DOI 10.7343/as-2024-755

ACQUE SOTTERRANEE
Italian Journal of Groundwater
journal homepage: https://www.acquesotterranee.net/

2024-AS51-755: 21 - 30

Evaluating groundwater residence time in arid aquifers: a crucial metric for monitoring sustainable water management

Valutazione del tempo di residenza delle acque sotterranee in acquiferi aridi: un parametro cruciale per la gestione sostenibile delle risorse idriche

AL MAMUN

Department of Physics, The College of Science, University of Hafr Al Batin, Al Jamiah, Hafr Al Batin 39524, Saudi Arabia.
email : *almamun@uhb.edu.sa*

ARTICLE INFO

Ricevuto/*Received*: 20 February 2024
Accettato/*Accepted*: 09 September 2024
Pubblicato online/*Published online*: 30 December 2024

Handling Editor:
Emma Petrella

Citation:
Al Mamun (2024) Evaluating groundwater residence time in arid aquifers: a crucial metric for monitoring sustainable water Management Acque Sotterranee - *Italian Journal of Groundwater*, 13(4), 21 - 30
https://doi.org/10.7343/as-2024-755

Correspondence to:
Al Mamun
almamun@uhb.edu.sa

Keywords: *age dating, groundwater, tritium, sustainability, liquid scintillation counter, sustainable water management.*

Parole chiave: datazione, acque sotterranee, tritio, contatore a scintillazione liquida, gestione sostenibile delle risorse idriche.

Riassunto

La valutazione del tempo di residenza delle acque sotterranee negli acquiferi delle regioni aride attraverso l'utilizzo dei radionuclidi naturali è fondamentale per prevedere le modalità di contaminazione delle acque, comprendere la dinamica degli acquiferi e garantire un utilizzo sostenibile delle risorse idriche. Questo studio si concentra sulla regione nord-orientale dell'Arabia Saudita, dove sono stati prelevati campioni d'acqua da pozzi adibiti a monitoraggio. A causa dei bassi livelli di trizio, l'acqua è stata sottoposta a un arricchimento elettrolitico da dieci a trenta volte rispetto ai valori iniziali tramite il processo di elettrolisi. I campioni arricchiti sono stati accuratamente analizzati utilizzando un contatore a scintillazione liquida in condizioni ottimali per determinare le concentrazioni di trizio. La validazione da parte di due laboratori internazionali accreditati ha ulteriormente confermato le concentrazioni stimate. Le concentrazioni di trizio sono state quindi utilizzate per stimare l'età delle acque sotterranee per ciascun pozzo di monitoraggio. L'analisi comparativa con i dataset internazionali suggerisce che le acque sotterranee raccolte nelle aree studiate abbiano probabilmente più di un secolo. In particolare, le età delle acque sotterranee mostrano significative variazioni in diverse località, anche all'interno dello stesso acquifero. Queste discrepanze derivano da differenze nella dinamica del flusso dell'acqua, nei tassi di ricarica e nella composizione geologica delle rocce e dei sedimenti attraverso i quali l'acqua defluisce. Al contrario, l'acqua proveniente da alcuni pozzi di monitoraggio ha mostrato un'età superiore a qualche centinaio di anni, classificandola come "acqua fossile" a causa di un prolungato tempo di permanenza nell'acquifero. Questa ricerca fornisce preziose informazioni sulla età delle risorse idriche sotterranee, contribuendo alla formulazione di strategie di gestione sostenibile delle acque nelle regioni aride.

Abstract

Assessing groundwater residence time in aquifers of arid regions by analyzing natural radionuclides is crucial for predicting water contaminants, understanding groundwater system dynamics and ensuring sustainable water utilization. This study focuses on the evaluation of groundwater residence time in northeastern Saudi Arabia using tritium as a tracer, where water samples were collected from monitoring wells. Due to the low levels of tritium, the water was reduced twenty to thirty- times from its initial values through the electrolysis process. The enriched samples were meticulously analyzed using a liquid scintillation counter under optimal conditions to determine tritium concentrations. Validation from two international commercial tritium laboratories further confirmed the estimated tritium concentrations. The tritium concentrations were then employed to estimate the groundwater age for each monitoring well. Comparative analysis with international datasets suggests that the collected groundwater in the studied areas is likely over a century old. Notably, groundwater ages display significant variations in different locations, even within the same aquifer. These disparities stem from differences in water flow dynamics, recharge rates, and the geological composition of the rocks and sediments through which the water travels. In contrast, water from selected monitoring wells exhibited an age exceeding a few hundred years, categorizing it as 'dead water' due to an extended residence time in the aquifer. This research contributes valuable insights into the longevity of groundwater resources, aiding in formulating sustainable water management strategies in arid regions.

Introduction

Evaluating the groundwater residence time is a crucial component of sustainable water management. It entails establishing the duration of a particular body of water entering a saturated zone (Grünenbaum et al., 2020; Post et al., 2013). Groundwater dating aids in identifying both the timing and origin of contamination, which can derive from human activities and actions on the land, on waterways and lakes, but also from insufficiently purified civil and industrial waste, from agriculture, from leaks of containers or landfills, from accidents with involuntary spills of substances (Bethke & Johnson, 2008; Sánchez-Úbeda et al., 2018). Older groundwater tends to undergo more extensive purification processes, thus making it "less polluted" than younger water. Therefore, groundwater age dating provides critical information to guide the sustainable management of groundwater resources.

Tritium has both anthropogenic and cosmogenic origins: it is produced in nuclear weapons tests and in nuclear reactors and is continuously generated by the interaction of high-energy cosmic rays with oxygen and nitrogen atoms in the upper atmosphere. The latter processes produce most of the world's natural tritium. It transforms into a He atom (^{3}He) by emission of particles with a half-life of 12.32 years ($T_{1/2}$). The concentration of tritium in surface water and groundwater is related to the amount of tritium in the atmosphere and the transfer time of rainwater from surface to groundwater, therefore tritium can easily be used as a tracer to estimate the age of groundwater (Gomes et al., 2017; Muhammad et al., 2013). Groundwater dating has been undertaken in various arid regions using isotopic techniques. For example, an isotopic technique was applied to examine groundwater from the Wajid aquifer in southern Saudi Arabia (Benaafi & Al-Shaibani, 2021). Groundwater recharge was determined to occur through local rainfall and inflow from nearby mountainous regions. The estimated groundwater age using environmental tracers ranged from up to 20 years. Okofo Boansi and colleagues employed a variety of environmental tracers to explore groundwater residence times and recharge processes in the northeastern region of Ghana. The findings indicated that the groundwater exhibits a broad spectrum of ages, spanning from less than one year to over 50 years (Okofo Boansi et al., 2022). Schlosser et al. (Schlosser et al., 1988) estimated groundwater ages in a shallow urban aquifer using environmental tracers and found a broad range of ages, spanning from less than a year to well over half a century, thus indicating the presence of young and old water within the aquifer. No relevant study has been reported in the northeastern arid regions of Saudi Arabia. In the present study, a scintillation counter was employed for tritium measurement. The estimated tritium activity concentration was used with Morgenstern and Pimenta to estimate the groundwater renewal time. This method is widely favored for its precision, reliability, and suitability for routine analysis of tritium levels in environmental samples.

In our previous studies, we reported an optimization method to minimize the detection limit of the liquid scintillation counter to measure low-level tritium activity in a water sample (Mamun & Alazmi, 2022a, 2022b, 2023). The low-level tritium and radon in groundwater samples were successfully identified after the successful enrichment of tritium level in water. This article reports the groundwater residence time using tritium as a tracing element with a "well-defined plot" by Morgenstern and Pimenta (Morgenstern & Taylor, 2009; Pimenta et al., 2017). By distinguishing between older and younger groundwater resources, the study sought to facilitate effective quality management practices to eliminate potential contamination risks for sustainable water utilization.

Study areas and experimental method

Geological and hydrogeological setting of the study areas

Groundwater samples were collected from the deep (800 m and above) and shallow (400 m and below) wells of three main cities in the northeastern arid regions of Saudi Arabia: Hafr Al Batin, Thybiyah, and Qaisumah. The study area is located in the largest country on the Arabian Peninsula, occupying the majority of its landmass (Figure 1a). The Arabian Peninsula is a vast region located in the Middle East, bordered by the Red Sea to the west, the Arabian Sea and the Gulf of Aden to the south, and the Persian Gulf to the northeast. The study areas are within the geographical coordinates of longitude 28o 26' 3" N and latitude 45° 57' 49" E (Fig. 1b). Hafr Al-Batin's geological setting is marked by its location on the Arabian Plate within a stable sedimentary basin, shaped by ancient seas and influenced by broader tectonic forces. The region's desert environment and rich groundwater resources also play a key role in defining its geology. Hafr Al Batin, also known as Al Batin Valley, derives its name from its location within the arid expanse of Wadi Al Batin. This valley constitutes a portion of the broader Wadi al Rummah, the most extensive and longest dry riverbed in the Arabian Peninsula, spanning a vast distance of approximately 2000 kilometers (El-Taher & Al-Turki, 2016; El-Taher et al., 2020). The central segment of Wadi Al Rummah courses through the Al Qassim oasis is recognized as one of Saudi Arabia's pivotal agricultural regions (Aly et al., 2015). The Saq Aquifer is a vital source of freshwater in Hafr Al-Batin, but its over-extraction has led to declining water levels and potential water quality issues. Sustainable management practices and careful monitoring are crucial to ensure groundwater's long-term availability. The prevailing climate in this area is characterized by extreme aridity and high temperatures during the summer, often between 40 and 50 °C. In contrast, during the winter nights, temperatures range from -2 to 8 °C. Rainfall is infrequent during winter, and no precipitation is recorded during summer.

The Saq Aquifer consists of sedimentary layers consisting primarily of sandstone, limestone, and porous formations. The aquifer's water is recharged primarily by infrequent and sporadic rainfall in the region. Due to its hydrogeological characteristics, the Saq Aquifer can store significant amounts

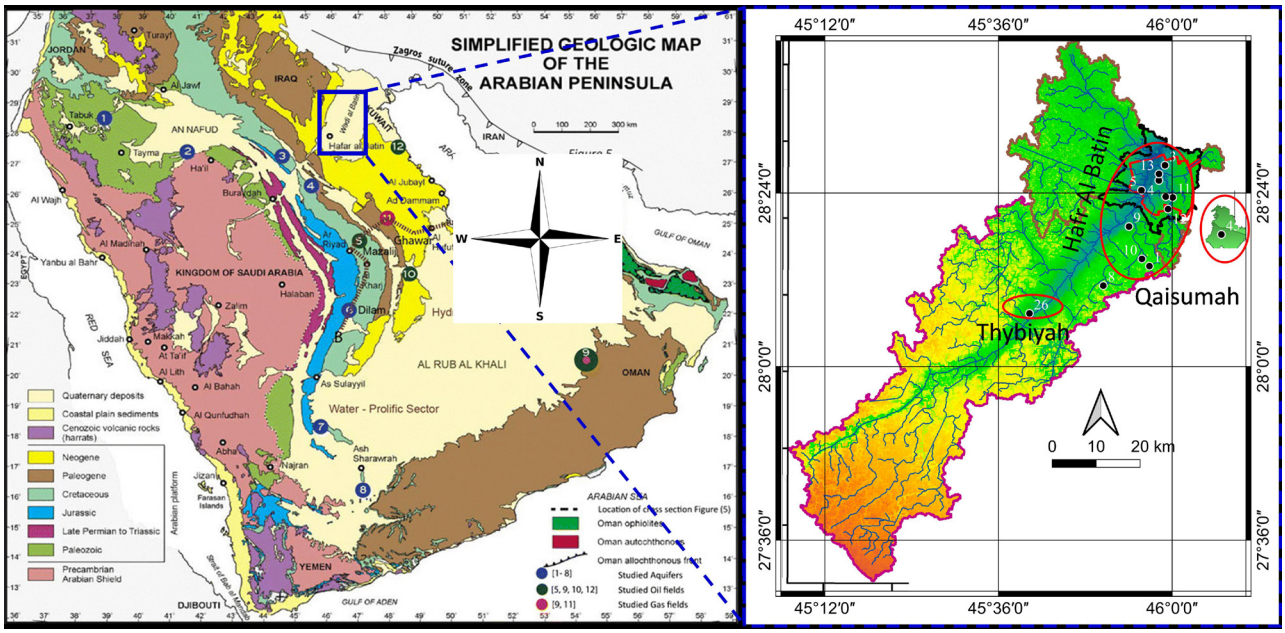

Fig. 1 - (a) Simplified geological map of the Arabian Peninsula, showing the aquifers and the regional cross-sectional areas with Wadi Al Batin (modified from Le Nindre et al., 2003) and (b) expanded areas of three cities Hafr Al Batin, Thybiyah, and Qaisumah, Northeast arid regions in Saudi Arabia. Color variation in the right image represent the elevation of the land and the black dot represent the location of the groundwater wells.

Fig. 1 - (a) Carta geologica semplificata della Penisola Arabica che mostra gli acquiferi e la sezione regionale passante per Wadi Al Batin (modificata da Le Nindre et al., 2023) e (b) dettaglio delle aree delle tre città Hafr Al Batin, Thybiyah e Qaisumah, della regione arida del nord-est dell'Arabia Saudita. La variazione di colore nell'immagine a destra rappresenta l'altitudine mentre i punti neri rappresentano la posizione dei pozzi.

of groundwater. According to Vincent (Vincent, 2008) and Alsharhan et al.'s report (Alsharhan et al., 2001), aquifers have characteristics with both primary and secondary permeability. The primary permeability aquifers include the Quaternary sands of the Wadi system, quartz sandstones, conglomerates with primary porosity, and calcarenite, coquinite, and oolitic limestone with secondary porosity (Alsharhan et al., 2001; Vincent, 2008). In Hafr Al Batin, a Quaternary sand aquifer is present, and deep wells in this area provide relatively good water compared to shallow wells.

To estimate the tritium activity concentration in groundwater and the corresponding groundwater age dating, the procedure outlined in Figure 2 was applied.

Electrolysis enrichment of water

Due to the low level of tritium, an electrolysis process was applied to increase the tritium level in groundwater samples. As regards the details of electrolysis, refer to Mamun (2023) (Mamun, 2023a). For convenience, a brief description of the electrolysis process is explained here. The electrolysis process involves four key steps. In the first step, groundwater is heated to its boiling point, creating steam. The steam is then collected, cooled, and condensed into liquid, leaving impurities and contaminants behind. The samples were distilled to eliminate naturally occurring dissolved ions and solids, such as Cl^-, SO_4^{2-}, Ca^{2+}, CO_3^{2-}, Mg^{2+}, Na^+, and K^+. Testing with a YSI 9500 photometer and Horiba LAQUAtwin (Kyoto, Japan) digital ion meters confirms the absence of these ions and salts, ensuring that they do not affect the subsequent electrolysis process.

After the distillation process, an enrichment process was employed using electrolytic cells. This process follows International Atomic Energy Agency (IAEA) guidelines and takes one to two weeks to enrich 500–800 ml of water. After enrichment, the final water sample was collected, with a calculated enrichment factor ranges of (25-30) ±0.5. An acidic substance (Carbonic acid) is added to the solution to counteract the alkalinity caused by electrolytes and salts. This reaction forms water and salt, neutralizing the alkalinity. It can be noted that maintaining a pH level of 7 (neutral) during

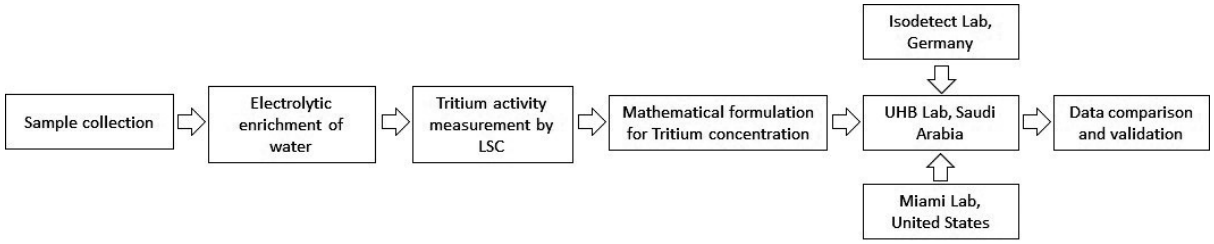

Fig. 2 - Schematic diagram of the experimental procedure for estimating tritium concentration and groundwater age dating with data validation.

Fig. 2 - Diagramma schematico delle procedure sperimentali per la stima della concentrazione di tritio per la datazione delle acque sotterranee con convalida dei dati.

this process is crucial to prevent excessive acidity. In the last step, after the electrolysis process, it is essential to confirm the absence of electrolytes in the solution, as they can interfere with subsequent measurements by the liquid scintillation counter. For this, the water is heated to its boiling point, and the resulting vapor is condensed back into water. Testing with a YSI 9500 photometer and Horiba digital ion meter further ensured the absence of electrolytes, and the water samples were sent for counting by a scintillation counter.

Tritium activity measurement and mathematical formulation

The details of the experimental procedure for tritium activity measurement, including mathematical formulation is explained in details (Mamun, 2023b). The step-by-step process, methodologies employed, and relevant parameters were thoroughly covered to understand the experimental design comprehensively. Here, a brief procedure is explained due to the convenience. A 10 ml water sample was mixed with an equal volume (10 ml) of Hidex scintillation cocktail (Aqualight Plus) from a United Kingdom-based company. This mixture converted the energy released during tritium decay into light flashes. The scintillation cocktail was selected for its outstanding performance in low-level tritium counting. To ensure the integrity of the samples, they were always stored in a cool and dark place and the solutions were kept for at least 4 hours before scintillation measurement to avoid the luminescence effect. Light flashes for tritium decay were counted by a liquid scintillation counter (Hidex 300 SL) operating on the triple-to-double coincidence ratio (TDCR) principle (supplementary Figure S1). Each sample was analyzed five times for 200 min. Before counting with the scintillation counter, the position of the liquid scintillation counter (LSC) was set to optimum conditions. For any drift, the measuring device's performance was assessed monthly by calibrating it with a standard source. Additionally, continuous monitoring of background radiation levels was maintained to ensure consistency. The background radiation can be ignored if measuring activities become approximately 1000 times higher than the background.

The efficiency of the scintillation counter was measured using the standard tritium source provided by Hidex. The measurements were conducted under the same experimental conditions as those for the unknown samples. The efficiency of tritium measurement (ε) was derived from the net count rate of the standard sample (Rn in s^{-1}), the known activity concentration of tritium (c in Bq/mL), and the volume of the sample (V in mL), as follows:

$$\frac{R_n}{c \cdot V} \qquad (1)$$

Flashes are measured in a liquid scintillation counter (Hidex 300 SL) in counts per minute (CPM). Each sample was measured five times for 200 minutes, and the average of the five runs was then determined. Standards and blanks (zero-value samples) are also estimated to evaluate the data with similar experimental conditions. The tritium activity concentration during the counting time by LSC was calculated using the following equation:

$$A_T = \frac{N_{SA} \cdot A_{ST}}{N_{ST} \cdot Z} \qquad (2)$$

where

AT: concentration activity of tritium at the counting time (Bq/L);

NSA: the net count rate of the sample (cpm);

NST: the net count rate of the standard (cpm);

AST: the tritium activity of the standard at the counting time (Bq/L) and

Z: is the enrichment factor.

It is important to note that one tritium unit (1 TU) equals 0.118 Bq/kg, and all the calculated units were converted into TU.

Decay correction, the radioactive decay between the time of sampling and that of measurement, is usually not needed for up to several months. However, the decay correction must be accounted for if the samples are left long before measurement. Therefore, the calculation uses the decay equation where the measured tritium concentration ^3H_t after some time, t, is equal to the initial concentration, ^3H_o times the exponential decay function:

$$^3H_t = {}^3H_o e^{-\lambda t} \qquad (3)$$

From the above, the decay term $\lambda = \ln 2/t_{½}$. Using tritium's half-life, $t_{½}$ = 12.3 years, this equation can be rewritten as:

$$t = -17.74 \ln \frac{^3H_1}{^3H_o} \qquad (4)$$

The decay curve visually represents the above equation. Since the above equation does not refer to the original tritium concentration at the time of sampling, it is, therefore, not a correction for post-sampling decay. But this equation can refer to the original tritium concentration in the water at the time of infiltration, which will help to determine the age.

Data comparison and validation

To ensure the accuracy and consistency of the collected data in our laboratory, identical groundwater samples were sent to two commercial tritium laboratories: "Isodetect Umwelmonitoring GmbH" in Germany and the University of Miami in the USA. Tritium analysis at the Isodetect laboratory was conducted using Quantulus W1220 equipment, while custom-built gas proportional counters were employed at the University of Miami. Both laboratories maintained almost similar experimental conditions throughout the sampling, distillation, and electrolysis. Each sample underwent ten separate analyses, each lasting 100 minutes and a total counting of 1000 minutes. The original water sample volume was subjected to electrolysis process, resulting in a reduced final volume in both laboratories, corresponding to approximately twenty-times tritium enrichment. This

rigorous methodology was applied consistently to ensure the reliability of the results. The experimental conditions for electrolysis process with efficiency is described in detail (Mamun, 2023a).

Results and Discussion

Measurement of tritium activity in groundwater samples

Measuring the efficiency of a scintillation counter is essential before any measurement. Efficiency measurements ensure that the scintillation counter provides accurate and reliable results when detecting and quantifying radiation. The detector of the Hidex 300SL liquid scintillation counter is confined with three photomultipliers, enabling the measurement of the TDCR ratio. This method determines the counting efficiency of an unknown sample without a standard source (Arun et al., 2021). The TDCR values of a typical sample as a function of the efficiency are plotted in Figure 3a. A linear relationship with efficiency was obtained, a characteristic of TDCR for the Hidex 300 SL device.

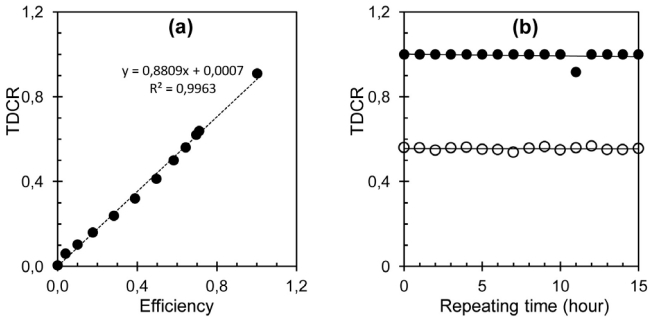

Fig. 3 - Triple-to-double coincidence ratio as a function of (a) efficiency and (b) repeating run (converted into time in hours) for a typical sample 12 for α-radiation (solid circle) and β-radiation (open circle).

Fig. 3 - Rapporto triplo-a-doppio in funzione di (a) efficienza e (b) ripetizione (convertita in tempo in ore) per un campione tipo 12 per radiazione alfa (cerchio pieno) e radiazione beta (cerchio vuoto).

Additionally, it is worth noting that a higher TDCR value was obtained for α-radiation than for β-radiation, as illustrated in Figure 3b. Conversely, there was no notable variation in the TDCR values during repeated runs. These findings suggest that the tritium activity concentration can be reliably measured using TDCR, even when conducting numerous repeated runs.

In groundwater samples, tritium levels are typically quite low and need a longer counting time to achieve the desired radiation. A counting time of 1000 minutes with five repetitions was chosen. This choice yielded an approximate detection limit of 0.27 tritium units (TU). A similar observation regarding the detection limit concerning counting time was made by Feng et al. (Feng et al., 2020). The estimated tritium concentrations for the groundwater samples of the monitoring wells, along with their corresponding standard uncertainties, determined using a liquid scintillation counter, were then further corrected for decay with sampling time.

Decay correction with sampling time

When a significant amount of time passes between sample collection and analysis, correcting the decay of the sample becomes crucial. If a sample is collected but analyzed later, the tritium concentration naturally decreases over the period. The correction factor is referred to as the decay correction factor (DCF), and it takes the form of an exponential function with a time constant of 17.745 years. The DCF is determined using the following formula (Salvato, 2003):

$$DCF = e^{(T/17,745)} \qquad (5)$$

Figure 4 shows the time-dependent DCF values for the samples analyzed in three laboratories (UHB in Saudi Arabia, Isodetect laboratory in Germany, and University of Miami in the United States). The solid line on the plot represents the DCF calculated based on the decay equation. The graph illustrates that substantial corrections are generally insignificant when samples are adequately sealed, stored, and counted by the Liquid Scintillation Counter (LSC) within a short time. However, a correction becomes essential for samples stored beyond one year, given that the DCF shows exponential growth with time. In the present study, most samples were counted within a month. Nonetheless, a few samples (indicated by open circles in Figure 4) underwent measurement after a year. A precise correction was implemented to compensate for the tritium decay in these cases, and it is tabulated in Table 1.

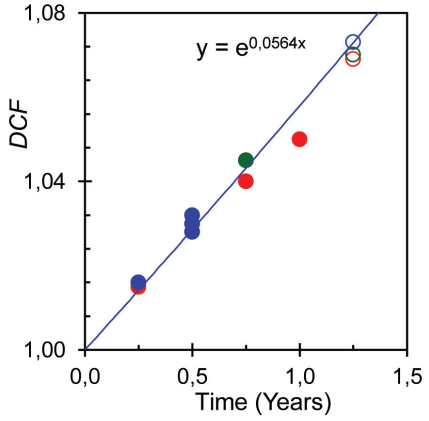

Fig. 4 - The decay correction factor (DCF) as a function of time. The samples represent our laboratory in Saudi Arabia (marked with red circles), the Isodetect laboratory in Germany (indicated by blue circles), and the University of Miami laboratory in the United States (represented by green circles). The solid line was calculated using the decay equation.

Fig. 4 - Fattore di correzione per il decadimento (DCF) in funzione del tempo. I campioni rappresentano: il laboratorio in Arabia Saudita (segnalati con cerchi rossi), il laboratorio Isodetect in Germania (indicato con cerchi blu) e il laboratorio dell'Università di Miami negli Stati Uniti (rappresentato con cerchi verdi). La linea continua è stata calcolata utilizzando l'equazione del decadimento.

Table 1 presents the measured tritium concentrations for 13 groundwater samples collected from the monitoring wells. The observed concentrations varied between 0.1 and 0.8 TU, with an average of 0.36 TU. Various national and international entities have a pivotal role in establishing comprehensive guidelines and safety thresholds for tritium

levels in groundwater, ensuring the protection of public health and environmental well-being on a global scale. These guidelines serve as essential benchmarks for assessing and managing tritium contamination risks. The United States Environmental Protection Agency (USEPA) has instituted a stringent threshold of 11.1 Bq/L (~93 TU) as the permissible limit for tritium concentration in groundwater (USEPA, 2000). This limit reflects the agency's commitment to safeguarding groundwater quality and safe drinking water sources. The UNSCEAR published a safe limit of 40 Bq/L (~338 TU) (UNSCEAR, 2000), while the European Commission (EC) and World Health Organization (WHO) have identified an action limit of 100 Bq/L (~847 TU) (EC, 2019; WHO, 2011). Remarkably, it is noteworthy that all the groundwater samples subjected to this study unequivocally exhibited tritium levels well below these internationally recognized limits, reaffirming the region's commitment to ensuring the safety of groundwater resources. Moreover, approximately 90% of the examined samples exhibited tritium concentrations markedly lower than those reported (1.0 to 80 TU) in previous studies documented in other regions in Saudi Arabia (Al-Jaseem et al., 2016; Aljaloud & ElBatouti, 2021; WHO, 2011).

Tab. 1 - Tritium activity in the groundwater collected from monitoring wells.

Tab. 1 - Attività del Tritio nelle acque sotterranee campionate nei pozzi di monitoraggio.

No	Sample ID	Depth of Wells	Tritium Activity (TU) UHB, Saudi Arabia	±TU
1	01Dd01	Deep	0.47	0.07
2	03DSt01	Deep	0.58	0.08
3	04DSt02	Deep	0.50	0.07
4	05DSt03	Deep	0.15	0.06
5	08d02	Shallow	0.40	0.06
6	09d03	Shallow	0.32	0.06
7	10d04	Shallow	0.42	0.07
8	11St06	Deep	0.15	0.07
9	12St07	Deep	0.12	0.05
10	13d05	Shallow	0.44	0.07
11	19ST08	Deep	0.15	0.06
12	26ST09	Deep	0.20	0.07
13	45D31	Shallow	0.78	0.09
Depth of the shallow wells: 400 m and below Depth of the deep wells: 800 m and above				

Data validation for tritium activity

Data validation is an essential step in the groundwater age dating process. The validation involves checking the accuracy and reliability of the obtained data to ensure future analysis. Several steps are considered in data validation, including error checking and comparison with known values. The first step was performed for data validation by checking the errors in the obtained data. This involves identifying any anomalies or outliers that could affect the accuracy of the results. Error checking was performed using statistical methods of regression analysis. The second step in data validation is to compare the obtained data with known values of spiked samples. Spiked samples are laboratory-prepared samples that contain a known amount of a specific tracer or isotope. The samples are used to calibrate the analytical methods and verify the accuracy of the obtained data. We found minor errors in the analytical methods by comparing the obtained data with the spiked samples. The details of the data validation using spiked samples have been published previously (Mamun, 2023b).

The ultimate phase of the data validation process involves a comparative assessment of the acquired data to ensure its accuracy and reliability. Two reputable international tritium laboratories validated this: Isodetect Umwelmonitoring GmbH in Germany and the University of Miami in the United States. The tritium activity obtained from these laboratories is tabulated in Table 2. In two cases, negative tritium values are listed in the table. Such numbers can occur because the net tritium count rate is, in principle, the difference between the count rate of the sample and that of a tritium-free sample (background count or blank sample). Given a set of "unknown" samples with no tritium, the distribution of net results should become symmetrical at approximately 0 TU. The negative values are reported to give the user an unbiased statistical treatment of data sets. For other applications, 0 TU should be used. By comparing the obtained data from three laboratories, it can be seen that the data are identical with a small error. The data collected independently from three separate laboratories exhibit complete consistency, providing strong evidence that the results obtained from all three laboratories are identical. This remarkable agreement in the collected data underscores the reliability and robustness of the experimental findings, as it reaffirms the accuracy and precision of the measurements conducted across these diverse research environments. Such uniformity in results not only lends credibility to the findings but also enhances the overall confidence in the validity of the scientific observations made in this study, reinforcing the significance of the research outcomes.

Groundwater age

Groundwater dating provides valuable information on the water sources within an aquifer. The estimated tritium activity of the monitoring wells was used to calculate the groundwater age. A well-defined plot by Morgenstern and Pimenta (Morgenstern & Taylor, 2009; Pimenta et al., 2017) was used to estimate the groundwater age. The tritium concentration estimated from the collected groundwater samples are plotted on a Morgenstern and Pimenta plot., which shows the renewal time against the tritium concentration, as shown in Figure 5 (solid black line). It can be found that most of the data points form a straight line with a consistent slope. This method used in hydrology and environmental science to estimate the age of groundwater. The method involves the use of environmental tracers, particularly tritium (^{3}H), to estimate the residence time of groundwater. This method assumes that the aquifer

Tab. 2 - Estimated tritium activity from two commercial laboratories.

Tab. 2 - Attività del tritio stimata da due laboratori accreditati.

No	Sample ID	Depth of Wells	Tritium Activity (TU) Isodetect, Germany	±TU	Tritium Activity (TU) Miami, USA	±TU
1	01Dd01	Deep	0.39	0.13	-	-
2	03DSt01	Deep	0.55	0.19	-	-
3	04DSt02	Deep	0.39	0.19	0.58	0.09
4	05DSt03	Deep	0.15	0.19	0.14	0.09
5	08d02	Shallow	0.35	0.13	-	-
6	09d03	Shallow	0.30	0.10	-	-
7	10d04	Shallow	0.39	0.12	-	-
8	11St06	Deep	0.16	0.13	-	-
9	12St07	Deep	0.10	0.01	0.04	0.09
10	13d05	Shallow	0.38	0.10	-	-
11	19ST08	Deep	-	-	0.06	0.09
12	26ST09	Deep	-	-	0.02	0.09
13	45D31	Shallow	-	-	0.70	0.09
Depth of the shallow wells: 400 m and below Depth of the deep wells: 800 m and above						

behaves as a linear system and that the relationship between hydraulic head and time follows a power-law relationship. It's important to note that while the Morgenstern and Pimenta plots can provide useful groundwater renewal time estimation, their accuracy depends on the validity of these assumptions and the quality of the data used. The tritium activity data from three different laboratories are embedded in the plot. The plot shows that the groundwater containing the lowest tritium activities has a longer renovation time; conversely, the higher value of tritium activities represents a shorter renovation time. However, the data from our laboratory (open red circle) show a wide variation in groundwater age, ranging from 80 to 600 years, indicating significant mixing between different water sources (Plummer & Glynn, 2013). According to the results, only the water from well no 13 is approximately one hundred years old, while the remaining wells have ages exceeding one hundred years, even several hundred years old. It is important to note that tritium has a relatively short half-life. Depending on the initial concentration and decay rate, it can be used for groundwater dating from several decades to a couple hundred years. However, beyond this temporal window, tritium concentrations diminish significantly, rendering accurate measurement challenging and, eventually, impractical. Consequently, tritium becomes unsuitable for estimating groundwater renewal time for older water sources. In the context of the present study, where, in some cases, tritium concentrations fall below 0.1 TU, the estimated renewal time is not reliable and does not have precision and significance (Jerbi et al., 2019). This suggests that groundwater sources with estimated renewal times exceeding 200 years (as indicated by the oval shape with an arrow) need further analysis utilizing alternative isotopic tracers with longer half-lives. Examples of such isotopes include carbon-14 and noble gases like helium-4. Carbon-14, with a half-life of around 5730 years, and noble gases, such as helium-4, can provide insights into groundwater age dating over longer time scales, ranging from hundreds to thousands of years. These isotopes undergo radioactive decay at rates conducive to dating ancient groundwater sources with greater accuracy. We are currently employing carbon-14 as a tracer with the same scintillation counter, but the result shows a few decades as an error. Further analysis with carbon-14 and future research could further clarify the relative age of these samples. Notably, a study conducted in the alluvial aquifer of the Rio Grande in the United States revealed diverse groundwater ages (Plassin et al., 2020; Plummer & Glynn, 2013). The complex hydrological processes controlling water movement in the aquifer were considered responsible.

In contrast, many studies have reported that Tritium serves as a versatile tracer for understanding groundwater renewal processes across a broad spectrum of temporal scales, ranging from relatively short-term to significantly longer intervals spanning several hundred years. In the context of longer timescales, tritium offers insights into the behavior of groundwater systems over more extended periods, reaching back hundreds of years. For example, Tritium activity was measured in groundwater wells in the upper Jequitibá River Basin, Municipality of Sete Lagoas, Minas Gerais, Brazil. Results showed that deep aquifer waters are 200 years old (Pimenta et al., 2017). Conversely, in the context of shorter timeframes, tritium's radioactive decay provides a means to track the movement and replenishment of groundwater over relatively recent periods, typically spanning from a few years to a few decades. For example, in Brazil, shallow aquifer waters are found to be less than 37 years old (Pimenta et al., 2017), while water from the Rock Island Aquifer of Tobago,

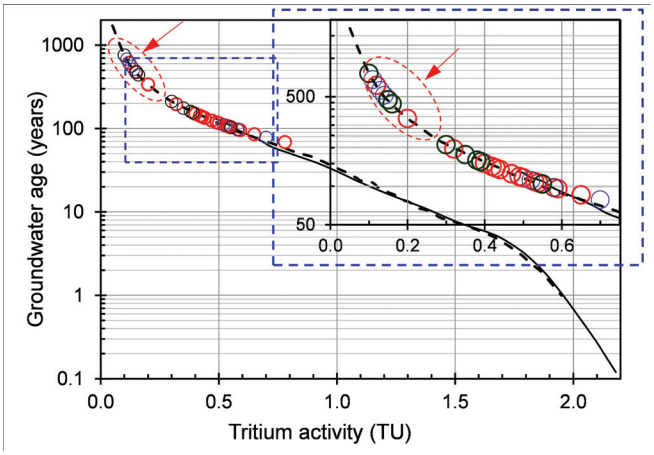

Fig. 5 - The age as a function of tritium activity (TU) was analyzed at various locations: our laboratory in Saudi Arabia (indicated by a red circle), the Isodetect lab in Germany (marked with a green circle), and the University of Miami lab in the United States (represented by a blue circle). The inset image shows an expanded area marked by a rectangular broken line. The solid and broken lines are the well-known "Morgenstern and Pimenta" curve for age dating (Jurgens et al., 2012; Morgenstern & Taylor, 2009; Pimenta et al., 2017).

Fig. 5 - Età dell'acqua in funzione dell'attività del trizio (TU) analizzata in diverse località: laboratorio in Arabia Saudita (indicato con un cerchio rosso), laboratorio Isodetect in Germania (segnalato con un cerchio verde) e laboratorio dell'Università di Miami negli Stati Uniti (rappresentato con un cerchio blu). L'immagine in dettaglio mostra il dettaglio contrassegnato dalla linea tratteggiata rettangolare blu. Le linee continue e tratteggiate nere rappresentano la nota curva "Morgenstern e Pimenta" per la datazione dell'età [30,31,34] (Jurgens et al., 2012; Morgenstern & Taylor, 2009; Pimenta et al., 2017).

West Indies, the age ranges between 18 and 60 - plus years (Allen & Boutt, 2023). Additionally, a study in the Ganges-Brahmaputra-Meghna delta in Bangladesh found that groundwater ages were relatively uniform across different wells, ranging from 7 to 28 years (Hoque & Burgess, 2012; Sadeak et al., 2023), due to the complex dynamics of aquifer systems in Bangladesh. Further examination of isotopic ratios and water chemistry variations is needed to verify the potential for groundwater to intermingle with water from diverse sources and factors that could influence age-dating results. Consequently, based on our analysis, we can assert that the groundwater within the surveyed region is quite old, with ages exceeding several hundred years.

Figure 6 shows the groundwater age distribution and describes the proportion of water at different ages within an aquifer. The results imply that relatively older water is in the monitoring wells in hillside areas on most of the northeastern side of the study area. In summary, the overall tritium levels within the surveyed site are quite low, indicating a substantially extended renewal period. Compared with tritium data from other countries, these findings suggest that most groundwater from the monitoring wells surveyed area is several hundred years old.

Conclusion

The tritium activity was measured using the liquid scintillation counter. Subsequently, the groundwater renewal time was calculated based on the interpretation of these tritium activity measurements. The process involved

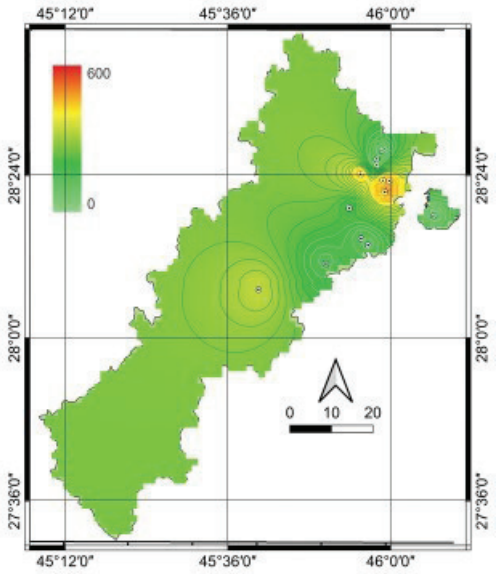

Fig. 6 - Spatial groundwater age distribution through the searched areas.

Fig. 6 - Distribuzione spaziale dell'età delle acque sotterranee nell'area di ricerca.

enriching groundwater samples from monitoring wells and enhancing their tritium content. Notably, groundwater ages exhibit substantial variability across different locations, even within the same aquifer. These disparities arise due to variations in water flow dynamics, recharge rates, and the geological composition of the rocks and sediments traversed by water. A very low level of tritium was found in the searched arid regions. Two renowned international tritium laboratories conducted verification to ensure the accuracy of the estimated tritium levels. The consensus reached by these laboratories suggests that the estimated tritium levels are quite precise, with minimal margin for error. Furthermore, when compared to other countries reporting analogous data, it becomes evident that the majority of groundwater from monitoring wells in the surveyed areas has ages exceeding a hundred years. The results imply that the groundwater in the surveyed regions is relatively ancient and has remained within the aquifer for an extended duration. Older groundwater is likely to be less affected by recent surface activities and may have better quality, whereas younger groundwater is more vulnerable to pollutants. Additionally, the estimated age helps to determine whether the water originates from recent precipitation or ancient sources, which is crucial for managing water resources, particularly in areas with scarce supplies. This information holds great potential for informing more effective water resource management practices undertaken by governmental authorities. We continuously assess and monitor groundwater using modern technologies; the variability of the tritium activity in the precipitates and the different mixing ratios of the different water portions will be reported in the future.

Acknowledgments

The author would like to thank the Deanship of Scientific Research at the University of Hafr Al Batin for granting access to the experimental facilities. Additionally, the research received financial support through the Institutional Funding Project (IFP-A-202-1-3), which was generously provided by the Ministry of Education in Saudi Arabia. Special thanks are to Isodetect Umwelmonitoring GmbH in Germany and the University of Miami in the USA for their prompt assistance in validating the data.

Funding source

The research received financial support through the Institutional Funding Project (IFP-A-202-1-3), which was generously provided by the Ministry of Education in Saudi Arabia.

Competing interest

The authors declare no competing interests.

Additional information

DOI: https://doi.org/10.7343/as-2024-755

Reprint and permission information are available writing to acquesotterranee@anipapozzi.it

Publisher's note Associazione Acque Sotterranee remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

REFERENCES

Al-Jaseem, Q. K., Almasoud, F. I., Ababneh, A. M., & Al-Hobaib, A. S. (2016, 2016/09/01/) Radiological assessment of water treatment processes in a water treatment plant in Saudi Arabia: Water and sludge radium content, radon air concentrations and dose rates. Science of The Total Environment, 563-564, 1030-1036. https://doi.org/https://doi.org/10.1016/j.scitotenv.2016.04.049

Aljaloud, K. B., & ElBatouti, M. (2021, 2021/02/01/) Statistical analysis of 222Rn concentration in Zamzam and other water sources in the Kingdom of Saudi Arabia. Heliyon, 7(2), e06057. https://doi.org/https://doi.org/10.1016/j.heliyon.2021.e06057

Allen, M., & Boutt, D. (2023) Environmental Tracers Tritium ^{3}H and SF6 Used to Improve Knowledge of Groundwater Sustainability of a Crystalline Rock Island Aquifer of Tobago, West Indies. Water, 15(24), 4231. https://www.mdpi.com/2073-4441/15/24/4231

Alsharhan, A.S., Rizk, Z.A., Nairn, A.E.M., Bakhit, D.W., & Alhajari, S.A. (2001) Preface. In Hydrogeology of an Arid Region: The Arabian Gulf and Adjoining Areas (pp. 287-309). Elsevier Science B.V. https://doi.org/https://doi.org/10.1016/B978-044450225-4/50000-2

Aly, A. A., Al-Omran, A. M., & Alharby, M. M. (2015, 2015/06/01) The water quality index and hydrochemical characterization of groundwater resources in Hafar Albatin, Saudi Arabia. Arabian Journal of Geosciences, 8(6), 4177-4190. https://doi.org/10.1007/s12517-014-1463-2

Arun, B., Viswanathan, S., Venkatesan, S., Jose, M. T., & Balasubramaniam, V. (2021, 04/29) Study of Triple to Double Coincidence Method for Tritium Measurements. Radiochemistry, 63, 221-226. https://doi.org/10.1134/S1066362221020120

Benaafi, M., & Al-Shaibani, A. (2021) Hydrochemical and Isotopic Investigation of the Groundwater from Wajid Aquifer in Wadi Al-Dawasir, Southern Saudi Arabia. Water, 13(13), 1855. https://www.mdpi.com/2073-4441/13/13/1855

Bethke, C., & Johnson, T. (2008, 05/01) Groundwater Age and Groundwater Age Dating. Annu. Rev. Earth Planet. Sci, 36, 121-152. https://doi.org/10.1146/annurev.earth.36.031207.124210

El-Taher, A., & Al-Turki, A. (2016, 11/01). Radon activity measurements in irrigation water from Qassim Province by RAD7. Journal of environmental biology, 37, 1299-1302.

El-Taher, A. M., Abojassim, A. A., Najam, L. A., & Mraity, H. A. A. B. (2020) Assessment of Annual effective Dose for Different Age Groups based on Radon Concentrations in the Groundwater of Qassim, Saudi Arabia. Iranian Journal of Medical Physics, 17(1), 15-20. https://doi.org/10.22038/ijmp.2019.37379.1476

Feng, B., Chen, B., Zhao, C., He, L., Tang, F., & Zhuo, W. (2020, 2020/12/01/) Application of a liquid scintillation system with 100-ml counting vials for environmental tritium determination: Procedure optimization, performance test, and uncertainty analysis. Journal of Environmental Radioactivity, 225, 106427. https://doi.org/https://doi.org/10.1016/j.jenvrad.2020.106427

Gomes, A. R., Abrantes, J., Libânio, A., Madruga, M. J., & Reis, M. (2017, 2017/11/01) Determination of tritium in water using electrolytic enrichment: methodology improvements. Journal of Radioanalytical and Nuclear Chemistry, 314(2), 669-674. https://doi.org/10.1007/s10967-017-5456-y

Grünenbaum, N., Greskowiak, J., Sültenfuß, J., & Massmann, G. (2020, 2020/08/01/) Groundwater flow and residence times below a meso-tidal high-energy beach: A model-based analyses of salinity patterns and ^{3}H-^{3}He groundwater ages. Journal of Hydrology, 587, 124948. https://doi.org/https://doi.org/10.1016/j.jhydrol.2020.124948

Hoque, M. A., & Burgess, W. G. (2012, 2012/06/11/) ^{14}C dating of deep groundwater in the Bengal Aquifer System, Bangladesh: Implications for aquifer anisotropy, recharge sources and sustainability. Journal of Hydrology, 444, 209-220. https://doi.org/10.1016/j.jhydrol.2012.04.022

Jerbi, H., Hamdi, M., Snoussi, M., Abdelmalek, M. B., Jnoub, H., & Tarhouni, J. (2019) Usefulness of historical measurements of tritium content in groundwater for recharge assessment in semi-arid regions: application to several aquifers in central Tunisia. Hydrogeology journal, 27(5), 1645-1660.

Jurgens, B. C., Böhlke, J. K., & Eberts, S. M. (2012) TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data [Report](4-F3). (Techniques and Methods, Issue. U. S. G. Survey. http://pubs.er.usgs.gov/publication/tm4F3

Le Nindre, Y.-M., Vaslet, D., Le Métour, J., Bertrand, J., & Halawani, M. (2003, 2003/02/10/) Subsidence modelling of the Arabian Platform from Permian to Paleogene outcrops. Sedimentary Geology, 156(1), 263-285. https://doi.org/https://doi.org/10.1016/S0037-0738(02)00291-9

Mamun, A. (2023a) Enrichment of Low-Level Tritium in Groundwater via an Electrolysis Process for Liquid Scintillation Counting Applications. Geosciences, 13(10), 290. https://www.mdpi.com/2076-3263/13/10/290

Mamun, A. (2023b) Estimation of Tritium Concentration in the Rain- and Groundwater in the Dry River of Hafr Al Batin, Saudi Arabia. Limnological Review, 23(2), 93-107. https://www.mdpi.com/2300-7575/23/2/6

Mamun, A., & Alazmi, A. S. (2022a) Advancement of a Liquid Scintillation Counter and Semiconductor Alpha Spectroscopy Detector to Estimate the Radon Concentration in Groundwater. Water, 14(23), 3849. https://www.mdpi.com/2073-4441/14/23/3849

Mamun, A., & Alazmi, A. S. (2022b) Investigation of Radon in Groundwater and the Corresponding Human-Health Risk Assessment in Northeastern Saudi Arabia. Sustainability, 14(21).

Mamun, A., & Alazmi, A. S. (2023) Risk Assessment of Radon Exposure by Ingestion and Inhalation of Groundwater Within Different Age Groups. Groundwater Monitoring & Remediation, 43(1), 69-77. https://doi.org/https://doi.org/10.1111/gwmr.12558

Morgenstern, U., & Taylor, C. B. (2009, Jun) Ultra low-level tritium measurement using electrolytic enrichment and LSC. Isotopes Environ Health Stud, 45(2), 96-117. https://doi.org/10.1080/10256010902931194

Muhammad, B., Nasiru, R., & Sumaila, A. (2013, 11/30) Procedure for Radio Dating of Water Using Nuclear Hydrological Isotopes Techniques. IOSR Journal of Applied Physics, 6. https://doi.org/10.9790/4861-06214953

Okofo Boansi, L., Adonadaga, M.-G., & Martienssen, M. (2022, 04/01) Groundwater age dating using multi-environmental tracers (SF6, CFC-11, CFC-12, $\delta^{18}O$, and δD) to investigate groundwater residence times and recharge processes in Northeastern Ghana. Journal of Hydrology, 610, 127821. https://doi.org/10.1016/j.jhydrol.2022.127821

Pimenta, R., Rocha, Z., Viana, J., Gardini, G., Duarte, M., & Moreira, R. (2017) Use of environmental tritium in groundwater dating in the upper jequitibá river basin, municipality of sete lagoas, minas gerais, brazil.

Plassin, S., Koch, J., Paladino, S., Friedman, J. R., Spencer, K., & Vaché, K. B. (2020, 2020/03/06) A socio-environmental geodatabase for integrative research in the transboundary Rio Grande/Río Bravo basin. Scientific Data, 7(1), 80. https://doi.org/10.1038/s41597-020-0410-1

Plummer, L. N., & Glynn, P. D. (2013) Radiocarbon dating in groundwater systems. Chapter 4. IAEA; Vienna (International Atomic Energy Agency (IAEA)); International Atomic Energy Agency, Division of Physical and Chemical Sciences, Vienna (Austria). https://doi.org/https://doi.org/ Other: ISBN 978-92-0-137210-9; TRN: XA13M0262055166 INIS

Post, V. E. A., Vandenbohede, A., Werner, A. D., Maimun, & Teubner, M. D. (2013, 2013/07/01/) Groundwater ages in coastal aquifers. Advances in Water Resources, 57, 1-11. https://doi.org/https://doi.org/10.1016/j.advwatres.2013.03.011

Sadeak, S., Al Amin, M., Chowdhury, T., Mia, M. B., Alam, M. J., Ahmed, K. M., & Khan, M. R. (2023, 2023/02/01/) Comparison of the groundwater recharge estimations of the highly exploited aquifers in Bangladesh and their sustainability. Groundwater for Sustainable Development, 20, 100896. https://doi.org/https://doi.org/10.1016/j.gsd.2022.100896

Salvato, C. (2003) The role of micro-strategies in the engineering of firm evolution. Journal of management studies, 40(1), 83-108.

Sánchez-Úbeda, J. P., López-Chicano, M., Calvache, M. L., Purtschert, R., Engesgaard, P., Martín-Montañés, C., Sültenfuβ, J., & Duque, C. (2018, 2018//). Groundwater Age Dating in Motril-Salobreña Coastal Aquifer with Environmental Tracers ($\delta^{18}O/\delta^{2}H$, $^{3}H/^{3}He$, ^{4}He, ^{85}Kr, and ^{39}Ar). Groundwater and Global Change in the Western Mediterranean Area, Cham.

Schlosser, P., Stute, M., Dörr, H., Sonntag, C., & Münnich, K. O. (1988, 1988/08/01/). Tritium/^{3}He dating of shallow groundwater. Earth and Planetary Science Letters, 89(3), 353-362. https://doi.org/https://doi.org/10.1016/0012-821X(88)90122-7

USEPA (2000) National Primary Drinking Water Regulations; Radionuclides; Final Rule. Fed. Reg., 65(236), 76708.

Vincent, P. (2008) Saudi Arabia: an environmental overview (1st Edition ed.). CRC Press. https://doi.org/https://doi.org/10.1201/9780203030882

Supplementary file - *File supplementare*

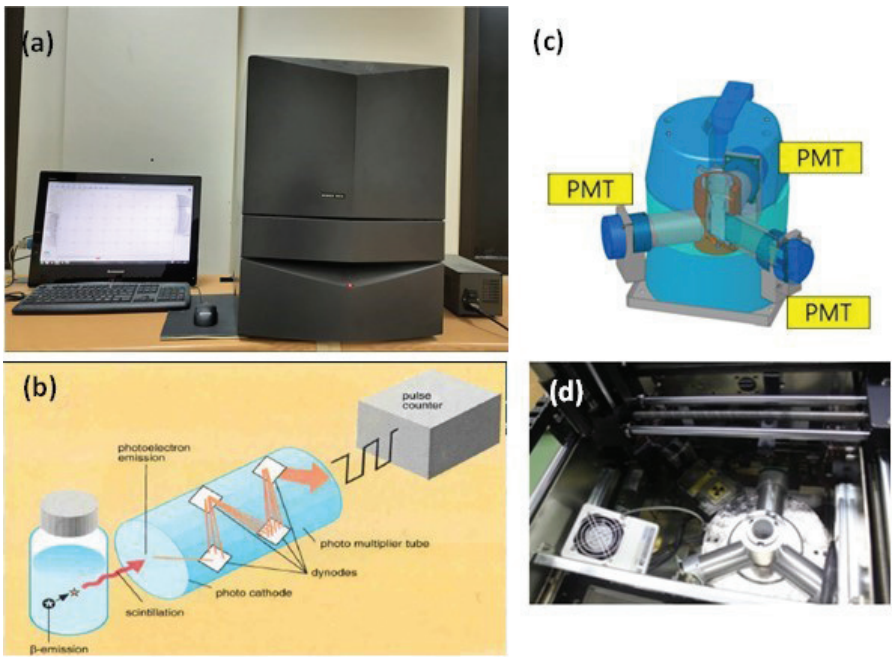

Fig. S1 - (a) The front view of the tritium-measuring device (Hidex 300SL), (b) a schematic representation of the scintillation principle, (c) the diagram of the photomultiplier, and (d) a photograph of the detector (Hidex 300SL).

Fig. S1 - (a) La vista frontale del dispositivo di misurazione del Trizio (Hidex 300SL), (b) una rappresentazione schematica del principio di scintillazione, (c) il diagramma del fotomoltiplicatore e (d) una fotografia del rilevatore (Hidex 300SL).