Universities Council on Water Resources
Journal of Contemporary Water Research & Education
Issue 159, Pages 78-104, December 2016

Application of Environmental Tracers in the Memphis Aquifer and Implication for Sustainability of Groundwater Resources in the Memphis Metropolitan Area, Tennessee

*Daniel Larsen, Brian Waldron, Scott Schoefernacker, Haley Gallo, John Koban, and Elizabeth Bradshaw

The University of Memphis, Memphis, TN, USA
**Corresponding author*

Abstract: Fourteen years of results from environmental tracer sampling for ^{3}H, He isotopes, noble gases, and SF_6 in production wells screened in the Memphis aquifer in Memphis, Tennessee, are presented and used to determine the age and mass proportion of modern water (<60 years old) pumped from this regionally important public supply aquifer. The results indicate persistent presence of modern water in water pumped from one or more production wells in most of the well fields sampled. The percentage of modern water is quantified by three methods: tritium-loading history, inverse geochemical modeling, and lumped parameter modeling. The mixing percentages and ages determined from each technique are generally in agreement, but also emphasize the unique information provided by each tracer and associated modeling approaches. The implications of the tracer data for sustainability and vulnerability are also considered, especially in regard to potential water quality threats to the water supply in the Memphis, Tennessee, metropolitan area.

Keywords: *aquifer, environmental tracers, modern water, public supply, sustainability, vulnerability*

Assessing sustainability of groundwater resources in urban areas presents challenges in regard to understanding hydrologic processes, water use, and vulnerability of water resources to contamination or loss of water quality. This contribution presents a case study of application of environmental tracers to assessing sustainability of groundwater resources in Memphis, Tennessee, U.S.A. The Memphis metropolitan area has a population of over 1 million people, for which all municipal and industrial water is pumped from groundwater resources, mostly from the Eocene Memphis aquifer (Figure 1). The Memphis aquifer is a semi-confined unconsolidated sand aquifer, partially confined by a silt and clay confining unit, which is in turn overlain by a sand and gravel shallow aquifer that is in direct hydrologic connection to surface water and near-surface contamination sources (Parks and Carmichael 1990; Parks 1990).

Water production began from the Memphis aquifer in 1886 and increased until 2005 when production peaked at 829,000 m^3/d (Kenny et al. 2009). Groundwater from the Memphis aquifer is a low total dissolved solids (32 to 333 mg/L, median 83 mg/L), mixed cation-bicarbonate water (Brahana et al. 1987), desirable for public supply and industrial applications in chemical manufacturing and food processing. Memphis enjoys some of the lowest municipal and industrial water costs in the United States (Memphis Light, Gas, and Water online), making its water supply a significant asset for economic development. In 2005, the State of Mississippi filed an action lawsuit against the City of Memphis and the major utility, Memphis Light, Gas, and Water (MLGW), in Tennessee, claiming that groundwater withdrawal from the Memphis aquifer by MLGW had caused diversion of groundwater from beneath Mississippi into Tennessee (Hood v. City

of Memphis 2009; Waldron and Larsen 2014). Although the 2005 case was dismissed without prejudice by the U.S. Supreme Court, the State of Mississippi has filed a subsequent lawsuit against the State of Tennessee on similar grounds, which is currently in litigation (State of Mississippi v. State of Tennessee 2015). Recognizing the economic benefit of groundwater resources of the Memphis aquifer as well as the vulnerability of the aquifer resources to legal apportionment, Mayor of Memphis, A.C. Wharton, created a community task force (Blue Stream Task Force - BSTF) in 2014 to determine how to protect, sustain, and best utilize groundwater resources in the Memphis area.

Assessment of sustainability is critical for determining long-term production rates of groundwater from an aquifer. Although sustainability can be equated with safe yield (amount that can be pumped regularly without dangerous depletion of the storage reserve) from an aquifer (Fetter 2001), aspects of water quality may present additional considerations. Considering the specific conditions of groundwater production from the Memphis aquifer in the Memphis area, the BSTF adopted the following operational definition of sustainability: *"the use, development and protection of the groundwater resource at a rate and manner that provides for current and projected needs without damage to*

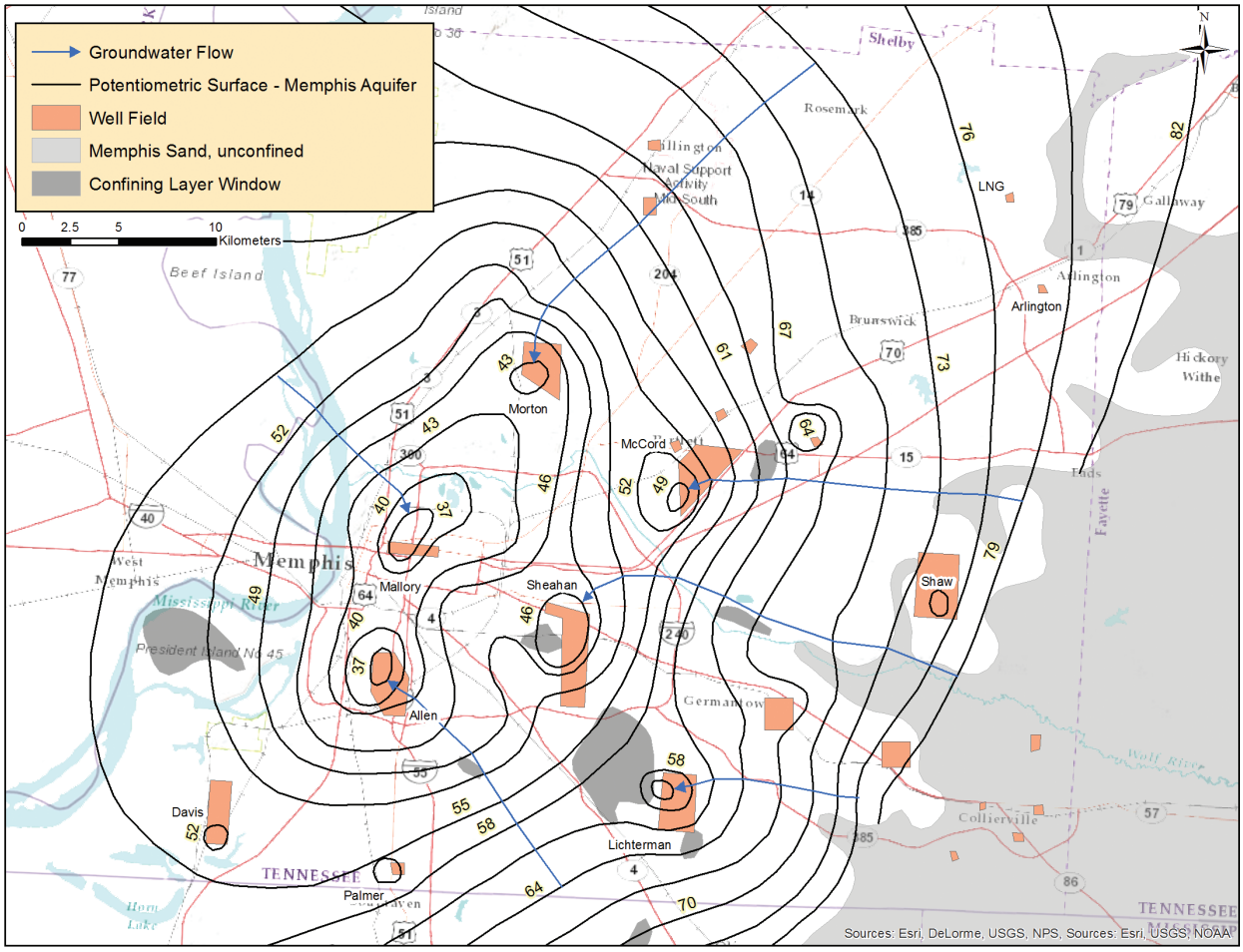

Figure 1. Study area in Memphis and Shelby County, Tennessee. Map shows Memphis and surrounding municipalities, 1995 potentiometric surface for the Memphis aquifer (Kingsbury 1996) (m above sea level, asl), groundwater flow direction, and the locations of public supply well fields for Memphis Light, Gas, and Water (MLGW), Bartlett, Collierville, Germantown, and Millington. Also shown are windows through the upper Claiborne confining unit and the Memphis Sand exposure area as mapped by Parks (1990).

the groundwater system or jeopardizing the ability to meet water needs in the future."

Pertinent aspects of the definition for the present work include determining a rate of production that will not "*damage the groundwater system*," which is interpreted as draining of the aquifer and inducing irreversible compaction or loss of storage, and not jeopardize *"the ability to meet water needs in the future*," which is interpreted as preserving water quality as well as capacity of the aquifer. Thus, the definition of sustainability applied to the Memphis aquifer appeals to balancing production rates while maintaining the desirable characteristics of the aquifer and its stored water resources. Groundwater flow modeling is commonly used to assess various production scenarios assuming known and optimized parameters of the groundwater system. Critical to such modeling endeavors is evaluation of leakage in or out of an aquifer from adjacent aquifers or confining units. In situations where leakage may derive from near-surface water sources, the quantity of leakage also has implications for changes in water quality as well as vulnerability of aquifer resources to contamination.

Environmental tracers are commonly applied to groundwater problems to assess recharge pathways and sources of water in aquifer systems (Cook and Böhlke 2000; Darling et al. 2012; Jurgens et al. 2014; Hagedorn 2015). Environmental tracers, such as chlorofluorocarbons, $^{3}H/^{3}He$, SF_6, and noble gases, are used to determine when groundwater obtained from wells was last exposed to the atmosphere, thus providing a groundwater age based on the atmospheric loading history and, for ^{3}H, radioactive decay. Although the systematics of the isotopic and chemical systems used for environmental tracing are subject to errors and assumptions of application, the resulting data provide independent constraints on both conceptual and numerical models of groundwater flow in aquifer systems. Environmental tracers, specifically combinations of inorganic chemicals, ^{3}H, ^{3}He, and SF_6, have been applied to groundwater systems in the Memphis area with success (Graham and Parks 1986; Parks et al. 1995; Larsen et al. 2003; Gentry et al. 2005; Gentry et al. 2006; Ivey et al. 2008; Koban et al. 2011; Barlow et al. 2012; Larsen et al. 2013), especially in identifying modern water in aquifer systems and leakage pathways between the Shallow and Memphis aquifers. Of particular importance for assessing sustainability, environmental tracers have been used to determine proportions of production well water that have recently been in contact with the atmosphere (modern water) and the likely sources for those modern waters (Larsen et al. 2003; Koban et al. 2011; Larsen et al. 2013).

In this paper we review the hydrogeology of the Memphis aquifer, discuss the application of the $^{3}H/^{3}He$ and SF_6 tracer systems to the Memphis aquifer, explore the results of 14 years of environmental tracer sampling of production wells in Shelby County, and discuss the implications of these data for groundwater sustainability, vulnerability, and policy.

Hydrogeologic Background

Memphis lies within the northern Mississippi embayment, a trough-shaped basin that plunges southward along an axis approximately parallel to the Mississippi River. The Mississippi embayment is filled with more than a thousand meters of sediments of Cretaceous, Tertiary, and Quaternary age (Moore and Brown 1969; Graham and Parks 1986). The early to mid-Tertiary-age geologic units beneath Shelby County dip gently to the west-northwest and include unconsolidated sand, silt, and clay with minor lignite laid down in a Coastal Plain setting. Pleistocene and Pliocene sand and gravel fluvial-terrace deposits, 0 to 20 m thick, unconformably overlie the mid-Tertiary units (Krinitsky 1949; Saucier 1987; Van Arsdale et al. 2008). Excluding the present-day tributary valleys, 3 to 20 m of loess (windblown silt and clay) overlie the fluvial deposits and mid-Tertiary sediments, and mantle the upland topography. Western Tennessee tributary valleys contain late Pleistocene to Holocene alluvium generally comprising as much as 15 m of sand and gravel capped by organic-rich silty sand and silty clay (Carmichael et al. 1997).

The geologic units beneath the Memphis and Shelby County area (Figure 1) are divided into a series of hydrostratigraphic units (Table 1). The loess and the upper part of the alluvium have similar textural and hydraulic properties (1.2×10^{-4} to

Table 1. Geologic and hydrostratigraphic units underlying Shelby County, Tennessee. (Adapted from Graham and Parks (1986) with modifications from Waldron et al. (2011)).

Series	Group	Stratigraphic Unit	Hydrostratigraphic Unit	Thickness (m)	Lithology
Holocene and Pleistocene		Alluvium	Shallow (Alluvial) aquifer	0-53	Sand, gravel, silt, and clay. Underlies the Mississippi alluvial plain and alluvial plains of tributary streams in western Tennessee. Thickest beneath the alluvial plain, where commonly between 30.5 and 45.7 meters thick; generally less than 15.2 meters thick elsewhere.
Pleistocene		Loess	Leaky confining unit	0-20	Silt, silty clay, and minor sand. Principal unit at the surface in upland areas of western Tennessee. Thickest on the bluffs that border the Mississippi alluvial plain; thinner eastward from the bluffs.
Pleistocene and Pliocene (?)		Fluvial terrace deposits	Shallow (Fluvial) aquifer	0-30	Sand, gravel, minor clay, and ferruginous sandstone. Generally underlies the loess in upland areas, but locally absent. Thickness varies greatly because of erosional surfaces at top and base.
Eocene	Claiborne	Jackson Formation	Upper Claiborne confining layer	0-110	Clay, silt, sand, and lignite. Because of similarities in lithology, the Jackson Formation and upper part of the Claiborne Group cannot be reliably subdivided based on available information. Most of the preserved sequence is the Cockfield and Cook Mountain Formations undivided.
		Cockfield and Cook Mountain Formations			
		Memphis Sand	Memphis aquifer	152-271	Sand, clay, and minor lignite. Thick body of sand with lenses of clay at various stratigraphic horizons and minor lignite. Thickest in the southwestern part of the Memphis area; thinnest in the northeastern part.
Eocene?	Wilcox	Flour Island Formation	Flour Island confining layer	49-94	Clay, silt, sand, and lignite. Consists primarily of silty clays and sandy silts with lenses and interbedded fine sand and lignite.
Paleocene		Fort Pillow Sand	Fort Pillow aquifer	38-93	Sand with minor clay and lignite. Sand is fine to medium. Thickest in the southwestern part of the Memphis area; thinnest in the northern and northeastern parts.
	Midway	Old Breastworks Formation	Old Breastworks confining layer	55-107	Clay, Silt, Sand, and lignite. Consists primarily of silty clays and clayey silts with lenses and interbedded fine sand and lignite.

2.1×10^{-3} m/day) (Robinson et al. 1997) and behave as a leaky confining unit, limiting direct infiltration into the underlying sediments. The fluvial-terrace deposits and lower part of the alluvium form the Shallow aquifer (Graham and Parks 1986). The Cockfield and Cook Mountain formations underlie the Shallow aquifer and form the upper confining unit, termed the upper Claiborne confining unit, for the Memphis aquifer. The clay beds in the confining unit range in thickness from 1 to 61 m

and have hydraulic conductivities of 1.5×10^{-6} to 3.0×10^{-4} m/day (Parks 1990; Robinson et al. 1997; Gentry et al. 2006). The Memphis aquifer is a sand-dominated aquifer, ranging in thickness from 122 to 274 m with an average transmissivity of 3.25×10^{3} m^2/day (Parks and Carmichael 1990; Brahana and Broshears 2001) or average hydraulic conductivity of 14.9 m/day (Waldron et al. 2011). The Flour Island Formation forms the lower confining layer for the Memphis aquifer and upper confining unit for the Fort Pillow aquifer, another water resource for the region.

Waldron and Larsen (2014) used historical water level data to reconstruct the predevelopment (prior to 1906) water table and potentiometric surface for the Memphis aquifer. Early studies suggested that the primary source of recharge to the Memphis aquifer was infiltration in upland regions, east and southeast of Memphis (Hosman et al. 1968), including the southeastern part of Shelby County (Criner et al. 1964). The hydraulic head in the aquifer was high enough to create flowing artesian conditions in downtown Memphis during the early years of Memphis aquifer water development. However, flowing artesian conditions soon dissipated and groundwater exploitation between 1886 and 2008 led to significant drawdown within the Memphis aquifer in Shelby and surrounding counties. Thus, prior to groundwater development, a strong upward vertical gradient existed between the Memphis aquifer and the overlying Shallow aquifer; however, groundwater pumping has reversed the gradient such that a downward vertical gradient exists between the Shallow and Memphis aquifers.

Pumping from the Memphis aquifer increased somewhat steadily from 1886 until 2005, but has declined in recent years, in part due to closure of a large food production facility in Memphis (MLGW, personal communication 2015). Pumpage from the Memphis aquifer in Shelby County increased from 0 to 150 million liters per day (MLD) during initial development from 1886 to 1920; however, pumping increased from 1920 to 1975 to reach 720 MLD (Criner and Parks 1976). Pumping remained at approximately 700 to 720 MLD from 1975 to 2005 (Kenny et al. 2009), but dropped to 654 MGL in 2010 (USGS, unpublished data). Long-term data from five observation wells show steady declines in water level until approximately 1975; after that date average yearly water levels have remained largely unchanged except in newly developed areas in the eastern part of Shelby County (Kingsbury 1996).

As groundwater usage increased in the Memphis area and urban growth extended east and southeast from the center of Memphis, evidence for vertical leakage (recharge) through the upper Claiborne confining unit arose from numerous studies (Criner and Armstrong 1958; Criner et al. 1964; Nyman 1965; Criner and Parks 1976; Parks 1990). Groundwater flow modeling of the Memphis aquifer in the Memphis area (Brahana and Broshears 2001) and regionally (Grubb 1998) suggest that substantial vertical leakage is required to accommodate the groundwater withdrawals in southwestern Tennessee. Water-table maps in Shelby County in 1988 (Parks 1990), 2005 (Waldron et al. in press), and 2015 (unpublished data), all show multiple anomalous depressions in the water-level contours, suggesting that leakage, in part, originates from cross-formational flow from the Shallow aquifer. No production wells exist in the Shallow aquifer in the areas of the anomalous depressions; thus, the depressions must originate from another mode of water loss from storage.

Environmental tracer studies have been conducted to establish groundwater age relationships and, specifically, the presence and quantity of modern water (<60 years old) in the Memphis aquifer. Initial studies utilized ^{14}C to demonstrate the dominance of older water (2000 - 3000 years old) in the Memphis aquifer and ^{3}H, which showed some wells where younger water was entering the Memphis aquifer in Shelby County (Graham and Parks 1986). Subsequent hydrogeologic studies showed the presence of numerous hydrogeologic windows in the upper Claiborne confining unit in Shelby County, which allow vertical recharge from the Shallow aquifer or surface water sources to the Memphis aquifer (Parks 1990; Bradley 1991). Hydrogeologic windows are intervals in the upper Claiborne confining unit that are thin due to erosion (e.g., Bradley 1991) or comprise predominantly sand facies rather than silt and clay (e.g., Larsen et al. 2003), such that water may be exchanged between the Shallow and Memphis aquifers. More recently, $^{3}H/^{3}He$ and geochemical data from production wells have shown a clear association of modern water in the

Memphis aquifer with proximity to hydrogeologic windows (Larsen et al. 2003; Gentry et al. 2005; Ivey et al. 2008; Koban et al. 2011; Larsen et al. 2013). Several of these studies using tracers and geochemical mixing models showed that as much as 75% of the water produced from some production wells is modern water, likely from a nearby surface water source (Larsen et al. 2003; Koban et al. 2011; Larsen et al. 2013; Gallo 2015).

The previous studies support a general conceptual model for groundwater flow in the Memphis area in which, prior to development, groundwater recharged into the Memphis aquifer in the hilly exposure belt of the Memphis Sand, 40 to 120 km southeast of the city of Memphis (Brahana and Broshears 2001). Groundwater flow was southeast to northwest toward the city of Memphis and supported flowing, artesian well conditions during the early years of water production from the aquifer in the late 1800's (Waldron and Larsen 2014). This groundwater is relatively old, with residence times ranging from about 1,000 to 3,000 years old based on ^{14}C data (data in Graham and Parks 1986). Following large-scale municipal water-supply development of the Memphis aquifer in the Memphis area, the potentiometric level dropped initially below the land surface and then, with increased pumping, below the base of the Shallow aquifer in the 1960's (Criner and Parks 1976). The drop in the potentiometric surface of the Memphis aquifer created optimal conditions for leakage of young, modern water from storage in the Shallow aquifer and infiltrated stream water through hydrogeologic windows where the upper Claiborne confining unit is thin or absent (Parks 1990). Larsen et al. (2003; 2013), Parks et al. (1995), Bradshaw (2011), Koban et al. (2011), and Gallo (2015) emphasize the importance of saturated alluvium in stream valleys as the long-term water source for leakage into the Memphis aquifer. Furthermore, evidence indicates that pollutants from industrial sites, landfills, and other sites near hydrogeologic windows have entered the Memphis aquifer (Parks 1990; Bradley 1991; Parks and Mirecki 1992; Gentry et al. 2005) and clarifies the need to understand the quantities and pathways by which modern water enters into the Memphis aquifer in the Memphis urban area.

Methods

Sampling

Selected production wells screened in the Memphis or Fort Pillow aquifer in the city of Memphis and Shelby County were sampled between 1999 and 2013. Typical production well design includes a stainless steel casing from the land surface to approximately 100 m depth or more and a screened interval 30.5 m long with a diameter of 0.3 m. Initially, most wells were sampled only for ^{3}H and major solute geochemistry to identify wells that had tritium contents greater than 0.2 tritium units (TU). Wells with ^{3}H contents above this threshold are likely to have a component of modern water (Clark and Fritz 1997), especially considering tritium decay over 1999 to 2013. Starting in 2000, one or more production wells were sampled each year or every other year for major solute geochemistry, ^{3}H, He isotopes, and noble gases. Due to decay of bomb-peak ^{3}H in near-surface groundwater reservoirs and associated loss of tracer utility, sampling of SF_6 was added as a tracer in 2009. Approximately five to seven production wells were sampled for tracers each year; however, no production well sampling was conducted during 2010, 2012, and 2014 due to budgetary limitations. Efforts were made during several of the sampling years to emphasize a specific well field; for example, during 2009 only wells in MLGW Allen well field were sampled. During other sampling years, for example 2011, wells from multiple well fields were sampled, sometimes including wells that had been sampled in previous years.

Water samples for geochemistry, ^{3}H, and SF_6 analyses were obtained from a sampling spigot located on the top of the production wells. Sampling generally commenced after the wells had been pumping for more than twelve hours; however, wells for the smaller utilities in Shelby County were pumped for less than three hours. Given that the pump discharge is approximately 4 m^3/min. and the well volume is generally less than 11 m^3, approximately 1,900 well volumes would be purged prior to sampling for a twelve hour purge period. Field chemistry measurements were made using calibrated probes in a YSI 6600 multi-parameter unit with a flow-through sampling cell:

pH, temperature, specific conductance, dissolved oxygen, and oxidation-reduction potential. In addition, field measurements were made in duplicate for alkalinity (using Hach titration kit) and dissolved oxygen content (using a factory-calibrated Hach 2000 spectrophotometer if probe-measured dissolved oxygen was less than 1 mg/L). As many as four water samples were obtained: 250 ml of raw water in a polypropylene bottle, 250 ml of filtered (0.45 micron filter) water acidified with 1 ml of concentrated ACS-certified nitric acid in a polypropylene bottle, 1 liter of raw water in an amber glass bottle for ^{3}H, and two 1-liter amber glass bottles for SF_6. U.S. Geological Survey protocols were followed for SF_6 sampling (Amber glass bottles were sealed with electrical tape as an added precaution). After collection, waters were stored in a cooler with ice until they were taken to the laboratory and placed in a refrigerator at 4°C.

Dissolved gas sampling required restricting the flow from the pump to the treatment plant to maintain a pressure of 40 to 45 (psi) and, thus, limit degassing during pumping. The gases were sampled in a flow-through cell in duplicate with a diffusion sampler (copper tube with a semi-permeable membrane attached to one end). The diffusion sampler was equilibrated with the flow of production well water for approximately 24 hours, although equilibration was as little as three hours for some of the smaller utilities in Shelby County. Upon retrieval, the copper tube portion of the sampler was sealed with a cold-weld crimper, tips of the tubes were sealed with electrical tape, and tubes were stored for later laboratory analysis. The total gas pressure in the water was measured using a calibrated probe and meter. The raw water samples in the amber glass bottles for ^{3}H and SF_6 and diffusion samplers for noble gas analysis were packed in a cooler and shipped to the Dissolved Gas Laboratory at the University of Utah.

^{3}H Analysis

Tritium activity is determined by the amount of ^{3}He accumulated in a sample over a series of three to four months (Clarke et al. 1976; Bayer et al. 1989). The practical detection limit for the helium in-growth method is 0.05 TU (Solomon and Cook 2000). Under typical conditions, the percent error for lab analysis of Tritium ranges from approximately ± 10% at 1 TU to ± 70% at the detection limit (Alan Rigby, personal communication 2006).

Dissolved Gas Analysis

Samples were analyzed in the Dissolved Gas Laboratory at the University of Utah using the method of Bayer et al. (1989). Reactive gases were removed using a SAES getter (degassing device) and heavy noble gases were sorbed onto charcoal at –180 ˚C for Ar, Kr, and Xe, and at –236 ˚C for Ne. Helium and other noble gas isotopes were then measured on a MAP 215-50 mass spectrometer to a precision of approximately ±0.5%.

Helium-3 dissolved in groundwater arises from four sources: atmospheric equilibration, ^{3}H decay, shallow subsurface nuclear reactions, and the mantle (Solomon and Cook 2000). The atmospheric component can be corrected for by using an excess air model to determine recharge temperature and then applying the appropriate gas-water equilibrium constants. Noble gas composition was used to determine the recharge temperature by applying a modified form of the closed-equilibrium model developed by Aeschbach-Hertig et al. (2000). Shallow subsurface nuclear reactions generate ^{3}He from fission of ^{6}Li produced during U- and Th-series decay. The resulting $^{3}He/^{4}He$ ratio from such reactions is approximately 1×10^{-8}, which is two orders of magnitude less than that of the atmosphere (1.36×10^{-6} at 10°C). Relatively large amounts of ^{4}He from shallow subsurface reactions must be present for this to be an important factor. Nonetheless, ^{3}He from shallow subsurface reactions are accounted for using $^{3}He/^{4}He$ ratio of terrigenic (crustal–produced) helium and using neon to correct for atmospheric ^{4}He contributions. Mantle helium has a $^{3}He/^{4}He$ ratio approximately ten times greater than that of atmospheric helium; thus, small contributions of mantle helium may be difficult to detect. Given the shallow groundwater flow paths inferred by groundwater flow modeling in the Memphis area (Brahana and Broshears 2001) and the cratonic tectonic setting, mantle-sourced helium is not likely to contribute significantly to the helium present in shallow Memphis aquifer waters.

The $^3H/^3He$ age of a groundwater sample is defined as:

$$t = \lambda^{-1} \times \ln(^3He_t/^3H+1) \quad \text{(Equation 1)}$$

where λ is the tritium decay constant, ^3He_t is tritiogenic ^3He, and t is the age in years of the modern (<60 years old) component of the water. Tritiogenic helium is calculated using Ne to correct for the excess atmospheric gas entrained during percolation of water through the vadose zone (Solomon and Cook 2000). The ratio R/R_a measures how closely the measured helium-isotope ratio is to that of air-saturated water. The R/R_a values approach 1 for young apparent age values and are progressively higher for older samples, which is consistent with domination of atmospheric helium contributions. Considering that all possible measures were taken to minimize error and gas loss, it is reasonable to assume, based on past sampling experience and replicate analyses, that the sum of the errors is less than 10% of the age determination.

SF_6 Analysis

SF_6 is analyzed by GC-ECD techniques to a precision of 1-3% at concentrations in excess of 1.0 fg/L to a maximum reporting level of 3.0 pg/L (Wanninkhof and Ledwell 1991; Law et al. 1994). This precision and detection limit permit groundwater dating applications from about 1970 to the present (Busenberg and Plummer 2000). Calculation of groundwater age uses the observed SF_6 concentration, recharge temperature obtained from the noble gas concentrations, recharge elevation approximated for the production well, and recharge salinity of 0 ‰. The partial pressure of SF_6 in groundwater is calculated based on Henry's Law solubility at a given temperature and then used to identify the year of recharge based on measured atmospheric compositions in North America (Busenberg and Plummer 2000). Measured SF_6 values beyond reasonable values for equilibration with atmospheric SF_6 concentrations are considered contaminated and excluded from age calculations. The precision of groundwater age calculated from SF_6 data depends on the analytical errors (generally ± 5%), error in the estimated recharge temperature (± 2°C = 1 to 3 years age difference), and error due to residence time in the unsaturated zone (as much as 8 to 12 years for unsaturated zone thickness of 30 m) (Busenberg and Plummer 2000).

Calculation of the Fraction of Modern Water

Three approaches are used to estimate the fraction of modern water in a sample: tritium loading, lumped parameter modeling, and inverse geochemical modeling. The tritium loading model is similar to that of Manning et al. (2005) in that the ground-water apparent age is used to determine a loading date, assuming that the modern water forms a single-age mode (a mass distribution of modern water centered about a single age). The mean monthly ^3H load for a given year was determined using the synthetic monthly ^3H values in precipitation determined by Ivey et al. (2008), which were calculated for the years 1953-1987 by spatial correlation of measured monthly ^3H values at locations outside the region, and approximated for years subsequent to 1987 using values from Hatteras, N.C. (Ivey et al. 2008). The mixing ratio is then determined by:

$$\%\ \text{modern water} = ((^3H+^3He_t))/((^3H\ load_{yr}))\times 100 \quad \text{(Equation 2)}$$

where ^3He_t is the tritiogenic, ^3He is determined using the noble gas data, and ^3H is the measured tritium activity in the samples. The recharge year is obtained by subtracting the apparent age of the modern water from the sampling year. The ^3H load from the recharge year (^3H $load_{yr}$) is determined from the compiled tritium loading history in Memphis (Ivey et al. 2008). The standard deviation of the ^3H $load_{yr}$ for the recharge year was propagated through the mixing calculations to estimate the uncertainty in the mixing ratio. The approach to uncertainty estimation is different than that of Manning et al. (2005) in that they evaluated uncertainty both by considering hydrodynamic dispersion along a flow path and by considering the maximum deviation of measured monthly ^3H values from the mean ^3H value in precipitation. Despite the difference in approach, the resulting magnitude of the uncertainty is similar (Koban et al. 2011).

Lumped parameter modeling (LPM) has been applied to the interpretation of environmental tracer data since the 1950's (see review in Jurgens

et al. 2014). These models represent simplified aquifer settings and groundwater flow dynamics, accounting for advective transport, dispersion during groundwater flow, and fluid mixing in the borehole. Comparative analysis of LPM and numerical groundwater modeling by Eberts et al. (2012) and Hagedorn et al. (2011) illustrate that apparent or piston-flow model ages from tracers can yield misleading descriptions of the age distribution of waters from some wells, especially public-supply wells with long well screens. Eberts et al. (2012) also show that the age distributions provided by application of an appropriate LPM for the geometry of the groundwater flow system can yield similar results to those from numerical groundwater flow modeling of the system. Models most appropriate for public-supply wells with long screened intervals include exponential piston flow and dispersion models (Ivey et al. 2008; Eberts et al. 2012). Alternatively, binary mixing models of discretely younger and older waters may be best modeled using a binary mixing model describing age distributions of waters flowing from two sources (Jurgens et al. 2014). Various LPM scenarios can be applied to a set of tracer data using the TracerLPM Excel worksheet (Jurgens et al. 2014), which allows for modeling of the age-distributions and percentages of binary mixing components. The worksheet requires applying a conceptual model that best fits the recharge conditions in the study area and iteratively solving the LPM expressions until a minimum relative error is obtained between model results and observed data.

Geochemical modeling is accomplished using PHREEQCi (Parkhurst and Appelo 1999), a speciation and reaction path modeling software package. Inverse geochemical modeling uses chemical species from initial and final water in a hydrologic flow system to predict mixing and mineral and gas transfer reactions in the system. Application of this approach evaluating mixing of modern and older waters is specific to individual wells and depends on the existence of significant chemical differences between the modern water component and the old water component. Successful applications of this approach have been used in several Memphis area well fields where modern water is leaking into the Memphis aquifer and mixing with older Memphis aquifer water (Parks et al. 1995; Larsen et al. 2003; Koban et al. 2011; Larsen et al. 2013; Gallo 2015).

Results

The environmental tracer data and apparent ages from production well waters in Shelby County, Tennessee from 2000 to 2013 are tabulated in Table 2. The data are organized by well field, year of sampling, and sampling date. In addition to samples from Memphis aquifer production wells, ^{3}H data from three wells screened in the Fort Pillow aquifer are presented. Supporting noble gas data are available from the primary author upon request.

Duplicate ^{3}H, $^{3}H/^{3}He$, and SF_6 samples were obtained during multiple sampling years to evaluate data consistency. Tritium duplicate values were generally within 0.10 TU; except when values were near the method detection limit (0.05 TU) and for MLGW 321, sampled in 2006, which had erratic pumping conditions during sampling. Duplicate $^{3}H/^{3}He$ age determinations in MLGW 203A in 2005 yielded age estimates within three years (31.9 and 29.3 years). Duplicate SF_6 age determinations in MLGW 708 in 2011 yielded age estimates within three years (26.8 and 24.3 years).

Tritium contents in excess of 0.2 TU (twice the duplicate activity of 0.1 TU) indicate a component of modern water in the upper production zone of the Memphis aquifer at 100±50 m depth in many well fields in the Memphis area (Figure 2). Production wells sampled from the Fort Pillow aquifer at depths of 320-340 m typically have ^{3}H values near the detection limit except for one well in Millington, which had a value of 0.27 TU. Many of the production wells with ^{3}H content in excess of 0.5 TU were subsequently sampled for $^{3}H/^{3}He$ and yielded apparent ages ranging from 12 to 50 years prior to the sampling date (Table 2). Sampling for SF_6 in production wells post-2009 yielded apparent ages from 6 to 40 years prior to the sampling date; however, these dates do not correspond well with $^{3}H/^{3}He$ apparent ages obtained from the same sampling event (Figure 3).

Table 2. Environmental tracer data and apparent ages.

Well field	Production well	Aquifer	Sample date	Top of screen (m)	R/Ra	^{3}H (TU)	^{3}He* (TU)	Age using Ne (yr)	SF_6 (fMol/L)	SF_6 age-piston flow (yr)
Allen	111A	Memphis	8/11/2004	87.2	1.10	0.64	4.20	36.4	nd	nd
	123	Memphis	8/11/2004	96.6	1.01	0.73	3.40	31.2	nd	nd
	109	Memphis	9/27/2006	96.6	1.08	0.48	4.90	43.4	nd	nd
	111A	Memphis	9/22/2006	87.2	1.08	0.97	2.60	23.3	nd	nd
	107	Memphis	9/22/2006	89.9	1.19	2.05	6.10	24.8	nd	nd
	109	Memphis	11/9/2007	96.6	1.04	0.60	1.70	25.2	nd	nd
	102	Memphis	11/12/2008	89.0	0.96	0.08	<0	nd	nd	nd
	111A	Memphis	11/12/2008	87.2	1.12	0.86	2.90	26.5	nd	nd
	114	Memphis	12/8/2008	90.5	1.46	2.10	13.6	36.1	nd	nd
	117	Memphis	12/8/2008	86.9	0.96	0.08	<0	nd	nd	nd
	103A	Memphis	12/11/2008	82.9	0.99	0.08	0.20	22.3	nd	nd
	114	Memphis	10/28/2011	90.5	1.35	1.94	11.6	34.9	0.13	40.3
	111A	Memphis	10/28/2011	87.2	1.12	0.86	5.00	34.4	0.67	35.8
Davis	432	Memphis	8/11/2004	106.7	1.20	1.62	8.10	32.1	nd	nd
	414	Memphis	8/12/2004	118.3	1.58	3.28	18.8	34.2	nd	nd
	432	Memphis	9/13/2005	106.7	1.17	nd	4.10	nd	nd	nd
	414	Memphis	9/13/2005	118.3	1.56	3.85	17.8	31.0	nd	nd
	432	Memphis	9/27/2006	106.7	1.12	0.47	1.60	26.2	nd	nd
Lichterman	321	Memphis	9/16/2005	69.8	1.06	0.57	0.50	10.7	nd	nd
	311	Memphis	9/16/2005	75.6	1.02	0.44	<0	nd	nd	nd
	311	Memphis	9/28/2006	75.6	0.99	0.04	<0	nd	nd	nd
	321	Memphis	10/1/2006	69.8	1.01	0.07	<0	nd	nd	nd
	324	Memphis	10/5/2006	88.4	1.24	0.62	6.40	43.4	nd	nd
	321	Memphis	11/13/2007	69.8	1.03	0.30	<0	nd	nd	nd
McCord	203A	Memphis	9/22/2005	85.4	1.17	1.10	5.40	31.9	nd	nd
	232	Memphis	9/22/2005	119.2	1.22	1.83	6.80	27.9	nd	nd

Table 2 Continued.

Well field	Production well	Aquifer	Sample date	Top of screen (m)	R/Ra	^{3}H (TU)	^{3}He* (TU)	Age using Ne (yr)	SF_6 (fMol/L)	SF_6 age-piston flow (yr)
McCord	203A duplicate	Memphis	9/22/2005	85.4	1.16	0.97	4.00	29.3	nd	nd
	217	Memphis	11/17/2009	122.0	1.03	0.19	2.26	45.9	5.84	4.5
	233	Memphis	11/17/2009	115.9	1.13	0.70	4.12	34.6	3.37	15.4
	206	Memphis	11/18/2009	97.6	1.06	0.45	3.76	40.1	4.26	11.6
	201	Memphis	11/20/2009	102.4	0.97	0.02	1.18	>55	1.02	28.4
	202	Memphis	11/20/2009	89.3	1.09	0.45	4.33	42.4	4.77	9.4
	203A	Memphis	8/7/2013	85.4	1.18	0.85	5.91	37.1	0.41	29.6
	209	Memphis	8/7/2013	86.6	1.21	0.75	6.68	41.2	0.48	27.6
	218	Memphis	8/8/2013	125.0	0.96	nd	0.12	nd	nd	nd
Morton	602	Memphis	11/28/2003	111.0	0.90	0.0	0.60	>40	nd	nd
Shaw	704	Memphis	11/1/2011	76.2	1.05	0.25	2.57	43.3	1.96	6.3
	708	Memphis	11/1/2011	91.5	1.10	0.69	4.11	34.9	0.50	26.8
	708 duplicate	Memphis	11/1/2011	91.5	nd	0.59	nd	nd	0.63	24.3
Sheahan	99	Memphis	11/19/2002	108.2	1.01	0.29	4.87	51.6	nd	nd
	88	Memphis	11/20/2002	103.4	1.04	1.0	1.73	18.0	nd	nd
	87A	Memphis	11/20/2002	94.8	1.11	1.38	4.24	25.2	nd	nd
	78B	Memphis	11/20/2002	125.3	0.94	0.04	<0	nd	nd	nd
	80A	Memphis	11/20/2002	126.5	0.97	0.18	5.11	60.6	nd	nd
	87A	Memphis	11/14/2007	94.8	1.14	1.0	4.80	32.0	nd	nd
	86R	Memphis	11/3/2011	129.6	1.02	0.36	2.17	34.9	0.67	23.6
	99	Memphis	11/3/2011	108.2	1.05	0.32	2.62	39.9	1.61	10.6
Bartlett	P3, W1	Memphis	10/4/2006	125.0	1.05	0.93	4.80	32.7	nd	nd
	P4, W3	Memphis	11/14/2007	149.4	0.98	0.20	<0	nd	nd	nd
Collierville	402	Memphis	12/9/2003	68.6	1.07	0.40	2.20	34.7	nd	nd
Germantown	J2	Memphis	12/10/2003	62.8	1.06	0.40	2.20	34.7	nd	nd
	10	Memphis	12/11/2003	94.5	0.98	0.10	<0	nd	nd	nd
	J2	Memphis	11/10/2011	62.8	1.05	0.42	2.82	36.8	0.81	22
	J10	Memphis	11/10/2011	172.3	0.98	0.05	1.03	>60	0.06	nd

nd = not determined

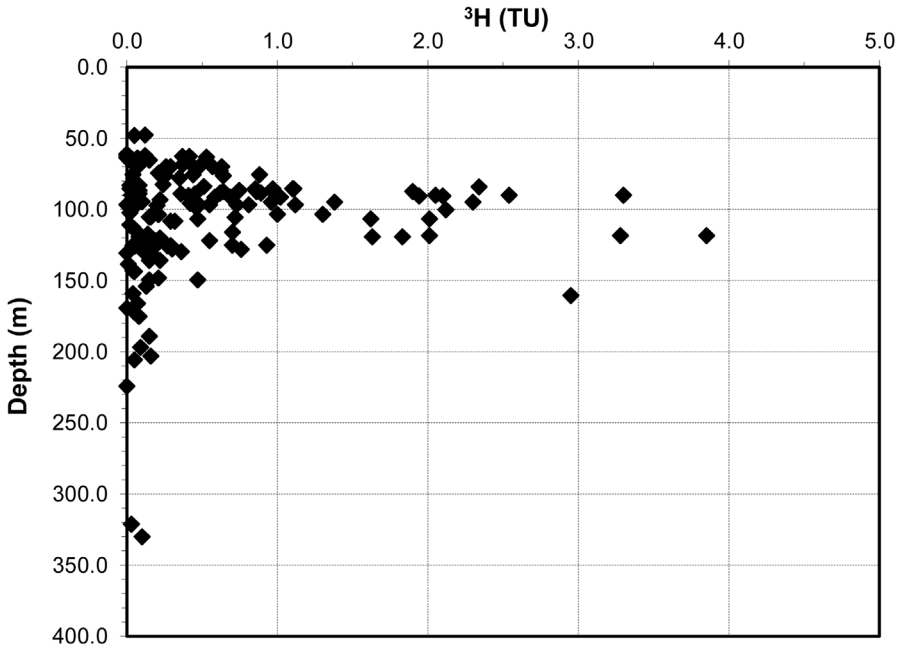

Figure 2. ^{3}H contents in production wells in Shelby County sampled between 2000 and 2013. The depth value plotted is the top of the screened interval, which is 24 to 30 m long for most wells.

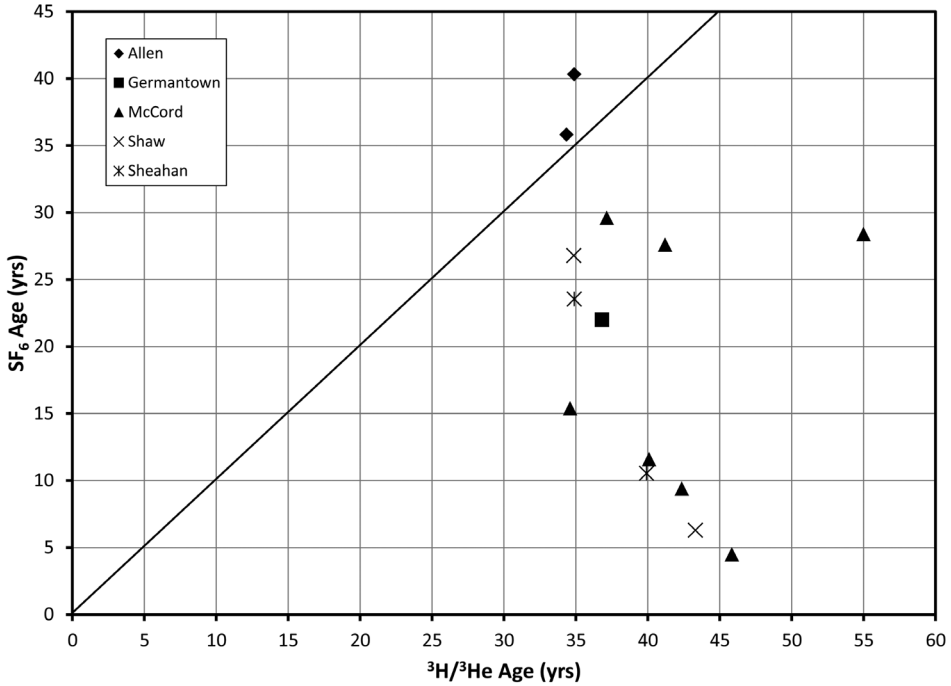

Figure 3. Crossplot of apparent ages determined by ^{3}H/^{3}He and SF_6 for water samples from Memphis aquifer production wells.

Discussion

Data Validation

A scatter plot of N_2 and ^4He is used to evaluate whether the gas data follow the expected water solubility relationships in groundwater equilibrated with the atmosphere (Solomon and Cook 2000). Waters from production wells in the Memphis aquifer plot in a region consistent with excess air saturation and equilibrium recharge temperatures ranging from 5 to 25˚C (Figure 4), with most data indicating equilibration temperatures between 8 and 15 ˚C. The mean annual temperature in the Memphis area is 17.6 ˚C (NCDC 2010) and most recharge is believed to occur during the cooler winter months. The values of R/R_a are generally between 1.0 to 1.6, which are consistent with atmospheric helium values augmented by bomb-pulse tritiogenic ^3He (Solomon and Cook 2000).

The SF_6 values for water from production wells are generally low, close to the lower limit of detection (0.01 fMol/L), but above background concentrations (0.05 fMol/L) of waters equilibrated with atmospheric SF_6. The Memphis aquifer is primarily composed of quartz sand (Lumsden et al. 2009; Larsen and Brock 2014) and is not likely to have significant SF_6 accumulation from igneous and metamorphic rocks (e.g., Busenberg and Plummer 2000). Based on these observations and evidence for the noble gas equilibration with the atmosphere at temperatures reasonable for the Memphis area, the SF_6 data appear to be useful for assessing residence time of young groundwater.

Apparent Age of Modern Water and Mixing with Old Water

The apparent age of groundwater sampled from public-supply wells with long screen intervals is known to comprise a mixture of old and young waters, commonly from one of more transmissive zones within the screened interval (Nelms et al. 2003; Manning et al. 2005; Eberts et al. 2012. The mixing fractions determined by the tritium loading model yield as much as 75% modern water in some wells producing from the Memphis aquifer, with most samples containing between 10 and 40% modern water (Table 3 and Figure 5). Not surprisingly, the apparent ages of these young water components tend to cluster between 20 and 45 years before the date of sampling, an age region

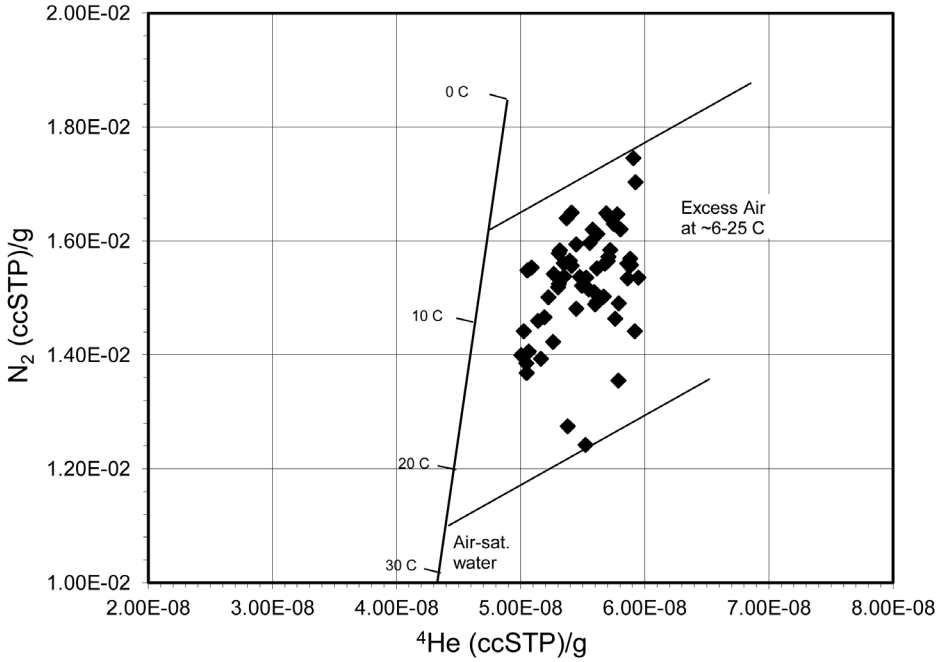

Figure 4. Plot of N_2 and ^4He dissolved gas contents of water from Memphis aquifer production wells.

for which the $^{3}H/^{3}He$ system is most sensitive to bomb peak atmospheric tritium loading (Solomon and Cook 2000). Because the piston-flow model assumes no dispersion or multimodality of the tracer loading history, the mixing fractions of modern water determined by tritium loading may be overestimates because of the strong influence of small quantities of bomb-pulse tritium.

Mixing fractions determined from inverse geochemical modeling of production well waters in the Sheahan (Larsen et al. 2003; Ivey et al. 2008), Davis (Koban et al. 2011), and McCord (Gallo 2015) well fields are plotted in Figure 6 with mixing fraction determined by the piston-flow $^{3}H/^{3}He$ model. Although the mixing fractions determined from the two independent methods crudely correlate, some of the results (for example, 2009 samples from McCord well field) yield significantly different mixing fractions. Because of the non-unique nature of the inverse geochemical model results, slight changes in water chemistry or choice of end-member wells can produce significantly different mixing fractions (Gallo 2015). Another consideration is that geochemical mixing model results may represent the mixtures of modern water with differing chemistry and sources. For example, Larsen et al. (2013) showed modern waters from two sources may be contributing to leakage in the Sheahan well field: modern water drained from storage in the Shallow aquifer and infiltrated modern stream water flowing through the Shallow aquifer to a window location.

Hydrogeologic and geochemical data from several studies of leakage near Memphis area public supply well fields (Parks et al. 1995; Larsen et al. 2003; Ivey et al. 2008; Koban et al. 2011; Larsen et al. 2013) provide hydrogeologic justification for a conceptual model of vertical leakage required for LPM analysis. Groundwater flow for the modern component is modeled using a range of models from a piston flow model (PFM) (the simplest case) to an exponential piston flow model (EPM), in which recharge enters the Memphis aquifer through a hydrogeologic window of width (x) and nearest distance (x*) (Cook and Bohlke 2000; Ivey et al. 2008). The EPM parameter (EPMP), x*/x, constrains aspects of the geometry of the window and is used in the model with idealized

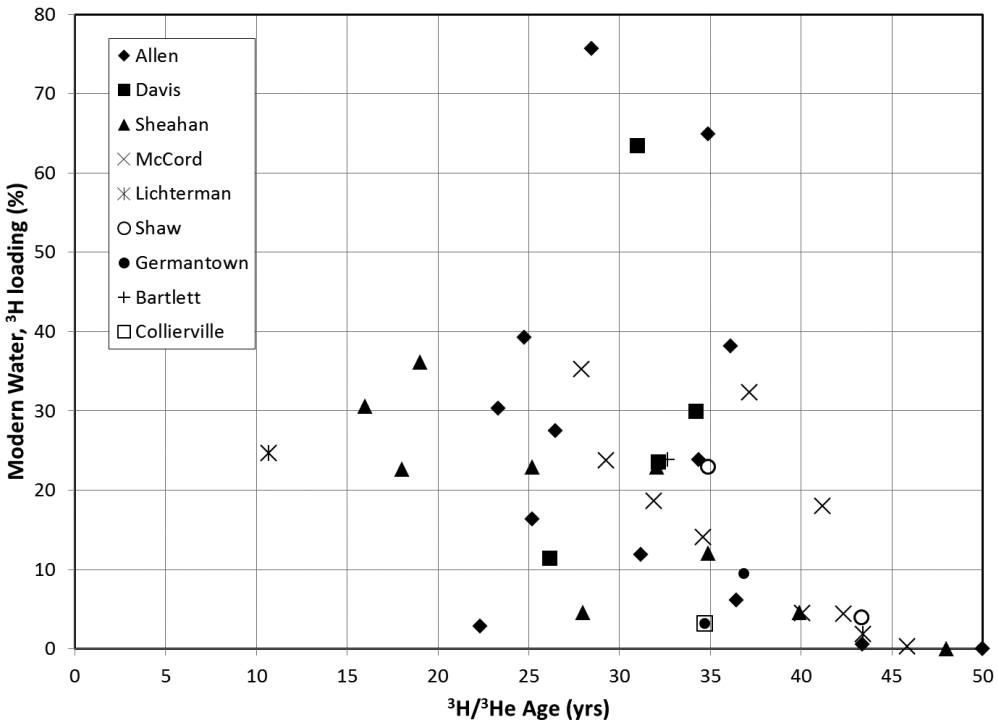

Figure 5. Plot of mixing percentage of modern water, determined by ^{3}H loading method, and $^{3}H/^{3}He$ apparent age for water samples from Memphis aquifer production wells.

tracer loading histories to match the observed tracer data (Jurgens et al. 2014). Groundwater flow for the pre-modern component in the Memphis aquifer is interpreted to follow a dispersion flow model (DM), in which hydrodynamic dispersion broadens the age distribution of a volume of water as the water flows downgradient from a distant recharge source. The age of the older water component was set at 2000 years for wells in all well fields except Shaw and Germantown (which were set to 1000 yrs), based on ^{14}C dating results of Memphis aquifer water sampled from observation wells throughout Shelby County (Graham and Parks 1986). The dispersion parameter, DP, is the ratio of the dispersion coefficient and advective flow over a distance, x (Zuber and Maloszewski 2001). The DP was fixed at 0.5 for all models. Given that advection likely dominates solute transport in the porous sand media of the Memphis aquifer and the 10s of km distance of travel from the outcrop region to the well fields, hydrodynamic dispersion is assumed to be about half as effective as advection in solute transport. Random variation of DP in a typical model resulted in little sensitivity in the model results. The source of most modern water contributions to the Memphis aquifer is closely tied to streams (Bradley 1991; Larsen et al. 2003; Bradshaw 2011; Larsen et al. 2013; Gallo 2015); thus, the travel time in the vadose zone is considered to be negligible.

The LPM results generally indicate a younger mean age of the modern water component than those from the $^{3}H/^{3}He$ and SF_6 apparent ages (Tables 3 and 4), but similar mixing fractions of modern water to those determined by the tritium loading model (Figure 7). The younger value of the mean modern water age is expected from the EPM due to contributions of modern waters from the 1960s and younger to model the observed apparent ages (e.g., Cook and Bohlke 2000). Although the EPMP is based on the conceptual model, in practice the model value is based on fitting the results to the specified model with the least error. The primary issue is that the width of the window, x, is poorly constrained, even in situations where the distance to the window, x*, is constrained by other data (e.g., Sheahan well field, Larsen et al. 2003; 2013; Ivey et al. 2008). However,

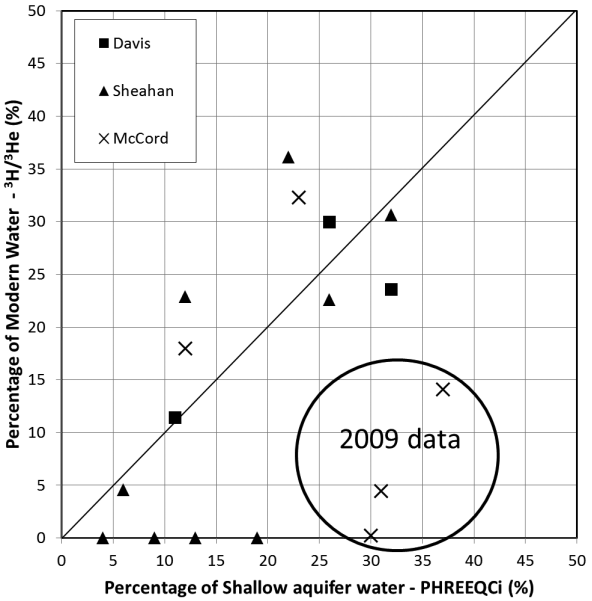

Figure 6. Plot of mixing percentage of modern water, determined by ^{3}H loading method, and mixing percentage of Shallow aquifer water, determined by inverse geochemical modeling with PHREEQCi, for water samples from three Memphis aquifer pubic supply well fields.

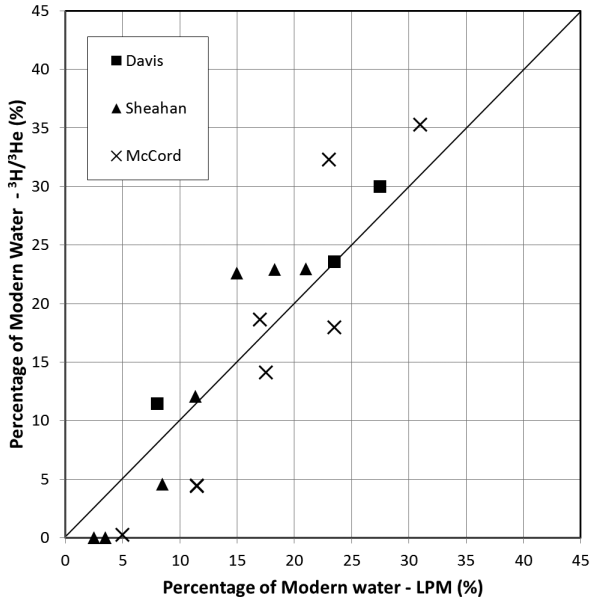

Figure 7. Plot of mixing percentage of modern water, determined by ^{3}H loading method, and mixing percentage of modern water, determined by LPM, for water samples from three Memphis aquifer public-supply well fields.

Table 3. Percentage modern water and adjusted SF_6 apparent age.

Well field	Production well	Aquifer	Sample date	$^3H+^3He^*$ (TU)	Age using Ne (yr)	Recharge year	Recharge yr ^3H load	% Modern ^3H load	% Modern Geochem	% Modern LPM	SF_6 age LPM mix (yr)
Allen	111A	Memphis	8/11/2004	4.9	36.4	1968	79.6	6	nd	nd	nd
	123	Memphis	8/11/2004	4.2	31.2	1973	35.0	12	nd	nd	nd
	107	Memphis	9/22/2006	8.2	24.8	1981	20.8	39	nd	nd	nd
	111A	Memphis	9/22/2006	3.6	23.3	1983	11.8	30	nd	nd	nd
	109	Memphis	9/27/2006	5.4	43.4	1963	937.5	1	nd	nd	nd
	107	Memphis	11/9/2007	12.4	28.5	1979	16.4	76	nd	nd	nd
	109	Memphis	11/9/2007	2.2	25.2	1982	13.7	16	nd	nd	nd
	114	Memphis	12/8/2008	15.7	36.1	1972	41.3	38	nd	nd	nd
	103	Memphis	12/11/2008	0.3	22.3	1986	9.8	3	nd	nd	nd
	111A	Memphis	11/12/2008	3.8	26.5	1982	13.7	28	nd	nd	nd
	114	Memphis	10/28/2011	13.6	34.88	1976	20.9	65	nd	25.6	29.8
	111A	Memphis	10/28/2011	5.9	34.4	1977	24.6	24	nd	21.4	22.3
Davis	432	Memphis	8/11/2004	9.7	32.1	1972	41.3	24	32	23.5	nd
	414	Memphis	8/12/2004	22.1	34.2	1970	73.8	30	26	27.5	nd
	414	Memphis	9/13/2005	21.7	31.0	1974	34.2	63	7	39.8	nd
	432	Memphis	9/27/2006	2.0	26.2	1980	17.7	11	11	8	nd
Licherterman	321	Memphis	9/16/2005	1.0	10.7	1994	4.2	25	nd	nd	nd
	324	Memphis	10/5/2006	7.0	43.4	1962	372.9	2	nd	nd	nd
McCord	203	Memphis	9/22/2005	6.5	31.9	1973	35.0	19	nd	17	nd
	232	Memphis	9/22/2005	8.7	27.9	1977	24.6	35	nd	31	nd
	203 duplicate	Memphis	9/22/2005	5.0	29.3	1976	20.9	24	nd	nd	nd
	217	Memphis	11/17/2009	2.4	45.9	1963	937.5	0	30.0	5.0	4.6
	233	Memphis	11/17/2009	4.8	34.6	1974	34.2	14	37.0	17.5	15.4
	206	Memphis	11/18/2009	4.2	40.1	1969	94.1	4	31.0	11.5	11.6
	201	Memphis	11/20/2009	1.2	>55	1954	4.0	nd	nd	nd	nd
	202	Memphis	11/20/2009	4.8	42.4	1967	108.3	4	nd	11.5	9.4
	203A	Memphis	8/7/2013	6.8	37.1	1976	20.9	32	23.0	23.0	7.6
	209	Memphis	8/7/2013	7.4	41.2	1972	41.3	18	12.0	23.5	4.1

Table 3 Continued.

Well field	Production well	Aquifer	Sample date	$^3H+^3He^*$ (TU)	Age using Ne (yr)	Recharge year	Recharge yr ^3H load	% Modern ^3H load	% Modern Geochem	% Modern LPM	SF_6 age LPM mix (yr)
Shaw	704	Memphis	11/1/2011	2.8	43.3	1968	79.6	4	nd	7.0	17.3
	708	Memphis	11/1/2011	4.8	34.9	1976	20.9	23	nd	19.5	24.8
Sheahan	87	Memphis	10/20/2000	7.5	nd	nd	nd	nd	22	nd	nd
	80	Memphis	10/20/2000	1.6	nd	nd	nd	nd	9	nd	nd
	78A	Memphis	10/21/2000	1.9	nd	nd	nd	nd	6	nd	nd
	88	Memphis	10/21/2000	3.7	nd	nd	nd	nd	32	nd	nd
	55B	Memphis	10/21/2000	1.3	nd	nd	nd	nd	4	nd	nd
	99	Memphis	11/19/2002	5.2	51.6	1950	4.5	nd	19	3.5	nd
	80	Memphis	11/20/2002	5.3	60.6	1941	4.5	nd	13	2.5	nd
	87A	Memphis	11/20/2002	5.6	25.2	1977	24.6	23	12	18.3	nd
	88	Memphis	11/20/2002	2.7	18.0	1984	12.1	23	26	15	nd
	87	Memphis	11/14/2007	5.7	32.0	1975	25.0	23	nd	21	nd
	86R	Memphis	11/3/2011	2.5	34.9	1976	20.9	12	nd	11.4	23.1
	99	Memphis	11/3/2011	2.9	39.9	1971	64.6	5	nd	8.5	19.6
Bartlett	P3, W1	Memphis	10/4/2006	5.7	32.7	1973	35.0	24	nd	nd	nd
Collierville	402	Memphis	12/9/2003	2.6	34.7	1968	79.6	3	nd	nd	nd
Germantown	J-2	Memphis	12/10/2003	2.6	34.7	1968	79.6	3	nd	nd	nd
	J-2	Memphis	11/10/2011	3.2	36.8	1974	34.2	9	nd	11	24
	J-10	Memphis	11/10/2011	1.1	>60	1951	4.0	nd	nd	nd	nd

LPM = Lumped Parameter Model
nd = not determined

Table 4. Lumped Parameter Modeling results.

Well field	Production well	Sample date	LPM model	Vadose zone travel time (yr)	Mean age of modern water (yr)	EPMP	Mixing % of modern water	Mean age of pre-modern water (yr)	Tracers optimized	Relative error (%)
Allen	114	10/28/2011	BMM-EPM-DM	5.0	26.1	6.0	25.6%	2000	^3H, ^3He_t, SF_6	0.0%
	111A	10/28/2011	BMM-EPM-DM	0.0	20.0	16.0	21.4%	2000	^3H, ^3He_t, SF_6	101.7%
Davis	432	8/11/2004	BMM-EPM-DM	0.0	20.0	10.2	23.5%	2000	^3H, ^3He_t	0.0%
	414	8/12/2004	BMM-EPM-DM	0.0	23.2	3.2	27.5%	2000	^3H, ^3He_t	0.1%
	414	9/13/2005	BMM-EPM-DM	0.0	24.2	5.8	39.8%	2000	^3H, ^3He_t	0.0%
	432	9/27/2006	BMM-EPM-DM	0.0	14.8	9.8	8.0%	2000	^3H	0.0%
McCord	203A	9/22/2005	BMM-EPM-DM	0.0	6.0	17.1	17.0%	2000	^3H, ^3He_t	0.0%
	203A	*9/22/2005*	*BMM-EPM-DM*	*0.0*	*5.9*	*5.0*	*17.0%*	*2000*	*^3H, ^3He_t*	*0.0%*
	232	9/22/2005	BMM-EPM-DM	0.0	15.8	6.3	31.0%	2000	^3H, ^3He_t	0.0%
	217	11/17/2009	BMM-EPM-DM	0.0	6.6	23.3	5.0%	2000	^3H, ^3He_t	155.8%
	217	*11/17/2009*	*BMM-PFM-DM*	*0.0*	*4.7*	*na*	*4.5%*	*2000*	*^3H, ^3He_t*	*155.9%*
	233	11/17/2009	BMM-EPM-DM	0.0	5.7	10.6	17.5%	2000	^3H, ^3He_t	26.5%
	206	11/18/2009	BMM-EPM-DM	0.0	6.1	13.2	11.5%	2000	^3H, ^3He_t	46.1%
	202	11/20/2009	BMM-EPM-DM	0.0	6.2	10.1	11.5%	2000	^3H, ^3He_t	27.0%
	203A	8/7/2013	BMM-EPM-DM	0.0	7.1	6.1	23.0%	2000	^3H, ^3He_t, SF_6	14.9%
	209	8/7/2013	BMM-EPM-DM	0.0	9.9	14.9	23.5%	2000	^3H, ^3He_t, SF_6	45.7%
Shaw	704	11/1/2011	BMM-EPM-DM	0.0	7.9	15.3	7.0%	1000	^3H, ^3He_t, SF_6	204.2%
	704	*11/1/2011*	*BMM-EPM-DM*	*0.0*	*7.7*	*16.8*	*7.0%*	*2000*	*^3H, ^3He_t, SF_6*	*202.6%*
	708	11/1/2011	BMM-EPM-DM	0.0	7.9	24.3	19.5%	1000	^3H, ^3He_t	27.5%
	708	*11/1/2011*	*BMM-EPM-DM*	5.0	*14.0*	*20.0*	*12.3%*	*2000*	*^3H, ^3He_t, SF_6*	*25.9%*

Table 4 Continued.

Well field	Production well	Sample date	LPM model	Vadose zone travel time (yr)	Mean age of modern water (yr)	EPMP	Mixing % of modern water	Mean age of pre-modern water (yr)	Tracers optimized	Relative error (%)
Sheahan	99	11/19/2002	BMM-EPM-DM	0.0	5.5	9.2	3.5%	2000	^3H, ^3He_t	21.1%
	80	11/20/2002	BMM-PFM-DM	0.0	7.9	na	2.5%	2000	^3H, ^3He_t	16.4%
	87A	11/20/2002	BMM-EPM-DM	0.0	3.2	8.4	18.3%	2000	^3H, ^3He_t	21.9%
	88	11/20/2002	BMM-EPM-DM	0.0	2.1	8.5	15.0%	2000	^3H, ^3He_t	201.7%
	87A	11/14/2007	BMM-EPM-DM	0.0	3.3	6.5	21.0%	2000	^3H, ^3He_t	3.3%
	86R	11/3/2011	BMM-PFM-DM	0.0	9.8	na	11.4%	2000	^3H, ^3He_t, SF_6	228.8%
	99	11/3/2011	BMM-EPM-DM	0.0	6.9	11.0	8.5%	2000	^3H, ^3He_t	114.9%
Germantown	J-2	11/10/2011	BMM-PFM-DM	0.0	6.6	na	10.5%	1000	^3H, ^3He_t	153.5%
	J-2	*11/10/2011*	*BMM-PFM-DM*	*0.0*	*6.8*	*na*	*10.7%*	*2000*	*^3H, ^3He_t, SF_6*	*176.7%*

LPM = Lumped Parameter Model
EPMP = Exponential Piston Flow Model Parameter
na = not applicable
italics = repeated model run for sample above with either different EPMP value, LPM model, or mean age of pre-modern water

the actual sensitivity of the EPM results on the EPMP is minimal in some cases. For example, model runs with different initial values for mean age, EPMP, and mixing % in well 203A sampled in 2005 (Table 4) converged with similar relative error yielding almost identical mean modern water ages and mixing percentages (6.0 and 5.9 yrs; 0.0% for both), but different values of EPMP (17.1 and 5.0). In addition, the effect of using a PFM or EPM for the modern water component is minimal in some cases. For example, a PFM for well 217 sampled in 2009 yielded similar relative error to the EPM and a slightly younger mean modern water age and mixing % (Table 4). Some wells did not fit any model using $^{3}He_{t}$ very well, resulting in high model error (>100%), commonly because observed $^{3}He_{t}$ values are less than all model values. Good examples of this behavior are wells 217 and 704, which yield excessive error for all models with $^{3}He_{t}$. The model sensitivity to the age of the pre-modern water component is generally minor for the Germantown and Shaw wells sampled (Table 4).

Unlike the apparent age results from the $^{3}H/^{3}He$ system, SF_6 data do not provide independent information of mixing fractions of modern and pre-modern waters. Thus, the poor correlation of apparent ages for production well waters based on $^{3}H/^{3}He$ and SF_6 is expected (Figure 3). Correction of the SF_6 apparent age data for mixing fractions using the LPM mixing percentages in Table 4 does not improve the correspondence to the $^{3}H/^{3}He$ apparent age data, but generally produces younger ages for the modern water component. Several explanations can be considered, including error in the mixing quantification, erroneous $^{3}H/^{3}He$ or SF_6 apparent age data, or differences in the sensitivity of each tracer to the age of modern water. Although errors in the dating and mixing calculations may obscure relationships, the bias of the SF_6 system toward younger apparent age relative to the $^{3}H/^{3}He$ system seems to be the most reasonable explanation for the general shift toward younger SF_6 apparent ages.

Implications for Wellhead Protection and Policy

The results of the past 14 years of environmental tracer analysis in production wells in Memphis and Shelby County, Tennessee, provide strong evidence for vertical recharge of modern water to the Memphis aquifer. However, each tracer provides somewhat different information. The $^{3}H/^{3}He$ system provides the greatest information through the apparent age determination and coupling of assumed atmospheric ^{3}H loading and ^{3}He daughter product retention to calculate mixing relationships (Manning et al. 2005). However, the decay and dispersion of bomb-peak ^{3}H in recently recharged groundwater limits the utility of this system for the youngest recharge. Furthermore, tracer-tracer plots of $^{3}He_{t}$ and ^{3}H or SF_6 commonly show apparent depletion in $^{3}He_{t}$, suggesting the potential for helium loss during sampling. Both of these issues bias the $^{3}H/^{3}He$ apparent age results toward older dates. Because of the increasing atmospheric concentration of SF_6 and resiliency to retarding or decay processes (Busenberg and Plummer 2000; Darling et al. 2012), SF_6 should provide the more useful tracer for the youngest recharge. However, correction for mixing with pre-modern water (lacking a terrestrial source of SF_6) may present challenges, especially in the absence of independent verification. Inverse geochemical models for mixing of modern and pre-modern waters may provide independent verification of mixing fractions under ideal conditions whereby only two chemically distinct water sources are mixing in the subsurface.

Despite the potential errors in calculated mixing proportions of modern water produced from production wells in Shelby County, it is clear from the current studies as well as regional modeling that vertical leakage of modern water occurs at windows in the upper Claiborne confining unit near streams and is a significant component of long-term sustainability of water supplies in the Memphis aquifer. The tracer data verify and detail the results of regional groundwater flow modeling of Brahana and Broshears (2001) that show as much as 50% of the water withdrawn from the Memphis aquifer in 1980 was derived from vertical leakage. Specific areas of prominent leakage are from the Shallow aquifer along the Wolf and Loosahatchie rivers and Nonconnah Creek watersheds, and along the Mississippi River alluvial valley. Based on the tracer results, the percentage of modern water produced is likely to be much less than 50%, except for the cases of the Allen and Davis well fields (Koban et

al. 2011). The LPM modeling results in Table 4 show that most wells affected by contributions of modern leakage have mixing proportions between 5 and 30% modern water. From the standpoint of sustainability of groundwater availability, the Memphis aquifer has great potential to continue to show stable groundwater levels, as demonstrated by Kingsbury (1996), and provide a steady water supply at current usage.

The prominence of vertical leakage of modern water in the Memphis aquifer mainly presents a challenge to water quality. United State Geological Survey studies of water quality in the Shallow aquifer and in urban streams in the Memphis area (Coupe 2000; Gonthier 2002; Barlow et al. 2012) demonstrate widespread loss of water quality from additions of nitrate, volatile organic compounds, and pesticides. In addition, specific areas of contamination of the Shallow aquifer are known in many parts of the Memphis area (see Parks 1990 for review), some of which clearly impact water quality in the underlying Memphis aquifer by vertical leakage through windows in the upper Claiborne confining unit (Parks and Mirecki 1992; Gentry et al. 2005; Doudrick 2008). Figure 8 shows a map of potential and historical contaminant sources in Shelby County assembled from U.S. Environmental Protection Agency (USEPA) facility registry services and publically available data from the Tennessee Department of Environment and Conservation. Potential sources of contamination are proximal to almost all of the public supply well fields and some are adjacent to hydrogeologic windows, which may provide a contaminant pathway to the Memphis aquifer.

The USEPA (EPA 1987) recommends that states implement wellhead protection area (WHPA) criteria for public water supplies. In compliance with USEPA and Safe Drinking Water Act regulations, the State of Tennessee established wellhead protection regulations for all public water supplies utilizing groundwater (TNPR 0400-45-01-.34). A wellhead protection plan (WPP) is developed by public water suppliers and must delineate primary and secondary zones of protection, or time of travel (TOT), zones for public supply wells. In practice, the duration of the TOT zones is agreed upon by the state regulators and utility or municipality so as to protect the groundwater supply. Most utilities utilize the USEPA WHPA code (Blanford and Huyakorn 1991) or the updated version, WhAEM (Wellhead Analytical Element Model) (Kraemer et al. 2007), to evaluate the TOT zones by employing simplified analytical models for determining the radius of effective protection of pumping wells under varying conditions.

Because of the simplified nature of the groundwater flow model in the USEPA WHPA and WhAEM codes, the complexities of the local hydrogeologic setting, such as windows in the confining unit (Parks 1990) or paleovalley channels in the Shallow aquifer (Larsen et al. 2013), cannot be incorporated readily into the modeling environment. The sources of modern water established by several environmental tracer and hydrogeologic studies of public supply wells in the Memphis area are streams or shallow aquifers connected to streams (Larsen et al. 2003, 2013; Bradshaw 2011; Koban et al. 2011; Gallo 2015), most of which are outside of the TOT zones developed from the WPP. Furthermore, it is unclear whether more complex modeling approaches such as applying MODFLOW (McDonald and Harbaugh 1988) would predict the degree of modern water influence, mainly because of limited hydraulic head and aquifer property data in the areas near the well fields (e.g., Sheahan well field). Thus, we argue that environmental tracers of modern water, such as $^{3}H/^{3}He$ and SF_6, provide essential information in any assessment of the WHPA, especially in areas where hydrogeologic complexities and limited hydraulic data diminish the resolution of analytical or numerical models.

The $^{3}H/^{3}He$, SF_6, and associated tracer data gathered during the past 14 years clearly show that the Memphis aquifer at many of the well fields in Shelby County is more vulnerable to contamination than is suggested by wellhead protection modeling. Several aspects of the hydrogeology and groundwater development history of the Memphis aquifer present intrinsic susceptibility to contamination through the existence of fast recharge pathways and a prominent downward vertical gradient between the Shallow and Memphis aquifers. Detailed environmental tracer case studies of the Sheahan (Larsen et al. 2003; 2013; Ivey et al. 2008), Davis (Parks et al. 1995;

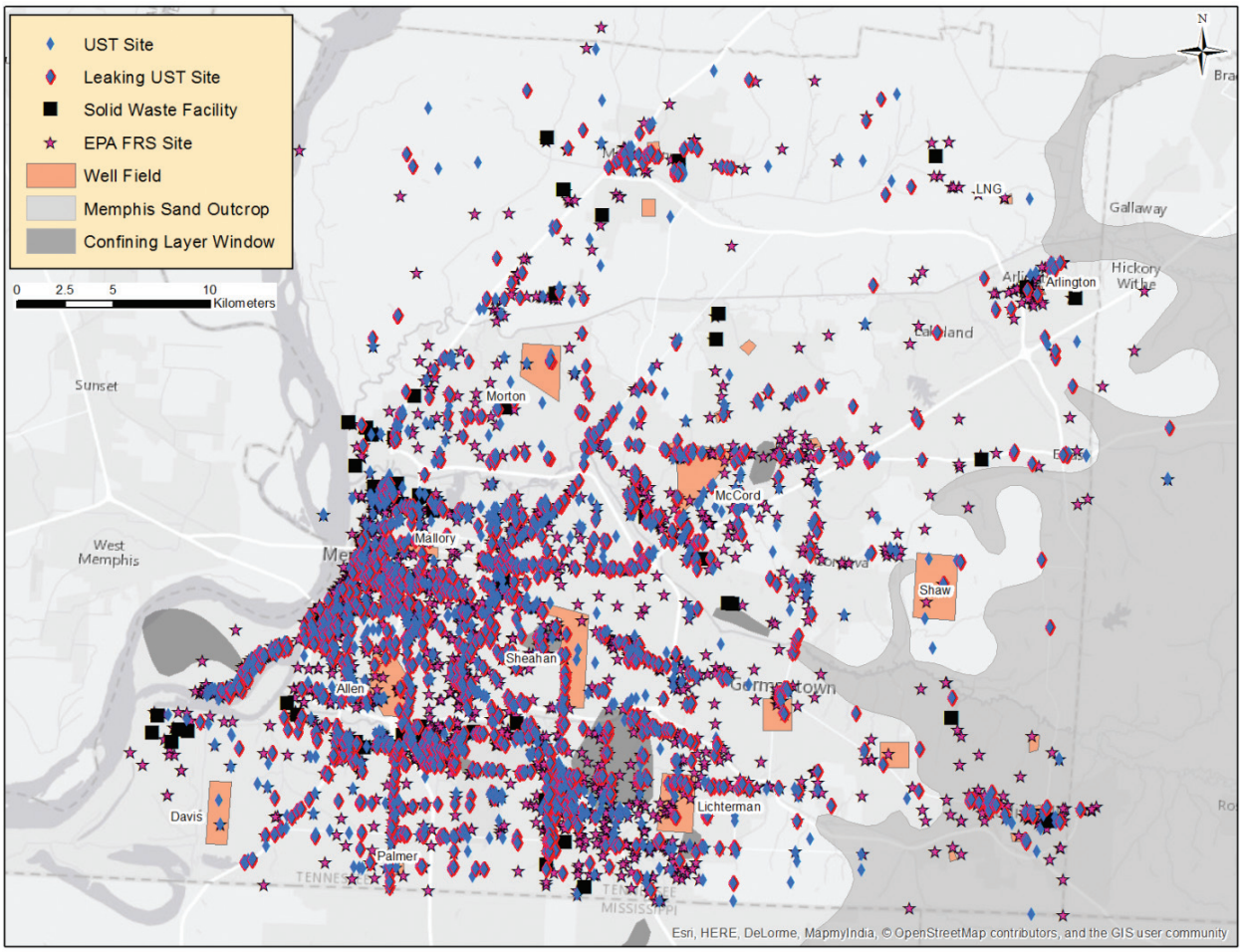

Figure 8. Map of Shelby County showing public supply well fields, hydrogeologic windows, and potential contaminant sources. UST is underground storage tank and FRS is federally registered site.

Koban et al. 2011), Allen (Bradshaw 2011), and McCord (Gallo 2015) well fields all indicate that substantial modern water fractions, mainly from nearby streams, are being drawn into the Memphis aquifer through hydrogeologic windows in the confining unit. However, the results also argue for a more comprehensive and continuous sampling plan rather than the piecemeal sampling approach so far utilized. As shown in figure 8, the number of potential contaminant sources adjacent to these well fields and nearby hydrologic windows creates significant aquifer vulnerability and concerns for the sustainability of water quality.

Conclusions

Environmental tracers (^{3}H, He isotopes, noble gases, and SF_6) have been sampled in production wells in Shelby County, Tennessee, to evaluate the presence of modern water in the semi-confined Memphis aquifer. The Memphis aquifer is a regionally important public supply source that has been shown to be locally susceptible to contamination. Use of groundwater from the Memphis aquifer since the late 1800's has caused the original upward hydraulic gradient in the aquifer to reverse in direction, such that modern water from the Shallow aquifer and local streams recharge the Memphis aquifer locally. Environmental tracers were used to specifically evaluate the age distribution of the modern water and quantity being withdrawn from public supply wells.

Tritium data from a large number of production wells show persistent presence of modern water in the Memphis aquifer, primarily in the upper 100 m. The ^{3}H/^{3}He and SF_6 apparent ages from affected wells in the Memphis aquifer show ages

of 20 to 45 years. The percentage of modern water in these wells using the tritium-loading method ranges from 0 to 75%, although most are less than 40% modern water. Inverse geochemical mixing models of a group of the wells from three well fields generally produce mixing percentages similar to those derived from the $^{3}H/^{3}He$ system; however, poor correspondence is indicated in some wells. Lumped parameter models (LPM) for binary mixtures of vertical recharge following an exponential piston flow behavior into long-flow path of deep Memphis aquifer water generally show mixing percentages similar to those from the tritium-loading method. However, the LPM mean ages of modern water are substantially younger than the apparent ages, mainly due to the application of the exponential piston flow model. Application of the LPM mixing percentages to the SF_6 apparent ages as a correction for dilution by pre-modern, non-tracer bearing waters results in younger SF_6 apparent ages than those from the $^{3}H/^{3}He$ system. The difference in the $^{3}H/^{3}He$ and SF_6 apparent ages is interpreted to reflect the differing sensitivities of these dating systems, with the $^{3}H/^{3}He$ system being more sensitive to older modern water and SF_6 being more sensitive to the youngest modern water.

The $^{3}H/^{3}He$ and SF_6 data and associated modeling verify and clarify the results of groundwater flow modeling in the Memphis aquifer by Brahana and Broshears (2001) that suggested as much as 50% of the water withdrawn from the aquifer in Memphis is from vertical recharge. The tracer-based mixing percentages indicate that quantities between 5 and 30% of modern water are being withdrawn from the Memphis aquifer in affected well fields. The tracer data combined with hydrogeologic information from case studies indicate the modern water source is mainly derived from local streams or shallow aquifers in hydraulic connection to the streams. Wellhead protection areas (WHPA) of the individual wells with significant percentages of modern water do not extend to the local streams, suggesting that the wells have greater inherent susceptibility to contamination than is indicated from WHPA modeling. Furthermore, the proximity of many potential contaminant sources to well fields and nearby hydrogeologic windows suggests significant vulnerability to contamination. The environmental tracer data provide essential information for evaluating WHPA that may not be gathered solely from traditional groundwater flow modeling, especially in cases where complexities in the hydrogeologic setting may be difficult to capture in modeling.

Although detailed groundwater flow modeling will undoubtedly provide greater insight to the flow dynamics and sensitivity of the local hydrologic systems, the environmental tracer data collected in the present study clarify the need for concern and further study. In addition, the connection between surface water and groundwater resources of the Memphis aquifer demand that a more holistic approach to water resources management be employed to ensure comprehensive sustainability.

Acknowledgements

Funding for this study was provided by a Tennessee Water Resources Research grant, the Shelby County Department of Health, and institutional funds from the Ground Water Institute (GWI) at the University of Memphis. This work could not have been possible without the assistance of public supply personnel in Shelby County, specifically, Tim Herndon (Bartlett), Richard McDaniel (Millington), Tim Overly (Collierville), Mike Sorenson (Germantown), and Arthur (Bubba) Vick (MLGW). Other collaborators whom have greatly assisted over the years on this project include Jerry Anderson and Randy Gentry. Thanks are extended to many graduate and undergraduate students at the GWI and Department of Earth Sciences at the University of Memphis that worked on data collection and analysis over the years. The manuscript was improved by consideration of the thoughtful insight from three anonymous reviewers.

Author Bio and Contact Information

Daniel Larsen is a professor and department chair for the Department of Earth Sciences at the University of Memphis. His interests are in hydrogeology, applications of chemical and isotopic tracers, and sedimentology. He is an affiliated research faculty member at the Center for Applied Earth Science and Engineering Research (CAESER) where he emphasizes hydrogeological studies of groundwater resources in the northern Mississippi embayment in the central U.S. He may be contacted at dlarsen@memphis.edu and his mailing address is 113 Johnson Hall, University of Memphis, Memphis, TN 38152.

Brian Waldron is an associate professor in the Department of Civil Engineering at the University of Memphis. His research interests are in groundwater and contaminant transport modeling, GIS analysis, and hydrology. He is the Director of the Center for Applied Earth Science and Engineering Research (CAESER) where he initiates and manages national and international research projects in water resources, GIS analysis, and geospatial data management. He may be reached at bwaldron@memphis.edu. His mailing address is Wilder Tower, suite 900, 3675 Alumni Drive, University of Memphis, Memphis, TN 38152.

Scott Schoefernacker is a project manager at the Center for Applied Earth Science and Engineering Research (CAESER). His primary research interests are in hydrogeology, especially in site evaluation, groundwater flow, and data collection studies. He is currently pursuing a Ph.D. in Earth Sciences emphasizing hydrogeologic and geophysical investigation of a closed landfill. He can be contacted at sschfrnc@memphis.edu and his mailing address is Wilder Tower, suite 900, 3675 Alumni Drive, University of Memphis, Memphis, TN 38152.

Haley Gallo is a research assistant at the Center for Applied Earth Science and Engineering Research (CAESER). Her research interests are in hydrogeology and groundwater flow modeling. She is currently pursuing a Masters Degree in Civil Engineering emphasizing groundwater flow modeling in sediments within the Mississippi embayment of the central U.S. To contact her, write to hggallo@memphis.edu or mailing address is Wilder Tower, suite 900, 3675 Alumni Drive, University of Memphis, Memphis, TN 38152.

John (Jack) Koban is a laboratory manager at Fugro Consultants, Inc. in Baton Rouge, Louisiana. His interests are in groundwater and wetland hydrology. He is currently pursuing a Ph.D. in Earth Sciences emphasizing the hydrologic role of Mississippi River islands in nitrogen cycling. He can be contacted at Jkoban@fugro.com and his mailing address is 4233 Rhoda Drive, Baton Rouge, LA 70816.

Elizabeth Bradshaw is an administrative assistant at Phillips Pet Food and Supplies in Lansing, Michigan. She completed a Masters Degree of Earth Sciences at the University of Memphis emphasizing GIS and tracer-based investigations of recharge to the Memphis aquifer at a municipal well field. Write to her at ebradshaw55@gmail.com.

References

Ackerman, D.J. 1996. *Hydrology of the Mississippi River Valley Alluvial aquifer, south-central United States.* U.S. Geological Survey Professional Paper 1416-D.

Aeschbach-Hertig, W., F. Peeters, U. Beyerle, and R. Kipfer. 2000. Palaeotemperature reconstruction from noble gases in groundwater taking into account equilibration with entrapped air. *Nature* 405: 1040-1044.

Barlow, J.R.B., J.A. Kingsbury, R.H. Coupe. 2012. Changes in shallow groundwater quality beneath recently urbanized area in the Memphis, Tennessee area. *Journal of the American Water Resources Association* 1-19. DOI: 10.1111/j.1752-1688.2011.00616.x. Accessed November 16, 2016.

Bayer, R., P. Schlosser, G. Bönisch, H. Rupp, F. Zaucker, and G. Zimmek. 1989. Performance and blank components of a mass spectrometric system for routine measurement of helium isotopes and tritium by the ^{3}He in-growth method. *Sitzungsberichte der Heidelberger Akademie der Wissenschaften, Mathematisch-naturwissenschaftliche Klasse* 5: 241-279.

Blanford, T.N. and P.S. Huyakorn. 1991. *US EPA WHPA*. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.

Bradley, M.W. 1991. *Ground-water Hydrology and the Effects of Vertical Leakage and Leachate Migration on Ground-water Quality Near the Shelby County Landfill, Memphis, Tennessee*. U.S. Geological Survey Water-Resources Investigations Report 90-4075.

Bradshaw, E.A. 2011. Assessment of ground-water leakage through the upper Claiborne confining unit to the Memphis aquifer in the Allen well field, Memphis, Tennessee. Unpublished M.S. Thesis, Department of Earth Sciences, University of Memphis, Memphis, TN.

Brahana, J.V., W.S. Parks, and M.W. Gaydos. 1987. *Quality of Water from Freshwater Aquifers and Principal Well Fields in the Memphis Area, Tennessee*. U.S. Geological Survey Water Resources Investigations Report 87-4052.

Brahana, J.V. and R.E. Broshears. 2001. *Hydrogeology and Ground-water Flow in the Memphis and Fort Pillow Aquifers in the Memphis Area, Tennessee*. U.S. Geological Survey Water Resource Investigation Report 89-4131.

Busenberg, E. and L.N. Plummer. 2000. Dating young ground water with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. *Water Resources Research* 36(10): 3011-3030.

Carmichael, J.K., W.S. Parks, J.A. Kingsbury, and D.E. Ladd. 1997. *Hydrogeology and Ground-Water Quality at the Naval Support Activity Memphis, Near Millington, Tennessee.* U.S. Geological Survey Water-Resources Investigations Report 97-4158.

Clark, I.D. and P. Fritz. 1997. *Environmental Isotopes in Hydrogeology.* Lewis Publishers, Boca Raton, Florida.

Clarke, W.B., W.J. Jenkins, and Z. Top. 1976. Determination of tritium by mass spectrometric measurements of ^{3}He. *International Journal of Applied Radioactive Isotopes* 27: 515-522.

Cook, P.G. and J.K. Bohlke. 2000. Determining timescales for groundwater flow and solute transport. In: *Environmental Tracers in Subsurface Hydrology*, P.G. Cook and A.L. Herczeg (Eds.). Kluwer Academic Publishers, Boston, pp. 397-424.

Coupe, R.H. 2000. *Occurrence of Pesticides in Five Rivers of the Mississippi Embayment Study Unit.* U.S. Geological Survey Water-Resources Investigations Report 99-4159.

Criner, J.H. and C.A. Armstrong. 1958. *Ground-water Supply of the Memphis Area*. U.S. Geological Survey Circular 408.

Criner, J.H. and W.S. Parks. 1976. *Historic Water-level Changes and Pumpage from the Principal Aquifers of the Memphis Area, Tennessee: 1886-1975.* U.S. Geological Survey Water-Resources Investigations Report 76-67.

Criner, J.H., P-C.P. Sun, and D.J. Nyman. 1964. *Hydrology of the Aquifer Systems in the Memphis Area, Tennessee*. U.S. Geological Survey Water-Supply Paper 1779-O.

Darling, W.G., D.C. Gooddy, A.M. MacDonald, and B.L. Morris. 2012. The practicalities of using CFC's and SF6 for groundwater dating and tracing. *Applied Geochemistry* 27: 1688-1697.

Doudrick, K.W. 2008. A predictive model of groundwater flow and contaminant transport of Cr(VI) and TCE in Collierville, Tennessee. Unpublished M.S. Thesis, Department of Civil Engineering, University of Memphis, Memphis, TN.

Eberts, S.M., J.K. Bohlke, L.J. Kauffman, and B.C. Jurgens. 2012. Comparison of particle-tracking and lumped-parameter age-distribution models for evaluating vulnerability of production well to contamination. *Hydrogeology Journal* 20: 263-282.

EPA (U.S. Environmental Protection Agency). 1987. *Guidelines for Delineation of Wellhead Protection Areas.* EPA-440/5-93-001. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.

Fetter, C.W. 2001. *Applied Hydrogeology*. Prentice-Hall, Upper Saddle River, NJ.

Gallo, H.G. 2015. Hydrologic and geochemical investigation of modern leakage beneath the McCord Well Field, Memphis, Tennessee. Unpublished M.S. Thesis, Department of Earth Sciences, University of Memphis, Memphis, TN.

Gentry, R.W., T.-L. Ku, S. Luo, V. Todd, D. Larsen, and J. McCarthy. 2005. Resolving aquifer behavior near a focused recharge feature based upon synoptic well field hydrogeochemical tracer results. *Journal of Hydrology* 323: 387-403.

Gentry, R., L. McKay, N. Thonnard, J.L. Anderson, D. Larsen, J.K. Carmichael, and D.K. Solomon. 2006. *Novel Techniques for Investigating Recharge to the Memphis Aquifer.* AWWARF Report 91137, American Water Works Association, Denver, Colorado.

Gonthier, G.J. 2002. *Quality of Shallow Groundwater in Recently Developed Residential and Commercial Areas, Memphis Vicinity, Tennessee, 1997*. U.S. Geological Survey Water-Resources Investigation Report 02-4294.

Graham, D.D. and W.S. Parks. 1986. *Potential for Leakage Among Principal Aquifers in the Memphis Area, Tennessee*. U.S. Geological Survey Water-Resources Investigations Report 85-4295.

Grubb, H.F. 1998. *Summary of Hydrology of the Regional Aquifer Systems, Gulf Coastal Plain, South-central United States*. U.S. Geological Survey Professional Paper 1416-A.

Hagedorn, B. 2015. Hydrochemical and ^{14}C constraints on groundwater recharge and interbasin flow in an arid watershed: Tule Desert, Nevada. *Journal of Hydrology* 523: 297-308.

Hagedorn, B., A.I. El-Kadi, A. Mair, R.B. Whittier, and K. Ha. 2011. Estimating recharge in fractured aquifer of a temperate humid to semiarid volcanic island (Jeju, Korea) from water table fluctuations, and Cl, CFC-12, and ^{3}H chemistry. *Journal of Hydrology* 409: 650-662.

Hood v. City of Memphis. 2009. 570 F.3d 625.

Hosman, R.L., A.T. Long, T.W. Lambert, and others. 1968. *Tertiary Aquifers in the Mississippi Embayment with Discussions of Quality of Water by H. G. Jeffery*. U.S. Geological Survey Professional Paper 448-D.

Ivey, S.S., R. Gentry, D. Larsen, and J.L. Anderson. 2008. Case study of the inverse application of

age distribution modeling using $^{3}H/^{3}He$: MLGW Sheahan Well field, Memphis, TN. *Journal of Hydraulic Engineering* 13: 1011-1020.

Jurgens, B.C., J.K. Bohlke, and S.M. Eberts. 2014. *TracerLPM (Version 1): An Excel Workbook for Interpreting Groundwater Age Distributions from Environmental Tracer Data.* U.S. Geological Survey Techniques and Methods 4-F3.

Kenny, J.F., N.L. Barber, S.S. Hutson, K.S. Linsey, J.K. Lovelace, and M.A. Maupin. 2009. *Estimated Use of Water in the United States in 2005*. U.S. Geological Survey Circular 1344.

Kingsbury, J.A. 1996. *Altitude of the Potentiometric Surface, September, 1995, and Historic Water-level Changes in the Memphis and Fort Pillow Aquifers in the Memphis Area, Tennessee*. U.S. Geological Survey Water-Resources Investigations Report 96-4278, 1 sheet.

Koban, J., D. Larsen, and S. Ivey. 2011. Resolving the source and mixing proportions of modern leakage to the Memphis aquifer in a municipal well field using geochemical and $^{3}H/^{3}He$ data, Memphis, Tennessee, USA. *Environmental Earth Sciences* 66: 295. DOI: 10.1007/s12665-011-1239-x. Accessed November 16, 2016.

Kraemer, S.R., H.M. Haitjema, and V.A. Kelson. 2007. *Working With WhAEM2000 Capture Zone Delineation for a City Wellfield in a Valley Fill Glacial Outwash Aquifer Supporting Wellhead Protection.* U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

Krinitzsky, E.L. 1949. *Geological Investigation of Gravel Deposits in the Lower Mississippi Valley and Adjacent Uplands*. U.S. Army Corps of Engineers, Waterways Experiment Station Technical Memorandum no. 3-273.

Larsen, D. and C.F. Brock. 2014. Sedimentology and petrology of the Eocene Memphis Sand and younger terrace deposits in surface exposures of western Tennessee. *Southeastern Geology* 50(4): 193-214.

Larsen, D., J. Morat, B. Waldron, S. Ivey, and J.L. Anderson. 2013. Stream loss contributions to a municipal water supply aquifer, Memphis, Tennessee. *Environmental and Engineering Geoscience* 19: 265-287.

Larsen, D., R.W. Gentry, and D.K. Solomon. 2003. The geochemistry and mixing of leakage in a semi-confined aquifer at a municipal well field. *Applied Geochemistry* 18: 1043-1063.

Law, C.S., A.J. Watson, and M.I. Liddicoat. 1994. Automated vacuum analysis of sulfur hexafluoride in seawater: Derivation of the atmospheric trend (1979-1993) and potential as a transient tracer. *Marine Chemistry* 48: 57-69.

Lumsden, D.N., K.R. Hundt, and D. Larsen. 2009. Petrology of the Memphis Sand in the northern Mississippi Embayment. *Southeastern Geology* 46(3): 121-133.

Manning, A.H., D.K. Solomon, and S.A. Thiros. 2005. $^{3}H/^{3}He$ age data in assessing the susceptibility of wells to contamination. *Ground Water* 43: 353-367.

McDonald, M.G., and A. W. Harbaugh. 1988. A modular three-dimensional finite-difference ground-water flow model. In: *Techniques of Water-Resources Investigations of the United States Geological Survey*, Book 6, Chapter A1, 586 p.

Memphis Light, Gas and Water, Residential Rates, Electronic document. Available at http://www.mlgw.com/residential/residentialrates. Accessed November 16, 2016.

Moore, G.K. and D.L. Brown. 1969. *Stratigraphy of the Fort Pillow Test Well Lauderdale County, Tennessee.* Tennessee Division of Geology Report of Investigations 26, 1 sheet.

NCDC, National Climate Data Center. 2010. *Climatology of the United States, No. 20, 1971-2000*. Electronic document. Available at https://www.ncdc.noaa.gov/climatenormals/clim20/wa/454572.pdf. Accessed November 16, 2016.

Nelms, D.L., G.E. Harlow, Jr., L.N. Plummer, and E. Busenberg. 2003. *Aquifer Susceptibility in Virginia, 1998–2000.* U.S. Geological Survey Water Resources Investigations Report 03-4278.

Nyman, J.D. 1965. *Predicted Hydrologic Effects of Pumping from the Lichterman Well Field in the Memphis Area, Tennessee*. U.S. Geological Survey Water Supply Paper 1819-B.

Parkhurst, D.L. and C.A.J. Appelo. 1999. *User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations*. U.S. Geological Survey Water Resources Investigations Report 99-4259.

Parks, W.S. 1990. *Hydrogeology and Preliminary Assessment of the Potential for Contamination of the Memphis Aquifer in the Memphis Area, Tennessee*. U.S. Geological Survey Water-Resources Investigations Report 90-4092.

Parks, W.S., J.E. Mirecki, and J.A. Kingsbury. 1995. *Hydrogeology, Ground-water Quality, and Source of Ground Water Causing Water-quality Changes in*

the Davis Well Field at Memphis, Tennessee. U.S. Geological Survey Water-Resources Investigations Report 94-4212.

Parks, W.S. and J.E. Mirecki. 1992. *Hydrology, Ground Water Quality, and Potential for Water-supply Contamination Near the Shelby County Landfill in Memphis Tennessee*. U.S. Geological Survey Water Resource Investigation Report 91-4173.

Parks, W.S. and J.K. Carmichael. 1990. *Geology and Ground-water Resources of the Memphis Sand in Western Tennessee*. U.S. Geological Survey Water-Resources Investigations Report 88-4182.

Robinson, J.L., J.K. Carmichael, K.J. Halford, and D.E. Ladd. 1997. *Hydrogeologic Framework and Simulation of Ground-water Flow and Travel Time in the Shallow Aquifer System in the Area of Naval Support Activity Memphis, Millington, Tennessee.* U.S. Geological Survey Water-Resources Investigations Report 97-4228.

Saucier, R.T. 1987. *Geomorphological Interpretations of Late Quaternary Terraces in Western Tennessee and Their Regional Tectonic Implications.* U.S. Geological Survey Professional Paper 1336-A.

State of Mississippi v. State of Tennessee. 2015. No. 143, Original, U.S. Supreme Court.

Solomon, D.K. and P.G. Cook. 2000. ^{3}H and ^{3}He. In: *Environmental Tracers in Subsurface Hydrology,* P.G. Cook and A.L. Herczeg (Eds.). Kluwer Academic Publishers, Boston, pp. 397-424.

Van Arsdale, R.B., R.P. Bresnahan, N.S. McCallister, and B. Waldron. 2008. The Upland Complex of the central Mississippi River valley: Its origin, denudation, and possible role in reactivation of the New Madrid seismic zone. In: *Continental Intraplate Earthquakes: Science, Hazard, and Policy Issues*, S. Stein and S. Mazzotti (Eds.). Geological Society of America Special Paper 425, Boulder, CO, pp. 177-192.

Waldron, B. and D. Larsen. 2014. Predevelopment groundwater conditions surrounding Memphis, TN (USA): Controversy and unexpected outcomes. *Journal of the American Water Resources Association* 51(1): 133-153. DOI: 10.1111/jawr.12240. Accessed November 16, 2016.

Waldron, B., D. Larsen, R. Hannigan, R. Csontos, J. Anderson, C. Dowling, and J. Bouldin. 2011. *Mississippi Embayment Regional Ground Water Study*. EPA 600/R-10/130. U.S. Environmental Protection Agency.

Waldron, B., S. Schoefernacker, D. Larsen, and M. Bradley. In press. *Altitude of Water Table in Shelby County, Tennessee, October 2005*. U.S. Geological Survey Open-File Report: 1 sheet.

Wanninkhof, R. and J.R. Ledwell. 1991. Analysis of sulfur hexafluoride in seawater. *Journal of Geophysical Research* 96(C): 8733-8740.

Zuber, A. and P. Maloszewski. 2001. Lumped parameter models. In: *Volume 6: Modeling in Environmental Isotopes in the Hydrological Cycle: Principles and Applications*. UNESCO, Paris, France, 39(1): 5-35.