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THE $^3H/^3HE$ GROUNDWATER AGE-DATING METHOD AND APPLICATIONS

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ABSTRACT

Groundwater age-dating is an important tool for quantifying and managing water resources. Groundwater age is the elapsed time between recharge (at the land surface or water table) and the time when groundwater is sampled. If groundwater is sampled at the point of discharge from an aquifer, then the age represents the groundwater transit time. Groundwater that has recharged in recent decades is considered young groundwater. In many areas, the quality and quantity of young groundwater has been impacted by human activities and groundwater age-dating is useful for quantifying current and historical water and contaminant fluxes into and through aquifers. This review is focused on the tritium-helium ($^3H/^3He$) method, which is a robust and widely applied age-dating technique for young groundwater. We present the development of the $^3H/^3He$ method and practical considerations for sampling groundwater in shallow unconfined aquifers. Along the way, we highlight available resources: (1) educational software for building intuition around groundwater age-dating and selection of sampling sites and (2) software that can be used to calculate $^3H/^3He$ age from noble gas and ^3H data. We also highlight strengths and potential uncertainties associated with the method. For example, while other age-dating techniques require a known historical record of tracer concentration in the atmosphere, the $^3H/^3He$ age-dating technique does not require such historical records. However, the $^3H/^3He$ method requires measurement of two tracers to produce a groundwater age estimate (“apparent age” or “tracer age”). Precise measurement of ^3H and noble gases, plus careful analysis of noble gas data to calculate the tritiogenic ^3He (i.e., the portion of ^3He derived from decay of ^3H in the aquifer) is required to calculate the groundwater apparent age. Sampling for noble gases is sometimes challenging and requires specialized sample containers and technique. We also introduce basic sampling methods in this review but highlight how practitioners should work closely with a noble gas laboratory to obtain the correct containers and assess field conditions and/or the overall feasibility of projects. Lastly, the review highlights recent applications of the $^3H/^3He$ method, including recharge rate estimation, characterization of contaminant input histories for aquifers, quantifying groundwater transit times by sampling at aquifer discharge points, and the use of isotope data to constrain and inform numerical and statistical models of groundwater and contaminant movement in the subsurface.

Keywords: Groundwater age; Isotope hydrology; Environmental tracers; Groundwater recharge; Contaminant transport; Aquifer characterization.

RESUMO

O MÉTODO DE DATAÇÃO $^3H/^3He$ E SUAS APLICAÇÕES PARA ÁGUAS SUBTERRÂNEAS. A determinação dos tempos de residências das águas subterrâneas é uma ferramenta importante na quantificação e gestão correta dos recursos hídricos. Por definição, a idade da água subterrânea indica o tempo decorrido entre a sua recarga no aquífero e o momento em que é tomada a amostra de água subterrânea. Se essa amostra for tomada no ponto de descarga de um aquífero, a idade representa o tempo de trânsito da água subterrânea. Águas subterrâneas recarregadas nas últimas décadas são consideradas jovens. Em muitas áreas, a qualidade e a quantidade dessas águas têm sido impactadas por atividades humanas, fazendo com que a datação dessas águas seja útil na quantificação dos fluxos de água e contaminantes para o interior e através dos aquíferos. Esta revisão enfoca a aplicação do método do trítio-hélio ($^3H/^3He$), uma técnica robusta e amplamente aplicada de datação dos tempos de residência de águas subterrâneas recentes. O artigo apresenta o desenvolvimento do método $^3H/^3He$ e considerações práticas relativas a amostragem de água subterrânea em aquíferos rasos não confinados. Ao longo do texto são enfatizados algumas ferramentas disponíveis: (1) *software* educacional para construir intuição em torno da datação da água subterrânea e seleção de locais de amostragem e (2) *software* que pode ser usado para calcular a idade $^3H/^3He$ a partir de dados de gases nobres e ^3H. Também são destacados os pontos fortes e as incertezas potenciais associadas ao método. Por exemplo, enquanto outras técnicas de datação requerem um registro histórico conhecido da concentração do traçador na atmosfera, a técnica de datação $^3H/^3He$ não requer tais registros históricos. Por outro lado, o método $^3H/^3He$ requer a medição de dois traçadores para produzir uma estimativa da idade da água subterrânea (“idade aparente” ou “idade do traçador”). Medições precisas de ^3H e gases nobres, além de uma análise cuidadosa dos dados de gases nobres necessários ao cálculo do ^3He tritiogênico (isto é, a porção de ^3He derivada do decaimento radioativo do ^3H no aquífero), são necessárias para calcular a idade aparente da água subterrânea. As técnicas de amostragem para gases nobres são desafiadoras e requer amostradores específicos. Também são abordados métodos básicos de amostragem nesta revisão, apesar da recomendação de que os trabalhos de campo devam ser efetuados em estreita colaboração com o laboratório responsável pelas determinações das concentrações de gases nobres, como forma de se utilizar amostradores corretos e avaliar as condições de campo e/ou a viabilidade geral dos projetos. Por último, a revisão destaca as recentes aplicações do método $^3H/^3He$, incluindo estimativa de taxa de recarga, caracterização de histórias de entrada de contaminantes para aquíferos, quantificação de tempos de trânsito de água subterrânea por amostragem em pontos de descarga de aquíferos e o uso de dados de isótopos para elaborar modelos numéricos e estatísticos de movimento da água subterrânea e contaminantes no subsolo.

Palavras-chave: Idade das águas subterrâneas; Hidrologia isotópica; Traçadores ambientais; Recarga; Transporte de contaminantes; Caracterização de aquíferos.

1 INTRODUCTION

Determining the age of young groundwater is highly valuable for characterizing aquifer resiliency and anthropogenic impacts on groundwater resources. Groundwater recharge rates, movement of contaminants through aquifers, and aquifer discharge of groundwater and contaminants all have temporal aspects that can be investigated using groundwater age-dating. Groundwater age is also valuable for characterizing confined versus unconfined aquifer systems and connectivity between surface water and groundwater.

The tritium-helium ($^3H/^3He$) age-dating method is a well-established and robust groundwater age-dating method for young groundwater (typically < 70 years old; COOK 2020a). The method relies on the determination of tritium (^{3}H, T) and tritiogenic helium (^{3}He$_{trit}$, the product of radioactive decay of ^{3}H) in groundwater samples. Based on the half-life of ^{3}H (12.32 years; LUCAS & UNTERWEGER 2000), the relative abundance of ^{3}He$_{trit}$ and ^{3}H can be used to determine the groundwater age, which is defined as the time elapsed since recharge. ^{3}H/^{3}He age-dating requires measurement of two tracers. ^{3}H is part of the water molecule and a near-ideal tracer. ^{3}He$_{trit}$ is a dissolved gas. Determination of ^{3}He$_{trit}$ requires application of noble gas thermometry and knowledge of other sources of ^{3}He. As with other tracer-based age-dating methods, groundwater age from ^{3}H/^{3}He is referred to as groundwater apparent age or tracer age to acknowledge uncertainty in tracer-based methods (COOK 2020b).

This review is intended as an introduction to the ^{3}H/^{3}He groundwater age-dating method. We introduce and define essential terminology and theory. We also highlight additional resources for learning more about the ^{3}H/^{3}He method including literature and freely available educational resources. Key applications of the ^{3}H/^{3}He age-dating method in hydrogeology are also summarized, with a focus on shallow unconfined, unconsolidated aquifers. These applications include determination of groundwater recharge rates, characterization of contaminant transport, determination of transit times for groundwater discharge from shallow aquifers to gaining streams, and constraining groundwater models. We also discuss tracer limitations and provide key resources for practitioners and scientists who would like to apply this method in Brazil.

2 THEORETICAL BACKGROUND

In this section we highlight the development of the ^{3}H/^{3}He method, the ^{3}H/^{3}He age equation, and some key considerations for applying the method.

2.1 Development of the ^{3}H/^{3}He method

Determination of the tritium-helium ratio is the basis of the ^{3}H/^{3}He age-dating method. The method was originally described by TOLSTIKHIN & KAMENSKY (1969). Subsequently, the method was applied to ocean waters (JENKINS & CLARKE 1976) and lakes (TORGERSEN et al. 1979). SCHLOSSER et al. (1988) and POREDA et al. (1988) eventually applied the ^{3}H/^{3}He technique to determine age of shallow groundwater samples. The tritium-helium method was then used to estimate groundwater recharge (e.g., SOLOMON & SUDICKY 1991, SOLOMON et al. 1993), characterizing patterns and timing of groundwater contamination (e.g., SZABO et al. 1996, SHAPIRO et al. 1999, BÖHLKE 2002), estimating transit times of groundwater that discharges to surface water bodies (STOLP et al. 2010, GILMORE et al. 2016), and constraining or calibrating models (e.g., SZABO et al. 1996, PORTNIAGUINE & SOLOMON 1998, MURPHY et al. 2011, WELLS et al. 2021).

2.2 Tritium, ^{3}H

Tritium is a radioactive isotope of hydrogen and occurs in precipitation as tritiated water (HTO), with an activity currently in the range of 1 to 10 tritium units (TU) in the Southern Hemisphere (Figure 1) (IAEA/WMO 2020). A tritium unit (TU) is defined as a tritium to hydrogen ratio of 10^{-18}. The time required for ^{3}H with activity of 1 to 10 TU to decay to < 0.1 TU is 41 to 82 years, respectively. A large peak in tritium activity occurred in the mid-20th century due to atomic bomb testing. As a result, ^{3}H has been used as a marker for

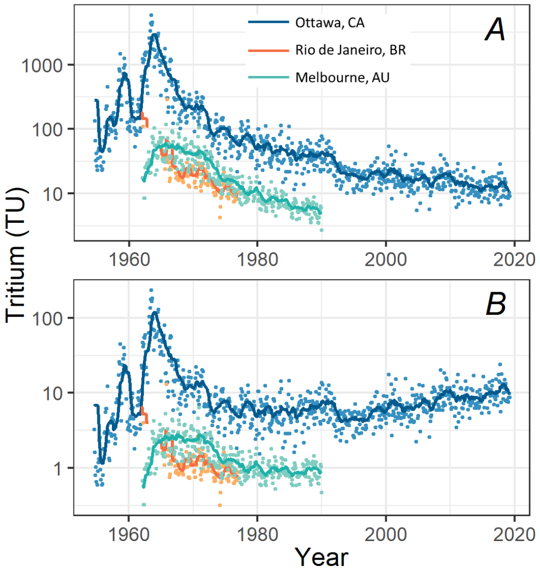

FIGURE 1 – (A) Historical ^{3}H activity in the precipitation in the Northern (Canada (CA)) and Southern (Australia (AU) and Brazil (BR)) Hemispheres. Filled circles show monthly tritium activities and smoothed curves show a running 1-year average. (B) ^{3}H activity in water if sampled in 2020 (i.e., activities shown in (A) have been decayed to year 2020). Note that vertical axes are log scale and the ranges are different for (A) and (B). Data were retrieved from IAEA/WMO (2020).

groundwater recharged in the late 1950s to early 1960s in the northern hemisphere. In the southern hemisphere, the “bomb peak” is less pronounced because most atomic testing was conducted in the northern hemisphere (GEYH et al. 2000) (Figure 1). Thus, the $^{3}H/^{3}He$ age-dating method is generally useful for ^{3}H investigations in shallow aquifers where groundwater is “young” (years to decades in age; nominally < 70 years for application of the $^{3}H/^{3}He$ method). Modest atmospheric ^{3}H can also occur naturally due to the bombardment of nitrogen and oxygen by the neutron flux from cosmic radiation and artificially from nuclear facilities. Trace amounts of tritium can occur in the crust from spontaneous fission of ^{6}Li from uranium and thorium decay (SCHLOSSER et al. 1989, LEHMANN et al. 1993).

2.3 Tritiogenic ^{3}He and the $^{3}H/^{3}He$ age equation

The decay of tritium will cause tritiogenic helium-3, $^{3}He_{trit}$, to accumulate in groundwater over time

$$^{3}He_{trit}(t) = {}^{3}H(t_0)(1 - e^{-\lambda t}) \tag{2.1}$$

where *t* is the time of interest (e.g., time of sample collection) and t_0 is the initial time (e.g., time of recharge) (SCHLOSSER et al. 1988). For example, $^{3}H(t_0)$ would correspond to ^{3}H shown in figure 1A, while for a groundwater sample collected in the year 2020, $^{3}H(t)$ would correspond to ^{3}H activities shown in figure 1B.

The radioactive decay rate, λ, is calculated as where 12.32 years is the half life of tritium (LUCAS & UNTERWEGER 2000). Assuming tritium and $^{3}He_{trit}$ travel together without mixing (i.e., piston-flow transport), the initial tritium concentration is equal to the sum of the remaining tritium concentration and the radioactive decay product tritiogenic helium.

$$^{3}H(t_0) = {}^{3}H(t) + {}^{3}He_{trit}(t) \tag{2.2}$$

Substituting equation 2.2 into equation 2.1 and solving for *t* yields the $^{3}H/^{3}He$ groundwater age equation. Note that in equation 2.3, the notation for groundwater age, τ, has been substituted for *t*, the time variable, and that the levels of tritium and tritiogenic helium are determined from the groundwater sample. Concentration units for equation 2.3 are tritium units (TU).

$$\tau = \lambda^{-1} \ln\left(1 + \frac{^{3}He_{trit}}{^{3}H}\right) \tag{2.3}$$

If the transport of the tracers in groundwater can be described as piston flow (MALOSZEWSKI & ZUBER 1996), then equation 2.3 gives the groundwater apparent age. Conditions under which these assumptions may be met are discussed further in Section 3.1. Methods for determination of $^{3}He_{trit}$ from noble gas data are described in Section 3.4.

2.4 Key considerations for applying the $^{3}H/^{3}He$ age equation

As seen in equation 2.3, the $^{3}H/^{3}He$ age-dating method is based on measurements of a radioactive tracer (^{3}H) and its decay product ($^{3}He_{trit}$). $^{3}He_{trit}$ readily diffuses within the atmosphere and is not retained in the water until after recharge, when water and tracers are transported below the water table. At this moment, the groundwater age “clock” begins at approximately time zero. Under these “closed system” conditions, $^{3}He_{trit}$ is retained in the groundwater because downward advection of $^{3}He_{trit}$ is the dominant transport mechanism and upward diffusion of $^{3}He_{trit}$ into the gas phase in the vadose zone is negligible or does not occur. Exceptions to the closed-system assumption may occur, however, if the recharge rate is exceptionally low and/or as water with very high ^{3}H activities cross the water table (Table 1). In this case, there may be sufficient $^{3}He_{trit}$ built up to create a concentration gradient and, in the case of low recharge rates, sufficient time for the $^{3}He_{trit}$ to diffuse back into the gas phase in the vadose zone.

Uncertainties in $^{3}H/^{3}He$ can also arise from diffusion of $^{3}He_{trit}$ during transport through the aquifer when high concentrations are produced from the bomb peak. Dispersive mixing may be an important process for samples containing substantial bomb-peak ^{3}H, adding significantly to uncertainty in apparent age (SOLOMON & SUDICKY 1991, SCANLON et al. 2002). Issues related to the bomb peak may be less critical when applying the method in the southern hemisphere where ^{3}H activities did not rise to the extreme levels observed in the northern hemisphere.

Knowing the ^{3}H input function over time (Figure 1) is useful for evaluating $^{3}H/^{3}He$ age-dating results, but the actual calculated groundwater age from equation 2.3 is independent of the tracer input function. This is a key characteristic of the $^{3}H/^{3}He$ method, and an advantage over transient age-dating tracers for young groundwater such as chlorofluorocarbons (CFCs; PLUMMER & BUSENBERG 1999) or sulfur hexafluoride (SF_6; BUSENBERG & PLUMMER 2000).

Groundwater age-dating with either CFCs or SF_6 requires a detailed historical record of atmospheric concentrations to estimate the recharge year and apparent age from groundwater tracer concentrations.

Another difference between SF_6 and ^{3}H/^{3}He age-dating is the uncertainty in very young groundwater ages (Table 1). For example, SF_6 concentrations in the atmosphere are much greater in the past few decades and increasing rapidly (BULLISTER 2021). As a result, very young groundwater has SF_6 concentrations much greater than analytical limits for SF_6 measurement. Because the ^{3}H/^{3}He method relies on a radioactive decay pair, $^{3}He_{trit}$ concentrations are low in very young groundwater. While the ^{3}He detection limits are extraordinarily low, the separation of $^{3}He_{trit}$ from other sources of ^{3}He is problematic for young water near the water table. Thus, there is greater uncertainty (on a percentage basis) in $^{3}He_{trit}$ concentrations and groundwater age in very young groundwater samples.

3 SAMPLING AND ANALYSIS

Proper application of ^{3}H/^{3}He age-dating in studies of young groundwater requires careful site selection, advanced field techniques, specialized sample containers, highly specialized analytical laboratories, and an understanding of processes that control noble gas concentrations in groundwater. In this section, we provide a brief introduction to each of these essential topics and point to additional, more detailed resources.

We encourage anyone interested in using the ^{3}H/^{3}He method to first contact a laboratory with expertise in ^{3}H and noble gas analyses and discuss the feasibility of the method, and the extent to which the laboratory will assist with determination of ^{3}H/^{3}He ages from raw data, during the proposal phase of the project. A partial list of laboratories capable of ^{3}H and noble gas analyses can be found in VISSER et al. (2014).

3.1 Selection of sampling sites

The ^{3}H/^{3}He method has been successfully applied in many hydrogeological settings, but careful selection of sampling sites is important if project goals include determination of apparent age for young groundwater. We note that noble gas and/or ^{3}H data can provide important insights beyond estimation of age for young groundwater, including identification of young and/or old groundwater and strengthening interpretation of multi-tracer datasets, but we are focused in this review on the specific sampling requirements for calculating groundwater apparent age using equation 2.3. Additional considerations for planning tracer-based field experiments can be found in COOK (2020d).

Criteria for sampling site selection include (1) the ability to collect groundwater without contact with a gas phase, such as the atmosphere, (2) identification of wells, springs, or other

TABLE 1 – Key considerations for ^{3}H/^{3}He age-dating method.

Consideration	*Processes involved and/or source of uncertainty*	*Nominal limits and/or practical considerations*	*Key resources*
Uncertainty in very young groundwater ages	determination of $^{3}He_{trit}$ from equation 2.4 is uncertain because $^{3}He_{trit}$ is a small component of the overall ^{3}He budgete	e.g., if initial ^{3}H is 3 TU, only 0.2 TU of ^{3}He is produced in 1.2 years.	SOLOMON & COOK (2000), GILMORE (2015)
Loss of ^{3}He from groundwater near the water table	diffusion	consider for low recharge rates; e.g., for recharge rate greater than 30 mm yr^{-1} ^{3}He loss is likely less than 20%; for recharge rates less than 3 mm yr^{-1} diffusion dominates transport of ^{3}He	See Figure 13.9 in SOLOMON and COOK (2000), equation 13.4 of SCHLOSSER et al. (1989), diffusion coefficient of SOLOMON et al. (1993); SCANLON et al. 2002
Applicable timescale for ^{3}H/^{3}He method for aquifers with deep water table	travel time in vadose zone may exceed timescale of ^{3}H decay	Times required for initial ^{3}H to decay to < 0.5 TU: 3 TU decays in 32 years 8 TU decays in 77 years	Calculated from equation 2.3 using ^{3}H half-life of 12.32 (LUCAS and UNTERWEGER 2000)

groundwater discharge points such as streambeds where mixing of different groundwater flowpaths is minimized, and (3) identification of sampling points that are likely to yield groundwater with ages that are within the applicable range of the method. In the following section, we illustrate mixing concepts using an idealized scenario of a simple unconfined aquifer with uniform geology and recharge. Additional insight to proper selection of sampling sites and the use of multiple tracers (including $^3H/^3He$) can be gained by reviewing groundwater age-dating studies in more complex geological environments (AESCHBACH-HERTIG et al. 1998, AVRAHAMOV et al. 2018, GIL-MARQUEZ et al. 2020, MOECK et al. 2021).

3.1.1 Considerations for sampling wells in a simple unconfined aquifer

Ideally, a groundwater sample collected for age dating would represent a discrete groundwater flow path and a narrow range of groundwater ages. This can be visualized conceptually as a narrow flow tube with a groundwater parcel moving through the flow tube as if pushed with a piston, and with no mixing with adjacent flow tubes before the groundwater is intercepted by a well screen (Figure 2). This idealized case is described as the piston-flow model (MALOSZEWSKI & ZUBER 1996). However, groundwater samples will always represent a range of groundwater ages (MCCALLUM et al. 2014). In the case where the groundwater sample is a mixture of water from a wide range of flow paths, such as a sample collected from a municipal supply well with a long screen (e.g., Figure 2A or Figure 2C), the age given by age-dating tracers is a composite age of the different sources of groundwater (TORGERSEN et al. 1979, POREDA et al. 1988, SCHLOSSER et al. 1988, SOLOMON & SUDICKY 1991). This composite age can be different than the true mean age of the sample (MALOSZEWSKI & ZUBER 1996, MANNING et al. 2005), especially when the relationship between time and concentration is not linear (BETHKE & JOHNSON 2008, COOK 2020c). In this case, multiple age-dating tracers may be required to constrain the mean age of the sample and/or determine the distribution of groundwater ages represented in the sample (e.g., VISSER et al. 2013, ÅKESSON et al. 2015).

A common approach used in many $^3H/^3He$ applications is to collect samples that are representative of as narrow a range in groundwater age as possible. In practice, wells with short screens are commonly used in unconfined aquifers to minimize the potential of intercepting groundwater with a wide range of ages (e.g., Figure 2E). In relatively simple unconsolidated shallow aquifers, well screens with length of one or two meters are often reasonable for age-dating groundwater with $^3H/^3He$, but the ideal screen lengths are highly dependent on the stratification of groundwater age in the aquifer (see COOK 2020d, their figure 14, for an illustration of age stratification). Age stratification is dependent on aquifer composition and geometry, and especially groundwater recharge patterns and rates. For example, groundwater age increases with depth in unconfined, unconsolidated aquifers, where recently recharged groundwater is located closer to the water table and older groundwater is found toward the base of the aquifer. If the groundwater recharge rate is 0.05 m yr^{-1} in an unconfined aquifer having a porosity of 0.3, then water entering at the bottom of a 3 m-long well screen could be nearly 20 years older than water entering near the top of the well screen.

Lumped-parameter models (LPM), which rely on simplified aquifer geometry, composition, and recharge characteristics to characterize groundwater age stratification, may be used as a first approximation of ideal monitoring well depths and screen lengths. Of course, the model assumptions must be a reasonable approximation for the study site. A commonly assumed LPM for simple unconfined aquifers is the exponential model (EM). The exponential model is based on assumptions of a homogeneous rectangular aquifer with uniform thickness, porosity, and recharge (VOGEL 1967, SOLOMON et al. 2006). For this simplified aquifer configuration, the groundwater age at a given depth (z) below the water table can be calculated as

$$t = \frac{L\theta}{R} \ln \frac{L}{L-z} \tag{3.1}$$

where t is groundwater age (years), L is saturated thickness of the aquifer (m), R is recharge rate (m yr^{-1}). This equation can also be used to evaluate groundwater ages that might occur for short-screened wells at different depths in an aquifer.

A partial exponential model (PEM; JURGENS et al. 2016) relies on the same assumptions as the EM but can be used to calculate the range of groundwater ages that would be intercepted by a given length of well screen. The

USGS Educational Web Tool (BÖHLKE et al. 2014, https://ca.water.usgs.gov/projects/gamactt/) relies on the PEM model, with values calculated as described in JURGENS et al. (2012). While it "should not be used for predictive purposes," the web tool is interactive and can be used to build intuition around stratification of groundwater age in aquifers and the extent to which different well screen lengths may intercept flow paths yielding groundwater with a range of ages (Figure 2).

LPMs such as the EM and PEM do not incorporate vadose zone transport times. For some study sites, vadose zone transport times may be an important consideration for application of $^3H/^3He$ age dating (Table 1). For cases where vadose zone transport time exceeds the dating range of $^3H/^3He$, little or no ^3H will remain in water that recharges the aquifer, and $^3H/^3He$ age dating will not be possible. In some cases, it may be appropriate to use a simple vertical transport equation to estimate approximate vadose zone transport times before selecting wells to sample as part of the monitoring well design. The vadose zone transport time equation is

$$t_{vz} = \frac{L_{vz}\theta_{vz}}{R} \tag{3.2}$$

where R is an estimated recharge rate for the study area (m yr^{-1}), t_{vz} is vadose zone transport time (years), θ_{vz} is mobile water content in the vadose zone (m^3 m^{-3}), and L_{vz} (m) is the vertical distance from land surface to the water table.

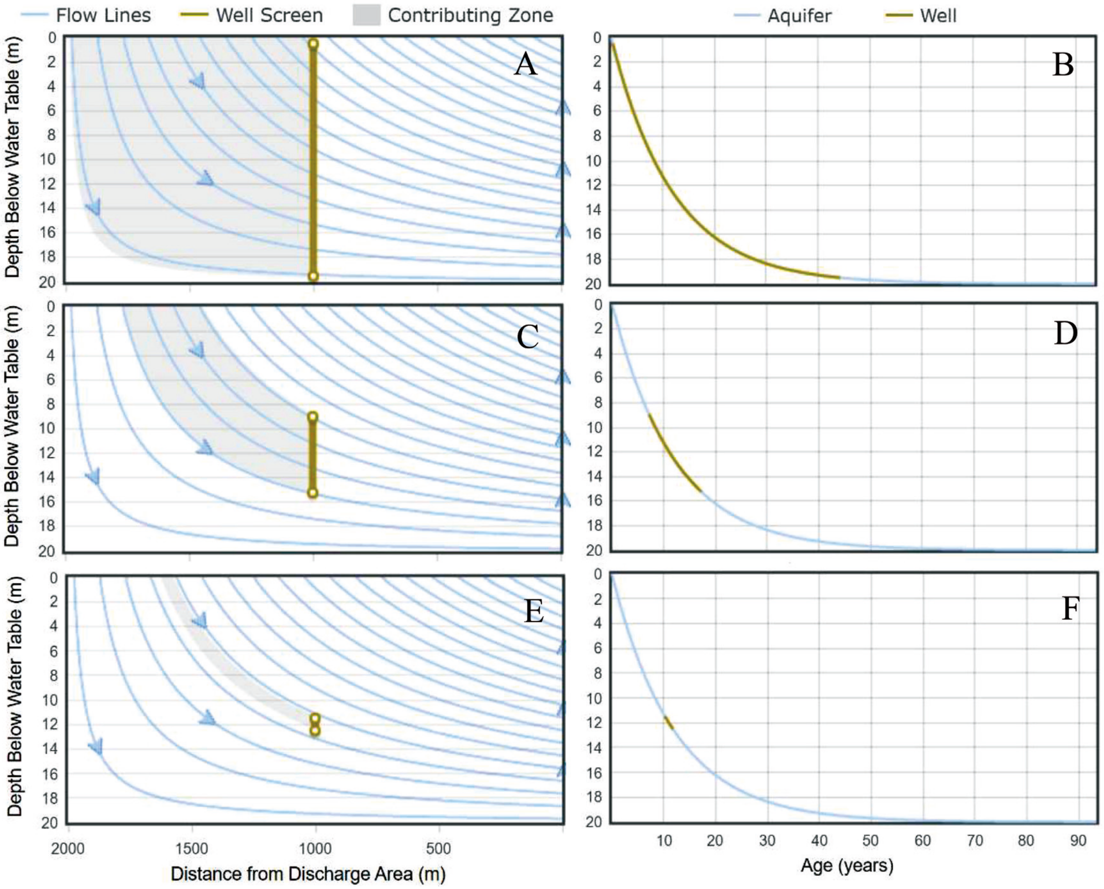

FIGURE 2 – Examples of modeled groundwater age mixtures intercepted by different well screen configurations, based on the PEM, with figures modified from https://ca.water.usgs.gov/projects/gamactt/). The modeled aquifer has saturated thickness of 20 m, porosity of 0.3, recharge rate of 0.5 m yr^{-1}, and mean groundwater age of 12 years. Plot (A) shows a screened interval from 0.5 to 19.5 meters below the water table. This screened interval intercepts groundwater with mean age of 11.1 years, with a range of 0.3 to 44.3 years, as shown in Plot (B). The screened interval in (C) is from 9 to 15 meters below the water table. The mean age of the intercepted groundwater is 11.5 years and the range of age shown in (D) is from 7.2 to 16.6 years. Plot (E) shows a screened interval from 11.5 to 12.5 meters depth, with mean age of 11 years and age range (F) of 10.3 to 11.8 years.

3.2 Basics of sampling

$^3H/^3He$ age dating requires collection of water that will be analyzed separately for ^3H and for noble gases (including helium isotopes). Sampling groundwater for analysis of ^3H is very straightforward. Sampling for noble gases can be more challenging because it requires specialized sampling equipment and procedures As described in AESCHBACH & SOLOMON (2013), successful sampling of noble gases requires minimizing the loss or gain of gases to the sample due to (1) gas exchange with the atmosphere (during sampling, via contact with atmospheric air and/or introduction of gas bubbles), (2) gas exchange prior to sampling (e.g., addition and/or loss of gases from the sample in a well bore or near a discharge point), and/or (3) improper sealing of the copper tubes. Further discussion of these issues and more detail on the following summarized sampling methods can be found in AESCHBACH & SOLOMON (2013).

As with any groundwater sampling, the well or piezometer being sampled should be purged until water quality parameters (e.g., pH, temperature, conductivity) are stabilized. It is ideal to purge the well with the pump placed near the top of the water column and then lower the pump closer to the screen during sampling. Lowering the pump decreases the chance of collecting air-equilibrated water from the top of the water column in the well. Water temperature and conductivity are critical parameters to measure because they are used in dissolved gas calculations. Total dissolved gas pressure and dissolved oxygen are also valuable field measurements (MANNING et al. 2003), to indicate potentially high gas concentrations and/or potential for degassing during sampling. Weather conditions and pump speed can adversely affect the quality of sample collected. For example, sampling during very hot weather with low flow rate provides an opportunity for the groundwater sample to increase in temperature as it passes through the pump tubing. Higher water temperature increases the possibility that dissolved gases will form bubbles and be lost from the sample.

3.2.1 ^3H and ^3He sample containers and basic process

3.2.1.1 ^3H sampling

^3H samples are collected in 500 ml or larger bottles (plastic or glass). Tritium samples may have a small amount of head space and samples can be stored at ambient temperatures.

3.2.1.2 Copper tube method for noble gas samples

Groundwater samples for noble gas analysis are often collected in refrigeration-grade Cu tubing with both ends sealed with refrigeration clamps (SOLOMON et al. 1992) (Figure 3). Clamps are machined to very tight tolerance that

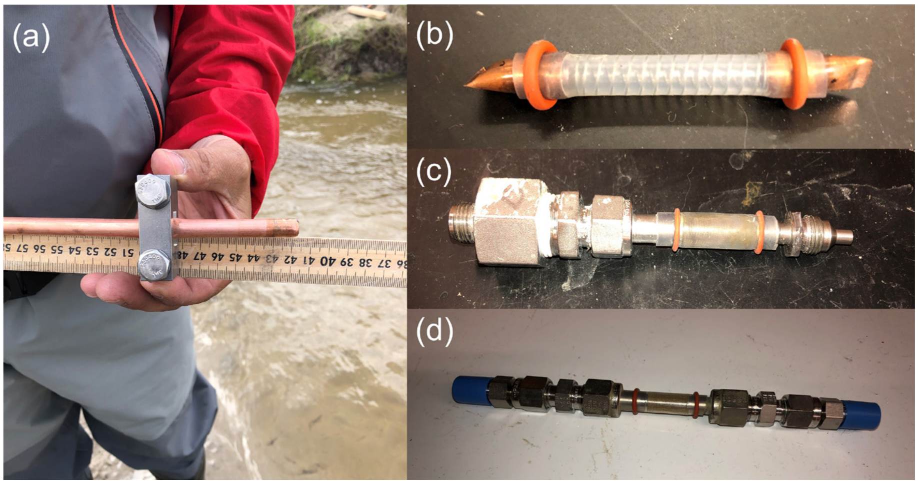

FIGURE 3 – (a) A Cu tube with clamp attached. Clamps should be place approximately 5 cm from the end of the tube to allow for sufficient sample volume and for connecting to a vacuum line in the laboratory. (b) Permeable tubing used for the standard diffusion sampler, after the two cold-welded Cu tube ends containing the gas sample have been removed. (c) and (d) show an advanced diffusion sampler. (Photos b, c, and d courtesy of Eric Humphrey, University of Utah Noble Gas Laboratory.)

must be compatible with the wall thickness of the copper tube. Tube and clamp configurations may differ between noble gas labs (AESCHBACH & SOLOMON 2013), therefore, it is important to coordinate in advance with a noble gas laboratory that can provide detailed sampling information and/or provide tubes and clamps (e.g., see https://noblegaslab.utah.edu/how-to.php). As an example, noble gas samples have been collected in 0.95 cm diameter copper (Cu) tubes about 50 cm in length, sufficient for sample volumes of approximately 18-20 ml (SOLOMON et al. 1992, SOLOMON et al. 1993).

When sampling using a submersible pump in a groundwater well, the inlet side of the Cu tube can be connected to pump tubing using a compression fitting (nylon ferrules can be removed and re-used if the fitting is not overtightened), or flexible tubing secured with a hose clamp (Figure 4A). The outlet side of the Cu tubing should be connected to an overflow line that remains full of sample water to avoid air contact with the water sample in the tube. To inspect for loss of air bubbles from the sample, it is important to use a piece of clear tubing on the outlet side of the Cu tube so bubbles can be observed (Figure 4B).

About one liter of water should be purged through the tubing before sampling. (UNIVERSITY OF UTAH 2021b). The water flowing through the tubing should be checked before sampling to ensure there are no air bubbles present. If there is a stream of bubbles in the tubing, the tubing connections should be checked to be sure they are airtight. Bubble formation may also be a sign of degassing of the sample, which may be partially mitigated by applying backpressure on the sample and/or, if sampling on a warm day, increasing pump speed to minimize residence time of groundwater in the pump tubing. Clamps should be place approximately 5 cm from the end of the tube, allowing sufficient tubing on the end to be attached to a vacuum system during laboratory analysis. The spacing of clamps is best achieved by using a metal channel to hold the clamps and tubing. After checking for bubbles in the outlet tubing, the wrench can be used to lightly tap the copper tubing and/or metal channel to dislodge any bubbles stuck in the tubing. Clamps should be tightened starting with the clamp on the outflow to ensure there is backpressure on the sample. Bolts should be gradually tightened, alternating between bolts on each side of the clamp until the clamp is

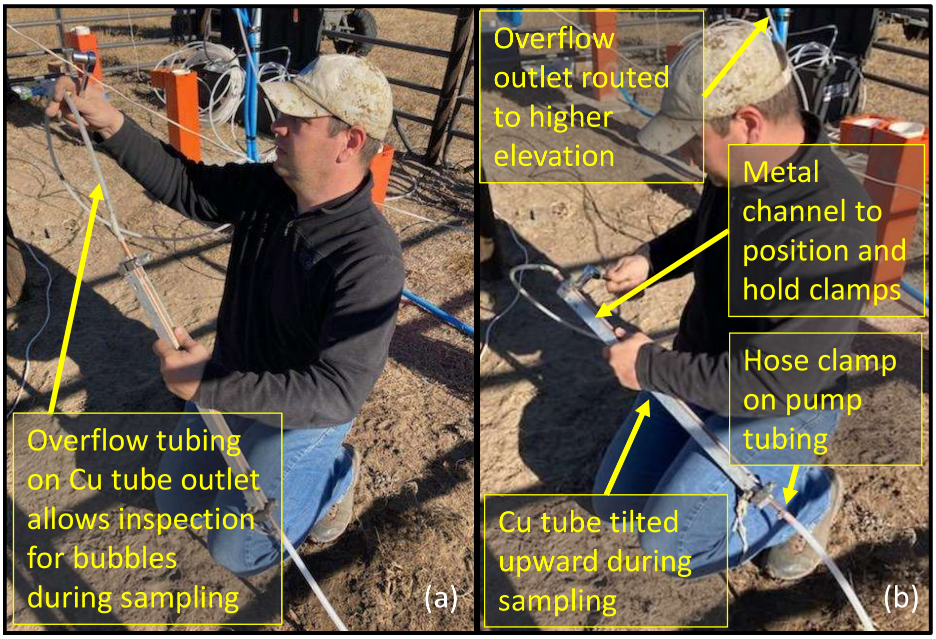

FIGURE 4 – (a) Inspecting for bubbles in overflow tubing during sampling and (b) Cu tube sample collection from a submersible pump in a groundwater observation well. Water flows through the white pump tubing into the Cu tube. A holder is used to keep the clamps and Cu tube stable while tightening clamps. Elevating the overflow tube outlet provides slight backpressure on the groundwater during collection, which can reduce potential degassing. (Photos courtesy of Griffin Nuzzo, University of Nebraska.)

completely closed. The bolts should be tightened completely to properly seal off the copper tube.

When sampling small diameter wells or piezometers in streambeds, sampling cannot be done with typical submersible sampling pumps. Instead, an inertial pump (e.g., Waterra check valve; see also SOLOMON et al. 1992) can be attached to the bottom of the Cu tube using flexible rubber tubing. The overflow tubing attached to the top of the Cu tube can be used to lower the inertial pump and Cu tube below the water level in the piezometer. After purging the piezometer and the Cu tube, the water level in the piezometer should be allowed to recover, and then pumping can be continued to collect the noble gas sample. The overflow line should be observed for gas bubbles, as with traditional well sampling. When the Cu tube has been purged, a three-way valve and syringe can be used to pressurize the overflow line. The pressure helps keep the check valve closed and also limits degassing. The overflow line is used to gently pull the Cu tube out of the piezometer. The Cu tube is then placed in the metal channel and clamps are tightened. In this scenario, the inlet side of the Cu tube (the side closest to the check valve) is clamped first to minimize leakage of air into the valve. Then the clamp on the outlet side is tightened.

Diffusion samplers

Diffusion sampling allows for passive gas extraction to avoid the problems with extraction sampling such as degassing. There are two types of diffusion samplers. The standard method for diffusion samples uses short Cu tubes (~8 cm) on either end of a short piece (~10 cm) of gas permeable tubing (silicone or Teflon). The Cu tubes are closed on the outer ends using cold welding (e.g., with a tungsten carbide pinch-off tool). The sampler is submerged in a well so gases exchange through the silicone tubing. This process takes approximately 24 hours. Once this process is completed the gas inside the sampler should be equilibrated with the groundwater's dissolved gas content (SANFORD et al. 1996). Once the samples are removed the ends are cold-welded using a specialized pinch-off tool (UNIVERSITY OF UTAH 2021c). Ends must be sealed quickly after removal from the well to eliminate gas exchange at the land surface.

The Cu tube for the advanced passive diffusion method is approximately 15 cm in length and 3 cm in diameter (GARDNER & SOLOMON 2009, UNIVERSITY of UTAH 2021a). The sampler contains four main components: the sample volume, where the gas sample is collected and stored, the gas exchange membrane, the gas-exchange piston and the hydraulic activation mechanism (GARDNER & SOLOMON 2009). Samplers are placed in wells for at least 24 hours before collection. This time allows for the gas exchange across the silicon membrane (GARDNER & SOLOMON 2009). Once 24 hours has passed the samples are collected and clamped. For sample retrieval a hand operated pump is used to increase valve tubing pressures, which closes the intake valves and prevents further gas exchange. Once the sample is pulled to the land surface the tubing is clamped shut which allows the sample to be stored long term (GARDNER & SOLOMON 2009).

3.3 Laboratory analysis

Estimates of groundwater age require laboratory measurements of ^{3}H and noble gases. Tritium concentrations are analytically determined either indirectly using the helium in-growth method or directly using the radiometric method. The radiometric or "counting" method involves measuring ^{3}H either with a gas proportional counter (GPC) or a liquid scintillation counter (LSC) (THEODORSSON 1999) (after electrolytic enrichment) which routinely reach a minimum detectable activity limit of 0.4 TU (PLASTINO et al. 2007) and lower than 0.05 TU with super electrolytic enrichment (MORGENSTERN & TAYLOR 2009). The in-growth method involves degassing, sealing, and storing water samples in stainless steel flasks for an extended period (typically 6-12 weeks) before the samples are analyzed for the ^{3}H daughter product, ^{3}He. The concentration of ^{3}He produced by the decay of tritium over a known period of time indicates the initial concentration of tritium in the water sample. The detection limit for the helium ingrowth method is typically near 0.01 TU although partially dependent on the amount of sample water and length of storage (SOLOMON & COOK 2000).

Water samples collected in copper tubes are also analyzed for the gas concentration of helium isotopes, ^{4}He and ^{3}He. Isotopic helium concentrations from copper tube and in-growth tritium samples are determined by large-radius sector-field mass spectrometry (SFMS). Other noble gases from copper tube samples are analyzed by quadrupole mass spectrometry (QMS) or by SFMS. For example, the noble gas laboratory at the University of Utah measures noble gases including ^{3}He and ^{4}He via cryogenic separation with a Mass

Analyzers Products Model 215-50 Magnetic Sector Mass Spectrometer. A faraday cup is used to measure ^{4}He, which is the major isotope, while an electron multiplier is used to measure the minor isotope, ^{3}He (UNIVERSITY OF UTAH 2021d).

3.4 Determination of $^{3}He_{trit}$

Determination of tritiogenic helium-3 ($^{3}He_{trit}$) concentrations in groundwater is informed by measured ^{3}He and ^{4}He, known ratios of ^{3}He/^{4}He for different sources of He, and other noble gas concentrations in the sampled groundwater. Laboratories may provide an estimate of tritiogenic helium-3 with the lab results. The procedure, starting with noble gas and ^{3}H data from the lab and ending with a $^{3}He_{trit}$ value for use in equation 2.3, is illustrated in figure 5. In practice, most calculations are done in spreadsheets (JURGENS et al. 2020) or other programs (JUNG and AESCHBACH 2018), so we focus here on the data checks and analysis steps in figure 5 without deriving or repeating detailed equations that are available in cited references.

Calculation of groundwater age from equation 2.3 requires quantification of $^{3}He_{trit}$ in the groundwater sample. As shown in Step 1 of figure 5, an initial check for evidence of $^{3}He_{trit}$ in the sample can be done by comparing the ^{3}He/^{4}He in the sample (R) with the ^{3}He/^{4}He in the atmosphere (R_a). R/R_a values greater than one are a preliminary indicator of $^{3}He_{trit}$ in the sample. R/R_a values less than one may suggest older groundwater that contains excess ^{4}He (although excess air can also cause $R/R_a < 1$), while R/R_a very close to one may reflect very young groundwater (i.e., there is not enough excess ^{3}He to affect the ratio). Low ^{3}H in the sample suggests older groundwater because most of the tritium present at recharge has since decayed. Conflicting values, such as $^{3}H > 0.5$ TU while $R/R_a < 1$, might suggest the sample is a mixture of young and old groundwater. These initial checks do not preclude further analysis of the data but can provide preliminary insight before proceeding with modeling groundwater ages.

Quantification of the $^{3}He_{trit}$ component of He in the sample involves steps 2 through 4 shown in figure 5. In the following sections, we expand on each of these three data analysis steps. The equation describing $^{3}He_{trit}$ determination from total ^{3}He ($^{3}He_{tot}$) measured in a water sample is

$$^{3}He_{trit} = \ ^{3}He_{tot} - \ ^{3}He_{atm} - \ ^{3}He_{terr} \tag{3.3}$$

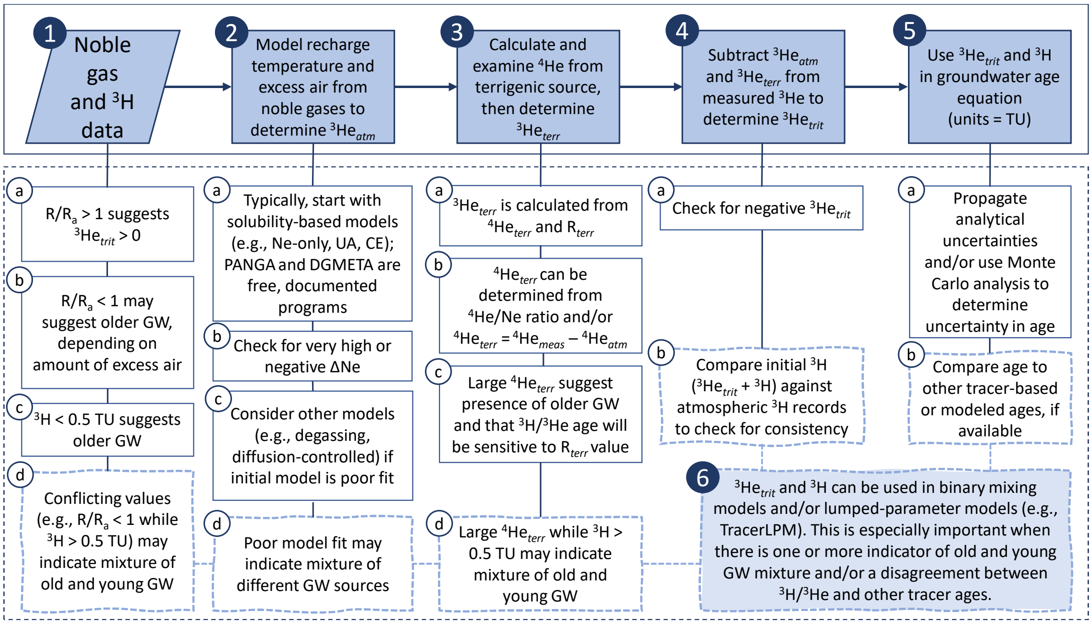

FIGURE 5 – Modeling process for determination of ^{3}H/^{3}He age of groundwater. Shaded boxes across the top show numbered steps in the process and text boxes below each step show key criteria to consider for each step. Dashed lines connect example observations that suggest the need to account for mixing of groundwater with substantially different ages (Step 6).

where $^3He_{sol}$ is from atmospheric sources, and $^3He_{terr}$ is from terrigenic sources.

In groundwater, there are often two sources of helium from the atmosphere (equation 3.4 and step 2 of figure 5). The first component is the solubility concentration obtained when the water was in equilibrium with the atmosphere. The second component is from entrainment of air bubbles during recharge and often has a composition similar to the atmosphere, hence the term "excess air" is used to describe this component (HEATON & VOGEL 1981).

$$^3He_{atm} = {}^3He_{sol} + {}^3He_e \qquad (3.4)$$

where $^3He_{sol}$ is the concentration calculated from solubility equilibrium with the atmosphere (at recharge temperature, pressure (based on elevation), and salinity. ^3He_e is the ^{3}He derived from excess air (SOLOMON & COOK 2000).

3.4.1 Determination of ^{3}He$_{atm}$ components using noble gases

Step 2 in figure 5 highlights the key components of recharge temperature and excess air in the noble gas modeling process. The atmospheric components in equation 3.4 can be computed from the temperature, salinity, excess air, and elevation where recharge occurred (often taken as the site elevation).

In some cases, the mean annual air temperature (+/- 1°C) can be used to estimate the recharge temperature because the water temperatures are closely related to soil and ground temperatures (STUTE & SCHLOSSER 1999). Neon concentrations can also be used to compute the excess air component of helium because it behaves similarly to helium but does not have an in-situ production term like helium (radiogenic helium). Thus, estimates of recharge temperatures from neon concentrations can provide the simplest method for calculating the ^{3}He$_{trit}$ component in water (SCHLOSSER et al. 1989; see also Appendix A). This simple model assumes that the ratio of He/Ne in excess air is the same as the atmosphere which is not always the case.

The recharge temperature and excess air values are often estimated or computed by inverse modeling with a suite of other dissolved gases measured in water. The most common noble gas models are based on solubility equilibrium at recharge temperature and the assumption that any excess air is of atmospheric composition and not fractionated. Conceptually, the model assumption is that any excess air is the result of a bubble of atmospheric air that was completely dissolved in groundwater. Studies have shown that these conditions are not always met (KLUMP et al. 2008), but in many cases these assumptions are reasonable. Thus, it is recommended to start the noble gas modeling process by first trying solubility-based models (JUNG & AESCHBACH 2018) such as the Ne-only model (SCHLOSSER et al. 1989, SOLOMON & COOK 2000), unfractionated excess air (UA) model, and the closed-system equilibration (CE) model (AESCHBACH-HERTIG et al. 2000). If the solubility-based model(s) result in poor model performance, then alternative models that include diffusive processes and partial dissolution of gases may be considered. All of these noble gas models are described in detail elsewhere, including in the documentation for the freely available Program for Analysis of Noble Gas data (PANGA) by JUNG & AESCHBACH (2018) and Dissolved Gas Modeling and Environmental Tracer Analysis (DGMETA) by JURGENS et al. (2020) and in the references therein (e.g., BALLENTINE & HALL 1999, AESCHBACH-HERTIG et al. 2000, KIPFER et al. 2002, AESCHBACH-HERTIG et al. 2008, AESCHBACH-HERTIG & SOLOMON 2013).

The UA model can be calibrated to multiple conservative noble gases, including Ne, Ar, Kr, and Xe, which provides a more robust estimate of excess air than the Ne-only method. An inverse fitting procedure is used to determine the recharge temperature and excess air values that best fit the UA model to several conservative noble gases (BALLENTINE & HALL 1999, AESCHBACH-HERTIG et al. 2000). As implemented in PANGA, the UA model is expressed as

$$C_i(T,S,P,A) = C_i^{eq}(T,S,P) + Az_i \qquad (3.5)$$

where T is temperature (°C), S is salinity (g/kg), P is pressure (atm), z_i is the mole fraction of the ith noble gas in dry air, and C is a noble gas concentration (cm^{3}STP/g), superscript "*eq*" indicates solubility equilibrium with the atmosphere, and A is the concentration of dissolved excess air (cm^{3}STP/g) (JUNG & AESCHBACH-HERTIG 2018). The concentration unit of cm^{3}STP/g can be visualized as follows. If a given gas (e.g., ^{4}He) is extracted from 1 gram of water, placed in a syringe, cooled to 273.15 K (standard temperature for gases) and then compressed to 1 atm (standard pressure), the volume of gas in the syringe will be the number of cm^{3}STP/g.

An important and simple variable for evaluating noble gas data is ΔNe (see Figure 5, Step 2b). ΔNe is calculated as

$$\Delta Ne = \left(\frac{Ne_{tot} - Ne_{sol}}{Ne_{sol}}\right) * 100 \qquad (3.6)$$

and indicates the presence of excess air (positive ΔNe). Excessively high ΔNe may be an indicator of a sampling artifact such as a bubble trapped in the copper tube during sampling. A negative ΔNe value may indicate that gas has been lost from the sample, in some cases due to degassing in the aquifer and/or during sampling (VISSER et al. 2007, AESCHBACH-HERTIG et al. 2008, NAKATA et al. 2019). One cause for degassing is the buildup of biogenic gases such as N_2 that is produced from denitrification (e.g., VISSER et al. 2009). When the dissolved gas pressure exceeds hydrostatic pressure, the gas bubbles may exsolve and cause the removal of not only the biogenic gas, but other atmospheric gases as well. These degassed samples are more difficult to evaluate and there is increased uncertainty in $^3He_{trit}$ values because the uncertainty in the atmospheric ^{3}He component becomes large. Analysis of degassed samples is more complex than excess-air-only cases because of unknowns that are difficult to evaluate. For instance, (1) how much excess air did the groundwater originally contain, and (2) when did the degassing occur? If degassing occurred just prior to sampling, then some $^3He_{trit}$ was lost from the sample. Not accounting for degassing could lead to an underestimation of groundwater age. If degassing occurred at the time of recharge (before any $^3He_{trit}$ could be accumulated in the sample), then noble gases would be lost from the sample, but no $^3He_{trit}$ would be lost. In this case, correcting $^3He_{trit}$ for degassing would lead to an overestimation of groundwater age. DGMETA provides a graphical way to identify samples that have been degassed (JURGENS et al. 2020).

The Closed-system Equilibration (CE) model is a more general model and can be used to model noble gases in degassed samples (AESCHBACH-HERTIG et al. 2008). The CE model formulation accounts for either excess air or degassing cases (the UA model is a special case of the CE model). This model is also available in PANGA and DGMETA, implemented in the form of:

$$C_i(T,S,P,A) = C_i^{eq}(T,S,P) + \frac{(1-F)A'z_i}{1+FA'z_i/C_i^{eq}} \qquad (3.7)$$

where variables and units are the same as for the UA model, except A' is the initial amount of entrapped air per unit mass of water (cm^{3}STP/g) and F is the dimensionless fractionation factor by which the size of the gas phase has changed during re-equilibration (JUNG & AESCHBACH 2018). As with other noble gas models, results of the CE model should be scrutinized to ensure that model parameters do not exceed realistic thresholds for excess air and/or degassing.

3.4.2 Accounting for $^3He_{terr}$

$^3He_{terr}$ may be composed of nucleogenic helium and/or sourced from the earth's mantle. ^{3}He/^{4}He ratios are different for mantle He (~10^{-5}), crustal (radiogenic) He (< 10^{-7}), and atmospheric He (~10^{-6}) (TORGERSEN et al. 1979; SOLOMON et al. 1993). Radiogenic helium may be produced from decay of U and Th in the subsurface. This decay causes nucleogenic ^{3}He production from ^{6}Li in Li-rich environments (ANDREWS 1985). Mantle sources are negligible for many groundwater systems (SCHLOSSER et al. 1989). For example, ^{4}He from the mantle is considered negligible or absent in groundwater sampled from the Guarani Aquifer in Brazil (AGGARWAL et al. 2015). An approach for the case where mantle helium is significant has been developed (referenced in SCHLOSSER et al. 1989) but is not discussed here as it requires a detailed understanding of the amount and isotopic composition of mantle He, which is typically not available.

Although the objective of Step 3 in figure 5 is to determine $^3He_{terr}$, the process starts by first determining $^4He_{terr}$. If the UA or CE model are used, $^4He_{terr}$ is determined by subtracting $^4He_{atm}$ from ^{4}He measured in the groundwater sample. Large values of $^4He_{terr}$ usually indicate the presence of old groundwater, and in the case where ^{3}H is also substantial (e.g., ^{3}H > 0.5 TU), a likely mixture of old and young groundwater. With $^4He_{terr}$ known, $^3He_{terr}$ is determined by multiplying $^4He_{terr}$ by the appropriate ^{3}He/^{4}He ratio (R_{terr}) based on the perceived source of terrigenic He (mantle or crustal). Thus, the choice of R_{terr} is especially important when $^4He_{terr}$ is high (Figure 3, Step 3c). DGMETA provides a graphical approach for determining sources of helium in an aquifer and the likely R_{terr} for correcting $^3He_{trit}$ calculations when terrigenic helium is present.

3.4.3 Determination of groundwater apparent age with $^3H/^3He$

The groundwater apparent age can be calculated using $^3He_{trit}$ ^3H, and equation 2.3. Figure 5 shows several useful checkpoints (Steps 1d, 2d, 3d, 4b, and 5b) to evaluate before concluding the $^3H/^3He$ age-dating process (at either Step 5 or Step 6). Most of these checkpoints describe potential indicators of groundwater mixing, whether due to (1) mixing within a long well screen in an unconfined aquifer (e.g., Figure 2A), (2) interception of a wide range of groundwater flowpaths that converge near an aquifer discharge point (e.g., streambed or spring), and/or in some cases (3) interception of distinct local and regional groundwater flowpaths (an example of a binary mixture). In the first two cases, it may be appropriate to use lumped-parameter models to determine groundwater age from $^3He_{trit}$, ^3H, and any other available age tracer data (e.g., SF_6, CFCs, ^{14}C). The second and third cases may be evaluated using a binary mixing model or a combination of binary mixing and lumped-parameter models (e.g, SOLOMON et al. 2010). TracerLPM (JURGENS et al. 2012) is a readily available and well-documented spreadsheet model that can be used for these procedures.

In general, uncertainty in $^3H/^3He$ apparent age is related to analytical uncertainties in noble gas and ^3H data, uncertainty in noble gas modeling, and uncertainties in the choice of R_{terr} values. Uncertainty in apparent age can be estimated by propagating uncertainties for these variables through the $^3H/^3He$ age equation, whether through classical error propagation methods or bootstrapping (Monte Carlo) methods (Figure 5, Step 5a). Uncertainty in groundwater apparent age based on the $^3H/^3He$ method is often in the range of 2-3 years (SCANLON et al. 2002), which can lead to substantial uncertainties for very young groundwater (Table 1; on a percentage basis, e.g., age of 1 year with uncertainty of 2 years yields 200% uncertainty). If lumped-parameter models are used instead of the $^3H/^3He$ age equation (Figure 5, Step 6), then additional uncertainties from the choice of model, uncertainty in the ^3H input function, and unsaturated zone travel time are all introduced, although some of these uncertainties may be offset by the use of additional age tracer data (e.g., CFCs, SF_6, ^{85}Kr; we also note that vadose zone transport of tracers may differ, see COOK and SOLOMON 1995), if available. Since the calculation of $^3He_{trit}$ involves small differences between larger numbers the absolute uncertainty for young waters (5 to 10 years) can be much greater than for older waters within the range of the tritium-helium method.

4 APPLICATIONS OF $^3H/^3HE$ AGE-DATING IN HYDROGEOLOGICAL AND ENVIRONMENTAL STUDIES

Groundwater age-dating can be used to characterize (1) groundwater recharge rates, (2) the movement of groundwater and solutes through aquifers, and (3) the eventual discharge of groundwater and solutes to wells, springs, or streams. In all these cases, groundwater age information can be useful for (4) informing more complex models of subsurface transport, through improved conceptual models, constraint of model inputs (e.g., recharge rate), and/or model calibration. The applicable timescale of $^3H/^3He$ age dating is ideal for investigating anthropogenic effects on the quantity and quality of groundwater resources since the mid-20th century.

Among the many recharge rate estimation methods reviewed by SCANLON et al. (2002), $^3H/^3He$ is a reliable method for groundwater recharge rates greater than about 30 mm yr^{-1}. SOLOMON & SUDICKY (1991) estimated recharge rates based on groundwater ages in multi-level wells that increased with depth below the water table (Figure 6). Subsequent studies were focused on both water

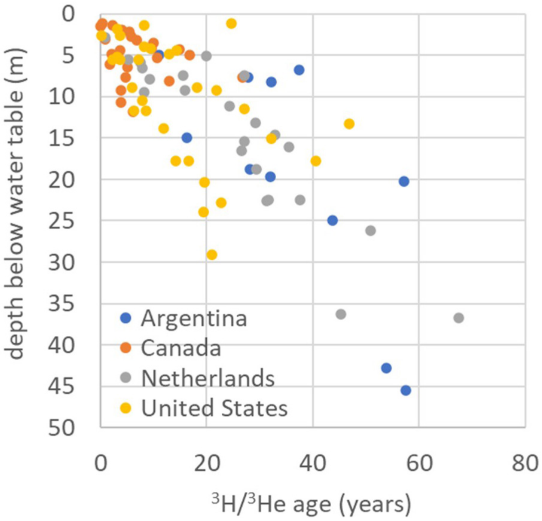

FIGURE 6 – Observations of increasing groundwater age with depth in aquifers. The selected study sites were in Argentina (MARTINEZ et al. 2016), Canada (SOLOMON et al. 1992), Netherlands (VISSER et al. 2013), and United States (EKWURZEL et al. 1994).

and contaminant fluxes into aquifers. For example, BÖHLKE (2002) analyzed groundwater ages beneath agricultural landscapes to estimate inputs of excess nitrate-nitrogen into shallow aquifers. More recently, groundwater recharge rates based on $^3H/^3He$ age have been used to observe how decadal-scale changes in water resources management (irrigation technology) have affected recharge rates (WELLS et al. 2018). Other studies have focused on point-source pollution by characterizing the transport rates and extents of groundwater contaminant plumes (e.g., SOLOMON et al. 1995). By combining groundwater age and contaminant concentrations observed from the same sampling points (wells or piezometers), contaminant histories can also be reconstructed. PUCKETT et al. (2011) used groundwater age and recharge nitrate concentrations (corrected for denitrification using N_2 gas and noble gas data) from groundwater wells to reconstruct recharge nitrate history in 20 agricultural watershed across the United States. Results showed how increased nitrogen fertilizer use for crop production was linked to decadal increases in nitrate concentrations in aquifers. LINDSEY et al. (2017) used ^3H-$^3He_{trit}$ data with lumped parameter models to show that concentration trends of methyl tert-butyl ether (MTBE) in many wells in northeastern USA were related to the groundwater age and the production history of MTBE.

Groundwater age-dating with $^3H/^3He$ has been done at various aquifer discharge points, including irrigation wells, municipal (drinking water) wells, springs, and gaining streams. As noted in Sections 3.1.1 and 3.2, sampling at points of groundwater discharge requires caution to avoid extensive groundwater mixing and/or gas exchange that could alter noble gas content in samples. Nonetheless, there have been many successful $^3H/^3He$ studies based on sampling long-screened, high-capacity wells (e.g., VISSER et al. 2013). These studies often involve the use of multiple age-dating tracers analyzed for each well sampled (e.g., ÅKESSON et al. 2015). Other studies have focused on more natural groundwater discharge zones, such as permeable streambeds in gaining stream reaches. Early studies relied mostly on CFC groundwater ages for groundwater collected from mini-piezometers temporarily installed in sandy streambeds overlying and alluvial aquifer (BÖHLKE & DENVER 1995). Results showed substantially different groundwater chemistry and age for samples collected from the same streambed, indicating that it was possible to collect groundwater from distinct groundwater flowpaths. As with groundwater age data from wells, the observations of, e.g., distinct groundwater nitrate (with correction for denitrification) and groundwater age allowed for reconstruction of historical nitrate inputs and an estimated range of groundwater lag times associated with delivery of nitrate to the stream. KENNEDY et al. (2009) and BROWNE & GULDAN (2005) later built on this streambed sampling concept by pairing the groundwater chemistry and age information with vertical groundwater flux estimates in the streambed (these studies relied on the CFC age-dating technique; GILMORE et al. (2016) later used $^3H/^3He$ age-dating in this same type of sampling), showing distinct groundwater ages and chemical fluxes at sub-meter spatial scales. Streambed sampling combined with vertical groundwater flux estimates at each sampling point is a powerful combination, allowing not only reconstruction of contaminant history (Figure 7A), but also for constructing groundwater transit time distributions (Figure 7B) and predicting future fluxes of nitrate from aquifer to stream (Figure 7C) (GILMORE et al. 2016).

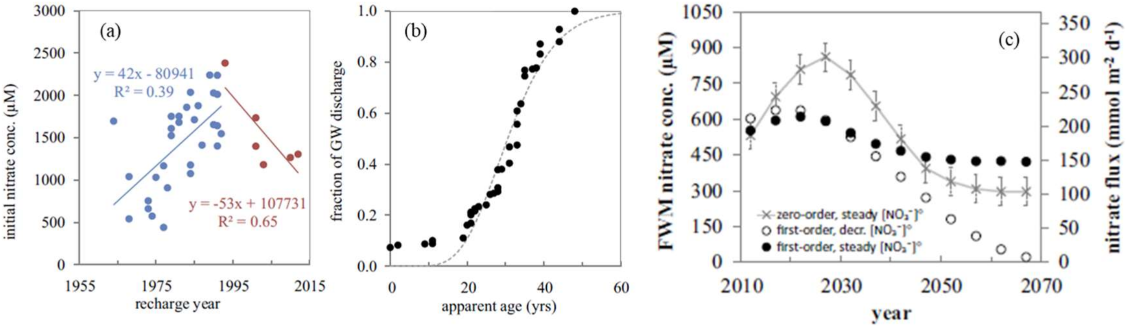

FIGURE 7 – (a) Initial (recharge) nitrate concentrations, corrected for denitrification, (b) groundwater transit time distribution, and (c) predicted future flow-weighted mean (FWM) nitrate concentrations and fluxes from streambed sampling in a 58m length stream reach in North Carolina, USA (modified from GILMORE et al. 2016).

Lastly, $^3H/^3He$ age-dating offers additional constraints and/or calibration targets for groundwater models, beyond the typical approach of using only groundwater head and/or stream discharge data. MCMAHON et al. (2010) found that even a small number of $^3H/^3He$ groundwater age estimates (6 out of 2574 field observations) had a major influence on refining a groundwater model. WELLS et al. (2021) used groundwater age estimates from previous studies (BÖHLKE et al. 2007, WELLS et al. 2018) as part of a machine learning framework for estimating groundwater and vadose zone transport rates for water and nitrate in an agricultural setting. Based on the vadose zone and groundwater transport rates derived from the Random Forest Regression, WELLS et al. (2020) could transform long-term groundwater quality monitoring data (Figure 8A) into a likely historical input history (where input is in this case at the time of infiltration below the root zone, rather than at recharge at the water table, Figure 8B) with similar characteristic shape as the long-term aquifer inputs of nitrate observed by PUCKETT et al. (2011) across the United States.

5 OPPORTUNITIES AND FUTURE PERSPECTIVES FOR APPLICATION OF $^3H/^3HE$ METHOD IN BRAZIL

To our knowledge, there has been very little application of groundwater age-dating for young groundwaters in Brazil, and seemingly no application of $^3H/^3He$ age-dating. While lower ^3H in precipitation (in the Southern Hemisphere, relative to the Northern Hemisphere) lead to lower values of $^3He_{trit}$ and larger uncertainties in groundwater age estimates, $^3H/^3He$ age-dating has been successful in Argentina (MATSUMOTO et al. 2017; we note, however, that ^3H was elevated due to a local source). Opportunities exist in Brazil to strengthen understanding of groundwater recharge processes in surficial aquifers, including recharge areas for the Guarani Aquifer or areas where

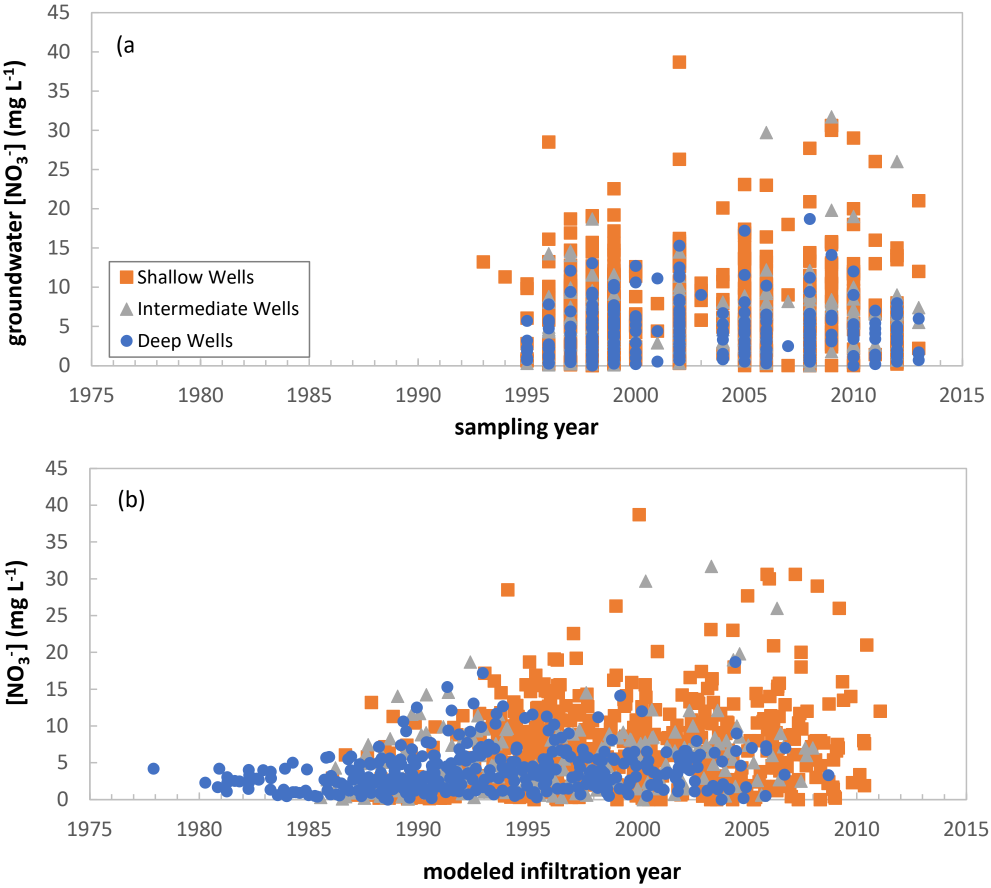

FIGURE 8 – (a) Groundwater nitrate monitoring data and (b) modeled infiltration year for nitrate in western Nebraska, USA (modified from WELLS et al. 2020).

groundwater development is ongoing or pending. Such investigations could complement the use of age-dating tracers for old groundwater (^{14}C, ^{81}Kr) used to improve conceptual models of groundwater flow in the Guarani Aquifer System or other groundwater systems, including poorly studied fractured aquifers. Study of both point-source (e.g., sewage in urban areas) and nonpoint-source (e.g., agrichemicals in agricultural areas) contaminants would be useful to determine not only the extent and magnitude of contaminant concentrations in groundwater but also the potential lag times (based on groundwater age) required for groundwater quality to improve. Groundwater-fed streams are also susceptible to groundwater contamination and human exploitation. Opportunities exist to increase understanding of groundwater and surface water interactions in Amazonia, for example. Groundwater age-dating, based on $^3H/^3He$ where appropriate, would strengthen understanding of the source and vulnerability of streams to human activities. Ultimately, the $^3H/^3He$ method is a robust approach for determining the apparent age of young groundwater, with potential applications for understanding and managing groundwater in Brazil.

6 ACKNOWLEDGEMENTS

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