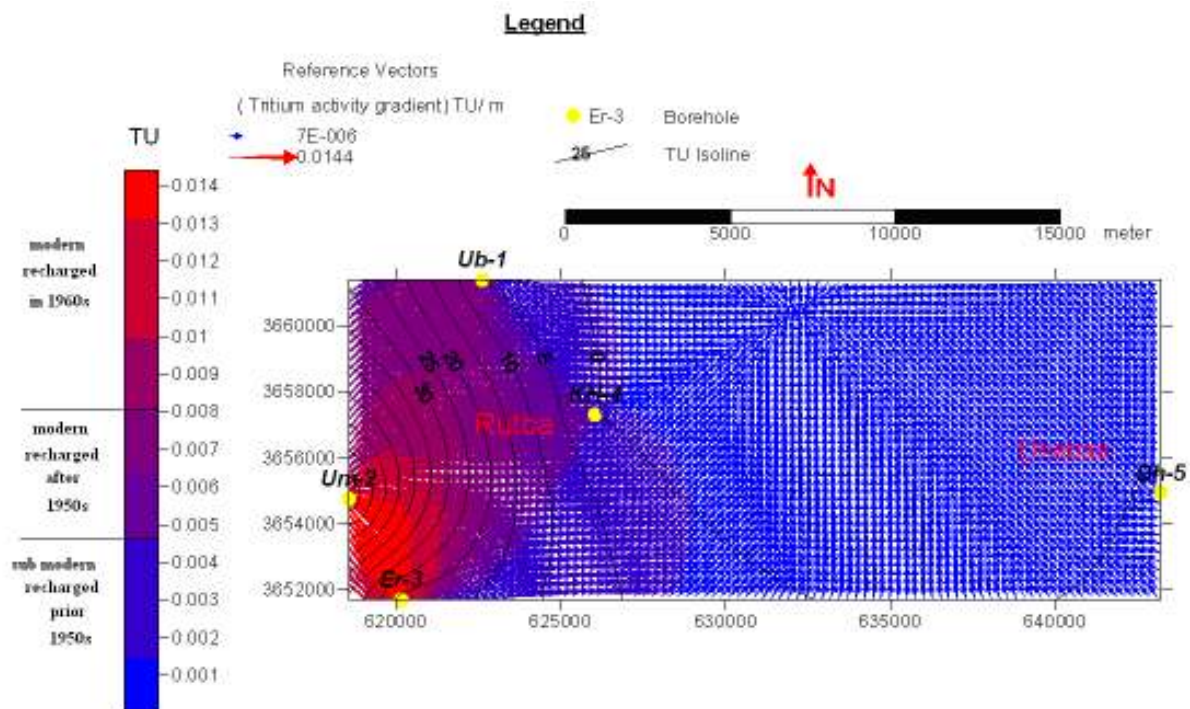
that gotten from the relation of ^2H and ^{18}O

2-The another two sites (Rumayla and Dhabaa) are not be well defined ,whether represent recharge or discharge zones , because the age is only prior 1950s,where this problem can be solved by interpretation of ^{14}C data (time since recharge) .

3-The spatial distribution phenomenon of decreasing tritium activity (TU) is nearly coincided with the groundwater flow in the same area as detected in traditional hydraulic technique, Fig(11).

Table-2 : Stable isotopes and Tritium results of groundwater(ECSAD-1983) .

B. H No.	Y UTM	X UTM	^3H TU	$\delta^{2\text{H}}$ ‰ per mil	$\delta^{13}\text{C}$ ‰ per mil	$\delta^{18}\text{O}$ ‰ per mil
Ub-1	3661416	622625	5	-29.0	- 8.5	-4.9
Um-2	3654774	618556	65	-19.9	- 10.5	-4.2
Er-3	3651713	620150	18	-25.3	- 8.9	-6.2
KH-4	3657331	626048	0.2	-32.0	- 7.6	-5.8
Dh-5	3654948	643206	0.3	-35.1	- 8.8	-5.4



Fig(10). Distribution map of Tritium in groundwater .

Carbon-13:

Carbon-13 data are expressed as ratios in delta notation (per mil) differences relative to the ratio of ^{13}C to ^{12}C in standard Vienna Pee Dee Belemnite (VPDB) (Gonfiantini, 1978) .

Measured delta ^{13}C composition of groundwater from wells of study area(Table-2) ranged from (-7.6 to -10.5) per mil. The delta ^{13}C values were increased (less negative) in water of well No.(Kh-4) , and decreased (more negative) in water of well No.(Um-2) with random distribution neither with hydraulic nor with hydrochemical phenomena . The random distribution may originated to the reactions within the aquifer which may add carbon that does not contain carbon-13 to the dissolved phase or remove carbon that may contain carbon-13 from the dissolved phase, and / or vice versa . Accordingly, in this study, the stable isotope of Carbon-13 (^{13}C),can not be used in chemical reactions evaluation that may occur within Mullusa aquifer. On other hand, the plotting of delta ^{13}C values on Mook schematic survey (Mook,2000) (Fig.12), shows that Carbon-13 data exist within the natural limits of their existence in groundwater HCO_3 zone (normal case).

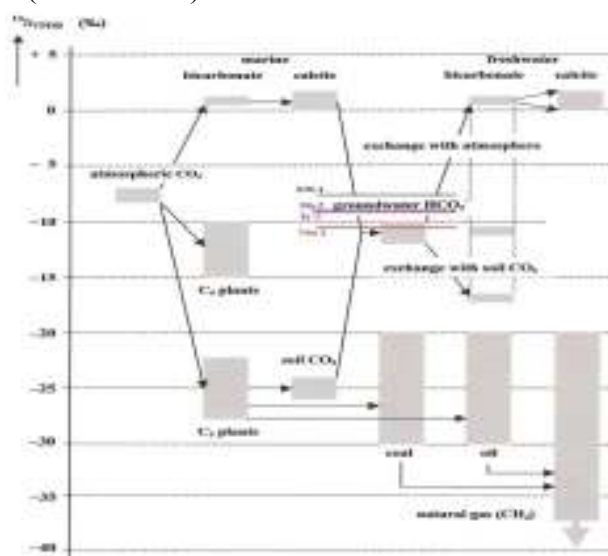


Fig.(12).Plotting of groundwater $^{13}\delta$ on the schematic survey of $^{13}\delta$ variations in nature

Carbon-14:

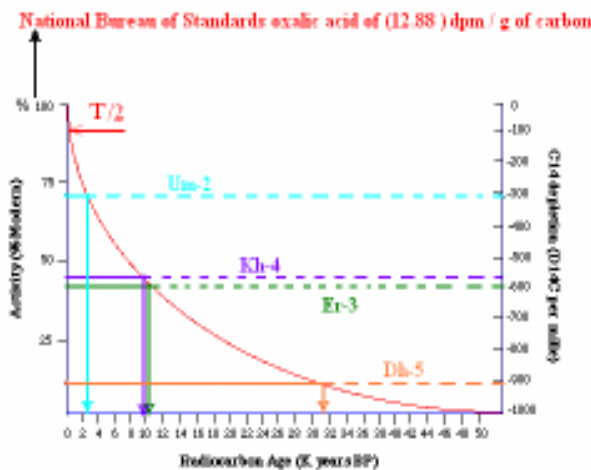
Carbon-14 (^{14}C) is a naturally occurring radioactive isotope of carbon having a half-life of about 5,730 years. Carbon-14 data are expressed as percent modern carbon by comparing carbon-14 activities to the specific activity of National Bureau of Standards oxalic acid of (12.88) disintegrations per minute per gram of carbon in the year 1950 equals 100 percent modern carbon(pMC).(Izbicki, etal,1998)

Atmospheric testing of nuclear weapons produced carbon-14 along with tritium. As a result, carbon-14 activities may exceed 100 percent modern carbon(pMC). In areas where ground water contains tritium. Carbon-14 activities are used to determine the age of ground water (time since recharge) on timescales ranging from recent to more than 45,000 years before present. Carbon-14 is not part of the water molecule, and unlike tritium, carbon-14 activities are affected by chemical reactions that occur between dissolved constituents and the aquifer matrix .

Measured carbon-14 activities in samples of groundwater from 4 wells in the study area ranged from 10 to 71 percent modern carbon(Table-3). In general, carbon-14 activities were highest in water from wells in the recharge areas, lower in water from wells in the discharge areas near Dhabaa Site. and lowest in water from deep wells that did not contain measurable tritium. Neglecting the chemical reactions that occur within the aquifer and assuming only radioactive decay and an initial carbon-14 activity of 71 percent modern carbon, the calculated ages (Table-3) of water from these wells range from about 2400 years before present for water from well Um-2 to about 31,500 years before present for well Dh-5 , as detected from Fig.(13),according to(Stuiver, M and Polach, H, 1977) method.

Table-3 : Activity of ^{14}C (%modern) results and age of groundwater(ECSAD-1983)

Borehole No.	Location	pMC %modern	$\delta^{14}\text{C}$ ‰	^{14}C (YEAR)
Ub-1	Ubayla	-	-	-
Um-2	Um Erdhuma	71	-310	2410 ± 80
Er-3	Emsad el Rutba	45	-600	10500 ± 200
KH-4	Rumayla	47	-570	9915 ± 120
Dh-5	Dhabaa	10	-910	31540 ± 1095

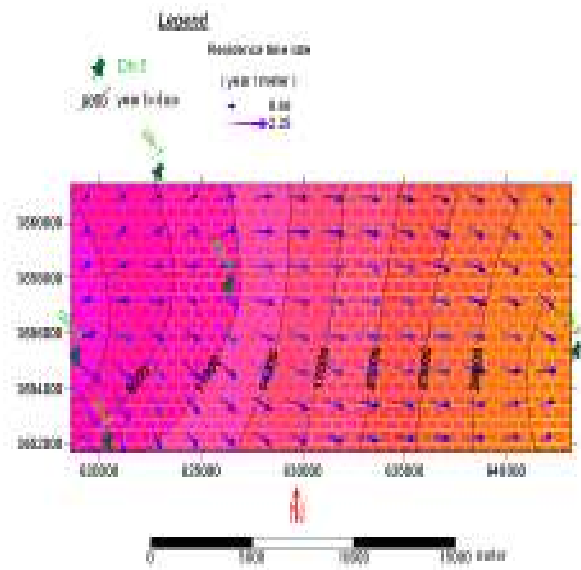
**Fig.(13)Radiocarbon age of groundwater within study area . on the base of (Stuiver, M and Polach, H, 1977).****Sources of Older Ground Water:**

Studies of oxygen, hydrogen, and carbon isotopes done for groundwater within the study area can help to resolve questions about groundwater especially about the source of groundwater .

Groundwater in Dhabaa site is isotopically lighter and older with respect to isotopes than groundwater of both Rumayla and Msad El Rutba sites, which is lighter than groundwater of Um Erdhuma site as discussed previously.

Groundwater from Dhabaa may be recharged at a time when the climate was cooler and the isotopic composition of water recharge was lighter, or the water may have been recharged at a different location and is associated with a different groundwater flow system.

Groundwater from Dhabaa well Dh-5 near the down gradient end of long flow paths through extant aquifer Fig(14), was found to have been recharged more than 31,500 years ago, which represents the residence time of ^{14}C

**Fig (14) Distribution map of groundwater age (carbon-14 dating) .**

in the groundwater within Mullusa aquifer. Possible sources for this recharge include infiltration of runoff from the wide drainage basin of Hauran valley ,where its drain areas of higher altitude in the southwest direction. Geyh, 1994 indicates that the groundwater recharge in Hamad region was interrupted in the past as a result of changing paleo-hydrologic conditions, e.g. after the termination of the humid periods in the Late Pleistocene and Early Holocene (Fig.15).

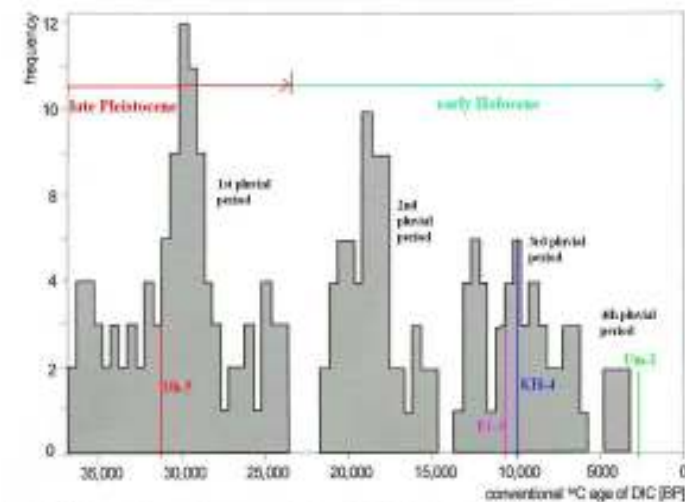


Fig (15) Plotting of groundwater age within paleohydrological situation in Hamad region.

From the abovementioned figure ,there are four main periods of pluvial periods, the first pluvial period (late Pleistocene age) of high frequency precipitation continued between (24000-37000) Years BP, which may represents the source of Dhabaa groundwater. The second pluvial period (early Holocene) of second frequency precipitation continued between (15000-22000) Years BP .

The third pluvial period (of third order frequency) continued between (6000-14000) Years BP, which may represents the recharge source of Rumayla and Msad El Rutba groundwater. Finally, the fourth lowest pluvial period of < 5000 Years BP, which may represents the source of Um Erdhuma groundwater .

Recharge to the upper 60-220 m of the regional carbonates Mullusa aquifer appears to originate largely near major washes that convey water from watersheds of Hauran Valley. The radioactive isotopes tritium (^3H) and radiocarbon (^{14}C) have appropriate half lives for the study of groundwater movement. Both isotopes are generated as a result of interaction between cosmic rays and ^{14}N in the upper atmosphere. The levels of both were also

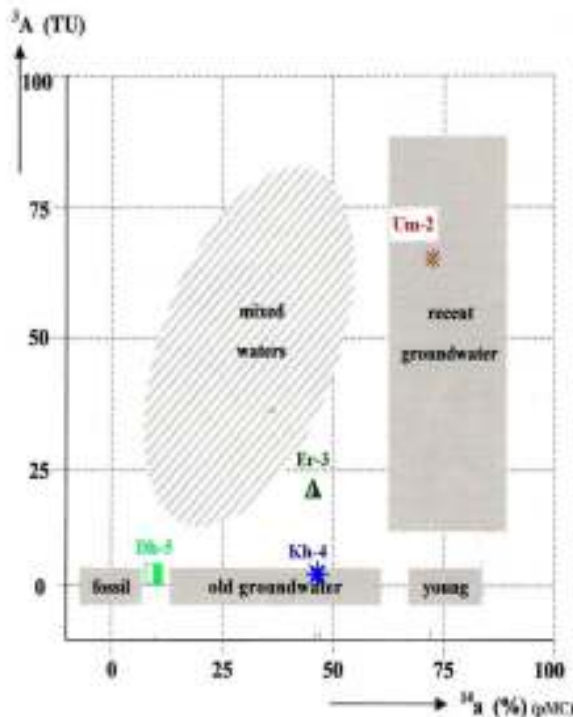
augmented by atmospheric testing of nuclear weapons ,particularly between 1960 and 1972 .

The presence or absence of tritium in the groundwater indicates accurate results about the age determinations. The mixing of older and younger waters after infiltration complicates the interpretations, in particular of using the calculation of ages from tritium data alone, so that ,it is necessary to use Carbon -14 with Tritium data to solve the complicated mixing mechanisms.

Accordingly, four cases are deduced from the application of ^{14}C and ^3H in recharge determination.

1. Water with measurable tritium(65 TU) and greater than (70 pMC) of ^{14}C , containing a significant fraction of water that fell as rain since 1950s is of recent recharge like which detected in Um Erdhuma site (Um-2) within Mullusa aquifer.
2. Water with measurable tritium(18 TU) and (45 pMC) of ^{14}C , containing a significant fraction of water that fell as rain since 1955s, is of recent recharge mixed with groundwater of old recharge in the ten centuries prior to 1950s , like which detected in Emsad El Rutba site (Er-3) within Mullusa aquifer.
3. Water with tritium below detection level (<0.2 TU), and (47pMC)of ^{14}C , ,containing a significant fraction of water that fell as rain potentially as prior to 1950s, is of old groundwater recharge within the ten centuries prior to 1950s , like which detected in Rumayla site (Kh-4) within Mullusa aquifer.
4. Water with tritium below detection level(<0.3 TU), and (10 pMC) of ^{14}C , containing little or no water that fell as rain in the few centuries prior to 1950s,but

of 30s centuries recharge BP(1950s). The abovementioned results are concluded in the schematic(Mook,2000). representation (Fig.16) .



Fig(16).Environmental setting of groundwater isotopes activity in the study area .

conclusions:

- 1- A three dimension hydrogeologic model achieved ,showing the spatial distribution of the hydrogeologic system and their hosted geologic formations.
- 2- Comparison between two different flow maps (prior 2000 and 2009),shows the effect of intense exploitation on the groundwater levels as dewatering mechanism in the area restricted between Rutba and Dhabaa Site
- 3- The spatial distribution map of hydraulic gradients indicates two obvious phenomena , the first is in Dhabaa site indicates artificial cone shape dewatering formed as a result of intense exploitation . The second phenomenon occurs (7 km) east of Rutba with a plume like shape terminated near Dhabaa Site probably connected with the cone of depression in

case of production excess . and may cause lateral and /or upward mixing mechanism.

- 4-The average transit time of groundwater between Hauran valley (recharge zone) and discharge zone in Dhabaa site is 29003 years .In term of isotopes the residence time detected by ^{14}C dating is 31500 years .This conclusion refers that the groundwater within Dhabaa site is not actively renewable ,which means the water wells of Dhabaa site product from fossil groundwater, which needs a proper pumpage plan .
- 5- Hydrochemical data is not sufficient to identify the source of groundwater, because of high similarity appeared in the groundwater types within study area. Therefore, available isotopic data are used to solve the source of ground water
- 6- As a result of $\delta(^{18}\text{O})$ and $\delta(\text{D})$ composition the ground-water recharge is mainly derived from the infiltration of inland rainfalls and surface water (stream water flow and sheet runoff)that not exposed to significant evaporation prior to recharge.
- 7- As a result of Tritium activity ,the groundwater within Dhabaa and Rumayla locations are classified as sub modern means of age prior 1950s, While the groundwater within Ubayla and Emsad el Rutba locations are classified as modern means of age after 1950s, finally the groundwater within Um Erdhuma location is recharged in the period of 1960s which is the newest one .
- 8- The spatial distribution phenomenon of decreasing tritium activity (TU) is nearly coincided with the groundwater flow in the same area as detected in traditional hydraulic technique.
- 9- On the base of Carbon-13 data ,the groundwater of the study area exists within the natural limits of their existence in groundwater HCO_3 zone (normal case).
- 10- Measured carbon-14 activities in samples of groundwater in the study area ranged from 10 to 71 percent modern carbon . Carbon-14 activities were highest

in water from wells in the recharge areas, lower in water from wells in the discharge areas near Dhabaa Site.

- 11- The calculated ages of ground water range from about 2400 years before present for water from well Um-2 to about 31,500 years before present for well Dh-5 , according to(Stuiver, and Polach, 1977) method .
- 12- The source of Dhabaa groundwater is originated to the first pluvial period (late Pleistocene age) of high frequency precipitation continued between (24000-37000) Years BP . The recharge source of Rumayla and Msad El Rutba groundwater is originated to the third pluvial period (of third order frequency) continued between (6000-14000) Years BP . Finally, the source of Um Erdhuma groundwater is originated to the fourth lowest pluvial period of < 5000 Years BP.

Recommendation :

Sustainable use of groundwater resources in Mullusa water-bearing systems requires that the resources be renewed naturally within a certain time, If the groundwater resource can be replenished in few dozens years.

It is showed that the hydrogeologic system of Mullusa aquifer has a certain degree close contact with meteoric water and a certain extent of natural renewal capacity in Rutba adjacent area, while Mullusa aquifer in Dhabaa Site cannot be replenished in few hundreds years, If the overtime (as detected from ¹⁴C dating)of groundwater reaches thirty thousands of years, that means there are poor relationship between hydrogeologic system and the naturally restorable meteoric water and little possibility to obtain nature recharge from meteoric water .

Accordingly, the production of groundwater from Dhabaa Site must be planned under preservation laws depends on groundwater management study, because the isotope study indicates that the

groundwater of Dhabaa Site is of ancient age originated to the first pluvial period (high intense rainfalls) which occurred before 31500 year BP(before present).

This result direct us to product the groundwater in a limit of human needs for Rutba people not excess, to be used for long time period, means the groundwater of Mullusa aquifer in Dhabaa Site is limited as fossil fresh water, and excess of exploitation depletes the storage and may cause quality deterioration .

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ABBREVIATIONS

DIC	Dissolve Inorganic Carbon
Year BP	Year before present (1950).
P	precipitation
PE	potential evaporation
ppm	part per million
pC/L	Pico curie per liter, one pC/L is equivalent to about 2.2 disintegrations of tritium per minute or about one tritium atom in 3.19×10^{17} atoms of hydrogen. Prior to 1952.
mg/L	milligram per liter
µg/L	microgram per liter
µS/cm	microseimen per centimeter at 25°C
TU	Tritium unit .(1TU = 3.19 pC / liter ,or 1 TU = 7.2dpm / liter)or (1TU=0.118 Bq/liter of water)

pMC ^{14}C contents are referenced to National Bureau of Standards oxalic acid of (12.88). disintegrations per minute per gram of carbon in the year 1950 equals 100 percent modern carbon (pMC).

δ (per mil) parts per thousand, as used with delta notation(‰)

$^2\text{H}/^1\text{H}$ VSMOW ($1.5575 \cdot 10^{-4}$) (Kendall. C and J. J. McDonnell, 1998)

$^{18}\text{O}/^{16}\text{O}$ VSMOW ($2.0052 \cdot 10^{-3}$) for water sample and VPDB ($2.0672 \cdot 10^{-3}$) for carbonate sample, where $\delta^{18}\text{O}_{\text{VSMOW}} = 1.03091 \cdot \delta^{18}\text{O}_{\text{VPDB}} + 30.91$ (Coplen et al., 1983):

$^{13}\text{C}/^{12}\text{C}$ * VPDB ($1.1237 \cdot 10^{-2}$)

VSMOW Vienna Standard Mean Ocean Water

UNEP United Nation of Environmental Program

GMWL Global meteoric water line

UTM Universal Transverse Mercator. The Conventional Radiocarbon Age BP is calculated using the radiocarbon decay equation: $t = -8033 \ln(\text{Asn}/\text{Aon})$, Where -8033 The mean lifetime of ^{14}C (Stuiver and Polach, 1977).

Aon

The activity in counts per minute of the modern standard,

Asn

The equivalent cpm for the sample.

In The natural logarithm

$\delta^{14}\text{C} = ((\text{Asn}/\text{Aon}) - 1)1000$ per mille

$\text{D}^{14}\text{C} = \delta^{14}\text{C} - 2(\delta^{13}\text{C} + 25)(1 + \delta^{14}\text{C}/1000)$ per mil

Radiocarbon age = $-8033 \ln(1 + \text{D}^{14}\text{C}/1000)$

$T(\text{bp}) = -(T_{1/2} / \ln 2) \ln(^{14}\text{A}_{\text{sample}} / ^{14}\text{A}_{\text{standard}}^0)$
 $= (-5568 / 0.693) \ln(^{14}\text{A}_{\text{sample}} / ^{14}\text{A}_{\text{standard}}^0)$

$= -8033 \ln ^{14}\text{a}_{\text{sample}}$ Where,
 $^{14}\text{a} = (^{14}\text{C decay rate in sample }) / (^{14}\text{C decay rate in reference })$, or
 $= (^{14}\text{C concentration in sample }) / (^{14}\text{C concentration in reference })$

*VPDB Vienna Pee Dee Belemnite The common reference for delta ^{13}C Marine Carbonate Standard was obtained from a Cretaceous marine fossil, *Belemnite Americana*, from the Pee Dee Formation in South Carolina. This material has a higher $^{13}\text{C}/^{12}\text{C}$ ratio than nearly all other natural carbon-based substances. For convenience it is assigned a delta ^{13}C value of zero, giving almost all other naturally-occurring samples a positive delta value.