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RESEARCH PAPER

Use of Isotope Technique in Groundwater Investigation around Erbil City- Northern Iraq

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A B S T R A C T:
The fundamental characteristics of environmental isotopes in water resources management is dependable on the nature of geographical region of the catchment boundaries. The method of applying different isotopes has a main character in quantity and quality estimations of water resources that sometimes cannot be achieved by old techniques. Nowadays the detailed inquiry of surface water or groundwater difficulties can practically have been explained against the support of performing the isotopes. In this study, the environmental isotopes were measured and are used to predict the residence time (age) of groundwater in the areas around Erbil city in Kurdistan region- Iraq. Or to predict some of ground water characteristics. A total of 22 (10 wells and 12 springs) samples of water were taken at different places starting from Haji-Omran to Barzan. The samples collected through a glass bottles and covered to prevent the evaporation then transported to the laboratory in Vienna for the purpose of measuring the isotope contents in water molecule. The results show that, groundwater saves the ^{18}O and deuterium (D) content out of which they were formed. The isotope content includes high degree in deuterium surplus (d) is about 20‰ which is representative for the areas having high elevation. also, the high concentration of isotopes was taken place at Haji-Omran and Jundian w that about 8.93 and 8.37 degrees respectively. The water in the well from Per-Daud has a ^{3}H content of 0.8 TU which means that is an old water and its age is more than 40 years. Whereas, the tritium content of water taken from Haji-Omran was 13.4 TU that can be accounted as young water due to quickly recharge rate and the effects of precipitation at this location.

KEY WORDS: Isotope technique, Groundwater dating, Erbil city.
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1. INTRODUCTION:

An isotope has exerting a great force in the field of engineering hydrology based on the natural water cycle. The environmental isotope either related to natural (stable isotopes) or they are artificial and unstable (radioactive isotopes). Water molecules carry unequaled isotopic fingerprints, based in part on differing ratios of the oxygen and hydrogen isotopes that establish the water molecule. isotopes include ^{1}H which is common hydrogen having only one proton, ^{2}H which is deuterium (D) which is heavy stable hydrogen and produced from addition of one and two neutrons. The frequent isotopes processed in hydrology are the natural isotopes of the water molecule (^{1}H, ^{2}H, ^{16}O, and ^{18}O). Other stable isotopes, such as ^{13}C and ^{15}N were greatly applied to find origination of water pollution, recharge rate and recharge mechanism, determination of flow velocity and its direction, separation of groundwater flow and baseflow with stream flow, the interconnections between aquifers, some aquifer characteristics and source of salinity.

Natural isotopes have applicability in many fields used for solving several problems in the environment. This means that this technique is not bounded only to engineering hydrology but also apply to other areas such as meteorology, oceanography, archaeology, animal migration, forensic and health studies.

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2. LITERATURE REVIEW:

2.1 Modifications of tritium (T) and oxygen-18 of different types of precipitation in Czechoslovakia:

Dencer and Martinic,1965 studied the variation of tritium (T) and oxygen-18 in precipitation, snowmelt and snowpack during the winter in a small mountain basin in northern Czechoslovakia. The results show that a significant altitude effect exists for oxygen-18 when the precipitation is not in the solid form. Evolution of the isotopic composition of the snowpack reflects the movement of water resulting from melted snow in the snowpack and its relation to the thermal conditions in the snowpack.

2.2 Distribution of deuterium (D) isotope in Canadian waters:

Brown,1970 investigated on the distribution of hydrogen isotope (especially deuterium) in Canadian waters like precipitation and surface water. In this investigation, the change in concentration of deuterium (D) and tritium (T) was determined. High concentration of deuterium and low concentration of tritium taken place near the land along the sea which absorb the first condensate from oceanic vapour due to reduction in temperature, recycle of surface water by evaporation, and resumed the involvement of atmospheric tritium. Storm-to-storm fluctuations in isotope content of precipitation at Ottawa reflect a variability in the origin of precipitating moisture. Seasonal variation of tritium, due to late spring feed-in from the stratosphere, has been particularly prominent and regular at Canadian latitudes. Declining annual peak concentrations since 1963 indicate depletion of the stratospheric reservoir with a half-time of 1.2 years.

2.3 Dating of young groundwater:

Plummer, 2003 In America investigated that the age of young groundwater is depends on the time elapse since recharge and the groundwater concentration, while different methods achieved that the age of young groundwater is ranged between (0-50 years). Base on this investigation the groundwater dating is related to three main processes:

a. Initial concentration of the radionuclide is recreated from the measured concentrations of the parent and daughter isotopes and then the groundwater age is illustrated from the decay equation.
b. Initial concentration of the radionuclide loaded again to the aquifer, and then the dating of groundwater is estimated from the measured concentration.
c. Age information is reasoning the atmospheric input function of an anthropogenic gas, its capability to soluble in water, and the measured concentration in the water sample.

Each technique has advantages and limitations therefore, a multi-tracer concept is proposed.

2.4 Radiocarbon dating of old groundwater:

Geyh, 2003 in Germany explained that, ^{14}C is the method that recognized to dating of groundwater based on estimations of geo-hydraulic characteristics of aquifers and aquitards. In aired and semi-aired zones, the age of groundwater changes due to renewability and non-renewability of its source.

2.5 Compound specific stable isotope analysis:

Lollar et. al., 2007 Charecterized the compound stable isotopes to evaluation the contamination dissolved in groundwater. The multi-isotopes of carbon and hydrogen was used and the results of this study found that stable isotope identified the source of contamination in groundwater.

2.6 Groundwater management strategies under semi-aired area in Morocco:

Mohammed et. al., 2015 investigated the groundwater under semi-aired catchment for the wadi ouazzi basin in morocco city. Results of isotope content in water molecule illustrates that there is low evaporation of precipitation during the infiltration process. Tritium value in the groundwater of the Ouazzi Basin are below 1.5 tritium unit (<1.5 TU).

2.7 Use of radioactive tritium (^3H) and radiocarbon (^{14}C) isotope hydrology in water resources:

Samie et. al., 2018 used the radioactive tritium (^3H) and radiocarbon (^{14}C) as a dating tools to determine the age of groundwater, residence time, and thus refreshing the groundwater. Isotope tracers in catchment analysis known as tracing concept such as chlorofluorocarbons, Freon (CFCs) and Sulfur hexafluoride (SF6), are used for dating young groundwater, whereas noble gases ($T/^3He$) are used for determining the age and the water temperature during groundwater recharge, and consequently mean elevation of groundwater recharge.

2.8 Futuristic isotope hydrology in the Gulf region:

Kumar and Hadi, 2018, used the isotope technique in applications of groundwater management at Arabian Gulf region. this investigation focused on the evaluation of aquifer storage and recharge with its recovery system. The results explained that in this region the quantity of groundwater includes the hydrocarbon pollution and the solute movement of water was in unsaturated zone.

3. METHODOLOGY OF THE STUDY:

The mass spectrometer is an analytical method used for measuring mass to charge ratio of ions, the spectra are used to find an isotopic fingerprint of each sample were taken. The details of this test are that the groundwater sample molecules break up t the positively charged ions or without ions. Then the ions will separate based on their mass to charge ratio that becomes a spectrum of the signal intensity of detected ions as a function of the mass-to-charge ratio. For the aim of this investigation, samples of groundwater between July 30th 2001 and August 24th 2001, 22 from springs and wells from the northern Iraq (Erbil city) were drawn by (Dana, 2003), to make ^{2}H, ^{3}H and ^{18}O measurements. The isotopic composition of water, determined by mass spectrometry device as explained earlier, it is expressed in per mil (‰) deviations from the standard mean ocean water (SMOW).

3.1 Sampling points:

Natural springs are usually ideal sites for drawing samples of groundwater and its dissolved components representing a continuous outflow. One must be careful and make sure that the sample was drawn as close to the spring discharge as possible in order to minimize the effects of atmospheric pollution and decarburization. Drill mixture can be deposited on the walls of the well or it can penetrate the aquifer due to hydraulic pressure. The zone from where the samples drawn was defined and the contingents from other zones excluded then wells rinsed thoroughly before drawing the samples.

a. Isotope analysis:

As shown in table 1, Samples at different locations taken for analysis of Deuterium (D) ^{2}H and ^{18}O is proportionality simple because none of two isotopes measured for chemical and biological processes. During the sampling, the evaporation caused by permeable bottle caps or by partly filled bottles were prevented because it could represent problem when the heavy isotopes can be enriched in the residual water. Also, the samples containing elusive organic components was marked and pre-treated in the laboratory because gasses made a problem during the mass spectrometry measurement. The volume of 100 ml (minimum 10 ml) was taken through a glass bottle that tightly closed to avoid evaporation as explained earlier the isotopes of Deuterium (D) and ^{18}O identified with isotope ration mass spectrometer. The samples drawn for tritium (^{3}H) measurements in the direct analysis method one can use 50-125 ml (50 ml is taken for this investigation) bottle for all three isotope determinations without being the need of filter method or any special conservation method. Whereas, in electrolytic enrichment method usually 1 liter is necessary.

Table 1: Summary of the sampling points for isotope measuring data within the time interval between July 30th 2001 and August 24th 2001.

No	Location	Type	Water Level (m)	Date	Altitude (m)	$\delta\,^{2}H$ ‰	$\delta\,^{18}O$ ‰	^{3}H (TU)
1	Haji-Omran	Spring	-	17.08.2001	1673	-51.1	-8.93	13.4
2	Rayat	Spring	-	17.08.2001	1480	-45.8	-8.11	8.6
3	Chuman	Spring	-	17.08.2001	1140	-44.2	-7.82	9.3
4	Rezanok	Spring	-	17.08.2001	750	-40.9	-7.34	9.5
5	Piera-sawed	Spring	-	17.08.2001	1050	44.6	-7.98	11.7
6	Jundijan	Wells	8-15	17.08.2001	570	-47.4	-8.37	10.8
7	Diana	Spring	-	17.08.2001	720	-44.6	-7.79	12.8
8	Gali-Ali-Bag	Spring	-	17.08.2001	670	-43.8	-8.01	9.1
9	Bekhal	Spring1	-	17.08.2001	640	-44.5	-7.98	10.7
10	Bekhal	Spring2	-	17.08.2001	644	-43.8	-7.99	11.0
11	Harir	Spring	-	17.08.2001	740	-39.9	-7.28	10.2
12	Mirawa	Wells	19-22	17.08.2001	775	-31.7	-5.79	7.4
13	Betrma	Wells	65-70	24.08.2001	845	-37.9	-7.15	13.9
14	Shaqlawa	Wells	60-70	24.08.2001	840	-39.0	-7.28	12.0
15	Kawanjan	Wells	50-60	24.08.2001	950	-36.8	-6.85	10.8
16	Hirjan	Spring	-	24.08.2001	840	-36.8	-6.87	12.8
17	Kore	Wells	19-22	24.08.2001	600	-36.8	-6.83	6.8
18	Malla-Omar	Wells	15-20	24.08.2001	550	-33.2	-5.93	3.5
19	Per-Daud	Wells	30	24.08.2001	400	-29.5	-5.28	0.8
20	Kasnazan	Wells	15-20	30.07.2001	420	-29.1	-5.17	4.9
21	Bila	Wells	30-40	30.07.2001	700	-38.4	-7.27	11.2
22	Barzan	Spring	-	30.07.2001	720	-39.0	-7.30	9.9

Where:

- δ: the value of isotope content, referred to a standard.
- $\delta\,^{18}O$: δ value calculated from the oxygen isotope ration ($^{18}O/^{16}O$) and referred to Vienna V-SMOW standard. The absolute isotope ratio ($^{18}O/^{16}O$) ranges from 1:490 to 1:530.
- V-SMOW: Vienna Standard Mean Ocean Water, isotope standard for the determination of both $\delta\,^{18}O$ and $\delta\,^{2}H$ values of water and ice. It is submitted by IAEA (international atomic

energy agency in Vienna).

- δ^2H: δ value calculated from the hydrogen isotope ration ($^2H/^1H$) and referred to Vienna V-SMOW standard. The stable isotope ^2H is also named as Deuterium (D). The absolute isotope ratio ($^2H/^1H$) in groundwater ranges from 1:5800 to 1:10000.
- ^3H: is the tritium isotope and also named as (T).
- TU: is the tritium unit. 1 TU= 1 tritium atom per 10^{18} hydrogen atoms.

3.3 Transporting the samples to the laboratory:

The samples were transported to the (Arzinal) laboratory in Vienna/Namsa inside the suitable bottles. All samples from the province Erbil were drawn by trustworthy persons, Unfortunately, due to the political situation within this study, it had been impractical to personally access the sampling points of the springs and there is also no hydrological information about the sampled springs within the available technical literature. The subsequent description of the sampling points will therefore be considered provisional, and must be completed for further research by exact interpretation of the isotopic data.

4. Results and discussion:

4.1 Calculation of isotope measurements:

According to the equation that mentioned by (Dana,2003) the calculation was done. in column six in table (2), the Deuterium isotope (δ^2H) according to eastern Mediterranean meteoric water line (EMWL) founded by equation (1) as follow:

$\delta D = 8\ \delta^{18}O + 22$ ……….. (1)

whereas the global meteoric water line (GMWL) used the following equation to calculate δ^2H in column seven:

$\delta D = 8\ \delta^{18}O + 10$ ……….. (2)

and the local meteoric water line (LMWL) equation for the northern Iraq based on the isotope data of the groundwater, equation (3) is applicable for column eight.

$\delta D = 8\ \delta^{18}O + 20$ ……….. (3)

This equation defines the Kurdish meteoric water line (northern Iraq, Erbil city and the surrounding region).

Finally, in the last column, the Deuterium surplus was defined by equation (4):

$d = \delta D - 8\ \delta^{18}O$ ……….. (4)

Table 2: calculated results of the sampling points for isotope measuring data.

No	Location	Measurements			Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)
		$\delta^{18}O$ ‰	δ^2H	^3H (TU)	δ^2H ‰	δ^2H ‰	δ^2H ‰	d ‰
1	Haji-Omran	-8.93	-51.1	13.4	-49.44	-61.44	-51.44	20.34
2	Rayat	-8.11	-45.8	8.6	-42.88	-54.88	-44.88	19.08
3	Chuman	-7.82	-44.2	9.3	-40.56	-52.56	-42.56	18.36
4	Rezanok	-7.34	-40.9	9.5	-36.72	-48.72	-38.72	17.82
5	Piera-sawir	-7.98	-44.6	11.7	-41.84	-53.84	-43.84	19.24
6	Jundijan	-8.37	-47.4	10.8	-44.96	-56.96	-46.96	19.56
7	Diana	-7.79	-44.6	12.8	-40.32	-52.32	-42.32	17.72
8	Gali-Ali-Bag	-8.01	-43.8	9.1	-42.08	-54.08	-44.08	20.28
9	Bekhal	-7.98	-44.5	10.7	-41.84	-53.84	-43.84	19.34
10	Bekhal	-7.99	-43.8	11	-41.92	-53.92	-43.92	20.12
11	Harir	-7.28	-39.9	10.2	-36.24	-48.24	-38.24	18.34
12	Mirawa	-5.79	-31.7	7.4	-24.32	-36.32	-26.32	14.62
13	Betrma	-7.15	-37.9	13.9	-35.2	-47.2	-37.2	19.3
14	Shaqlawa	-7.28	-39	12	-36.24	-48.24	-38.24	19.24
15	Kawanjan	-6.85	-36.8	10.8	-32.8	-44.8	-34.8	18
16	Hirjan	-6.87	-36.8	12.8	-32.96	-44.96	-34.96	18.16
17	Kore	-6.83	-36.8	6.8	-32.64	-44.64	-34.64	17.84
18	Malla-Omar	-5.93	-33.2	3.5	-25.44	-37.44	-27.44	14.24
19	Per-Daud	-5.28	-29.5	0.8	-20.24	-32.24	-22.24	12.74
20	Kasnazan	-5.17	-29.1	4.9	-19.36	-31.36	-21.36	12.26
21	Bila	-7.27	-38.4	11.2	-36.16	-48.16	-38.16	19.76
22	Barzan	-7.3	-39	9.9	-36.4	-48.4	-38.4	19.4

4.2-Comparison of measured readings with Mediterranean and global meteoric water line:

As calculated in Table 1, the value of deuterium surplus (d) are mainly higher than 10, this finding was also determined by (Craig, 1961 cited in Dana, 2003) for a large number of measuring stations all around the world. This relatively high deuterium surplus is typical for the Mediterranean Sea region. The highest deuterium surplus in the research area is thus attributed to the humidity coming from the Mediterranean Sea. The cause of this surplus is the low relative air humidity prevailing in the Mediterranean Sea region. as shown in figure (1), most of the measure values from this study remain close to the Eastern Mediterranean Meteoric Water Line (EMWL) and others present some variations.

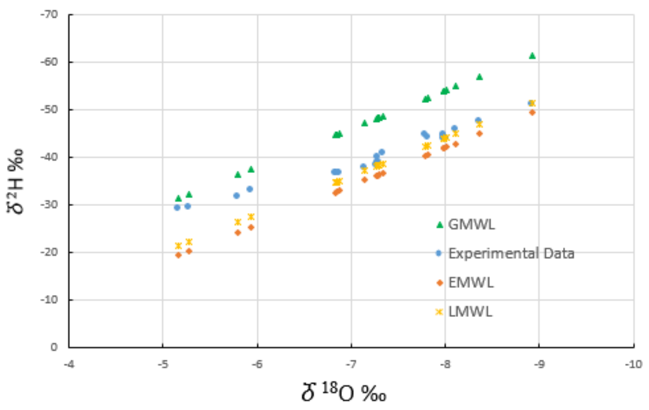

Figure (1). Relation between δ ^{2}H ‰ and δ ^{18}O ‰ and comparing it with different standards.

4.3 Constitution of ^{2}H and ^{18}O in groundwater:
The isotope composition of groundwater samples from ten wells and twelve springs. Usually the isotope composition of groundwater presents a large range as a result of influencing variables such as altitude, temperature, quantity of precipitation, and evaporation because the samples were taken in summer. Besides, it is assumed that groundwater systems store the ^{18}O and deuterium (D) content.

4.4 Deuterium excess (d):
The value of deuterium excess (d) was changed with climate, the warmer places have greater (d). it was lower than 15‰ are from Mirawa, Malla-Omar, Per-Daud, Kasnazan. These findings can probably be attributed to an isotopic enrichment due to the evaporation influences. The highest deuterium excess is about 20‰ was determined at sampling points at high altitude.

4.5 Concentration of heavy isotope (δ ^{18}O):
The concentration of heavy isotopes was at points from Haji-Omran, and Jundian which are -8.93 and -8.37 respectively. Both sampling points were the lowest values lie in higher catchment basins. From the point of view of the measured accuracy, Bekhal 1 and Bekhal 2 was -7.98 and – 7.99 respectively are presents no differences in their isotope ratio.

4.6 Tritium (^{3}H) content in spring water and groundwater:
Tritium is the only isotope that is part of water molecule. Its half-life is 12.32 years (Terwey, 1984). The tritium is important to allow the determination of groundwater dwell time up to 100 years. As shown in table 3, the tritium content was varied at different catchments in Kurdistan region. Its highest value was recorded in the groundwater from the mountain regions, while the lowest value was seen in the plain basin near Erbil city. Table 3 illustrates that the water age results from the law of the radioactive decomposition.

Table 3. Age of water with different TU (Dana, 2003).

^{3}H (TU)	10	5.7	3.3	1.9	1.1	0.6	0.4
Age (year)	0	10	20	30	40	50	60

As explained in table 4, the interpolating measurement values listed in table 2 with values in table 3 shows the water age at each position.

Table 4. Groundwater age at different location in Erbil city.

Location No.	Location	^{3}H (TU)	Interpolated age of water (Year)
1	Haji-Omran	13.4	0
2	Rayat	8.6	3.26
3	Chuman	9.3	1.63
4	Rezanok	9.5	1.16
5	Piera-sawir	11.7	0
6	Jundijan	10.8	0
7	Diana	12.8	0
8	Gali-Ali-Bag	9.1	2.09
9	Bekhal	10.7	0
10	Bekhal	11	0
11	Harir	10.2	0
12	Mirawa	7.4	6.04
13	Betrma	13.9	0
14	Shaqlawa	12	0
15	Kawanian	10.8	0
16	Hirjan	12.8	0
17	Kore	6.8	7.44
18	Malla-Omar	3.5	19.17
19	Per-Daud	0.8	46
20	Kasnazan	4.9	13.33
21	Bila	11.2	0
22	Barzan	9.9	0.23

the water in the well from Per-Daud has a ^{3}H content of less than 1 TU (0.8 TU) which allows the discussion that the water is older than 40 years (about 46 years). Also, for sampling point at Malla-Omar, the tritium content was measured as 3.5 TU which means that the age of water at this location is older than 10 years (about 19 years). In case of this proportionally long retention time of groundwater, there is a danger of a lake of balance between the natural supply and the extraction from the wells.

5. **Conclusions**:

The investigation of Appling an isotope technique on the groundwater in northern Iraq was the first step of determination the origin and dwell time of the respected water. this could be of great help for the further development of the region especially for the population, agriculture, industry and economy. The main key points of this investigation were summarized in the following points:

- The comparison of measured readings with Mediterranean and global meteoric water line has a slight difference that can be ignored due to the local climate at our region.
- The groundwater systems store the ^{18}O and deuterium (D) content out of which they were formed.
- From Mirawa, Malla-Omar, Per-Daud, Kasnazan, the value of deuterium excess (d) was smaller than 15 per mil due to the effect of evaporation at these places.
- The heavy concentration of □ ^{18}O isotope were -8.93 and 8.37 per mil were from Haji-Omran and Jundian respectively.
- The tritium (^{3}H) content from Per-Daud was 0.8 TU, the dwell time of water was older than 40 years.

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