

Available online at www.sciencedirect.com



Applied Geochemistry 18 (2003) 1043-1063

Applied Geochemistry

www.elsevier.com/locate/apgeochem

The geochemistry and mixing of leakage in a semi-confined aquifer at a municipal well field, Memphis, Tennessee, USA

Daniel Larsen^{a,*}, Randall W. Gentry^b, D.K. Solomon^c

^aGround Water Institute and Department of Earth Sciences, University of Memphis, Memphis, TN, 38152, USA ^bDepartment of Civil and Environmental Engineering, The University of Tennessee, Knoxville, TN 37996-2010, USA ^cDepartment of Geology and Geophysics, University of Utah, Salt Lake City, Utah, 84112, USA

> Received 13 February 2002; accepted 10 October 2002 Editorial handling by A. Welch

Abstract

The Memphis aquifer in southwestern Tennessee is confined to a semi-confined unconsolidated sand aquifer and is the primary municipal water source in the Memphis metropolitan area. Past studies have identified regions in the metropolitan area in which the overlying upper Claiborne confining unit lacks significant clay and provides a hydraulic connection between the shallow aquifer and the Memphis aquifer. In this study, major solute chemistry, ³H, and 3 H/ 3 He groundwater dating are used to investigate the extent and chemical effects of leakage through the confining unit to the Memphis aquifer in the vicinity of a municipal well field. The ³H/³He dates and geochemical modeling of the chemical data are used to constrain mixing fractions and the timing of modern recharge. Tritium activities of as much as 2.8 TU are observed in shallow production wells, but deeper production wells have ${}^{3}H$ activities that approach the detection limit. Trends in water chemistry indicate vertical mixing in the aquifer of shallow Na-SO₄-Cl-rich water and deeper Ca-Mg-HCO₃-rich water. Water chemistry does not vary consistently with seasonal pumping, but ³H activity generally decreases during low use periods. Stable O and H isotopes show little variation and are not useful groundwater tracers for this study. The ³H-bearing, Na–SO₄–Cl-rich water is interpreted to reflect recharge of modern water through the upper Claiborne confining unit. The ${}^{3}H/{}^{3}He$ dates from 5 production wells indicate modern recharge, that infiltrated 15-20 a ago, is present in the shallow production wells. Geologic data and hydrologic boundary conditions suggest that the most likely source for continued leakage is a nearby stream, Nonconnah Creek. Geochemical reaction modeling using the NETPATH computer code suggests that proportions of shallow aquifer water leaking into the Memphis aquifer range from 6 to 32%. The ${}^{3}H/{}^{3}He$ dating and NETPATH modeling results correlate well, suggesting that these complementary analytical tools provide an effective means to evaluate proportions of modern water leaking into semi-confined aquifers. These results also indicate a need to carefully consider connections between surface water and semi-confined groundwater resources in wellhead protection programs.

© 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Leakage of water through confining units is an important source of recharge for some confined or leaky confined aquifers (Bredehoeft et al., 1983; Fortin et al., 1991). Geochemical processes occurring as water passes through confining units can significantly modify the

* Corresponding author. Fax: +1-901-678-2178. *E-mail address:* dlarsen@memphis.edu (D. Larsen). chemical and microbiological composition of leakage and aquifer water (Back, 1986; Pucci et al., 1992; Chapelle, 1993; Wicks and Herman, 1994; McMahon, 2001). The chemical processes associated with leakage induced by extensive groundwater pumping from underlying confined aquifers are less understood (e.g., Mazari and Mackay, 1993). In urban areas, such leakage can degrade water quality and provide an avenue for contaminated surface water to reach potable groundwater supplies.

^{0883-2927/03/\$ -} see front matter O 2002 Elsevier Science Ltd. All rights reserved. P11: S0883-2927(02)00204-4

Memphis, Tennessee, and surrounding municipalities in southwestern Tennessee use groundwater from the confined to partly confined Memphis aquifer as a major source of potable water (Figs. 1 and 2). The Memphis aquifer is observed near the surface in southeastern Shelby County, but is present below the surface and overlain by the upper Claiborne confining unit throughout the remainder of Shelby County (Kingsbury and Parks, 1993). Throughout much of the Memphis area, the extensive thickness of clay in the confining unit (as much as 43 m of clay) protects the water resources of the Memphis aquifer by preventing water from seeping directly from the surface into the aquifer. However, several studies (Graham and Parks, 1986; Parks, 1990; Kingsbury and Parks, 1993) have documented that the clay is absent in some areas (Fig. 2). Instances of contaminants in water from the Memphis aquifer (Parks, 1990) and evidence of groundwater leakage from the surface aquifer to the Memphis aquifer (Parks and Mirecki, 1992; Mirecki and Parks, 1994; Parks et al., 1995) have elevated concerns that the Memphis aquifer may be susceptible to contamination.

The purposes of this contribution are to (1) describe the geochemical effects and age of leakage influencing



Fig. 1. (A) Map of the United States showing the location of Fig. 1B in the south-central United States. (B) Map showing the location of the Mississippi Embayment aquifer system and Memphis, Tennessee.



Fig. 2. Map of Shelby County Tennessee showing the potentiometric surface of the Memphis aquifer (Kingsbury, 1996), distribution of recharge area and windows (Parks, 1990), and location of Sheahan well field. The potentiometric surface is measured in m above sea level. SCL is the Shelby County landfill.

groundwater that is being pumped from the Memphis aquifer at a municipal well field, and (2) demonstrate the combined application of ³H/³He dating and NET-PATH geochemical modeling to estimate leakage fractions of modern water. Tritium and ³H/³He are used to determine the wells most affected by leakage and to calculate a weighted average age for the modern water that has leaked into the Memphis aquifer. The age estimates are evaluated with hydrogeologic data to identify a leakage-source flowpath from a nearby creek. Aquifer reactions along the flowpath and mixing proportions of modern leakage and deep Memphis aquifer water are investigated using geochemical modeling with NET-PATH (Plummer et al., 1991). The NETPATH results provide an indication of the geochemical reactions affecting pumping-induced leakage as it passes through a leaky confining unit. Although the water quality

changes created by leakage are minor at present, identification of leaky areas contributing recharge to the semiconfined Memphis aquifer may affect future development plans by clarifying hydraulic connections to leakage sources.

2. Background

2.1. Geology and hydrogeology

Memphis lies in the center of the northern Mississippi embayment, a trough-shaped basin that plunges southward along an axis that approximates the Mississippi River (Fig. 1). 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 to the west and include unconsolidated sand, silt, and clay with minor lignite (Table 1). Pleistocene and Pliocene(?) fluvial terrace deposits unconformably overlie the mid-Tertiary units (Krinitsky, 1949; Saucier, 1987). Excluding the present-day tributary valleys, 3-20 m of loess (windblown silt and clay) overlie the fluvial deposits and mantle the underlying topography. The Pleistocene loess is thickest near the Mississippi River bluffs and thins eastward. Present-day valleys of Big and Nonconnah creeks, and the Loosahatchie and Wolf rivers (Fig. 2) contain as much as 18 m of alluvium (Strom, 1997; Carmichael et al., 1997). The alluvium typically contains sand and gravel near the base and fines upward into sandy and clayey silt (reworked loess).

The geologic units beneath the Memphis and Shelby County area are divided into a series of hydrostratigraphic units, each with its own hydraulic characteristics. The loess and the upper part of the alluvium have similar textural and hydraulic properties (Robinson et al., 1997) and behave as a leaky confining unit. The fluvial terrace deposits and the sand and gravel in the lower part of the alluvium comprise the shallow (fluvial) aquifer. The Cockfield and Cook Mountain Formations comprise the lower confining unit for the shallow aquifer and upper aquitard for the Memphis aquifer; this unit is termed the Upper Claiborne confining unit. The thickness of clay beds in the confining unit varies from 61 m to 1 m, suggesting that areas of hydrologic connectivity exist between the underlying Memphis aquifer and the overlying fluvial aquifer (Parks, 1990). The Memphis aquifer is a thick sand-dominated aquifer, ranging from 122 to 274 m thick where it is not eroded. Average withdrawals from the Memphis aquifer in Shelby County were reported at 617×10^6 l/day in 1995 (Hutson, 1999). Long-term data from 5 observation wells show steady declines in water level until approximately 1975; after that date average yearly water levels have remained largely unchanged except at newly developed areas in the eastern part of Shelby County (Kingsbury, 1996). The Flour Island Formation forms the lower confining layer for the Memphis aquifer and is present throughout the county. It forms the upper confining unit for the Fort Pillow aquifer, another water resource for the region.

2.2. Evidence for leakage

Early studies suggested that the primary source of recharge to the Memphis aquifer was infiltration in upland regions, east of the Mississippi River in western Tennessee (Hosman et al., 1968), including the southeastern part of Shelby County (Criner et al., 1964). As groundwater usage increased 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 water-supply studies. Some early hydraulic indications of vertical recharge included a decline of water levels in shallow aquifers (Criner et al., 1964; Nyman, 1965), excess water recovery during pumping tests (Criner and Armstrong, 1958), and decreasing water-level declines in the cone of depression under Memphis (Criner and Parks, 1976). Using borehole log and water-level data, Parks (1990) showed that a strong downward vertical gradient exists between the shallow and Memphis aquifers throughout much of Shelby County and identified numerous areas where the upper Claiborne confining unit was thin or absent, termed windows. Modeling efforts 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. Some clear examples of vertical recharge through windows or otherwise leaky areas in the upper Claiborne confining unit have been shown through detailed geological, radioactive tracer (14C and 3H), and geochemical studies (Graham and Parks, 1986; Parks, 1990; Bradley, 1991; Parks and Mirecki, 1992; Mirecki and Parks, 1994; Parks et al., 1995).

2.3. Sheahan well field

The Sheahan well field (Figs. 2 and 3) has been in operation since 1932. The well field currently includes 24 wells and the pumping station has a treatment capacity of 35×10^6 gallons (132.5×10^7 I) per day. Tritium analysis of water from the Sheahan well field in the mid-1980s revealed that a component of modern water was being pumped from the well field, specifically from two wells in the south Sheahan well field (Graham and Parks, 1986). Later studies (Parks, 1990) revealed by contouring geologic data that potential windows through the confining unit exist adjacent to the Sheahan well field. Most recently, Ivey (1997) used Ba concentrations to estimate that 8% of the water in the shallow Memphis aquifer was derived from downward leakage of water from the overlying shallow aquifer.

3. Methods

All available production wells in the Sheahan well field were sampled in the fall of 1999 and late spring through early summer 2000. In addition, 5 production wells were sampled in the fall of 2000. Water samples for geochemistry, ³H, and stable isotope analyses were obtained from a sampling spigot located on the top of the production wells. Sampling commenced after the wells had been pumping for more than 12 h. Given that the pump discharge is on the order of 3 m³/min and the

Series Hydrostratigraphic unit Group Stratigraphic unit Thickness (m) Lithology Holocene and Pleistocene Alluvium Shallow (alluvial) aquifer 0 - 53Sand, 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 0 - 20Silt, 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 - 30Sand, 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 Oligocene? Eocene Jackson Formation Claiborne Upper Claiborne confining layer 0 - 110Clay, silt, sand, and lignite. Because Cockfield and Cook of similarities in lithology, the Jackson Mountain Formations Formation and upper part of the Claiborne Group cannot be reliable subdivided based on available information. Most of the preserved sequence is the Cockfield and Cook Mountain Formations undivided 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

Table 1 Geologic and hydrostratigraphic units underlying Shelby County, Tennessee

D.

Larsen et al. | Applied Geochemistry 18 (2003) 1043-1063

and lignite

well volume is generally less than 11 m³, approximately 200 well volumes would have been purged prior to sampling. The following field chemistry measurements were made using probes in a flow-through sampling cell: pH, temperature, specific conductance, and Eh. In addition, field measurements in duplicate were made for alkalinity (using Hach titration kit), dissolved O₂ content (using a factory-calibrated Hach 2000 spectrophotometer or a calibrated YSI dissolved O₂ probe), total Fe (using a factory-calibrated Hach 2000 spectrophotometer), and total NO_3^- (using a factory-calibrated Hach 2000 spectrophotometer). Three water samples were obtained: 11 of raw water in a polypropylene bottle, 250 ml of filtered (0.45 µm filter) water acidified with 1 ml of concentrated HNO₃ in a polypropylene bottle, and 11 of raw water in amber glass bottle. After collecting waters were stored in a cooler with ice until they were taken to the laboratory and placed in a refrigerator at 4 °C.

Dissolved anion analyses were performed on raw filtered water with a Dionex 2000I ion chromatography module. Anion (Cl⁻, NO₃⁻, and SO₄²⁻) concentrations were determined using an AS14 column and NaHCO₃-CO₃ eluent. Precision based on multiple analyses of inhouse standards was within 10% (1 σ) of the mean for Cl⁻ and SO₄²⁻ and within 30% of the mean for NO₃⁻. Cation analyses were performed on filtered and acidified water with a Varian AA10 atomic absorption spectrometer. Reproducibility based on multiple analyses of inhouse standards was within 10% (1 σ) for Na, K, Ca, and Mg, and within 4% for Fe and Mn. Charge errors were within 8% of balance.

For the fall 1999 and spring-summer 2000 sampling events, the raw water samples in the amber glass bottles were packed in a cooler and shipped to the Center for Applied Isotope Studies, University of Georgia for ³H analysis. Tritium enrichment was utilized to obtain a detection limit of 0.1 to 0.3 ³H units (TU). Duplicate sample analyses for the spring-summer 2000 event were within 0.2 TU for samples with approximately 1.0 TU (Table 2); however, triplicate sample analyses for the fall 1999 event had a minimum 2σ error of 0.3 TU. For the fall 2000 sampling event, the raw water samples in the amber glass bottles were packed in a cooler and shipped to the University of Utah for ³H analysis by the He in-growth method. In this method, ³H activity was determined by the amount of ³He accumulated in a sample over a series of 3 to 4 months (Clarke et al., 1976; Bayer et al., 1989). The practical detection limit for the He in-growth method is 0.05 TU (Solomon and Cook, 2000). The percent error ranges from approximately $\pm 10\%$ at 1 TU to $\pm 70\%$ at the detection limit (Table 3).

Gas sampling of 5 production wells was conducted in fall 2000. The flow from the pump to the treatment plant was constricted to retain higher pressures and limit any degassing during pumping. The gases were

Series	Group	Stratigraphic unit	Hydrostratigraphic unit	Thickness (m)	Lithology
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
		Old Breastworks formation	Old Breastworks confining layer	55-107	northeastern parts Clay, Silt, Sand, and lignite. Consists primarily of silty clays and clayey silts with lenses and interbeds of fine sand and lignite

Table 1 (continued)

Adapted from Graham and Parks, 1986.



Fig. 3. Map of Sheahan well field and nearby Nonconnah Creek. The locations of MLGW wells as well as UR-13s (used in modeling) are shown.

sampled in a flow-through cell in triplicate with a diffusion sampler (Cu tube with a semi-permeable membrane attached to one end). The diffusion sampler is equilibrated with the flow of production well water for approximately 24 h. Once the gas volume within the sampler had reached equilibrium with the water in the flow-through cell, the Cu tube portion of the sampler was sealed and stored for later laboratory analysis. Samples were analyzed in the Noble 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 $-180 \degree C$ for Ar, Kr, and Xe, and at -236 °C for Ne. Helium and other noble gas isotopes were then measured on a MAP215-50 mass spectrometer to a precision of approximately $\pm 0.5\%$.

Samples for O and H stable isotope analysis were sent to the stable isotope laboratory at the University of Tennessee at Knoxville. Three ml sample volumes were equilibrated with H₂, using a Pt-catalyst, or CO₂ on a Finnigan MAT HDO Equilibrator and Delta plus mass spectrometer (Roether, 1970; Horita et al., 1989). The values are reported relative to VSMOW with precision of $\pm 0.1\%$ for δ^{18} O and $\pm 1.0\%$ for δ D.

4. Results

4.1. Tritium and helium-3

Tritium activities from the fall 1999 and springsummer 2000 sampling events range from below detecTable 2

Tritium and stable O and H isotope data collected from production wells in the Sheahan well field during fall 1999 and spring-summer 2000

MLGW Well	Depth ^a (m)	Tritium (TU) fall 1999	Tritium (TU) spring–summer 2000	% Change tritium	δ ¹⁸ O spring–summer 2000	δ ² H spring–summer 2000
52	189	0.76	< 0.33	>-56	-5.3	-29
54	113	0.81	0.49	-40	nd ^b	nd
55	166	1.8	0.46	-75	-5.2	-29
57	112	0.94	0.87, 1.1	-7, 18	nd	nd
63	96	1.9	1.4	-23	-5.1	-30
70	140	0.48, < 0.4, 0.71	0.44	-8.3, >10, -38	nd	nd
71	126	0.86	0.58	-32	nd	nd
72	nd	< 0.4	0.32	>-20	nd	nd
74	154	< 0.4	< 0.3	>-25	nd	nd
76	91	2.0	1.4	-29	nd	nd
78	125	0.99	0.76	-23	nd	nd
79	199	0.43	< 0.33	>-23	nd	nd
80	127	1.2	0.72	-40	-5.3	-30
87	95	2.8	1.5	-46	-5.2	-30
88	103	1.09	nd		-5.3	-31
91	159	0.79	0.79	0	nd	nd
93	210	0.94	< 0.35	>-63	nd	nd
95	237	< 0.4	< 0.4		-5.4	-31
96	211	< 0.4	0.6	50	nd	nd
97	144	0.79	nd		nd	nd
98	149	< 0.4	< 0.33		-5.2	-29
99	108	1.02	< 0.27	>-73	nd	nd

^a Depth of the top of the screened interval of production well.

^b Not determined.

Table 3				
Tritium and gas analysis data from	n sampling production	wells in Sheahan	well field d	uring fall 2000

MLGW Well	N_2 (cc/g)	²⁰ Ne (cc/g)	⁴ He (cc/g)	³ H (TU)	³ He*a (TU)	³ H + ³ He* (TU)	$R/R_{\rm a}^{\rm b}$	Apparent Age (years)
78	1.63E-02	2.06E-07	5.75E-08	0.29 ± 0.06	1.6	1.89	0.973	28
55	1.56E-02	2.04E-07	5.86E-08	0.07 ± 0.05	1.2	1.27	0.944	51
80	1.62E-02	2.03E-07	5.58E-08	0.08 ± 0.05	1.5	1.58	0.984	48
87	1.65E-02	2.02E-07	5.41E-08	2.3 ± 0.3	5.2	7.5	1.119	19
88	1.64E-02	2.04E-07	5.37E-08	1.3 ± 0.1	2.4	3.7	1.052	16

^a ³He* is tritiogenic ³He.

^b R is the ³He/⁴He ratio of the sample; R_a is the ³He/⁴He ratio of air (1.384×10⁻⁶).

tion to 2.7 TU and decrease with depth (Fig. 4, Table 2). Considerable scatter is observed in the data as the detection limits are approached. Given this observation and the stated errors, the results from ³H enrichment and standard counting are considered qualitative for activities below 1.0 TU. However, the same trend of decreasing activity with depth is observed for the fall 2000 samples (Table 3), which were analyzed by the more accurate and precise ³H in-growth method (Solomon and Cook, 2000). Despite the clear decrease in ³H activity with depth, no systematic lateral variations in ³H are observed. Tritium activities vary

depending on the season. Higher activities are generally observed during the fall than the spring-summer sampling events (Fig. 4).

The He and other gas isotope analysis are presented in Table 3. Co-relations between N₂, Ne, and He indicate that the waters are supersaturated with air, assuming no subsurface sources of Ne or N₂. The apparent ages are calculated assuming ³H decay and He supersaturation results from air entrapment only (Solomon and Cook, 2000). The ratios of ³He/⁴He in the samples to ³He/⁴He in the atmosphere are approximately 1; thus, crustal ⁴He and ³He contributions are minimal. The



Fig. 4. Plots of (A, B) 3 H activity and (C, D) Cl⁻ concentration with depth (m) in production wells within the Sheahan well field sampled during fall, 1999 and spring–summer, 2000. Depth plotted is the top of the screened interval for the well.

apparent ages of 51 and 48 a obtained for MLGW 55 and 80, respectively, are at the limit of detection for the ${}^{3}H/{}^{3}He$ dating method and represent background (${}^{3}H +$ tritiogenic ${}^{3}He$) values. Only two of the samples, MLGW 87 and 88, contain significant (${}^{3}H +$ tritiogenic ${}^{3}He$) over background. An apparent age of 28 a is obtained for MLGW 78; however, the low ${}^{3}H$ activity and limited tritiogenic He concentration over background are problematic and discussed in a subsequent section. Similar to the ${}^{3}H$ data, apparent ages decrease systematically with depth.

4.2. Water chemistry

The chemical compositions of the well waters are generally mixed cation-HCO₃ waters (Fig. 5). Proportions of major ions vary systematically along linear trends (Fig. 5), reflecting contributions from Ca–Mg–

 HCO_3 and Na– SO_4 end members. Chloride and SO_4^{2-} concentrations and ³H activity decrease with depth along curvilinear trends (Figs. 4 and 6); however, depth trends for other solutes are more variable (Fig. 6).

Tritium is part of the water molecule and is considered geochemically conservative (Solomon and Cook, 2000). The similarity in concentration versus depth trends for ³H and Cl⁻ indicates that Cl⁻ is behaving conservatively, a common observation in groundwater systems (for review see Herczeg and Edmunds, 2000). The smooth, curvilinear decrease in Cl⁻ concentrations with depth suggests mixing, by some combination of diffusive and advective processes, of 2 chemically distinct waters.

Cation/Cl⁻ and anion/Cl⁻ concentration ratios versus depth shown in Fig. 7 illustrate the degree of non-conservative behavior for each constituent during mixing: linear, invariant trends indicate conservative



Fig. 5. Piper diagrams for major ion concentrations in groundwater from the Sheahan well field sampled during (A) fall, 1999 and (B) spring-summer, 2000.

behavior, whereas, linear, variant and curved trends indicate non-conservative behavior. Na⁺/Cl⁻ and K⁺/Cl⁻ exhibit nearly linear trends, although the Na⁺ data shows considerable scatter. Ca²⁺/Cl⁻, Mg²⁺/Cl⁻, and HCO₃⁻/ Cl⁻ show similar curvilinear trends that increase in value with depth. SO₄²⁻/Cl⁻ shows a C-shaped trend with higher values at shallow and deep levels. Fe²⁺/Cl⁻ and NO₃⁻/Cl⁻ show similar C-shaped or reverse C-shaped trends with depth, but have more scatter in the data. Eh generally decreases with depth, but pH shows no consistent trend with depth (Fig. 6). Eh and pH are not correlated, but, rather, cluster at or below saturation with amorphous Fe hydroxide solubility (Fig. 8). SO_4^{2-} and NO_3^{-} increase with increasing Eh, although, Fe^{2+} , another redox-sensitive species, shows no trend with Eh. Dissolved O_2 is higher than expected given the measured Eh values and the range of total dissolved Fe concentrations. Though redox dis-



Fig. 6. Plots of solutes and Eh with depth (m) in groundwater from the Sheahan well field sampled during fall, 1999: (A) pH, (B) NO₃, (C) Eh, (D) Fe²⁺, (E) Ca²⁺, (F) SO₄²⁻. Depth plotted is the top of the screened interval for the well.



Fig. 7. Plots of (A) anion/ Cl^- and (B) cation/ Cl^- with depth in production wells within the Sheahan well field sampled during fall, 1999. Trend lines are plotted to assist with pattern identification. Depth plotted is the top of the screened interval for the well.

equilibrium is not unusual, correlation of dissolved O_2 values to bubbling from the sampling line suggests that the dissolved O_2 values may not reflect subsurface conditions.

4.3. Oxygen and hydrogen isotopes

The O and H isotope data are invariant with depth (Table 2). The mean values $[\delta D = -29.9\% \pm 0.8 (1 \text{ S.D.})]$ and $\delta^{18}O = -5.24\% \pm 0.09 (1 \text{ S.D.})]$ are practically indistinguishable from mean values obtained from the

shallow aquifer $[\delta D = -29.2\% \pm 1.2 \text{ (1 S.D.)}$ and $\delta^{18}O = -5.26\% \pm 0.10 \text{ (1 S.D.)}$ (US Geological Survey WATSTORE database).

5. Discussion

5.1. Isotopic and geochemical indicators of leakage

Several isotopic and geochemical indications of vertical groundwater leakage through the upper Claiborne



Fig. 8. Eh-pH diagram for Pt electrode Eh values and field pH values for fall 1999 and spring–summer 2000. The solution composition constraints approximate those of waters sampled from the Sheahan well field. Stability fields for Fe species are also shown (thermodynamic data from Geochemist's Workbench, Bethke, 1998).

confining unit in the Sheahan well field area are present in the results. Tritium activities measured in the shallow aquifer in 1997 range from < 0.3 to 14 TU (n=32); however, the mean value upgradient from the Sheahan well field is 3.3 TU (n=10) (US Geological Survey WATSTORE database). Tritium activity in deep Memphis aquifer water is below detection, even using the He in-growth measurement method. The presence of ³H activities approaching 2.7 TU and the overall decrease in ³H activity with depth in the Memphis aquifer (Fig. 4) suggest that water from the shallow aquifer is leaking vertically and mixing with older Memphis aquifer water. Groundwater flow studies suggest travel times of 50-150 a from an upgradient, identified window in the confining unit at the Shelby County landfill (Fig. 2) to the Sheahan well field (Parks and Mirecki, 1992). Water travelling along this path would have a ³H activity below 0.5 TU by the time it reached the Sheahan well field (assuming an initial activity of 5 TU and plug flow); thus, a shorter flow path is required. Areas located immediately south of the Sheahan well field where clay layers in the confining unit are thin or absent (Parks, 1990) may provide shorter flow paths between the shallow and Memphis aquifers. The shallow aquifer beneath the Sheahan well field is unsaturated presently and infiltration to the shallow aquifer is limited by extensive urban land coverage and concrete channelization of tributaries. Thus, in the absence of shallow aquifer storage and infiltration, continued leakage requires a continuous water source. The nearest and most appropriate constant head boundary for the shallow aquifer in the Sheahan well field is Nonconnah Creek, to the south of the well field (Figs. 3 and 9). Subsurface data suggests that paleovalley systems at the base of the shallow aquifer may provide a hydrogeologic connection between the alluvium in the Nonconnah Creek valley and terrace deposits beneath the Sheahan well field (Larsen et al., 2001). Furthermore, past studies of the Nonconnah Creek basin suggest that stream flow losses are recharging the shallow aquifer south of the Sheahan well field (Nyman, 1965; Graham and Parks, 1986).

Chloride, Na^+ , and SO_4^{2-} all show curvilinear decreases in concentration with depth similar to that of ³H. The chemistry of groundwater in the shallow aquifer is variable, but recent analyses from the Nonconnah Creek area contain greater Cl⁻, Na⁺, and SO₄²⁻ concentrations than those in the Memphis aquifer. Another source of Cl⁻, Na⁺, and SO₄²⁻ may be from silt and clay lenses in the upper Claiborne confining unit. The confining unit locally contains pyrite concretions and may include beds that were deposited in brackish or saline water. Reaction of fresh, oxygenated water with these deposits would liberate Cl⁻, SO₄²⁻, Fe²⁺, and Na⁺ from cation exchange. The decrease in SO_4^{2-} concentrations with depth may also reflect SO_4^{2-} reduction; however, Eh values suggest the conditions in the Memphis aquifer are not reducing enough to drive this reaction (Fig. 8). No measureable dissolved sulfide was detected by spectrophotometric field tests. The strong downward vertical hydraulic gradient from the shallow to the Memphis aquifer could potentially extract and transport Cl⁻- and Na⁺-rich formation water from storage in the confining unit to production wells in the Memphis aquifer. Higher Cl^{-} and Na^{+} , and SO_{4}^{2-} concentrations have been observed in other aquifers immediately below or above aquitards and inferred to reflect leakage (or diffusion) contributions to the aquifer (Bredehoeft et al., 1983; Back, 1986; Hendry and Schwartz, 1991; Fabryka-Martin et al., 1991; Rudolph et al., 1991; Wicks and Herman, 1994). Highly systematic variations with depth, such as those observed in the Memphis aquifer, may be typical of aquifers with extensive pumping stresses. As reviewed by Herczeg and Edmunds (2000) and discussed below, interpretation of such results by mixing processes is complicated by understanding of end-member compositions and geochemical reactions.

The stable O and H isotope data are invariant with depth and show no effects of leakage. Stable O and H isotope data are commonly used to identify mixing between waters of either differing age or source (e.g., Muir and Coplen, 1981; Hendry and Schwartz, 1988; Thomas et al., 1996; Davisson et al., 1999). The use of stable O and H isotopes as groundwater tracers in western Tennessee probably is limited because flow paths to the Memphis aquifer are too short and the isotopic variations in precipitation in the region too small. The lack of an appreciable decrease in H and O isotopic values in water from near the base of the Memphis



Fig. 9. Conceptual diagram illustrating potential groundwater flow from Nonconnah Creek to the Memphis aquifer in the Sheahan well field. Arrows illustrate potential flow paths.

aquifer suggests that upward leakage from the underlying Fort Pillow aquifer, which is known to have Pleistocene-age water (Graham and Parks, 1986), is minimal.

Pumpage in the Sheahan well field varies cyclically through the year (Fig. 10); however, ³H activities and solutes that indicate leakage show variable patterns depending on the well. Well 87 shows the expected pattern of higher tritium and SO_4^{2-} following the high water-demand summer months and lower ³H and SO₄²⁻ following the low water-demand spring months (Fig. 10). Other solutes, for example Ca2+, show no consistent trend with time for a given well. Other wells, such well 55B, show variable behavior with regard to the solutes, but the ³H values (considering only the values from ³H enrichment) always decrease following the low waterdemand months (Table 2). The ³H results suggest that the quantity of leakage varies according to pumping stress. The variable behavior of the solutes is interpreted to reflect geochemical and hydrogeologic processes that complicate mixing between the shallow and Memphis aquifer waters.

5.2. Timing of leakage

Tritium and ³He are useful groundwater age tracers for estimating the timing of modern recharge into aquifer systems (Solomon et al., 1992; Eckwurzel et al., 1994; Solomon and Cook, 2000). Previous studies have established that the deep groundwater in the Memphis aquifer is pre-modern (Graham and Parks, 1986; Parks et al., 1995) and was recharged perhaps hundreds or thousands of years ago. Assuming that mixing in the Memphis aquifer involves only two components (modern leakage and pre-modern Memphis aquifer water) the apparent age reflects only the timing of the leakage. The pre-modern water contributes no ³H and minimal tritiogenic ³He and, as discussed above, little or no crustal ³He. Thus, when young (tritiated) water mixes with older water, both ³H and tritiogenic ³He are diluted to the same extent. As a result, the apparent ³H/³He age is that of the young component. The apparent ages are interpreted to represent weighted average timing of recharge that leaked into the Memphis aquifer.

MLGW wells 87 and 88 yielded apparent ages of 19 and 16 a (Table 3), respectively, and represent two wells with chemical indications of a significant leakage component. MLGW well 78 yielded an apparent age of 28 a; however, the ³H content was low (0.29 TU) and sum (³H + tritiogenic ³He) is only slightly above background. This may be accounted for if only a small proportion of leakage affected this well. MLGW wells 55 and 80 yielded apparent ages that approach the limit of the ³H/³He dating method and appear little affected by leakage.

5.3. Geochemical reactions and mixing associated with leakage

The evidence discussed above suggests that modern water is leaking from the shallow aquifer through the upper Claiborne confining unit and mixing with deeper "native" Memphis aquifer water. Geochemical reactions along the flow path from the shallow aquifer to the Memphis aquifer are also possible. Geochemical reac-



Fig. 10. Time series plots showing changes in pumpage, ³H activity, and concentrations of Cl⁻, SO_4^{2-} , and Ca in wells (A) MLGW 55 and (B) MLGW 87 from April 1999 to December 2000. Pumpage is from Memphis Light, Gas, and Water records and is plotted as millions of gallons×0.01. Tritium activity is in ³H units and concentrations are in mg/l. Pumpage data were not collected in June 2000.

tion modeling using NETPATH (Plummer et al., 1991) was implemented to assess the feasibility of various geochemical reactions and mixing proportions. Information required for NETPATH mixing and mass balance modeling includes 2 initial water compositions, final water compositions, and reacting phases along the flow path. The chemical data from the 5 wells analyzed for ${}^{3}\text{H}/{}^{3}\text{He}$ (fall 2000 sampling) were used as final water

compositions so that mixing results could be compared with recharge timing and inferred modern leakage (Table 4).

The initial Memphis aquifer water composition was chosen to be from fall 1999 sampling of MLGW 95 (Table 4). The top of the screened interval in this well is at 238 m below land surface. MLGW 95 extracts water from the lower part of the Memphis aquifer and consistently shows little influence, chemical or isotopic, of leakage. The initial shallow aquifer water is more problematic. Complete water analyses are not available for Sheahan monitoring wells screened in the shallow aquifer and were not collected prior to 1987. Furthermore, the monitoring wells in the shallow aquifer within the Sheahan well field are presently dry or nearly so. A series of monitoring wells were constructed and sampled by the U.S.G.S. in 1996 and 1997 through the National Water Quality Assessment Program. One of the wells (UR-13S) was placed in the floodplain of Nonconnah Creek approximately 6 km SE of Sheahan well field (Fig. 3). An analysis from the 1997 sampling of well 13S was used as the initial water composition from the shallow aquifer (Table 4). It is not clear whether this analysis is representative of the chemistry of the shallow aquifer water in the past, but it is similar in composition to other recent analyses from the shallow aquifer in the Nonconnah Creek basin (US Geological Survey WAT-STORE database).

Reactive mineral phases and chemical constituents vary among the different hydrogeologic units. The shallow aquifer contains substantial silt and sand, within which reactive dolomite, kaolinite, illite, smectite, vermiculite, and Fe hydroxide are present along with less reactive quartz and K feldspar (Spann, 1997). The mean cation exchange capacity (CEC) of the sand is 14 meq/ 100 g (Spann, 1997). The textural variability and mineralogical composition of the upper Claiborne confining unit and Memphis aquifer are not well established at present. In a limited sampling of these units, Spann (1997) indicated a clay fraction dominated by kaolinite with minor illite and smectite. The mean CEC is 13.4 meq/100 g. Other field observations and recent drilling indicate substantial heterogeneity in the upper Claiborne confining unit in the Nonconnah Creek basin and

Table 4

Chemical and ³H data from fall 2000 sampling of production wells in the Sheahan well field and additional data used for NETPATH modeling

Well ^a	Date	Depth ^b (m)	рН	Eh (mV)	<i>T</i> (°C)	Cond ^c (µS/cm)	Na ⁺ (mg/l)	K ⁺ (mg/l)	Mg ²⁺ (mg/l)
Initial									
UR-13S	5/14/1997	7.6	6.3	nd ^d	17.6	287	34	1.3	7.6
95	9/30/1999	237	6.59	204	19.6	117	4.6	0.9	3.9
Final									
55	10/21/2000	166	5.59	234	18.2	102	5.9	0.5	3.6
78	10/21/2000	125	5.38	210	17.9	105	8.8	0.6	3.1
80	10/20/2000	127	5.52	42	17.4	109	9.8	0.6	3
87	10/20/2000	95	5.49	174	17.1	129	13	0.7	3.2
88	10/21/2000	103	5.4	339	17.7	151	13	0.8	4.6
Well	Ca ²⁺	Fe ²⁺	Cl-	SO_4^{2-}	NO_3^-	HCO_{3}^{-}	Charge	O ₂	³ H
	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	Balance	(µg/l)	(TU)
Initial									
UR-13S	14	1.4	11	31	< 0.05	102	+4.7	0.2	7.5
95	10.2	0.26	1.3	2.8	0.2	68	-6.8	2.6 ^e	< 0.4
Final									
55	8.1	0.23	2.6	4	0.2	46	+3.8	0.39	0.07
78	6.4	0.62	3.4	5.5	0.2	44	+4.2	0.32	0.29
80	6.3	0.48	4.2	5.9	0.1	43	+4.5	0.46	0.08
87	6.6	0.61	6	9.1	0.6	40	+7.8	0.66	2.3
88	9.1	0.18	7.4	12	0.5	50	+5.4	0.37	1.3

^a All MLGW wells except UR-13S.

^b Depth of top of screened interval.

^c Specific conductance.

^d Not determined.

^e Gas bubbles observed during sampling.

Sheahan well field including: chemically reduced (gley and olive colors), lignite-bearing, locally pyritic, deltaic sands, silts, and clays, oxidized (light gray with red Feoxide bands), kaolinitic clay and clayey sand, and clayey sand paleosols. The reactive mineral phases in the upper Claiborne confining unit and Memphis aquifer are considered to be the clay minerals, pyrite, and Fe hydroxides.

The potential reactants along the flow path used in NETPATH modeling include calcite, dolomite, goethite, Ca-Mg-Na exchange on clay minerals, Na-montmorillinite, CO₂ gas, and pyrite. Dolomite and pyrite were only allowed to dissolve because these phases are likely to be depositional in origin. Goethite is used to approximate Fe oxyhydroxide and hydroxide (Fig. 8) that are commonly observed as oxidation products of pyrite and reduced dissolved Fe. Mass was balanced using C, S, Ca, Mg, Cl-, Na, and Fe. Redox values from the Pt electrode measurements were used because these data are more consistent with the dissolved Fe concentrations. Chloride was balanced using the following methods: (1) Na and Cl⁻ were introduced using halite as a reactive phase to simulate solutes from brackish water potentially trapped in the clays and silts of the confining unit or (2) Cl⁻ was used as a mixing parameter.

The most reasonable model results are presented in Table 5. The best models are judged based on geochemical criteria, including those that require minimal precipitation of kinetically slow precipitating phases, such as Na-montmorillinite, and do not violate constraints, such as allowing pyrite precipitation. The models that balance Cl- with halite achieved the best results in that the mixing fraction of shallow aquifer water correlates with other indicators of leakage such as ³H and SO_4^{2-} . The models that balance Cl⁻ by mixing fraction yielded erratic results and did not balance Clviolating one or more constraints (typically, pyrite precipitation was required). All of the most reasonable models required substantial dissolution of CO₂ gas and precipitation of a small quantity of calcite. The increase in P_{CO₂} could be accommodated by dissolution of soilderived CO₂, oxidation of organic material in the alluvium, and oxidation of disseminated lignite in the confining unit and Memphis aquifer. The precipitation of calcite is more problematic and may reflect the complex ion exchange changes that might occur along a flow path involving marine and terrestrial deposits (e.g., Appelo, 1994), but which are not possible to model using NETPATH. Most of the models require precipitation of varying quantities of goethite and Namontmorillinite. Although precipitation of goethite (or ferrihydrite) is common in soils and near-surface sediments, the precipitation of clay minerals is less well documented. Again, the Na-montmorillinite may reflect more complex exchange phenomena than can be modeled

with NETPATH. It is also possible that Al–Si-rich clay precursors, such as those discussed recently by Penn et al. (2001) in Atlantic coastal plain sediments, could precipitate along the flow path.

The apparent ${}^{3}H/{}^{3}He$ dates and the mixing fractions are plotted in Fig. 11. The model results that use halite to balance Cl⁻ show the best relationship to the ${}^{3}H/{}^{3}He$ dates, where mixing fractions of shallow aquifer water decrease with increasing apparent age. The model results that use Cl⁻ as a mixing parameter show a more erratic relationship to apparent age. Assuming that the models that use halite to balance Cl⁻ are a more realistic approximation to actual processes, the mixing fractions of shallow aquifer water being pumped from the Memphis aquifer in the Sheahan well field range from 6 to 32%. These model results suggest that all production wells in the well field may have at least a small component of shallow aquifer water contributing to the pumped water mass.

5.4. Implications for future water development

Using stream flow data from a section of Nonconnah Creek just south of the Sheahan well field, Nyman (1965) estimated losses due to underflow of $0.17 \text{ m}^3/\text{min}$, which is equivalent to approximately 25 m³/day. Using assumptions regarding leakage influence and pumping rates, the degree to which this stream loss accounts for leakage into the Memphis aquifer can be estimated. Assume that the 10 wells screened above 130 m depth, which consistently show ³H concentration above detection limits, are contributing to the leakage. Each well pumps at approximately 5.5×10^3 m³/day and is pumping approximately 25% of the time. The proportion of shallow aquifer water contributing to the pumpage varies for each well, but can be assumed to be approximately 15%. Using these assumptions, 2.0×10^3 m³/day of stream loss would be required to account for the amount of leakage estimated from the shallow aquifer. This flux is approximately 8.3 times greater than the stream loss that Nyman reported. Considering that the shallow aquifer is presently dry across much of the Sheahan well field, drainage of water from the shallow aquifer and upper Claiborne confining unit has undoubtedly contributed to the volume of leakage. However, the long-term source of leakage must largely come from Nonconnah Creek. Further work is required to more thoroughly evaluate total stream loss from Nonconnah Creek, but these initial studies clarify the need to examine hydraulic connections to nearby surface water in assessment of the groundwater resources in the Sheahan well field.

Identification of hydraulic connections between surface-water and groundwater, such as those inferred near the Sheahan well field, needs to be considered for future urban development in order to ensure protection of groundwater resources. The isotopic, che-

Table 5 Results of NETPATH modeling

Final well	NaCl used for Cl balance (water or phase) ^a	Mixing fraction (by mass) or mass ^b (mmol/kg H ₂ O)	Cl determines mixing fraction (water or phase)	Mixing fraction (by mass) or mass (mmol/kg H ₂ O)
55	UR-13S	0.043	UR-13S	0.134
	MLGW 95	0.957	MLGW 95	0.866
	Calcite	-0.038	Calcite	-0.032
	NaCl	0.025	Goethite	0.010
	Goethite	-0.002	Pyrite	-0.013 ^c
	Exchange	0.038	Exchange	0.065
	Na-mont. ^d	-0.123	Na-mont.	-0.204
	CO ₂	3.534	CO ₂	3.359
78	UR-13S	0.063	UR-13S	0.216
	MLGW 95	0.937	MLGW 95	0.784
	Calcite	-0.058	Calcite	-0.049
	NaCl	0.042	Goethite	0.019
	Pyrite	0.005	Pyrite	-0.018 ^c
	Exchange	0.085	Exchange	0.132
	Na-mont.	-0.079	Na-mont.	-0.210
	CO ₂	6.061	CO_2	5.766
80	UR-13S	0.094	UR-13S	0.299
	MLGW 95	0.906	MLGW 95	0.701
	Calcite	-0.055	Calcite	-0.043
	NaCl	0.056	Goethite	0.026
	Pyrite	0.002	Pyrite	-0.028
	Exchange	0.103	Exchange	0.165
	Na-mont.	-0.092	Na-mont.	-0.268
	CO_2	3.931	CO_2	3.537
87	UR-13S	0.223	UR-13S	0.134
	MLGW 95	0.777	MLGW 95	0.866
	Calcite	-0.048	Calcite	0.032
	NaCl	0.071	Goethite	0.010
	Dolomite	0.014	Pyrite	-0.013 ^c
	Goethite	0.002	Exchange	0.065
	Exchange	0.153	Na-mont.	-0.204
	CO_2	3.603	CO_2	3.359
88	UR-13S	0.323	UR-13S	0.629
	MLGW 95	0.677	MLGW 95	0.371
	Calcite	-0.038	Calcite	-0.020
	NaCl	0.084	Dolomite	0.033
	Dolomite	0.054	Goethite	0.031
	Goethite	-0.008	Pyrite	-0.045°
	Exchange	0.149	Exchange	0.199
	CO_2	6.118	CO ₂	5.574

^a UR-13S and MLGW 95 are the initial waters, the remainder are phases dissolved in or precipitated from the final water.

^b Numbers for UR-13S and MLGW-95 are mixing fractions. For the phases, positive number indicates phase is dissolved in water and negative numbers indicate phase precipitates from water.

^c Dissolution only constraint for pyrite is violated.

^d Na-montmorillinite.

mical, and geologic data presented herein indicate that shallow groundwater has leaked in the past or is currently leaking from the shallow aquifer to the semi-confined Memphis aquifer near the Sheahan well field. Continued leakage requires a constant source of shallow groundwater, presumably derived from infiltration of Nonconnah Creek water (Fig. 9), as discussed above. At present, the water-quality effects of the



Fig. 11. Plot of ${}^{3}H/{}^{3}He$ apparent age versus proportion of shallow aquifer water contributing to water in 5 production wells in the Sheahan well field. Apparent age data are from Table 3 and mixing proportions are from Table 5. The two sets of symbols reflect differences in mixing model assumptions (see text for details).

leakage are minor and do not substantially diminish the potability of the Memphis aquifer water. Continued urban growth in the southeastern part of Shelby County may, however, impact the water quality of Nonconnah Creek and, in turn, the Memphis aquifer more than at present. The results of the present study indicate an approximately 15-20 a lag time between infiltration and appearance in municipal water supplies. The travel time from subsurface contamination sources may be significantly less than that indicated by groundwater dating methods. Identification of complex flow paths such as that suggested between Nonconnah Creek and the Memphis aguifer in the Sheahan well field are not currently considered in wellhead protection zone delineation. The importance of groundwater movement along such "fast paths" between unconfined and semi-confined aquifer resources may be underestimated in other municipalities that use semi-confined aquifer water resources.

6. Conclusions

Tritium, ³He, and major solute data are used to identify the extent, timing, and water-quality effects of leakage on water in the Memphis aquifer pumped from the Sheahan well field, Memphis, Tennessee. The results from individual wells in the Sheahan well field indicate mixtures of two end-member types of water in the Memphis aquifer: a Na–SO₄–Cl-rich end member derived from leakage and Ca–Mg–HCO₃-rich end member reflecting "native" water in the Memphis aqui-

fer. The Na–SO₄–Cl-rich water tends to have the highest ³H values (as much as 2.8 TU) and is pumped from the shallower wells (typically 85–130 m depth), whereas, the Ca–Mg–HCO₃-rich water tends to have lower ³H values (generally, less than 0.8 TU) and is pumped from the deeper wells. The major solute chemistry does not vary systematically with seasonal pumping changes; however, ³H activity decreases slightly with decreased pumping. Stable O and H isotopes do not vary with depth or season and do not provide useful groundwater tracers in the Memphis aquifer system.

The timing of modern recharge to the semi-confined Memphis aquifer is estimated using ${}^{3}H/{}^{3}He$ dating. Of the 5 wells tested, only two yielded substantial ${}^{3}H$ and ${}^{3}He$. These wells have the shallowest screened intervals and gave apparent ages of 16 and 19 a. The deeper wells yielded either problematic results or ages of approximately 50 a, the limit of detection for the ${}^{3}H/{}^{3}He$ method. Because the "native" Memphis aquifer water was recharged prior to 50 a ago, the apparent ages obtained from water in the shallow wells reflect the timing of modern recharge or leakage.

Based on geologic data and hydrologic boundary conditions affecting the Sheahan well field, leakage is inferred to flow from a nearby stream, Nonconnah Creek, through the shallow aquifer and conductive parts of the upper Claiborne confining unit to the Memphis aquifer. Geochemical reactions and mixing along this flow path were modeled using the NETPATH computer code. The most reasonable model results require addition of Na and Cl⁻, interpreted to diffuse from marine or brackish water trapped in silts and clays in the confining unit. Dissolution of CO_2 gas, precipitation of calcite, variable precipitation of goethite and Na-montmorillinite, dissolution of dolomite and pyrite, and Ca-Mg-Na exchange are predicted to occur along the flow path. Mixing fractions of shallow aquifer water range from 6 to 32%. The mixing fractions are inversely correlated to apparent ${}^{3}H/{}^{3}He$ ages.

The combined application of ³H analysis, ³H/³He dating, and geochemical modeling results provides an effective method for assessing the extent and timing of modern leakage to the Memphis aquifer in the Sheahan well field. This combined approach is likely to be useful for assessing modern leakage to other semi-confined aquifers that are used for municipal, industrial, or agricultural water supplies, especially for identification of fast groundwater flow paths. The results also emphasize the need to consider potential hydraulic connections to surface water as part of groundwater resource protection plans for semi-confined aquifers.

Acknowledgements

This research was funded by grants from the Shelby County Health Department and Tennessee Water Resources Research Center, and contributions from the Ground Water Institute. Field, laboratory, and computational assistance was provided by Alexa George, Stacey Hudgins, Stephanie Ivey, Merrie Salyers, Amanda Semko, and Brian Waldron. Many thanks to Norbert Thonnard for assistance with the design of the gas sampling fittings for the production wells. Jerry Anderson assisted with student support and grant administration. Discussions with Jack Carmichael and Mike Bradley of the U.S.G.S. Water Resources Division in Nashville assisted interpretations of the data. We appreciate the assistance from Memphis Light Gas and Water personnel for well access and cooperation with sampling schedules. The manuscript was improved by thorough reviews by June Mirecki and Carl Thodal

References

- Appelo, C.A.J., 1994. Cation and proton exchange, pH variations, and carbonate reactions in a freshening aquifer. Water Resour. Res. 30, 2793–2805.
- Back, W., 1986. Role of aquitards in hydrogeochemical systems: a synopsis. Appl. Geochem. 1, 427–437.
- Bayer, R., Schlosser, P., Bonisch, G., Rupp, H., Zaucker, F., Zimmek, G., 1989. Performance and blank components of a mass spectrometric system for routine measurements of helium isotopes and tritium by the ³He in-growth method. Sitzungsberichte der Heidelberger Akademie der Wissenschaften, Mathematisch-naturwissenschaftliche Klasse 5, 241–279.

- Bethke, C.M., 1998. The Geochemist's Workbench, Release 3.0. University of Illinois, Champaign, IL.
- Bradley, M.W., 1991. Ground-Water Hydrology and the Effects of Vertical Leakage on Ground-Water Quality Near the Shelby County Landfill, Memphis, Tennessee. US Geol. Surv. Water Resour. Invest. Rep. 90-4075.
- Brahana, J.V., Broshears, R.E., 2001. Hydrogeology and Ground-Water Flow in the Memphis and Fort Pillow Aquifers in the Memphis Area, Tennessee. US Geol. Surv. Water Resour. Invest. 89-4131.
- Bredehoeft, J.D., Neuzil, C.E., Milly, P.C.D., 1983. Regional flow in the Dakota aquifer: a study of the role of confining layers. US Geol. Surv. Water-Supply Pap. 2237.
- Carmichael, J.K., Parks, W.S., Kingsbury, J.A., Ladd, D.E., 1997. Hydrogeology and ground-water quality at Naval Support Activity Memphis, Millington, Tennessee. US Geol. Surv. Water Resour. Invest. 97–4158.
- Chapelle, F.H., 1993. Ground-water Microbiology and Geochemistry. New York, Wiley.
- Clarke, W.B., Jenkins, W.J., Top, Z., 1976. Determination of tritium by mass spectrometric measurements of ³He. Int. J. Appl. Radiat. Isot. 27, 515–522.
- Criner, J.H., Armstrong, C.A., 1958. Ground-water Supply of the Memphis Area. US Geol. Surv. Circ., p. 408.
- Criner, J.H., Parks, W.S., 1976. Historic Water-Level Changes and Pumpage from the Principal Aquifers of the Memphis Area, Tennessee: 1886–1975. US Geol. Surv. Water Resour. Invest. 76–67.
- Criner, J.H., Sun, P.-C.P., Nyman, D.J., 1964. Hydrology of the Aquifer Systems in the Memphis Area, Tennessee. US Geol. Surv. Water-Supply Pap. 1779-O.
- Davisson, M.L., Smith, D.K., Kenneally, J., Rose, T.P., 1999. Isotope hydrology of southern Nevada groundwater: stable isotopes and radiocarbon. Water Resour. Res. 35, 279–294.
- Eckwurzel, B., Schlosser, P., Smethie, W.M., Plummer, L.N., Busenberg, E., Michel, R.L., Weppernig, R., Stute, M., 1994.
 Dating of shallow groundwater: comparison of the transient tracers ³H/³He, chlorofluorocarbons, and ⁸⁵Kr. Water Resour. Res. 30, 1693–1708.
- Fabryka-Martin, J., Whittemore, D.O., Davis, S.N., Kubik, P.W., Sharma, P., 1991. Geochemistry of halogens in the Milk River aquifer, Alberta, Canada. Appl. Geochem. 6, 447–464.
- Fortin, G., van der Kamp, G., Cherry, J.A., 1991. Hydrogeology and hydrochemistry of an aquifer-aquitard system within glacial deposits, Saskatchewan, Canada. J. Hydrol. 126, 265–292.
- Graham, D.D., Parks, W.S., 1986. Potential for Leakage among Principal Aquifers in the Memphis Area, Tennessee. US Geol. Surv. Water-Resour. Invest. Rep., 85-4295.
- Grubb, H.F., 1998, Summary of Hydrology of the Regional Aquifer Systems, Gulf Coastal Plain, South-Central United States. US Geol. Surv. Prof. Pap. 1416-A.
- Hendry, M.J., Schwartz, F.W., 1991. Hydrogeology and hydrochemistry of the Milk River aquifer system, Alberta Canada: a review. Appl. Geochem. 6, 369–380.
- Hendry, M.J., Schwartz, F.W., 1988. An alternative view on the origin of chemical and isotopic patterns in groundwater from the Milk River aquifer, Canada. Water Resour. Res. 24, 1747–1763.
- Herczeg, A.L., Edmunds, W.M., 2000. Inorganic ions as tracers. In: Cook, P.G., Herczeg, A.L. (Eds.), Environmental

Tracers in Subsurface Hydrology. Kluwer, Boston, pp. 31–37.

- Horita, J., Ueda, A., Mizukami, K., Takatori, I., 1989. Automatic D and ¹⁸O analyses of multi-water samples using H₂and CO₂-water equilibration methods with a common equilibration set-up. Appl. Radiat. Isot. 40, 801–805.
- Hosman, R.L., Long, A.T., Lambert, T.W., Jeffery, H.G., 1968. Tertiary Aquifers in the Mississippi Embayment. US Geol. Surv. Prof. Pap. 448-D.
- Hutson, S.S., 1999. Public Water-Supply Systems and Associated Water Use in Tennessee, 1995. US Geol. Surv. Water Resour. Invest. 99-4052.
- Ivey, S.S., 1997. The Use of Barium as a Natural Tracer for Leaky Aquifers. MS thesis, Univ. Memphis, Memphis, TN.
- Kingsbury, J.A., 1996. Altitude of the Potentiometric Surfaces, September 1995, and Historical Water-Level Changes In The Memphis and Fort Pillow Aquifers in the Memphis Area, Tennessee. US Geol. Surv. Water Resour. Invest. 96-4278.
- Kingsbury, J.A., Parks, W.S., 1993. Hydrogeology of the Principal Aquifers and Relation of Faults to Interaquifer Leakage in the Memphis Area, Tennessee. US Geol. Surv. Water-Resour. Invest. Rep. 93-4075.
- Krinitsky, E.L., 1949. Geological Investigation of Gravel Deposits in the Lower Mississippi Valley and Adjacent Uplands. US Army Corps of Engineers Waterways Experiment Station Technical Memorandum 3-272.
- Larsen, D., Gentry, R.W., Waldron, B., Ivey, S., Hudgins, S., Salyers, M., Jones, A.J., 2001. Variations in water quality and tritium in the Sheahan and Morton well fields, Memphis, Tennessee, USA. In: Proc. 11th Ann. Tennessee Water Resour. Symp. Oo, 1A1–1A7.
- Mazari, M., Mackay, D.M., 1993. Potential for groundwater contamination in Mexico City. Environ. Sci. Technol. 27, 794–802.
- McMahon, P.B., 2001. Aquifer/aquitard interfaces: mixing zones that enhance biogeochemical reactions. Hydrogeology Journal, Online First DOI 10.1007/s100400000109.
- Mirecki, J.E., Parks, W.S., 1994. Leachate geochemistry at a municipal landfill, Memphis, Tennessee. Ground Water 32, 390–398.
- Moore, G.K., Brown, D.L., 1969. Stratigraphy of the Fort Pillow test well, Lauderdale County, Tennessee. Tennessee Division of Geology, Report of Investigations 26.
- Muir, K.S., Coplen, T.B., 1981. Tracing Ground-Water Movement By Using The Stable Isotopes Of Oxygen And Hydrogen, Upper Penitencia Creek Alluvial Fan, Santa Clara Valley, California. US Geol. Surv. Water-Supply Pap. 2075.
- Nyman, D.J., 1965. Predicted Hydrologic Effects of Pumping from The Lichterman Well Field in the Memphis Area, Tennessee. US Geol. Surv. Water-Supply Pap. 1819-B.
- Parks, W.S., 1990. Hydrogeology And Preliminary Assessment Of The Potential For Contamination Of The Memphis Aquifer In The Memphis Area, Tennessee. US Geol. Surv. Water-Resour. Invest. Rep. 90-4092.

- Parks, W.S., Mirecki, J.E., 1992. Hydrogeology, Ground-Water Quality and Potential for Water-Supply Contamination Near the Shelby County Landfill in Memphis, Tennessee. US Geol. Survey Water-Resour. Invest. Rep. 91-4173.
- Parks, W.S., Mirecki, J.E., Kingsbury, J.A., 1995. Hydrogeology, Ground-water Quality, and Source of Ground Water Causing Water-Quality Changes in the Davis Well Field at Memphis, Tennessee. US Geol. Surv. Water-Resour. Invest. Rep. 94-4212.
- Penn, R.L., Zhu, C., Xu, H., Veblen, D.R., 2001. Iron oxide coatings on sand grains from the Atlantic coastal plain: highresolution transmission electron microscopy characterization. Geol. 29, 843–846.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1991. An Interactive Code (NETPATH) for Modeling net Geochemical Reactions Along a Flow Path. US Geol. Surv. Water-Resour. Invest. Rep. 91-4078.
- Pucci, A.A., Ehlke, T.A., Owens, J.P., 1992. Confining unit effects on water quality in the New Jersey coastal plain. Ground Water 30, 415–427.
- Robinson, J.L., Carmichael, J.K., Halford, K.J., Ladd, D.E., 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. US Geol. Surv. Water-Resour. Invest. Rep. 97-4228.
- Roether, W., 1970. Water-CO₂ exchange set-up for the routine ¹⁸Oxygen assay of natural waters. Int. J. Appl. Radiat. Isot. 21, 379–387.
- Rudolph, D.L., Cherry, J.A., Farvolden, R.N., 1991. Groundwater flow and solute transport in fractured lacustrine clay near Mexico City. Water Resour. Res. 27, 2187–2201.
- Saucier, R.T., 1987. Geomorphological Interpretation of Late Quaternary in Western Tennessee and Their Regional Tectonic Implications. US Geol. Surv. Prof. Pap. 1336-A.
- Solomon, D.K., Cook, P.G., 2000. ³H and ³He. In: Cook, P.G., Herczeg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology. Kluwer, Boston, pp. 397–424.
- Solomon, D.K., Poreda, R.J., Schiff, S.L., Cherry, J.A., 1992. Tritium and helium-3 as groundwater age tracers in the Borden aquifer. Water Resour. Res. 28, 741–756.
- Spann, E.W., 1997. Selected Sediment and Geochemical Properties of Quaternary and Tertiary Sediments from Five Boreholes in Shelby County, Tennessee: Implications for Contaminant Retardation Potential. MS thesis, Univ. Memphis, Memphis, TN.
- Strom, E.W., 1997. Hydrologic Interpretations Of Natural-Gamma Logs for 31 Shallow Wells in the Memphis, Tennessee, area. US Geol. Surv. Water-Resour. Invest. Rep. 97-4181.
- Thomas, J.M., Welch, A.H., Dettinger, M.D., 1996. Geochemistry and Isotope Hydrology of Representative Aquifers in the Great Basin Region of Nevada, Utah, and Adjacent States. US Geol. Surv. Prof. Pap. 1409-C.
- Wicks, C.M., Herman, J.S., 1994. The effect of a confining unit on the geochemical evolution of ground water in the Upper Floridan aquifer system. J. Hydrol. 153, 139–155.