

## Sampling and Analysis

Following the standard sampling procedures used previously (USEPA, 2017; USGS, 2011), the groundwater monitoring wells were purged before sampling. Purging followed low-flow rate protocols (less than 0.5 liters per minute), and water parameters were monitored during the process. Specifically, water from both wells were simultaneously monitored for pH, electrical conductance, and temperature until stable values were obtained, whereupon the samples were collected.

During sampling, water samples for measurement of dissolved gas and noble gas composition were collected in refrigeration-grade copper tubes that were flushed in-line with at least 50 volumes of sample water prior to sealing with brass clamps (Darrah et al., 2014b; Harkness et al., 2017a; Harkness et al., 2017b). In the laboratory, the fluid was extracted from the copper tubes on a vacuum line (at a pressure of  $< 10^{-6}$  torr) and sonicated for ~30 minutes to ensure complete transfer of dissolved gases to the sample inlet line (Solomon et al., 1995). Major gas components (e.g., N<sub>2</sub>, O<sub>2</sub>, Ar, CH<sub>4</sub>) were measured using an SRS quadrupole mass spectrometer (MS) and an SRI gas chromatograph (GC) (Darrah et al., 2013; Hunt et al., 2012).

The isotopic analyses of noble gases were performed using a Thermo Fisher Helix SFT mass spectrometer following methods reported previously (Darrah and Poreda, 2012; Darrah et al., 2013; Hunt et al., 2012). Standard analytical errors were  $\pm 3\%$  for noble gas concentrations ( $[^4\text{He}]$ ,  $[^{22}\text{Ne}]$ ,  $[^{40}\text{Ar}]$ ). Isotopic errors were approximately  $\pm 0.01$  times the ratio of air (or  $1.384 \times 10^{-8}$ ) for  $^3\text{He}/^4\text{He}$  ratio,  $< \pm 0.5\%$  and  $< \pm 1\%$  for  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$ , respectively, and  $< \pm 0.5\%$  for both  $^{38}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$ . Tritium analyses were measured by the in-growth of  $^3\text{He}^*$  using a Thermo Fisher Helix SFT mass spectrometer by methods reported previously (Solomon et al., 1995; Solomon et al., 1992).

## *Noble Gas Systematics*

The elemental abundances of noble gases (e.g., helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe)) and the isotopic compositions of He, Ne, and Ar provide a set of non-reactive geochemical tracers. In effect, the original noble gas composition of the groundwater is preserved independent of microbial activity, chemical reactions (e.g., sulfate reduction), or changes in oxygen fugacity, salinity, or electrical conductivity. The inert nature, low terrestrial abundance, and well-characterized isotopic composition of noble gases in the mantle, crust,

hydrosphere, and atmosphere enhance their utility as geochemical tracers of crustal fluids (Ballentine et al., 2002). Noble gases are useful indicators of the residence time of groundwater in systems where pre-modern (non-tritiogenic) and modern (tritium-active) waters exist (Clark and Fritz, 1997; Darrah et al., 2014a; Schlegel et al., 2011), because noble gases are relatively inert and are unaffected by microbial processes, redox conditions, and mineral reactions unlike more labile species (e.g.,  $^{14}\text{C}$ ) (Ballentine et al., 2002).

The noble gas composition in groundwater is derived dominantly from two primary sources: the atmosphere (air-saturated water (ASW): e.g.,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ,  $^{84}\text{Kr}$ ) and the crust ( $\text{U} + \text{Th} \rightarrow ^4\text{He}$  and  $^{21}\text{Ne}^*$  and  $^{40}\text{K} \rightarrow ^{40}\text{Ar}^*$ , where the \* denotes the proportion derived from radioactive decay) (Ballentine et al., 2002). Atmospheric noble gases (AIR) dissolve in groundwater when meteoric water equilibrates with the atmosphere prior to groundwater recharge into the subsurface (commonly termed air-saturated water or ASW) at concentrations proportional their abundance in the atmosphere according to Henry's Law of solubility (i.e., solubility increases with atomic mass:  $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ ) (Weiss, 1971a; Weiss, 1971b). Because the meteoric source for this ASW is constant globally, the concentrations of ASW components in groundwater are a well-constrained function of local temperature, salinity, and atmospheric pressure (elevation) (Weiss, 1971a; Weiss, 1971b).

Typically, shallow groundwater in unconfined aquifers in the environmental conditions of Augusta, GA have ASW noble gas levels of  $[^4\text{He}] = 40\text{-}45 \times 10^{-6} \text{ cm}^3 \text{ STP/kg}$ ;  $[\text{Ne}] = 185\text{-}190 \times 10^{-6} \text{ cm}^3 \text{ STP/kg}$ ; and  $[\text{Ar}] = 0.31\text{-}0.35 \text{ cm}^3 \text{ STP/kg}$ . Isotopically, each ASW gas component that dissolves into groundwater is similar to atmospheric compositions (i.e., helium:  $^3\text{He}/^4\text{He} = 1.36 \times 10^{-6}$  or  $\sim 0.985R_A$ , where  $R_A$  is the ratio of a sample relative to the ratio of helium isotopes in AIR =  $1.384 \times 10^{-6}$ , neon:  $^{20}\text{Ne}/^{22}\text{Ne}$  (9.78) and  $^{21}\text{Ne}/^{22}\text{Ne}$  ( $\sim 0.0289$ ), and  $^{40}\text{Ar}/^{36}\text{Ar}$  ( $\sim 295.5$ )). Only helium ( $0.985 R_A$ ) displays an isotopic effect related to fractionation related to preferential partitioning of  $^3\text{He}$  and  $^4\text{He}$  during Henry's Law dissolution into meteoric water that is larger than the analytical measurement errors.

Crustal noble gases are produced *in-situ* within the Earth's crust from the decay of U, Th ( $^4\text{He}$  and  $^{21}\text{Ne}^*$ ), and K ( $^{40}\text{Ar}^*$ ) (e.g., Ballentine and Burnard, 2002). As groundwater interacts with the Earth's crust, the noble gas composition changes according to the radiogenic nature and geologic history of the rock protolith in which the fluids form and through which they migrate (Ballentine et al., 2002). Typical isotopic ratios of crustal noble gases are  $^3\text{He}/^4\text{He} = \sim 0.01\text{-}0.02R_A$ ,

$^{20}\text{Ne}/^{22}\text{Ne}$  (~9.6-10.0),  $^{21}\text{Ne}/^{22}\text{Ne}$  (~0.029-0.060), and  $^{40}\text{Ar}/^{36}\text{Ar}$  (~295.5-1100), respectively (e.g., Ballentine et al., 2002). In relatively old groundwater (>300 years), the diffusional release of crustal  $^4\text{He}$  can provide an estimate of groundwater residence time.

Because the mantle acquired significant quantities of primordial  $^3\text{He}$  during the accretion of the Earth (e.g., Ballentine et al., 2002), elevated [ $^3\text{He}$ ] and  $R/R_A$  ( $^3\text{He}/^4\text{He}_{\text{sample}}/(^3\text{He}/^4\text{He}_{\text{air}})$ ) measurements can be used to distinguish the presence and/or proportion of relatively small contributions (~1%) from mantle-derived components in shallow groundwater or other crustal fluids or identify inputs from the decay of  $^3\text{H}$  (Poreda et al., 1986). Mantle helium isotopic endmembers can range from ~3-8 $R_A$  ( $^3\text{He}/^4\text{He}_{\text{air}}$ ) for Mid-Ocean Ridge Basalt (MORB) -like contributions, which are common in extensional tectonic regimes and rift environments, but are not expected in the geological setting of the Alvin W. Vogtle Electric Generating Plant Site near Augusta, GA.

In addition to the  $R/R_A$  value, the relative abundance of helium and other heavier noble gases such as neon (i.e.,  $\text{He}/\text{Ne}$ ) can provide important insights on the source of fluids. Air-saturated water (ASW) and excess atmospheric air have relatively low  $\text{He}/\text{Ne}$  that range from 0.219 to 0.247 (ASW) and ~0.288 (AIR), respectively. By comparison, mantle- and crustal-derived fluids typically have  $\text{He}/\text{Ne}$  of >1,000 or more (e.g., Craig et al., 1978). Mantle-derived helium isotopes are not expected in this region and the current study area was previously known to contain helium isotopic values (elevated  $R/R_A$ ) consistent with the decay of tritium ( $^3\text{H}$ ). Thus, the  $\text{He}/\text{Ne}$  ratio provides a useful metric for differentiating between excess  $^3\text{He}$  from mantle sources, ASW, and tritium decay to  $\text{He-3}$  ( $^3\text{H} \rightarrow ^3\text{He}^*$ ). Based on the near-ASW ratios of  $\text{He}/\text{Ne}$ , we can assume that the measured concentrations of  $^3\text{He}$  in the current data set reflect contributions from ASW with all additional  $^3\text{He}$  stemming from the decay of  $^3\text{H}$  (wherein the tritiogenic component of  $^3\text{He}$  is denoted by  $^3\text{He}^*$ ) (Figure 5).

### ***Tritium/Helium-3 Systematics***

Tritium, with a half-life of 12.43 years, is a long-established isotopic tracer commonly used to estimate residence times of young groundwater (<80 years old) in the subsurface. Tritium measurements are especially useful for distinguishing modern and pre-modern (i.e., before 1950's) ground water. Tritium's usefulness as a modern tracer stems from the fact that the level of tritium in the atmosphere increased several orders of magnitude above background levels from the 1950's to mid-1960's because of atmospheric nuclear testing. Tritium-helium age dating is applied mostly

for dating young waters with environmental levels of  $^3\text{H}$ . However, the technique is well-suited for studies that seek to determine the age of groundwater for problems associated with elevated tritium contents (e.g., tritium releases associated with nuclear power plants).

Because tritium ( $^3\text{H}$ ) decays to helium-3, paired measurements of the mother and daughter pair provide a useful basis for robustly calculating how long ago the tritiated water reached the saturated zone and the linear groundwater velocity from recharge area to the point of sampling. This calculation assumes that the tritium content of the source waters was not diluted by hydrodynamic dispersion or matrix diffusion in fractured rock. In other words, our calculations assume conservative “plug flow” of the groundwater with mixing or other forms of mass transport.

The infiltration of tritium-rich rainwater into aquifers, the known decay rate of tritium, and the quantifiable accumulation of  $^3\text{He}^*$  have been extensively used for determination of groundwater ages globally (e.g., Solomon et al., 1995; Solomon et al., 1992). The method includes incubation of water samples and ingrowth of  $^3\text{He}^*$  from the decay of even small concentrations of tritium. The levels of  $^3\text{He}^*$  and  $^3\text{H}$  provides the basis for estimating groundwater ages.

The tritium-helium ( $^3\text{H} \rightarrow ^3\text{He}^*$ ) age-dating technique is based on the premise that tritium atoms provide a conservative tracer of groundwater flow because the tritium atom is part of the water molecule and hence behaves conservatively in the hydrologic cycle. As a result, the radioactive tritium atom is transported at the rate at which water moves without adsorption, retardation, or the influence of other reactions, except on occasion, dispersion and diffusion.

In the environment, tritium is sourced from a variety of natural (cosmic ray produced interactions with gases (i.e.,  $\text{N}_2$ ) in the earth’s atmosphere) and anthropogenic (e.g., releases from nuclear power plants, testing of nuclear weapons, such as stratospheric nuclear testing, or exit signs) sources. Rain entering the vadose zone has some measurable concentration of tritium and trace, but quantifiable concentrations of helium-3. In the atmosphere, vadose zone, or at the water table, the  $^3\text{He}$  in water equilibrates with the dominant amount of  $^3\text{He}$  in the atmosphere (about 7.3 parts per trillion). At the water table, this exchange of helium with the atmosphere is governed by Henry’s Law and results in about  $60 \times 10^{-12} \text{ cm}^3\text{STP}$  per liter of water (or  $1.69 \times 10^9$  atoms of  $^3\text{He}$  per liter of water) at  $19^\circ\text{C}$  (approximate mean annual temperature at sample location). Precipitation infiltrates down to the water table (slowly) and recharges at the water table to become part of the flowing groundwater.

Once a parcel of water is isolated from the atmosphere below the water table,  $^3\text{He}^*$  from

tritium decay begins to accumulate as a dissolved constituent in the groundwater. Neither the partial pressure of  $^3\text{He}$  (i.e.,  $^3\text{He}^*$  plus  $^3\text{He}_{\text{ASW}}$ ),  $^4\text{He}$ , nor other noble gases is high enough for them to occur as a gas phase. In other words, these tracers remain dissolved in the water. Thus, they behave as conservative tracers moving with that parcel of water. In this respect,  $^3\text{He}$  behaves like other dissolved, conservative species (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$ ) subject only to advective flow and dispersion/diffusion caused by porous medium heterogeneity and concentration gradients in the water, respectively.

There is a difference in diffusion coefficients between tritium and  $^3\text{He}$ . However, these are only relevant in systems where the water is not flowing or flowed over a long distance in fractured rocks. Neither of these exceptions apply to the hydrogeologic setting at the Alvin W. Vogtle Electric Generating Plant Site. In a simple system, the ratio of  $^3\text{He}^*/^3\text{H}$  on a per atom basis can be used to determine a groundwater age (also commonly termed groundwater residence time) based on the equation  $t = (1/\lambda) \ln[(^3\text{He}^*/^3\text{H}) + 1]$  where  $t$ =time,  $\lambda$  is the reaction rate constant for the decay of tritium, and  $^3\text{He}^*$  is the tritiogenic component of  $^3\text{He}$ , which equals  $^3\text{He}_{(\text{total})} - ^3\text{He}_{(\text{ASW})}$ , and  $^3\text{H}$  equal the concentration of tritium.

Key features of the tritium-helium ( $^3\text{H} \rightarrow ^3\text{He}^*$ ) age-dating technique have been discussed previously Darrah et al., 2020:

1. The tritium-helium ( $^3\text{H} \rightarrow ^3\text{He}^*$ ) “age” is zero at the water table because tritiogenic  $^3\text{He}$  [i.e.,  $^3\text{He}^*$ ] is zero and the water is in solubility equilibrium with the atmosphere;
2. Along a simple groundwater flow line, intersected by groundwater monitoring wells, screened over a narrow interval, the farther the water migrates from the source of the equilibration with the atmosphere, the older the water;
3. Along a given groundwater flow line, the spatial age gradient can be interpreted to provide the groundwater velocity;
4. The  $V(z)$  (vertical groundwater velocity)  $\times \Phi$  (porosity) =  $r$  (recharge in feet/year) where recharge is the amount of water which reaches the water table;
5. From the spatial distribution of recharge and flow paths determined from distribution of hydraulic heads, one can define the horizontal groundwater velocity ( $V(x)$ ) and direction of plume migration.