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RESEARCH PAPER

Estimating Mean Residence Time of Groundwater in Central Basin/Erbil using Environmental Isotopes

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A B S T R A C T:
The average time of input water needs to recharge the groundwater basin and reach a catchment outlet, whether it follows a vertical or horizontal flow direction, is known as the mean residence time (MRT). This study aims to identify the theory concepts of estimation MRT of groundwater in a well using environmental isotope technique. For this purpose, the spatiotemporal data of oxygen-18 of precipitation in Erbil city were taken from Global Network of Isotopes in Precipitation (GNIP). Furthermore, a well named (HWL) in Erbil city that located at central basin of groundwater were selected. Because of $\delta^{18}O$ measured as a natural tracer for estimation MRT in groundwater, the sample analyzed for isotope by using the cavity ring down spectrometer. The derivation of sine wave regression was used to measure $\delta\ ^{18}O$ variations in both precipitation and groundwater.
Decreasing isotopic amplitude of $\delta^{18}O$ due to the phase shift from input (precipitation) which is 5.74 ‰ to output (groundwater) to 0.277 ‰ can solve by sine wave equation to estimate MRT of groundwater in aquifer. Results showed that, by temporal response of groundwater to precipitation inputs, MRT from HWL well in Erbil city estimated was 1202 days. This concluded that groundwater spent about 1202 days for recharging HWL well.
2The comparison of $\delta^{18}O$ in precipitation and groundwater in Erbil city range from -10.1 to -2.4 per mill for rainfall. These values varied from -7.05 to -6.86 when inters groundwater from HWL well which are typically affected by a reflection of the current state climates.

KEY WORDS: Isotopes in Erbil, Oxygen-18, Groundwater, Residence Time.
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1. INTRODUCTION:

Groundwater can be characterized by using environmental isotope interpretations. it's very important to implement the isotope technique to find the MRT for recharging any well, this will involves frequently sampling at the same well over a period. Estimates of groundwater residence times are required for the management of groundwater resources in an environmentally responsible manner. Tracer methods are recomme-*-nded* among several hydraulic, hydrogeological, and hydrological methodologies to enhance groundwater dwell duration calculations. Because of long duration of in-situ measurement, shipping the samples to nearest laboratory and cost of testing, this topic was not investigated widely by researchers in comparing to the other hydrological studies. Spatially, in Kurdistan region of Iraq country the MRT for groundwater at wells was not studied yet. Some publications were explained in the following section.

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2. LITERATURE REVIEW:

(***Tekzleab et al.*, 2014)** studied for (^{18}O) and deuterium (^{2}H) in two catchments in Ethiopia's Blue Nile basin, Chemoga (358 km^2) and Jedeb (296 km^2). Data sets for streamflow taken from gauge stations between July 1, 2009, and October 31, 2011. Regression models were used to create rating curves based on stage discharge relations. The MRT in the Chemoga and Jedeb catchments, respectively, are calculated to be 4.1 and 6.0

months based on the seasonal fluctuation in ^{18}O in precipitation and streamflow.

(Seeyan, 2014) The water chemistry (cations and anions) and isotope technique were investigated in a recharge area in Kurdistan region (shaqlawa and Harrir) basin located at northeast of Erbil city and the Safin anticline at the southwest. The total of 100 samples of deep groundwater, river water and spring water were drawn during wet and dry seasons. The samples of total inorganic carbon and dissolved organic carbon also samples for Radiocarbon (^{14}C) collected in polyethylene bottle. The experiments of isotope compositions such as (^{18}O, ^{2}H and ^{14}C) were done in Poznan Radiocarbon Lab., Poland. The procedure of converting ^{14}C to the percent of modern carbon (pmC) was implemented in the laboratory by using accelerator mass spectrometer device. Results of this study focused on the groundwater age, direction of water and the interface between aquifers. The relation between (^{18}O and ^{2}H) for all samples located above the GMWL with slope of 7.7 due to either evaporation or water-rock interaction. The local deuterium excess was 14.4‰ which is higher than global value (d=10‰) due to the humidity of this basin. The increase of altitude due to Safin, Pirmam and Harrir mountain leads to decrease in delta valve of ^{18}O of water samples.

(Kavousi and Raeisi 2015) This investigation not used the isotope techniques, but used an average-weighted by discharge to get the mean residence time for the Sheshpeer Spring located near to Zagros Mountain in Iran. The Sheshpeer unconfined aquifer's catchment area contains 259 holes. The suggested technique resulted in a mean residence duration that was around one year longer than that of the uranine dyed tracing. The suggested method's mean time is reflective of all active circulating water throughout the whole aquifer, unlike the tracer mean time, which represents flowing water between the injection and emergence stations.

(Shah et al., 2017) Used tritium, sine wave models, and tracer testing for finding the mean residence time (MRT) of karst groundwater in three mountainous catchments of the Western Himalaya. Water samples were taken from streams, karst, glacier melt, and precipitation. When compared to the results of the sine wave model, the MRT calculated using the tritium approach has longer MRT in warm karst springs and shorter MRT in cold karst springs. The tracer breakthrough curves (TBC) collected for various springs indicated quick channel flow and brief groundwater travel times.

(Jeelani et al., 2018) identified the areas of groundwater/springs that receive recharge in mountainous catchment of the western Himalaya. The total of 8 samples of precipitation and 6 for groundwaters collected. The sampling period runs monthly from November 2010 to January 2012. Using an isotope ratio mass spectrometer, the geographical and temporal distribution of ^{18}O and ^{2}H values were examined. Based on amount weighted mean precipitation isotopic values, the results showed that a mean altitude gradient of -0.15 and -1.16 per 100 m change in elevation for oxygen-18 (^{18}O) and Hydrogen-2 that named as Deuterium (D), respectively, was detected.

(Zhou et al. 2021) variations of stable isotope in river water among four sub-catchments in Tuojiang River catchment in China was investigated. Water sampled from four sub-catchments (Yazi River catchment, Shiting River catchment, Jiangxi River catchment, and Pihe River catchment). From May 2018 to April 2019, 113 precipitation samples in total were taken. 116 river water samples were taken between May 2018 and April 2019 at the outlets of four sub-catchments. The result shows that Pihe River has depleted isotope value and the lowest slope of river water line. The seasonal patterns in ^{18}O are modelled using a sine-wave technique. The Yazi River, Shiting River and Jiangxi River catchments all have estimated MRTs that range from 346 to 374 days, whereas the Pihe River catchment has a larger MRT of 493 days.

(Hssaisoune *et al.*, 2022) isotopic analysis performed for 67 groundwater samples from the karst aquifer in the Rif Mountains in Morocco. The measurable tritium levels (>2.7 TU) discovered in groundwater are consistent with this little residence duration. The Rif Mountains' groundwater contains recent recharge (within the last 60 years), according to this evidence. The relationship was made for showing the correlations between springs' altitude and the ^{18}O concentration of precipitation. The elevation of the recharge area was determined to be 0.18 per mil per 100 m altitude based on δ^{18}O measurements.

(Kuo et al. 2022) estimated the MRT of two types of groundwater in Taiwan. two wells at depths of 160 and 2200 meters were sampled over the course of 18 months. Stable isotopes concentration of oxygen-18 and deuterium was analyzed to find the groundwater dwell time due to seasonal change. Lighter isotope composition values are seen in deeper wells. The estimated MRTs for wells with a depth of 2200 m and 160 m are 1148 days and 150 days, respectively. This suggests that groundwater recharged both wells at separate times as150 and 1148 days, respectively.

(Wang et al. 2022) employed sine-wave exponential modeling to predict water MRT in a high-altitude permafrost catchment (5,300 m a.s.l.) in the middle Tibetan Plateau. In this area, direct precipitation had a major impact on the stable isotope compositions of stream and supra-permafrost water. During the observation period from June to October, 416 precipitation samples were taken in high volume collectors. In the Xiaoliuyu watershed, 755 stream water samples and 296 supra-permafrost water samples were collected every year from June to October at intervals of around one day. According to the results, the MRT for water from streams and supra-permafrost estimated to be 100 and 255 days, respectively.

(Schmidt et al. 2022) estimated the travel time of four groundwater monitoring wells and two surface water spots by using four different stable and unstable isotope elements like (Radon-222, Sulfur-35, Tritium, and oxygen-18). These tracers have different concentration in water samples, the Radon-222 concentration is higher than other used isotopes. The Sulfur-35 concentration measured in surface water was about 4 times higher than the concentration in groundwater. While the median oxygen-18 fingerprint in surface water was similar to the signature found in groundwater. This finding reveals that groundwater mean residence times varies between 5 and 6 months based on The Sulfur-35 and oxygen-18.

3. MODEL THEORY:

The reduction of seasonal fluctuations in ^{18}O and ^{2}H during infiltration and groundwater flow is influenced by the physical/hydraulic characteristics of the unsaturated zone and/or aquifer medium. The main factor that controls the MRT is the seasonal amplitude in ^{18}O and ^{2}H of the sine wave curve which is minimized after groundwater recharge.

It is necessary to idealize groundwater flow in the geo-hydraulic system taking into account the physical qualities of the used isotopes and the flow parameters. There are three main conditions of groundwater movement involving the piston (closed system) flow movement of groundwater in confined aquifers without and with dispersion, as well as the exponential model. In figure (1), the piston flow model is schematically depicted which presents the most basic hydrological phenomenon. The flow in confined aquifers is typically well described by the piston-flow model. when the duration of the groundwater recharge exceeds the groundwater's maximum residence time in the aquifer.

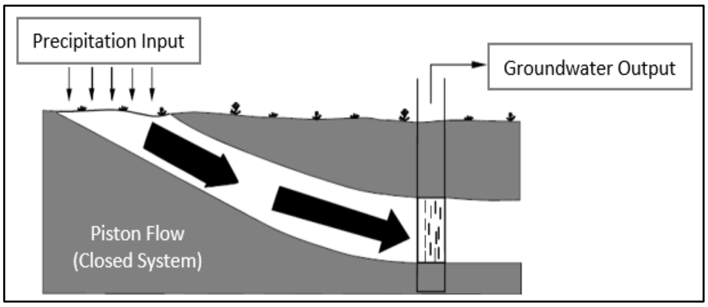

Fig. 1 Piston flow for groundwater movement (Texas Department of Transportation 2016).

The dwell time can be calculated using the seasonal variation in ^{18}O in precipitation and groundwater over frequently sampling period. (Zhou et al., 2021) shows equation (1) according to dwell time distribution f(τ), the groundwater outputs composition at any given time $\delta_{out}(t)$, consists of previous inputs that have lagged $\delta_{in}(t-\tau)$, where (τ) is the difference in time in the composition of the input and output tracers.

$$\delta_{out}(t) = \int_0^\infty f(\tau)\ \delta_{in}(t-\tau)\, d\tau \quad \ldots\ldots\ldots\ldots 1$$

And, in piston flow model, the response function is given by the well-known (Dirac function) δ which is:

$$f(\tau) = \delta\ (t-\tau)$$

For exponential model, we assume that there is no tracer exchange between the flow lines and then obtain the following response function:

$$f(\tau) = \frac{1}{\tau_m}\ e^{(\frac{\tau}{\tau_m})} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

where τ is the transit time, t is the time of tracer exit from the catchment and $(t-\tau)$ represents the time of tracer enter into the catchment, τ_m is MRT and $f(\tau)$ is a representation of the transfer function. An approach that indicated in the aforementioned equation is only appropriate when the system is steady and the mean flow pattern is stable. The proportional weighting of how an isotope tracer exits a watershed is characterized by the residency time distribution $f(\tau)$.

In the current investigation, the variation of $\delta^{18}O$ in groundwater compared to the sinusoidal input from precipitation that modelled on the catchment area in Erbil city. The $\delta^{18}O$ contents of Erbil city precipitation represent the seasonal variability, which is frequently passed on to groundwater. With respect to displacement of input and output isotope concentration in groundwater systems, its decreasing amplitude in groundwater can be based on the sinusoidal function as shown in figure (2), which is a sine wave approach.

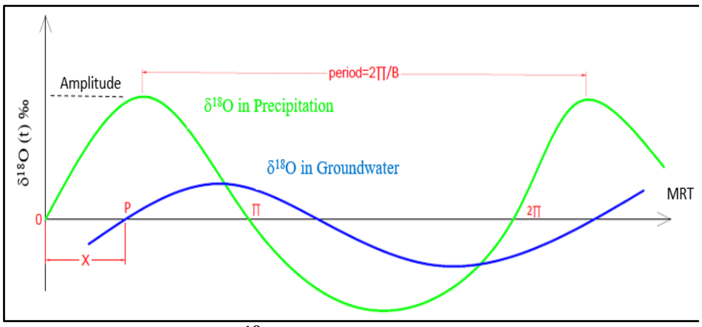

Fig. 2 Variation of $\delta^{18}O$ in groundwater compared to the sinusoidal input from precipitation.

This approach is written below (Clark and Fritz 2013):

For precipitation, the displacement equation of $\delta^{18}O$ in precipitation at point (O) is:

$$\delta_p(t) = A_p \sin \omega t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

While this equation for groundwater at point (p) will become:

$$\delta_g(t) = A_g \sin (\omega t + C) \quad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

where:

$\delta_p(t)$ and $\delta_g(t)$ is the input and output isotopic composition at time (t). A_p and A_g represent the amplitude (in ‰) of the precipitation and groundwater variations, respectively. ω is the angular velocity of wave and C is the phase shift of the output function as compared to the input function (phase difference of precipitation and groundwater at points (O and P).

To write the equation for groundwater in another form, for (L) length of wave, the phase difference is 2π. Therefore, for a unit length, the phase shift will be $(2\pi/L)$ which is the wave number, and for any shifting length of wave (x), the phase difference (C) will be defined as:

$$C = 2\pi x/L \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

And, angular velocity (ω) = distance / time. For a unit length of (2π) is:

$$\omega = 2\pi/B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

The sine-wave function was used in this study to predict the seasonal variations in $\delta^{18}O$ to fit the seasonal variations in precipitation and groundwater, which defined by equation below:

$$\delta^{18}O(‰) = y_o + A \sin\left[\frac{2\pi}{B}t + C\right] \quad \ldots\ldots\ldots 7$$

where y_o is vertical shift of curve which is the weighted average annual value of $\delta^{18}O$ in ‰, A is the seasonal amplitude of $\delta^{18}O$ in ‰, B is the angular frequency constant (B= $2\pi/153$ = 0.0411 rad/day) in this study, the variation of $\delta^{18}O$ used in is five months which is period of the seasonal cycle and t is time in days.

In terms of a watershed's temporal response to precipitation inputs, the MRT of a catchment offers a straightforward description of the effects of storage and mixing within the catchment. The commonly used exponential model, which assumes that precipitation inputs would quickly mix with resident water to produce surface and groundwater, is used to estimate MRT. (McGuire and McDonnell, 2006) cited by (Wang et al. 2022) solved analytically of the MRT (τ_m) for the exponential model can be derived by combining equation (1) with equation (7).

$$\tau_m\,(MRT) = \frac{1}{2\pi} \times \sqrt{\left(\frac{A_g}{A_p}\right)^{-2} - 1} \quad \ldots\ldots\ldots 8$$

Where:

The above equation is measured the mean residence time by years (Kralik 2015)?.

4. INVESTIGATION SITE AND DATA COLLECTION:

The Erbil basin in Kurdistan region of north-east of Iraq country Iraq, is a groundwater reservoir in Erbil province. This basin divided into three sub-basins named as Kapran, Central and Bashtapa. The current investigation focused on the well in central sub-basin of groundwater. As shown in figure (3), the boundary of catchment area draws with support of google earth which covers about 1315 km^2. The well in (New Hawler) domain named as (HWL) was selected for sampling which located between Erbil city center and Kasnazan district. It is about 6.4 km far from Erbil citadel and 7 km far away from Kasnazan district. The coordinates of the well are (longitude: 44.078781, latitude 36.201199 decimal degrees) with an altitude of 483 m above sea level.

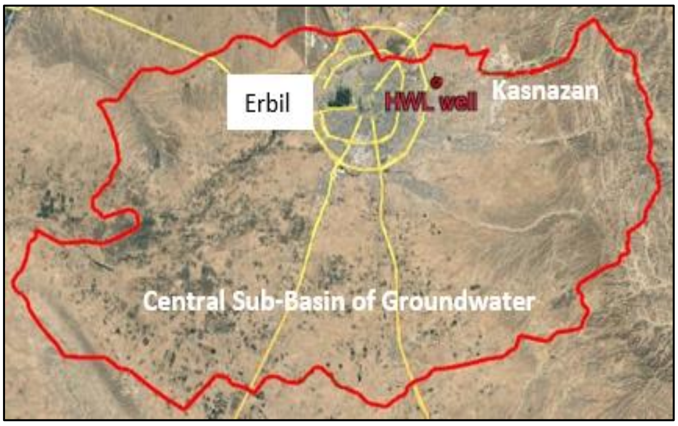

Fig. 3 Location of the HWL well in Central basin of groundwater in Erbil city.

This well is built at 2011 for a depth of 300 m. Total product was 95 gal/min used a source of fresh water supply for people's daily usage at this zone. During pumping test, the static water level is 90 m, while at the time of sampling the water depth recorded as 96.2 m by water level sounder. This means that about, the water level lowered at this well about 6 m during last eleven years.

For sampling procedure Firstly, it is important to accurately record the coordinates of well location using *global positioning system* device (GPS). Before sample drawn, the well needs to be pumped out about three well volumes to purge the well with a pump. Then, a volume of one litter of water collected in the polyethylene bottles used that screwed tightly and identical information on the bottles was written. The main data which wrote on the bottles include: (date and time of sampling, field code, well name, field measurements, sample size and type of analysis). Then transferred to isotopic laboratory named DSI at Ankara/ Turkey.

The determination of isotope composition oxygen-18 was made using Cavity ring down spectrometer device (CRDS). It runs the water samples with excellent results thus far, for approximately a month (long-term external precision of 0.04 for oxygen and 0.19 for hydrogen). It includes 105 microplates to put the water sample inside it as the instrument is type two which is faster high-precision. This instrument provides a platform for advanced research into all aspects of the water cycle: water vapor, liquid water, or water trapped in solids. The accuracy of this method, which is based on Beer-law Lambert's and non-dispersive laser absorption, is greater than 0.5 for δD and 0.15 for $\delta^{18}O$.

Then oxygen-18 results are reported as parts per thousand (‰) with respect to V-SMOW using the delta notation (δ) below and the analytical error of ± 0.1‰.

$$\delta\,(‰) = \left(\frac{R_{\,sample}}{R_{\,standard}} - 1\right) \times 1000 \quad .... \; 7$$

where; R is the isotope ratio of oxygen ($^{18}O/^{16}O$). Harmon Craig (1961a) cited in (Clark and Fritz 2013) introduced standard mean ocean water (SMOW) as a baseline for measurements of ^{18}O and ^{2}H in water.

Frequently $\delta^{18}O$ value of groundwater at HWL well were used to find the MRT to recharge this well. The precipitation data taken from (Waterisotopes.org) that has a web link with global network for isotopes in precipitation (GNIP). GNIP Introduced in 1960 by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) as the worldwide isotope tracking network of hydrogen and oxygen isotopes in precipitation. Basic information for the use of isotopes in hydrological investigations within the context of water resources assessment, planning, and development is provided by the analysis of the temporal and spatial fluctuations of environmental isotopes in precipitation (primarily oxygen-18 and deuterium).

Monthly value $\delta^{18}O$ variation in precipitation can find based on the coordinate system of Erbil city. In the precent study 5-months data from March to July 2022 were used.

5. WAVE FORM EQUATION:

By using regression analysis to fit equation (5) for measuring experimental data, parameters in that equation like (Y, A_g, and C) were computed. in this study the SigmaPlot (V.15) software was used to identify the values of model fitting parameters that result in the smallest value of the squared sum of the residuals between model output and data measured. The software performed different iteration for precipitation and groundwater to report the parameters of waveform equation. By calculating the fitted sine with 95% wave's amplitude's confidence interval, the uncertainty of the MRT estimates was measured. Specifically, using Eq. (3) to produce MRT error (the upper and lower 95% confidence bounds of the predicted MRT) by applying the 95% confidence of the fitted sine-amplitude wave's. This software is specialized tool for data analysis and scientific graphing. utilized as a nonlinear curve fitting and to create all different kinds of graphs and charts. It uses vector-based programming as its language. Additionally, SigmaPlot offers access to statistical tests that can be used for essential data analysis.

6. RESULTS AND DISCUSSION:

The general findings and analyses of the present investigation is the determination of MRT to recharge the well in Erbil city by using environmental isotopes. The seasonal variations of oxygen-18 concentrations in both precipitation and groundwater from HWL well were analyzed.

6.1 Residence time of groundwater:

This method is common in natural groundwater systems, that are subjected to interaction with surface water, like mixing of groundwater of different age. Using this method has some difficulties to complete it like long duration sampling of both precipitation and groundwater and transporting samples to the laboratory for analyzing stable isotopes is another complexity of the study. The groundwater's isotope composition takes some time to respond to the isotope composition of the precipitation.

As shown in figure (4), the sine wave curve fitted with observed precipitation data after performing 15 iterations. Results obtained the amplitude of $\delta^{18}O$ for precipitation variation was to be 5.74 ‰ with excellent determination coefficient of the relation (R^2 = 1).

For groundwater at HWL well data analysis and fitting results of SigmaPlot software, the parameters estimated after performing 14 solved iterations and the amplitude of $\delta^{18}O$ for groundwater was found to be 0.277 ‰. Results of experimental data and fitting model was shown in figure (5) with a good determination coefficient of the sine wave relation as (R^2 = 0.994).

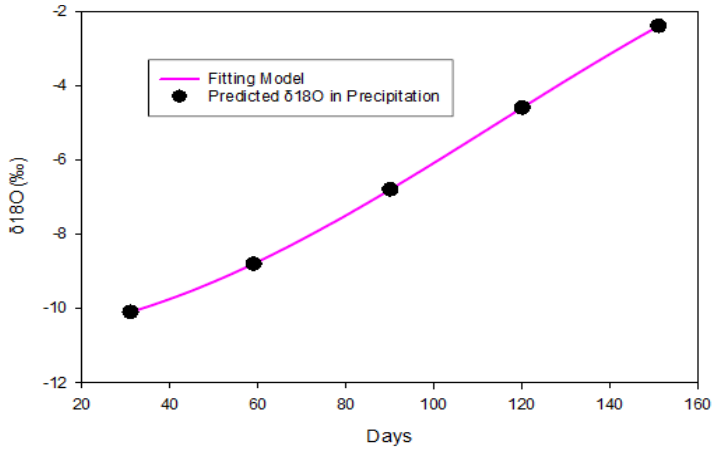

Fig. 4 Sinusoidal wave for $\delta^{18}O$ variation in precipitation.

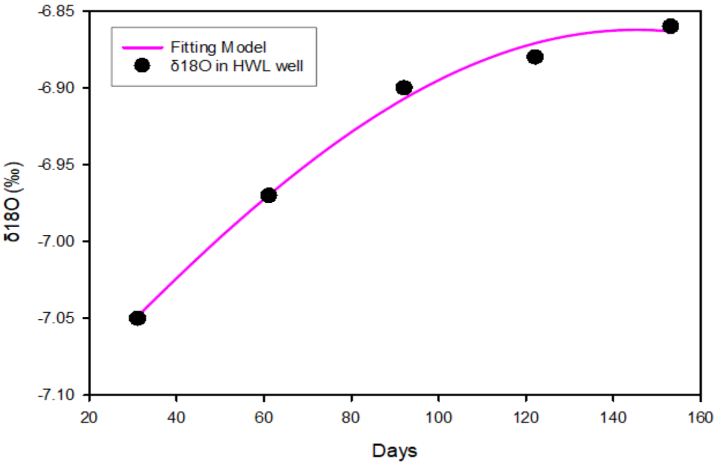

Fig. 5 Sinusoidal wave for $\delta^{18}O$ variation in groundwater.

Generally, a short MRT of the stream water shows that surface water reacts to precipitation very quickly than that of groundwater. On the other hand, the longer MRT indicates more complicated soil water recharge and storage processes

Furthermore, using equation (6) to estimate MRT from HWL well illustrates that the estimated MRT is about 1202 days which means that the groundwater spent about 1202 days for recharging HWL well. This result is an estimation that controlled by the amplitude of sinusoidal wave of $\delta^{18}O$ for both precipitation and groundwater that may have some errors due to some topography and catchment climatic change.

6.2 Comparison of Oxygen-18 Variations in Precipitation and Groundwater:

In this section, A box and whisker diagram that shows the distribution of a data set as five numerical summaries, such as the upper quartile (Q_1), median(Q_2) and lower quartile (Q_3) values in the middle box span, was created. The box's whiskers, on the other hand, lines that extend from each end to indicate the minimum and maximum observations.
Figure (6) illustrates the comparison of isotope of $\delta^{18}O$ for both precipitation and groundwater in Erbil city. Results showed that the groundwater has higher values of $\delta^{18}O$ contents. This likely represents seasonal variability and meteorological conditions in which the precipitation formed. Lower $\delta^{18}O$ values correspond to larger rainouts of the air mass, observed as depletion of the heavier isotope ^{18}O in rain in both seasons, summer and winter.

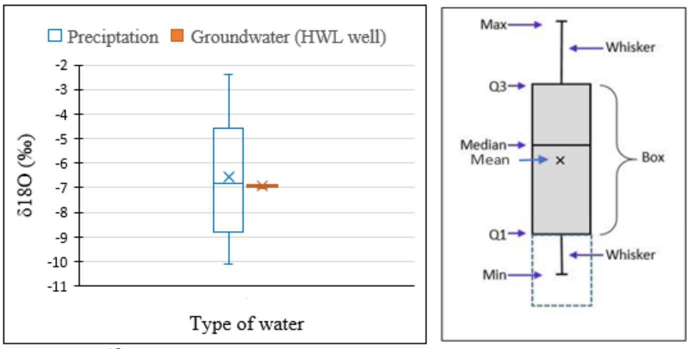

Fig. 6 $\delta^{18}O$ Variations in precipitation and groundwater.

The $\delta^{18}O$ values of precipitation in Erbil city during spring season of five months range from -10.1 to -2.4 ‰ with a mean value of -6.54 ‰. The negative value indicates lower abundances of rare isotope in the sample than in standard which is (VSMOW: Vienna standard mean ocean water). VSMOW is baseline for measurements of ^{18}O and ^{2}H in water. While in groundwater from a well in HWL these values ranged from -6.86 to -5.77 ‰ with a mean value of -6.186 ‰. This concluded the isotope values of groundwater, which is typically a mixture of precipitation.

7. CONCLUSION:

MRT can be considered as the typical length of time that water passes in an underground system before reaching a certain location. In order to successfully estimate the MRTs of sub-surface water, the samples should be taken at least four times a year, but monthly samples are more likely to show the maximum groundwater variation. Both (precipitation and groundwater) or (precipitation and River water) contents of $\delta^{18}O$ show notable seasonal changes. MRT was estimated based on these seasonal variations. In this study, the seasonal fluctuation of $\delta^{18}O$ in precipitation and groundwater flow were used to determine MRT of groundwater in the HWL well near Kasnazan district. The estimated residence time was about 1202 days. The duration of 3.3 years is not long period for researching this well. This demonstrated that the groundwater in the Kasnazan catchment area can easily be contacted by precipitation.

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