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RESEARCH PAPER

A Review of Modern Isotope Applications in Engineering Hydrology

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A B S T R A C T:
Climate change can affect water systems in general by varying rainfall quantities and distribution, increasing air and water temperatures, and eventually affecting groundwater sources. Hydrology is a water science of studying the occurrence and distribution of water on the planet and in its atmosphere. In this regard, isotope technology has arisen as an effective scientific approach for addressing water-related concerns such as groundwater recharging, process improvement, surface water research, salinization and pollution investigations, and so on.

The current paper emphasizes the importance of isotope technology and applications for water management in changing climatic conditions by reviewing a series of publications including four investigations in Kurdistan region of Iraq and eight other studies at (California, China, Romania and Taiwan) that focus on the variation of oxygen-18 and deuterium isotopic concentrations, as well as the various factors that influence them. Also, the methods of estimating the dwell time of groundwater in an aquifer by using stable isotope behind the dating criteria with radioactive carbon and tritium in water molecules.

KEY WORDS: Isotope hydrology, stable isotopes, radioactive, groundwater applications.
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1. INTRODUCTION:

The isotope technique in modern engineering hydrology is the most effective method for achieving the exact solutions of problems in water resources management. (Clark and Fritz, 2013) explains that the terminology of isotope comes from Greek language in which (isos means equal and topos means the place) and suggests that there were several isotopes for a given element around the turn of the century. In engineering hydrology, the isotope composition of water (Oxygen and Hydrogen) will be used as tracers in different application. Generally, isotopes were divided into two parts like stable isotopes that naturally produced and unstable (radioactive isotopes).

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The characteristics of environmental isotopes in water resources management is depends on the nature of geographical region of the catchment boundaries. Therefore, this modern method has a main role in quantity and quality estimations of water resources that sometimes cannot be achieved by old fashion techniques.

The most famous organization established in 1957, which supports the development of nuclear energy is (IAEA) means (international atomic energy agency) located at Vienna which is capital of Austria. The program of this organization consists of science and technology field, and the isotopes have a meaningful publication in hydrological investigations which played a progress role in recognizing and development of isotope procedure in the sustainability and management of both surface water and groundwater throughout different engineering applications.

In the current research, the literature summarized and the main critical evaluation of what researchers have published about isotope hydrology. Then, each point of view was examined, as well as any strengths or faults discovered in the research methodology or finding based on the problems that have a more compact with water resources engineering.

2. USE OF ISOTOPE TECHNIQUE:

Before analyzing any hydrological problem, it is required to first understand the background of the tritium (^{3}H composition in water which is radioactive isotope) concentration in local surface water such as precipitation and river water. Due to atomic and hydrogen bomb experiments in the 1962, results the tritium quantity display in water is due to a cosmic ray on atmospheric nitrogen therefore natural tritium levels increased dramatically.

The following are the most common uses of isotopes in engineering hydrology (Clark and Fritz, 2013):

- Groundwater origin.
- The time it takes for water to get from the recharge area to the aquifer.
- Calculate the groundwater basin capacity.
- Determining the flow path and velocity.
- Interfere between different aquifers (recognizing the boundary).
- Interconnection between surface and groundwater.
- Groundwater dating
- Investigations concerning groundwater contamination.
- Origin and mechanism of groundwater salinity and pollution.

The most important reasons to employ environmental isotopes identify in what kind of hydrological fields can be used:

- Its low cost when compared to the expense of traditional hydrological techniques, as the cost of an isotope test is frequently rather low. The variation of costs depends mainly on the laboratory instructions for completing each isotope test.

- The isotopes often reveal information that other techniques may not be able to provide. On the other words, results which are exceedingly precise and do not require any interpretation in the isotope procedure. For example, we can confirm exactly where this water comes from by evaluating at its age, whether it comes from the hydrological cycle or from before it.

- In addition, the experiments in conventional procedures of any hydrological study will take longer time in compared to the isotope testing.

3. REVIEWED INVESTIGATIONS IN KURDISTAN CATCHMENTS:

The following section includes the overall studies on the assessment of the water quality at different locations in Kurdistan region of Iraq through implementing the engineering isotope tools.
The main points of review focused on the study area, type of water sample (spring water, groundwater, runoff water … etc.), types of isotope composition, the laboratory for testing the isotope compositions, field measurement data.
Water samples sent to an European country because there were no isotope laboratories in our country. A summary of these studies is showed in table (1). The EC is electrical conductivity of the samples.

Table (1) information on the reviewed investigations in Kurdistan region of Iraq.

No.	Author	Study Area	Type of water	No. of Samples	Isotope Type	Laboratory for Isotope tests	Field measurement
1	Mawlood, 2003	Haji-Omeran to Barzan	Groundwater from wells and springs	22	^{18}O (Oxygen-18) ^{2}H (Deuterium) ^{3}H (Tritium)	Austrian research and test center Arsenal in Vienna	Temp. PH EC
2	Ali et. al., 2012	Ganau Lake, Ranya	Surface water	2	^{18}O (Oxygen-18) ^{2}H (Deuterium) ^{3}H (Tritium)	Uni. Of Waterloo Env. Isotope Lab. (Canada)	Temp. PH EC
3	Seeyan & Merkel, 2014	Shaqlawa-Harrir basin (and Safin anticline at southwest)	Deep Groundwater, Spring water, and river water	100	^{18}O (Oxygen-18) ^{2}H (Deuterium) total inorganic carbon, dissolved organic carbon ^{14}C (Radiocarbon)	Poznan Radiocarbon Lab., Poland	
4	Mustafa et. al., 2015	Karst Springs of Makook Anticline (Ranya) ≈ 400 km^2	Spring water	48	^{18}O (Oxygen-18) ^{2}H (Deuterium)	Technische Universität Bergakademie Freiberg, Germany	Temp. PH EC

The main points of finding of the aforementioned investigation are include: the recharge area, age dating, movement of water … etc. as described below for each author:

(Mawlood, 2003) found the large compositions of isotopes in water due to the effect of sea level, temperature as well as precipitation and evaporation changes. The relation between ^{18}O and ^{2}H named as global meteoric water line made by (Craig, 1962 cited at (Clark and Fritz, 2013))

were plotted by using the local meteoric water line (LMWL) equation (as written below: equation 1) for the northern Iraq based on the precipitation data and the value of deuterium excess in this region found to be about 20 per mille (‰).

$$\delta D = 8\ \delta\ ^{18}O + 20 \quad \ldots \quad (1)$$

Furthermore, the dwell time of groundwater at 22 locations were investigated. The groundwater in Per-Daud site has a tritium concentration (^{3}H) of 0.8 TU (Tritium unit) the calculations mean that the water is old because their age excess 40 years. The tritium content of water obtained from Haji-Omran was 13.4 TU, indicating that it was not about current water.

Also, the effect of altitude on the δ ^{18}O value in this study area is around -0.23‰ per each 100 m of altitude.

(Ali and Aziz, 2012) Used Erbil MWL by (Mawlood, 2003) and compared with the values from global meteoric water linear. Results showed the similar composition of isotope values as written below:

- The age of water samples explained to be two types such as modern water and old water based on the tritium value such as: (^{3}H > 0.3 TU is Modern water, while (^{3}H ≤ 0.3 TU is old water). Spring water at Ganau lake at Ranya found to be recharged water (modern spring water).

- Relation between oxygen-18 and hydrogen-2 indicates that the water in Ganau-1 lake at Ranya located below GMWL (global meteoric water line) due to large surface water evaporation but for Ganau-2 it falls between GMWL and Erbil MWL (Mawlood,2003).

- The isotope composition reveals that Ganau lake at discharging of the deep artesian water. the aquifer assumed to be semi-confined therefore the fresh water and brine solution is flowing through fault planes to the Ganau lake.

(Seeyan S, 2014) focused on the groundwater age 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.

(Mustafa, Merkel and Weise, 2015) Determined the source and residence duration of water moving toward the aquifer. The water quality of this area has low salinity content and its suitable for drinking water and agricultural purposes. The isotopic behavior of the area's precipitation reveals temperature and quantity effects. The hydraulic and hydrodynamic features of karst aquifers are influenced by stable isotope enrichment.

4. REVIEWED INVESTIGATIONS OUTSIDE OF KURDISTAN:

The hydrological investigation of water isotopes that conducted throughout different locations surrounding Iraq cities and in the European countries are reviewed in the followings:

(Muir and Coplen, 1981) studied the groundwater movement in a valley named (Santa-Clara) at the northern of California. The samples of three different types of water were drawn along twenty-four different sites throughout different durations starting of March/1975 to April/1977. Oxygen-18 and hydrogen-2 isotopes were found in parts per thousand as written in table (2). The relative amounts of native groundwater and refilled foreign water pumped out from wells were calculated using oxygen and hydrogen to trace the flow of withdrawn water in the area extending.

Table (2) Isotope compositions by Muir & Coplen, 1981.

Water Sample Type	δ ^{18}O ‰	δ D ‰
Local runoff	-6.00	-40.00
Local native groundwater	-6.10	-41.00
Withdrawn water	-10.20	-74.00

Results of isotope composition of oxygen was proportionate to the SMOW (standard mean ocean water) in parts per thousand (‰). In a specified gradient direction, the California water was diluted with local groundwater.

Two wells have approximately 74 percent northern California water, while six wells yield more than 50 percent. As well as, the delta values of Oxygen and Deuterium compositions of local runoff obtained at surface-water sites reveal that they are reasonable for middle-latitude, near-ocean, lowland, meteoric precipitation.

(Davis & Bentley, 1982) explained different isotope elements for groundwater dating. The isotopes of carbon-14, krypton-85, chlorine-36 and chlorofluorocarbon has some disadvantages like requiring large sample size, complex chemical analysis and special instrument that available only in few laboratories.

According to their research the best element is Tritium radioactive traces for dating which measured by liquid scintillation counter. Natural mean tritium levels varied from 2 to 8 TU prior to atmospheric nuclear weapon testing in the 1950s. Atmospheric nuclear bombing response to new 1.13×10^{9} TU to the northern hemisphere, with the highest tritium concentrations. In 1963, it reached its pinnacle.

Tritium concentrations have decreased since the end of atmospheric nuclear testing. TU levels have reduced to between 12 and 15 TU. Tritium-based groundwater age assessment only offers semi-quantitative values shown in table (3). Tritium concentrations were lowered to eight times between 1963 and 2000.

Table (3) Tritium values and types of water (DAVIS and BENTLEY, 1982).

Tritium values in (TU)	Water Age
< 0.8 TU	Sub-modern (earlier to 1950s)
0.8 to 4 TU	mix of sub-modern and modern
5 to 15 TU	modern water (5 to 10 years)
15 to 30 TU	Some bomb tritium
>30 TU	Water recharged in the 1960s to 1970s

The shallow groundwater recharge age can be determined more accurately using the tritium-helium-3 (^3He) method. Mass spectrometry can be used to quantify tritium and ^3He. T/^3He ratios are important for groundwater dating group from several months to roughly 30 years (but no further out than about 50 years). The accuracy of T/^3He ratios ranges from one to three years. The following equation can be used to calculate the age of groundwater:

$$Age = -17.8 \ \ln \left(1 + \frac{^3He}{^3H}\right) \ \ldots\ldots\ldots\ldots\ldots (2)$$

Where: Age in year, 3He is the helium component derived from tritium decay, adjusted for other helium origins, and ^3H is the tritium concentration in TU.

(Liu *et al.*, 2006) Used the mass spectrometer device of type Delta S-Thermoqest in the laboratory of Chiba university to measure the isotope compositions of oxygen and hydrogen. Thirty different locations along the river channel were selected in a basin (Huaishahe) located in northwest of (Beijing) city in China. The samples include spring water and shallow groundwater. In the field the water PH as well as the relative conductivity were measured in which the analytical accuracies were ±1.0 and ±0.1‰ for both $\delta^{18}O$ and δD respectively. The investigation area is semi humid and it was about 158 km^2. The annual average precipitation taken as 645 mm. The recharge rate to groundwater were found out and the relation between oxygen-18 and deuterium isotope contents were found to be:

$$\delta D = 7.82 \ \delta^{18}O + 8.48 \ \ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

Furthermore, Spring water was primarily recharged by evapotranspirated precipitation and surface water was primarily replenished by spring water which is at a higher elevation.

(Costinel *et al.*, 2009) investigated for the isotope compositions for both ^2H and ^{18}O in rainwater as well as the Bistrita river water in Raureni-Valcea region in Romania city. The method of continue flow isotope ratio mass spectrometry (CF-IRMS) used for sampling measurements of water compositions during two years. The CO_2-H_2O equilibration method is the most popular sample preparation procedure for $^{18}O/^{16}O$ in water and the isotopic exchange can convert the $^2H/^1H$ ratio of a water sample to H_2 according to the equations below:

$$H_2^{18}O + C^{16}O_2 \Leftrightarrow H_2^{16}O + C^{18}O^{16}O$$
$$^2H^1HO + {}^1H_2 \Leftrightarrow {}^1H_2O + {}^2H^1H$$

During the sampling collections, the average temperature and humidity was recorded so as to illustrate their effects on the variation of isotope compositions in the same period. Results shows that Rainwater has a different isotope of oxygen and hydrogen depending on the small seasonal variation.

(IAEA Guidelines, 2014) This report under the title (guidelines on the applications of nuclear technique for flood mitigation and management) explains some information to found the flood mitigation strategies of integrate soil, water, mineral, crop, and animal management flood mitigation. The radioactive isotope of phosphorus (^{32}P) and stable isotopes of (^{16}O, ^{18}O, ^{14}N, and ^{15}N) were commonly used as a trace to the resistance of flooding event due to the combination of surface water and soil. It's critical to figure out what influence ecosystems' soil-water-plant-animal interactions, as well as their resilience for flooding.
Stable isotopes pose no safety risks, whereas the use of radioactive isotopes necessitates to avoid the adverse effects of radiation on living creatures and the environment, strict safety precautions and protective methods in respect of transportation and storage, source handling, sampling, analysis, and waste disposal must be implemented.

Flooding in low-lying flood plains is widespread in many tropical Asian regions, and this can deliver a beneficial effect, such as the deposit of fertile sediments to enrich soil fertility and increase agricultural yield, according to the

Guidelines. In addition, the guideline outlined two main primary topics, which are described below.

- As a result of improper land use and deterioration, floodplains have formed.

- Improve the creation of flood-resistant agricultural varieties by diagnosing animal diseases, assessing feed and food quality, ensuring public health and food safety, and supporting animal reproduction.

(Sharma *et al.*, 2015) described the essential role of isotope technique in the management of water resources with changing climate conditions to achieve a sustainable environment. This study defines the isotope as a key method that has a knowledge to solve and assess the hydrological problems. The investigation explained that the climatic change affects the amount and duration of the precipitation which changes the isotope composition of water molecule. Since 1961, the Global Network for Isotopes in Precipitation (GNIP) has been tracking water isotopes. Except for some sections of the world, the GNIP dataset contains sufficient temporal and spatial density of stations to provide the foundation for spatial modeling.
Furthermore, there are two important aspects on which groundwater flow and natural hydro-chemical processes are dependent. The first is the geological-ecological structure, and the second is the lithosphere's petrological composition, both influence the hydro-chemical properties of groundwater. As stated below in the table (4), the principal isotope elements have been categorized based on water-related applications.

Table (4) Isotope ratio that applied for hydrological topics (Sharma *et al.*, 2015)

Isotope	Ratio	Hydrological study
Hydrogen (^{2}H)	$^{2}H/^{1}H$	Source of water
Oxygen (^{18}O)	$^{18}O/^{16}O$	Source of water
Carbon (^{13}C)	$^{13}C/^{12}C$	Groundwater dating
Nitrogen (^{15}N)	$^{15}N/^{14}N$	Organic contamination in groundwater body
Chlorine (^{37}Cl)	$^{37}Cl/^{35}Cl$	Groundwater pollution

(Kuo *et al.*, 2022) For the purpose of determining the oxygen and hydrogen stable isotopes of Taiwan's surface water and thermal water, two wells at depths of 160 and 2200 meters were sampled over the course of 18 months. Stable isotopes concentration used to estimate the mean groundwater residence time (MRT) due to seasonal change. Lighter isotope composition values are seen in deeper wells. The values of model fitting parameters that result in the minimum value of the squared sum of the residuals between model output and data measured were determined using the curve-fitting algorithm of SigmaPlot software and the Marquardt-Levenberg process. The estimated MRT 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 China) and long-term stable isotopic data to identify runoff components. 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.

5. FUTURE DIRECTION OF ISOTOPE STUDIES:

Over the last 40 years, the use of isotopes to track the origins and movement of water in catchments has resulted in a significant advance in our understanding of watershed systems. This is particularly true in small, experimental catchments with extensive apparatus and long data records. Recent trends show that isotopic applications to answer practical challenges in hydrology and water resource management in larger catchments are gaining in popularity that sometimes cannot be controlled by traditional methods or being high duration and cost required. Application of isotope technologies is now a potential study field. Due to the decreasing nuclear tritium signal in natural systems, new techniques for tracing older waters are being developed

Although a trend toward multi-isotope studies is desirable, many academics and sub-communities remain fixed on a single isotope. Novel applications of isotopes combined both solutes and artificial isotopic in complex methods also hold a lot of promise. In addition, isotopic uses could considerably improve process and parameter interpretation in the calibration and validation of rainfall-runoff catchment models. Large basins are highly diverse, with a wide range of runoff processes driving them. As a result, strategies developed in tiny natural catchments may be constrained when applied to big basins. Techniques and indicators that characterize the main processes in vast catchments without requiring spatially dense experimental datasets are needed.

6. CONCLUSION:

Climate change has had a substantial impact on water resources around the world in recent decades. The international scientific community is concerned about the long-term durability of water resources. As can be seen from the above discussion, isotope technology is an important tool for the long-term sustainability and management of water resources, as well as for water resource characterization, groundwater pollution research, groundwater renewability, and groundwater salinization studies. New methods for quantifying and integrating runoff indicators in catchments, as well as evaluating their ability for sustainability, should be developed.

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