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Stream Loss Contributions to a Municipal Water Supply Aquifer in Memphis, Tennessee

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ABSTRACT

Leakage of water into the semi-confined Memphis aquifer near the Sheahan well field in Memphis, Tennessee, has been suggested by many studies extending back to the 1960s. A leakage pathway from Nonconnah Creek to the Sheahan well field was investigated over a 1-year period using multiple approaches: (1) stream discharge data, (2) hydraulic head data, (3) geochemical and environmental tracer $(^{3}H/^{3}He$ and chlorofluorocarbon) studies, and (4) geochemical modeling. The stream loss data strongly support the conclusion that losses from the creek contribute at least $2,600 \text{ m}^3$ /d to the shallow aquifer, and hydraulic head data consistently indicate the majority of this infiltrated surface water flows within the shallow aquifer toward the Sheahan well field. Tritium-³He data from shallow aquifer monitoring wells within the Sheahan well field are composed of modern water with ages that generally increase with distance from the creek toward the well field. The leakage pathway from the creek to the well field is interpreted to involve seepage of creek waters into the shallow aquifer, mixing with other water sources and chemical reactions as the infiltrated waters flow in the shallow aquifer along a paleovalley toward the Sheahan well field, as well as leakage from the shallow to the Memphis aquifer through a hydrologic window in the upper Claiborne confining unit. The results of this work emphasize the utility of multiple investigative approaches in studies of groundwater flow to well fields, but they

also illustrate the complexity of groundwater flow and groundwater vulnerability in a stressed water-supply aquifer system.

INTRODUCTION

Groundwater resources in semi-confined aquifer systems are vulnerable to water quality problems and contamination from infiltration of polluted surface and soil waters. These problems can be exacerbated in urban areas where pronounced downward vertical head gradients from groundwater pumping facilitate deep infiltration of urban runoff or contamination from waste sites. A key problem in these settings is determining the hydrologic pathways between water sources and well fields, especially where complex subsurface geology generally limits hydrologic communication between shallow and underlying semiconfined aquifers.

In this contribution, the results of a multifaceted approach are presented to test a hypothesized surface water source for leakage to a municipal well field in Memphis, Tennessee (Figure 1). Previous studies (Larsen et al., 2003a; Ivey et al., 2008) have shown as much as 30 percent modern water contributing to groundwater pumped in the Sheahan well field from the semi-confined Memphis aquifer, the municipal water source in much of western Tennessee. Studies (Larsen et al., 2003a; Gentry et al., 2005) of multiple tracers show that several geochemical reactions, especially oxidation–reduction reactions, take place during the recharge process. Although Ivey et al. (2008) demonstrate a leakage location into the Memphis aquifer proximal to the Sheahan well field, the overlying shallow aquifer receives little direct recharge and is almost completely unsaturated,

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Figure 1. Study area in Memphis, Tennessee. (A) Map of southwestern Tennessee showing Memphis and surrounding municipalities, potentiometric surface for the Memphis aquifer (meters above sea level, asl), and the location of the Memphis Light Gas and Water (MLGW) Sheahan well field. Also shown are windows through the upper Claiborne confining unit, as mapped by Parks (1990). (B) Map of the Sheahan well field and nearby reach of Nonconnah Creek. Also shown are production wells in the Sheahan well field as well as shallow aquifer wells and discharge sites along Nonconnah Creek investigated in the current study. In addition, part of the 2005 water table map for the shallow aquifer in Shelby County (from Narsimha [2006]) is shown.

indicating a more distant water source. The closest perennial surface water source to the well field is Nonconnah Creek, which flows east to west approximately 4 km south of the Sheahan Pumping Station. Discharge data for Nonconnah Creek, in addition to water level, water chemistry, and tracer data from monitoring wells screened in the shallow aquifer near the Sheahan well field and Nonconnah Creek, are presented to test the hypothesis that water lost from Nonconnah Creek flows through the shallow aquifer and enters the Memphis aquifer through a hydrogeologic window in the upper Claiborne confining unit. The results present important implications for investigative approaches to complex groundwater pathways as well as consideration of wellhead protection mapping and vulnerability assessment for municipal well fields.

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. 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. Pleistocene and Pliocene fluvial-terrace deposits, 0– 20 m thick, unconformably overlie the mid-Tertiary units (Krinitzsky, 1949; Saucier, 1987; and Van Arsdale et al., 2008). Within Shelby County, the fluvial-terrace deposits are thickest along buried paleovalley features and modern tributary valleys (McClure, 1999). Excluding the present-day tributary valleys, 3–20 m of loess (windblown silt and clay) overlie the fluvial deposits and mantle the underlying 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 (Robinson et al., 1997) and behave as a leaky confining unit. The fluvial-terrace deposits and lower part of the alluvium are interpreted to form the shallow aquifer (Graham and Parks, 1986; McClure, 1999). The sand and gravel in the lower part of the alluvium have a range of hydraulic conductivity from 37 to 119 m/d (Ackerman, 1996). Typical hydraulic conductivities for the fluvial-terrace deposits are approximately 2–3 m/d (Robinson et al., 1997; Larsen, unpublished data). The Cockfield and Cook Mountain formations comprise the lower confining unit for the shallow aquifer and upper confining unit for the Memphis aquifer; this unit is termed the upper Claiborne confining unit. The clay beds in the confining unit range in thickness from 1 to 61 m and have hydraulic conductivities of 1.5 \times 10⁻⁶ to 3.0 \times 10⁻⁴ m/d (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 m²/d (Parks and Carmichael, 1990; Brahana and Broshears, 2001). 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.

Western Tennessee accounts for over 75 percent of the total daily usage of groundwater for the entire state, with approximately 712 million liters per day, on average, pumped from the Memphis aquifer for use in the city of Memphis and surrounding Shelby County (Figure 1) (Webbers, 2003). 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).

Early studies indicated 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 (Criner and Armstrong, 1958; Criner et al., 1964; Nyman, 1965; Criner and Parks, 1976; and Parks, 1990). Modeling efforts in the Memphis area (Brahana and Broshears, 2001) and regionally (Grubb, 1998) indicate that substantial vertical leakage is required to accommodate the groundwater withdrawals in southwestern Tennessee. Some clear examples of vertical recharge through windows in the upper Claiborne confining unit have been shown through detailed geological, radioactive tracer (14 C and 3 H), and geochemical studies (Graham and Parks, 1986; Parks, 1990; Bradley, 1991; Parks and Mirecki, 1992; Mirecki and Parks, 1994; Parks et al., 1995; Larsen et al., 2003a; and Koban et al., 2011).

Series	Group	Stratigraphic Unit	Hydro-Stratigraphic 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 m thick; generally less than 15.2 m 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 Cockfield and Cook Mountain formations	Upper Claiborne confining layer	$0 - 110$	Clay, silt, sand, and lignite. Because of similarities in lithology, the Jackson For- mation 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.
		Memphis Sand	Memphis aquifer	$152 - 271$	Sand, clay, and minor lignite. Thick body of sand with lenses of clay at various strati- graphic 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 interbeds of 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 interbeds of fine sand and lignite.

Table 1. Geologic and hydrostratigraphic units underlying Shelby County, Tennessee. Adapted from Graham and Parks (1986), with modifications from Waldron et al. (2007).

Climate and Stream Hydrology

The Memphis area has a humid, subtropical climate with four distinct seasons. Mean annual temperature is 16.8° C, with hot and humid summers and mild to chilly winters (NCDC, 2010). Mean annual precipitation is 138.8 cm, with precipitation distributed relatively evenly throughout the year, though August through October tends to be drier (NCDC, 2010). Soil moisture loss is greatest from May through September, with soil moisture recharge occurring primarily in October and November. Soil water excess exists from December through April, resulting in more extensive runoff and groundwater recharge (Flowers, 1964).

Nonconnah Creek is a westerly flowing tributary of the Mississippi River with headwaters in northern Mississippi and western Tennessee. The stream is inset within alluvium along most of its course, although locally it traverses directly over fluvialterrace deposits of the shallow aquifer. Nonconnah Creek was channelized along most of its course during the mid- to late 20th century. Discharge in Nonconnah Creek within the Memphis area is characteristically flashy, with a measured peak discharge of 414 m^3 /s during the past 41 years, but the discharge typically flows at less than $0.3 \text{ m}^3/\text{s}$ (USGS, 2010). Based on a 37-year record of daily median values, base flow is approximately $0.3 \text{ m}^3/\text{s}$ during December through May but decreases to

Figure 2. Conceptual model for leakage from the shallow aquifer to the Memphis aquifer near the Sheahan well field (modified from Larsen et al. [2003a]).

values approaching 0.03 m^3 /s during October and November (USGS, 2010).

Sheahan Well Field

The Memphis Light, Gas and Water (MLGW) Sheahan well field (Figure 1) has been in operation since 1932. The well field currently includes 24 production wells and a water treatment plant with a treatment capacity of 0.13 million m^3/d . The screen depth for production wells ranges from 91 to 236 m below the ground surface, with well screens generally 24–30.5 m in length.

Nyman (1965) suspected that leakage from the shallow aquifer was contributing water to the Memphis aquifer south of the Sheahan well field because of a loss of discharge in Nonconnah Creek. The creek was observed to be dry during fall months in this area, although upstream and downstream reaches still had measurable flow (Nyman, 1965). Tritium analysis of water from Sheahan wells revealed that a component of modern water was being pumped from the well field, specifically from two wells in the southern part of the Sheahan well field (Graham and Parks, 1986). Parks (1990) later identified a depression in the water table immediately west of the Sheahan well field, indicating that a window in the upper Claiborne confining unit in that area provides a conduit for vertical migration of waters from the shallow to the Memphis aquifer. More recently, Larsen et al. (2002, 2003a) showed a strong correlation between water quality and modern water (as indicated by tritium activity and ${}^{3}H/{}^{3}He$

apparent ages) in Sheahan production wells. Inverse geochemical modeling with the computer program NETPATH showed mixing of as much as 32 percent shallow aquifer water in water produced from the Memphis aquifer in the Sheahan well field. A conceptual model derived from these studies shows a potential path for how stream losses from Nonconnah Creek may contribute to leakage to the Memphis aquifer (Figure 2). Ivey et al. (2008) used an inverse age-distribution model along with estimated mixing ratios of shallow and Memphis aquifer water and measured ${}^{3}H/{}^{3}He$ data to simulate vertical recharge fluxes to the Memphis aquifer and derive a probable recharge window location. The recharge window location of Ivey et al. (2008) is partially coincident with the window location estimated by Parks (1990) and is consistent with a paucity of clay layers in the upper Claiborne confining unit within the central part of the well field (Larsen et al., 2002; Gentry et al., 2005). Although the above studies established the probable location for leakage into the aquifer near the Sheahan well field, no detailed hydrologic studies have been conducted of the probable recharge source, Nonconnah Creek.

METHODS

Groundwater Level Measurement and Water Quality

Sampling

Hydraulic head was measured in monitoring wells screened in the shallow aquifer in the Sheahan well

Figure 3. Scale diagram of well installation and stilling well at the NC cluster along Nonconnah Creek. (A) Well NC-3; (B) well NC-2; (C) well NC-1; (D) stilling well box; (E) well head and cover; (F) 10-cm–thick concrete pad; (G) concrete-filled post-holes; (H) aluminum well casing; (I) 5-cm–diameter vertical polyvinyl chloride (PVC) pipe; (J) concrete bags with penetrating rebar support for slope stability; (K) 5 cm–diameter horizontal PVC pipe with 1.5-m screened interval in creek; (L) 20-cm–diameter PVC pipe for screen protection; (M) limestone boulder pile on 20-cm protective pipe; and (N) water level in stilling well.

field and at a well cluster installed adjacent to Nonconnah Creek (NC cluster) (Figure 1). The NC cluster comprises three monitoring wells (NC-1, NC-2, and NC-3) with screened depths from 7.6 to 15.5 m (Figure 3) and a stilling well installed in Nonconnah Creek. Prior to construction of the stilling well at the NC cluster, the water level in Nonconnah Creek was measured from a surveyed location on the Getwell Road Bridge. Water levels in all wells were measured manually during seasonal sampling events. In addition, water levels were recorded hourly during part of 2004 and 2005 using Solinst 3001 water-level data loggers (Junior Edge LT F15 M5, accuracy \pm 5 mm) deployed in several of the monitoring wells in the shallow aquifer (NC-1, NC-3, K-75, and MLGW 99s) as well as monitoring wells in the Memphis (K-66) and Fort Pillow aquifers (K-45) (Figure 1). Impacts of barometric pressure on water levels were corrected using a barometric pressure data logger deployed at the NC cluster. Because the transducer record is incomplete, the hourly water levels and temperatures recorded using the Solinst transducers were used to confirm trends observed in the manual measurements.

Water samples for major solute chemistry were obtained quarterly from Nonconnah Creek during base flow conditions and selected monitoring wells (NC cluster, K-75, 96s, and 99s-Figure 1). Samples were taken after three well volumes were purged from the wells and after temperature, pH, specific conductance, and dissolved oxygen values had stabilized. Values for temperature, dissolved oxygen (D.O.), total dissolved solids (TDS), specific conductance $(S.C.), pH, NH₄⁺, and oxidation-reduction potential$ (Eh) were measured using calibrated probes installed in a YSI 6600° flow-through sonde. Dissolved oxygen and redox potential were also measured with external calibrated probes: D.O. with a $YSI^@$ 51B probe and redox with an Orion® 250A meter and platinum probe. Duplicate alkalinity titrations were performed in the field, along with duplicate spectroscopic analysis of Fe, D.O. (if $\lt 1.0$ mg/L), NO₃, and $NO₂⁻$ using a portable Hach® spectrophotometer DR2400. Sulfide was determined spectroscopically during the last sampling event.

One raw and one filtered water sample $(0.45 \text{-} \mu \text{m})$ filter) preserved with 1 mL of concentrated nitric acid $(HNO₃)$ were collected in 250-mL Nalgene bottles. Duplicate and field blank samples were taken during each sampling event. The samples were stored on ice and returned to the University of Memphis water quality lab for chemical analysis. The raw water samples were analyzed for dissolved anion $(Cl^-,$ NO_3^- , F^- , and SO_4^{2-}) concentrations using a Dionex[®] DX-120 ion chromatograph. Precision of SO_4^{2-} analyses was within 4 percent, but precision was within 17 percent for Cl^- , NO_3^- , and F^- . Accuracy was within 13 percent for all analytes within the concentration range of interest. The filtered and acidified water samples were analyzed for cation concentrations $(Mg^+, Ca^+, Na^+, K^+, Fe^+,$ and Mn⁺) within 6 months of sampling using a Varian 220 FS atomic absorption spectrometer. Analytical precision for analytes was within 10 percent, except for Fe^{2+} , which was within 15 percent.

Environmental Tracer Sampling

Environmental tracers (chlorofluorocarbons [CFC], 3 H $/{}^{3}$ He, and noble gases) were used to determine when groundwater obtained from the shallow wells was last exposed to the atmosphere. Tritium samples were obtained during the August 2004 sampling event in 1-L amber glass bottles and sent to the Dissolved Gas Laboratory at the University of Utah for tritium analysis using the helium in-growth method (Clarke et al., 1976). The practical detection limit for the helium in-growth method is 0.05 tritium units (TU) (Solomon and Cook, 2000). The percent error ranges from approximately ± 10 percent at 1 TU to ± 70 percent at the detection limit. Noble gas sampling, also conducted during the August 2004 event, used a diffusion sampler (two 3-cm–long copper tubes with a gas-permeable membrane connecting them) that was suspended for 1 week within the well screen interval, which had been previously purged. Upon retrieval, the diffusion sampler was immediately cold-sealed and packed in Nalgene bottles for shipment to the Dissolved Gas Laboratory. Total gas pressure was measured in the well water using a total gas probe following retrieval. Isotopic measurements were made using a Stanford Research SRS–Model RGA 300 quadrapole mass spectrometer (QMS) for $^{28}N_2$, ^{36}Ar , ^{40}Ar , ^{20}Ne , ^{22}Ne , ^{78}Kr , ${}^{84}\text{Kr}, {}^{86}\text{Kr}, {}^{126}\text{Xe}, {}^{129}\text{Xe}, {}^{131}\text{Xe}, {}^{132}\text{Xe}, {}^{134}\text{Xe}, \text{ and}$ 136Xe and a Mass Analyzers Products–Model 215-50 Magnetic Sector Mass Spectrometer (MSMS) for 3 He and 4 He. The precision of QMS is between 2 and 5 percent for the gases of interest, whereas precision for the MSMS is 1 percent.

Helium-3 dissolved in groundwater arises from four sources: atmospheric equilibration, ³H 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 ³He from fission of ⁶Li produced during U- and Th-series decay. The resulting ³He/⁴He ratio from such reactions is approximately 1×10^{-8} , which is two orders of magnitude less than that of the atmosphere (1.36 \times 10⁻⁶ at 10^oC). Relatively large amounts of ⁴He from shallow subsurface reactions must be present for this to be an important factor. Nonetheless, ³He from shallow subsurface reactions are accounted for using the ³He/⁴He ratio of terragenic (crustal-produced) helium and using neon to correct for atmospheric ⁴He contributions. Mantle helium has a ³He/⁴He ratio approximately 10 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 3 H $/{}^{3}$ He age of a groundwater sample is defined as

$$
t = \lambda^{-1} \times \ln(\,^{3} \text{He}_{t}/^{3} \text{H} + 1) \tag{1}
$$

where λ is the tritium decay constant, ³He_t is tritiogenic 3 He, and t is the age in years of the modern (<50 years old) component of the water. 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 percent of the age determination.

For CFC sampling the well was purged using 0.1 cm–diameter copper tubing until three well volumes had been extracted, and stable chemical and physical values were obtained using the YSI 6600 sonde. Outflow from the copper tubing was used to fill a 2- L glass beaker until full (approximately 5 minutes). Glass sampling bottles and foil-lined caps were placed in the beaker and allowed to be thoroughly rinsed by outflow water. The sampling bottles were

filled and capped under the water surface of the beaker. Four samples were obtained; each sample was examined to assure that no air bubbles were observed, sealed with electrical tape, and placed on ice upside down. The samples were immediately sent to the University of Utah Dissolved Gas Laboratory for analysis. Calculation of CFC ages used the observed CFC concentrations for CFC-11, CFC-12, and CFC-113; recharge temperatures obtained from the noble gas concentrations; recharge elevations approximated as that of a monitoring well; and a recharge salinity of 0%. Partial pressures of CFC compounds in groundwater are 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 (Plummer and Busenberg, 2000). Measured CFC values that were beyond reasonable values for equilibration with atmospheric CFC concentrations were considered contaminated and were excluded from age calculations. The precision of groundwater ages calculated from CFC data depends on the analytical errors (generally ± 3 percent), error in the estimated recharge temperature ($\pm 2^{\circ}C = 1$ to 3 years of age difference), and error due to residence time in the unsaturated zone (as much as 8–12 years for unsaturated zone thickness of 30 m) (Plummer and Busenberg, 2000).

Stream Gaging and Discharge: Measurements

Stream discharge in Nonconnah Creek was measured seasonally during the project year at three locations (Figure 1) with a Swoffer[®] current velocity meter and measuring tape; the float method was used during low-flow conditions at the Winchester Road site. A float measurement was also made in the concrete channel near the terminus of Johns Creek, the only significant tributary to Nonconnah between the U.S. Geological Survey (USGS) gage station at Winchester Road and the Getwell Road site. The float method is less accurate than the gaging method, but our experience indicates that differences between float and gaging measurements are generally less than 10 percent for small streams in well-defined channels.

Hydraulic Testing

Slug tests were performed on the three monitoring wells at the NC cluster as well as two other monitoring wells (MLGW 99s and K-75). The slug tests were completed in duplicate by rapidly filling the well bore with tap water and monitoring head change back to static conditions using both manual head

measurements and a water-level data logger (measurements made at 2-second intervals). Hydraulic conductivity was calculated using the Hvorslev or Bouwer and Rice methods, as appropriate based on well geometry. Hydraulic conductivity was also calculated by the Hazen method (Kasenow, 1997) from grain-size analysis of core materials obtained during drilling of the NC cluster boreholes. Grain-size analysis of the sediment was completed using a method modified from Gee and Bauder (1986).

Geochemical Modeling

Geochemical modeling was completed using PHREEQCi (Parkhurst and Appelo, 1999), which is 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. In the present application, input water compositions from Nonconnah Creek and wells are used to predict mixing and mineral transfer reactions occurring during flow through the shallow aquifer and into the Memphis aquifer.

RESULTS

Stream Hydrology

Discharge measurements were made at three locations along Nonconnah Creek during 2004– 2005 to assess stream flow loss or gain. USGS gage station data at the upstream location (Winchester Road) for the project area show typical baseflow conditions of 0.03 to 0.3 m³/s throughout most of the year, with lower discharge occurring during July and August. Figure 4 shows stream discharge measurements along the study reach. The discharge at Mt. Moriah Road is the sum of discharge from Nonconnah and Johns creeks. Discharge increases from Winchester Road to Mt. Moriah Road and then decreases from Mt. Moriah Road to Getwell Road. The average downstream loss for these three measurements is 0.03 m^3 /s, which equates to approximately 2,600 m³/d. Given that additional minor tributaries contribute flow between the Mt. Moriah Road and Getwell Road sites, the recorded losses represent a minimum.

Groundwater Hydrology

Hydraulic head measurements in the stilling well and adjacent monitoring wells at the NC cluster (Figure 3) decrease from surface water levels in Nonconnah Creek to increasing well screen depths

Figure 4. Line plot of discharge measurements at sites along Nonconnah Creek during 2004 and early 2005. The discharge at Mt. Moriah is the sum of that from Nonconnah and Johns creeks. Johns Creek is the only major tributary to enter Nonconnah Creek between Winchester Road and Getwell Road; however, many small tributaries exist along that reach.

(Figure 5). The values obtained from the stilling well and the Getwell Road Bridge were consistently more than 0.5 m higher than those in the monitoring wells, except during the high-water condition observed in November 2004. Furthermore, water levels observed in the monitoring wells decreased with successively deeper screen depths in all low-water measurements. During storm flow conditions (11/04/2004), the water levels in the monitoring wells increased over those observed during baseflow. However, the water levels decreased with screen depth, presumably as a result of instantaneous loading in the upper part of the aquifer and bank storage. The hydraulic data collected at the NC cluster indicate that a consistent downward gradient in the head exists between the surface and shallow groundwater.

North-south cross-sections of water level elevations collected in May 2004 and January 2005 are shown in Figure 6 along with the elevations of the land surface and base of the shallow aquifer (based on cuttings and drillers logs). The water level data illustrate a depression in the shallow aquifer centered on well 99s, which is roughly in the center of the well field. The magnitude of the depression did not vary significantly over the observational period, except in well 99s, which decreased by as much as 2 m during the fall but rebounded during the late spring. The base of the shallow aquifer rises abruptly to the north of well 99s to well OT51; however, because of lithologic heterogeneity in the underlying upper Claiborne confining unit (Larsen et al., 2002), it is possible that water in well OT51 is perched and not part of the local water table. The water table surface in the shallow aquifer is generally within 1 m above the base of the shallow aquifer (e.g., well 96s). However, well 99s was screened in the sandy upper part of the upper Claiborne confining unit at this site because no water was present in the shallow aquifer (Gentry et al., 2005); thus, in this well the water table is substantially below the base of the shallow aquifer. Given that the shallow aquifer has as much as 8 m of saturation at the NC cluster, a pronounced lateral gradient exists from the Nonconnah Creek to the Sheahan well field area in the shallow aquifer.

A regional water table map in Shelby County was constructed from water level measurements made primarily in the shallow aquifer in 2005 (Narsimha, 2006). Figure 1B shows part of the water table map in the Sheahan well field illustrating the pronounced

Figure 5. Water levels (in meters above sea level) measured in the NC cluster and from a survey point on the Getwell Road Bridge along Nonconnah Creek during 2004 and early 2005.

Figure 6. Water levels (in meters above sea level) measured in wells screened in the shallow aquifer and upper Claiborne confining unit in the Sheahan well field during May 2004 and January 2005. The base of the shallow aquifer and land surface profiles from well log data are also plotted. The anomalously high water level in well OT51 is thought to be due to perched water in the shallow aquifer.

anomalous depression in the water table in the vicinity of the well field. In Figure 7 the water table contours are overlain on a structure contour map of the top of the upper Claiborne confining unit (data from Stevens [2007]). Not all wells monitored during the 2004–2005 Nonconnah Creek study were utilized for the 2005 regional water table mapping; however, the overall trend of the water table depression in the Sheahan well field is the same. Furthermore, few monitoring wells exist immediately outside the Sheahan well field; thus, the contour expression of the water table depression is, in part, elongated as a result of the limited well control but also as the result of a paleovalley incised into the underlying upper Claiborne confining unit (McClure, 1999; Stevens, 2007). Anomalous water table depressions also exist adjacent to other well fields: an elongated depression west of the Lichterman well field (Figure 7) and another elongated depression west of the Sheahan well field related to pumping in the Allen well field (Bradshaw, 2011).

Flow through a window in the confining unit beneath the anomalous depression in the water table in the Sheahan well field can be estimated assuming steady-state conditions in the shallow aquifer and assuming a single value for hydraulic conductivity. If a single window at well 99s is assumed to act as a pumping well removing water from the shallow aquifer at that location and if the water level conditions in the shallow aquifer have reached a steady state as a result of loss, then the Thiem equation for steady radial flow can be applied to estimate loss from the shallow aquifer. Initial water level surface near well 99s is assumed to be flat and 76 m above sea level (asl), which is slightly higher than the measured 2004–2005 Nonconnah Creek

surface. The two observation wells are MLGW 96s and K-75, with steady-state water levels of 57 and 64 m asl and radial distances of 1,270 and 2,731 m from the window at well 99s, respectively. Slug tests conducted at the NC cluster and K-75 yielded hydraulic conductivities ranging from 0.3 to 3.0 m/d. A slug test at well 99s had a hydraulic conductivity too low $(<0.15$ m/d) to evaluate by slug test methods; however, this well is in the window and, thus, the focus of drawdown. Assuming a range of hydraulic conductivity of 0.3 to 3 m/d, the discharge through the window would range from 280 to $2,800 \text{ m}^3$ /d. Although the higher value $(2,800 \text{ m}^3/\text{d})$ is similar to that of the average daily measured loss from Nonconnah Creek $(2,600 \text{ m}^3/d)$, many assumptions are required to apply the Thiem equation. For example, the lower boundary of the shallow aquifer is clearly not horizontal (Figures 6 and 7). Furthermore, the elongate water table depression south of Nonconnah Creek indicates that part of the discharge loss from the creek may contribute to leakage to the upgradient Lichterman well field.

Hydrochemical Data

The hydrochemical data are tabulated in Table 2. The hydrochemical classification of the Memphis aquifer, shallow aquifer, and Nonconnah Creek waters sampled near the Sheahan well field ranges from mixed cation to Na+K bicarbonate-type waters (Figure 8). The waters in the Memphis aquifer plot along a linear array in the cation and anion triangles (Larsen et al., 2003a) (Figure 8), whereas the shallow aquifer and creek water compositions plot adjacent to or within the Memphis aquifer array. The composition of well 99s is more Na+K rich than are the

Figure 7. Map of 2005 water table surface (Narsimha, 2006) plotted over a structure contour map of the top of the upper Claiborne confining unit (data from Stevens [2007]; elevations in meters above sea level [asl]). The structure contour map was constructed using ordinary kriging of log-transformed data from 672 borehole data points in Shelby County; only those in the view of the map are shown. Also shown are production wells in the Sheahan and Lichterman well fields and shallow aquifer wells and discharge sites used in this study. Generalized groundwater flow paths in the shallow aquifer at the Sheahan well field and Shelby Farms Park site (Bradley, 1991; Parks and Mirecki, 1992; and Gentry et al., 2006) are shown as well as a suspected flow path toward the Lichterman well field. Water levels measured in meters asl.

Memphis aquifer waters, but the composition has similar HCO_3^- concentrations and elevated tritium activity (Figure 9A), consistent with mixing relationships described in Larsen et al. (2003a) and Ivey et al. (2008). Nonconnah Creek has slightly elevated HCO_3^- and Ca^{2+} and slightly lower Na⁺ concentrations relative to Memphis aquifer waters. The remaining shallow aquifer well waters have higher specific conductance and HCO_3^- and higher concentrations of most major solutes than do well 99s, Nonconnah Creek, or the Memphis aquifer waters. Sulfate concentrations of the shallow aquifer waters generally decrease with decreasing D.O. concentrations and Eh, except for well K-75, which has relatively high SO_4^{2-} and low D.O. and Eh. Nitrate concentrations are generally below 1.0 mg/L in Nonconnah Creek and the shallow aquifer wells, except for wells 96s and 99s, which have concentrations between 12 and 30 mg/L (Figure 9B). Well K-75 had a NO_3^- concentration of 24 mg/L for the October 2004 sampling but otherwise was below 0.2 mg/L. Conversely, field NH_4^+ values are generally at or above 1 mg/L for the reduced waters that have low $NO_3^$ concentrations, but otherwise meausre < 0.2 mg/L. Limited field S^{2-} data indicate values at or below detection $(\sim 1 \,\mu g/L)$ in all samples except water from well

I.D. $=$ identification; S.C. $=$ specific conductance; Eh $=$ oxidation-reduction potential; D.O. $=$ dissolved oxygen; na $=$ not applicable; $nd = not determined.$

99s, which measured 53 µg/L. Dissolved oxygen concentrations for Nonconnah Creek are close to saturation at the measured temperatures. The D.O. concentrations of most of the shallow aquifer wells are below 1.0 mg/L, except for wells 96s and 99s, which are consistently above 4.0 mg/L. The chemistry of the NC cluster waters consistently show higher S.C., major non– redox sensitive solute concentrations, decreasing SO_4^{2-} , and increasing NO_3^- and D.O. with higher screen depth, indicating complex chemical gradients and mixing relationships in the shallow aquifer near Nonconnah Creek.

Water quality characteristics vary seasonally in Nonconnah Creek and several of the wells. Dissolved oxygen is lowest in the fall, as are many dissolved constituents (Figure 10A). Seasonal changes in dissolved constituents in the shallow aquifer wells are generally less systematic than those of the surface water (Figure 10B). Water temperatures from the transducer data vary seasonally by less than 0.2° C in wells K-75 and 99s, with slightly warmer temperatures observed during the spring months. Water temperatures in NC-1 from the transducer data vary seasonally by less than 0.6° C, with warmer water temperatures observed during the winter and spring months.

Environmental Tracer Data

The noble gas, N_2 , ${}^{3}H$, and CFC data are tabulated in Table 3. Figure 11 shows the relationship of N_2 and ⁴He concentrations in the shallow and Memphis aquifer waters. The plot of N_2 and ⁴He in Figure 11 is used to evaluate whether the gas data follow the expected water solubility relationships in groundwater conditions (Solomon and Cook, 2000). Waters from the Memphis aquifer (data from Ivey et al. [2008]) plot in a region consistent with excess air saturation and recharge temperatures ranging from 5° C to 15[°]C. Several of the shallow aquifer wells (K-75, NC-1, and MLGW 96s) plot in a similar region to the Memphis aquifer waters; however, MLGW 99s waters have higher gas concentrations, consistent with cooler recharge temperatures and potential addition of crustal ⁴He. Considering that this well is screened in the upper Claiborne confining unit, it is possible that older helium-rich water is contributing to the noble gas composition. The noble gas results

I.D. $=$ identification; TDS $=$ total dissolved solids; Non. Cr. $=$ Nonconnah Creek; nd $=$ not determined.

Figure 8. Trilinear major ion (Piper) diagram of water compositions in the Memphis aquifer (2002 data; Ivey et al., 2008) and timeaveraged data from the shallow aquifer and Nonconnah Creek during 2004 and early 2005.

Figure 9. Cross plots of (A) tritium and HCO_3^- and (B) tritium and NO_3^- in the Memphis aquifer (2002 data; Ivey et al., 2008) and timeaveraged data from the shallow aquifer during 2004 and early 2005. The radius of the symbols is proportional to the total dissolved solids (TDS) in (A) and dissolved oxygen concentration (DO) in (B).

from well NC-2 yielded a poor fit to the temperature algorithm and produced very young or negative age results. Both wells NC-2 and NC-3 show high recharge temperatures and some of the most reducing redox conditions observed over the sampling period. The low gas concentrations in these wells may have resulted from gas stripping, as methane or H_2S were generated under the reducing conditions observed at that level in the shallow aquifer near Nonconnah Creek.

Nonconnah Creek and all of the shallow aquifer waters contained significant ³H activity. Sampling of Nonconnah Creek during May 2004 yielded a value of 2.9 TU, whereas all of the shallow aquifer wells were sampled in August 2004 and yielded values of 3.4 to 5.0 TU. The $3H/3He$ ages from the shallow

Figure 10. Line plots of selected water quality measurements in (A) Nonconnah Creek and (B) well 99s during May 2004 through February 2005.

Well	N_{2} (ccSTP/g)	^{40}Ar (ccSTP/g)	84 Kr (ccSTP/g)	20 Ne (ccSTP/g)	4 He (ccSTP/g)	R/Ra	Tritiogenic 3 He (TU)	Tritium 3 H (TU)	Apparent Mean Age (years)	Mean Recharge (year)
$NC-3$	0.0130	3.34E-04	$4.22E-08$	1.67E-07	4.34E-08	1.2	4.8	3.5	15	1990
$NC-2$	0.0118	3.05E-04	4.17E-08	1.40E-07	3.80E-08	1.0	1.0	3.8	4	na
$NC-1$	0.0151	3.97E-04	5.32E-08	1.86E-07	5.00E-08	1.1	4.3	3.4	15	1990
$K-75$	0.0157	3.59E-04	4.76E-08	1.85E-07	5.50E-08	1.4	15.8	5.8	24	1981
96s	0.0154	3.98E-04	5.12E-08	2.06E-07	5.87E-08	1.1	5.9	4.8	14	1990
99s	0.0184	4.46E-04	5.67E-08	2.34E-07	6.87E-08	1.3	13.6	3.4	29	1975
	³ H Load Recharge		Percent	Recharge		Total Gas	$CFC-11$		$CFC-12$	CFC-113
Well	$(TU) \pm 1 \sigma$		Modern	Temperature $(^{\circ}C)$		Pressure (atm)	Recharge (year)		Recharge (year)	Recharge (year)
$NC-3$	7.1 ± 2.7		110	16.9	0.991		cont		1960	nd
$NC-2$	na		na	23.6		0.997	1954		1961	$1977**$
$NC-1$	7.2 ± 3.4		110	8.6		1.024	1953		1956	nd
$K-75$	17.7 ± 3.2		120	12.7		1.068	1956		1988	nd
96s	7.2 ± 3.4		150	10.3		1.114	ns		ns	ns
99s	25 ± 8.0		67	6.7		1.182	1969		cont	1974

Table 3. Environmental tracer data.

 $TU = tritium units; na = not applicable.$

 $CFC = chlorofluorocarbon;$ na = not applicable; cont = contaminated; nd = not detected; ns = not sampled.

**Single sample result.

aquifer wells varied widely, from 4 years for NC-2 to 29 years for 99s. Using the ${}^{3}H/{}^{3}He$ ages to determine an average ³ H loading year and comparing to the total 3 H and tritiogenic 3 H (e.g., Manning et al., 2005; Koban et al., 2011), the shallow aquifer waters are of modern age in all wells but well 99s (Table 3), which, as discussed above, likely contains a significant proportion of pre-modern water. The ages generally increase with distance from Nonconnah Creek, with

the exception of well 96s, which gave an age of 14 years, similar to the ages of wells NC-1 and NC-3.

All shallow aquifer wells except for well 96s were sampled for CFC concentration. The CFC values represent the average of as many as four samples. Wells NC-1 and NC-2 gave similar ages for CFC-11 and CFC-12, with values ranging from 1953 and 1961. NC-3 gave uncontaminated ages for only CFC-12, with a value of 1960. Well NC-2 had one CFC-113

Figure 11. Cross plot of N_2 and ⁴He gases dissolved in groundwater from the Memphis aquifer (2002 data; Ivey et al., 2008) and the shallow aquifer (sampled in August 2004). Gas solubility curve plotted from data compiled in Ozima and Podosek (2002).

value of 1977. Well K-75 gave disparate ages for CFC-11 and CFC-12, with CFC-11 giving 1956 and CFC-12 giving 1988. Well 99s gave uncontaminated results only for CFC-11 with an age of 1969, but also had detectable CFC-113, which gave a value of 1974. CFC age estimates show no relationship to distance from Nonconnah Creek but they do correspond to redox conditions, with the youngest apparent ages in oxidized waters (well 99s) and older apparent ages in chemically reduced waters, consistent with microbial degradation under anaerobic conditions (Plummer and Busenberg, 2000). CFC-12 is less susceptible to anaerobic microbial degradation, which may explain why the CFC-12 age estimate of water from well K-75 is much younger than that from CFC-11. Only the age from the well with oxidized water shows a direct correlation to the ${}^{3}H/{}^{3}He$ ages (Table 3).

DISCUSSION

Loss from Nonconnah Creek

Several lines of hydrologic evidence point to consistent loss of flow from Nonconnah Creek to the shallow aquifer in the study area. The stream discharge measurements confirm water loss observed by Nyman (1965) and indicate a minimum average loss of $2,600 \text{ m}^3$ /d. Water conditions at the NC cluster indicate a persistent downward vertical gradient exists between the creek and shallow groundwater, even in an area where a competent underlying clay confining unit exists. A prominent anomalous depression in the water table is present beneath the Sheahan well field, with a lateral gradient from Nonconnah Creek. Calculated flow through a window in the confining unit beneath the Sheahan well field is estimated to be between 280 and 2,800 m^3/d , of which the maximum discharge is similar to the observed minimum loss from Nonconnah Creek.

Groundwater flow from the creek toward the well field in the shallow aquifer is likely to follow zones of high hydraulic conductivity, such as the paleovalley illustrated in Figures 6 and 7. The north-south cross section from Nonconnah Creek to the Sheahan well field illustrates little or no saturated thickness of the shallow aquifer at wells K-75 and 81s. However, approximately 2 m of saturated thickness is present at well 96s, which is south of the focus of production wells in the Sheahan well field. The paleovalley is mapped in the subsurface to connect with Nonconnah Creek downstream from the Mt. Moriah site (Figure 7) (McClure, 1999; Stevens, 2007). Water quality data also support the interpretation of prominent flow in the paleovalley, as both wells 99s and 96s contain water that is more oxygenated than that in similar wells (e.g., K-75). Wells 99s and 96s contain water with higher specific conductance than that of Nonconnah Creek, perhaps reflecting mixing with older, more chemically evolved modern and premodern waters in the shallow aquifer (see discussion below).

The 3 H $/{}^{3}$ He age estimates also support preferential and faster flow through the paleovalley. The ages for water from wells 96s and 99s yield plug-flow velocities of 0.18 and 0.13 km/yr, respectively, which are two to three times faster than the plug flow velocity for water in well K-75. Assuming effective porosity of 0.3 and 0.4, the calculated hydraulic conductivity values per unit area associated with these ages range from 40 to 50 m/d for 96s and from 20 to 30 m/d for 99s. Both of these values slightly exceed (96s) or are within the range (99s) of the highest hydraulic conductivity values measured by slug tests in the shallow alluvial aquifer of the Wolf River (Gentry et al., 2006). Unfortunately, none of the monitoring wells in the Sheahan well field intercepted a significant saturated thickness of strata in the paleovalley from which to conduct an aquifer test; however, the well log for well 96s shows a coarsening-down interval of gravel from 13.7 to 29 m in depth. The hydraulic conductivity estimate from Gentry et al. (2006) for coarse-grained basal alluvial strata is consistent with the thick, coarse-grained paleovalley fill observed at well 96s.

Water Chemistry

The chemistry of water in wells 96s and 99s is interpreted to relate closely to that of Nonconnah Creek waters, mainly through mixing and chemical reactions within the shallow aquifer. Well 99s has elevated D.O., Eh, and HCO_3^- values and lower S.C. values relative to the other shallow groundwaters; however, several other constituents have values in well 99s that are generally similar to those of Nonconnah Creek. Waters from wells 96s and 99s have relatively high D.O. and Eh values relative to the other wells, indicating a component of surface water is present in these waters. However, well 96s has higher S.C. and alkalinity than Nonconnah Creek water, indicating a more complex relationship to the infiltrated creek water. The best explanation for the overall chemical characteristics of waters from wells 96s and 99s supports the interpretation of the hydrologic data: a significant component of these shallow aquifer waters derives from oxygenated Nonconnah Creek water.

Differences in chemistry between the Nonconnah Creek water and water in well 99s are interpreted to be a result of chemical reactions and additions of other waters along the flow path. The major

differences between well 99s and Nonconnah Creek waters are the lower pH (5.7 versus 7.4), higher $Cl^-,$ $NO₃⁻$, and $Na⁺$ values and lower $SO₄²⁺$, $K⁺$, and $Ca²⁺$ values in well 99s. The lower pH and slightly lower D.O. and Eh values of the well water may reflect oxidation of organic matter in the alluvial deposits and upper part of the confining unit along a flow path. Dispersed organic matter and logs were observed in the alluvial strata at the NC cluster; similarly, lignite is commonly observed in the Eocene deposits (Carmichael et al., 1997; Gentry et al., 2006). Thus, the oxidation of organic matter as well as subsequent increased soil P_{CO2} are likely to be key processes affecting the pH of the shallow groundwater as it migrates from Nonconnah Creek along the paleovalley and passes vertically through the window in the upper Claiborne confining unit in the Sheahan well field. Higher Cl⁻ and NO₃^{σ} values in 99s water than in Nonconnah Creek are more difficult to associate with the creek water or flow path in the shallow aquifer because these constituents are not likely to arise from mineral reactions. A reasonable source, however, is urban runoff that could percolate through the loess surface soils or perhaps beneath one of several lakes and creeks on the land surface above the paleovalley. Studies (Larsen et al., 2009) of water chemistry in storm sewer systems in the Memphis area indicate chloride concentrations elevated over those observed in waters from the Memphis aquifer. Chloride may additionally arise from brackish clay beds in the confining unit (Larsen et al., 2003a). Perhaps more difficult to explain are the lower SO_4^{2-} , K^+ , and Ca^{2+} and higher Na^+ concentrations in well 99s waters, compared with those of the creek water. The variations in the cation concentrations may reflect cation exchange processes with the clays in the shallow aquifer strata and upper Claiborne confining unit, given that the cation charge equivalent concentrations of the creek and well waters are approximately equal. The lower SO_4^{2-} concentrations are consistent with the significant presence of S^{2-} , but both of these observations are unexpected given the oxidized nature of these waters.

Despite their proximity to the creek, the waters from the NC cluster have higher S.C. and HCO_3^- and lower pH, D.O., and Eh than do the creek waters. The systematic variations in redox species and decrease in alkalinity and S.C. (and TDS) with screen depth argue for a strong control of mineral reactions coupled with oxidation-reduction processes and increasing influence of creek loss with depth in the shallow aquifer. Water from NC-3 has higher TDS, alkalinity, and Ca²⁺, Mg²⁺, and Na⁺, indicating that the waters have reacted with carbonate minerals (probably dolomite) and clays, which are prominent in the upper alluvium in which this well is screened. In contrast, water from NC-1 has lower TDS, alkalinity, and cation concentrations, as well as a range of Cl^- concentrations that matches closely those of Nonconnah Creek, indicating that this water is well connected to that in Nonconnah Creek. Redox indicators yield inconsistent results, with Eh indicating the highest values in waters from NC-3 and D.O. having the highest values in waters from NC-1 (Figure 12). Sulfate and $NO₃⁻$ concentrations in all three NC wells are greatly depressed compared to those in Nonconnah Creek, indicating active sulfate- and nitrate-reducing bacteria. The limited S^{2-} and NH₄⁺ data from the NC well waters support a bacterial role in redox processes as well. However, dissolved Fe is highest in waters from NC-1, and dissolved Mn is highest in waters from NC-3. Redox disequilibria and comparison with creek levels indicate that D.O. and oxidized S and N species flux into the aquifer exceed reduction during runoff events, whereas reduction exceeds flux of these components during base flow periods. Vertical variations in Fe and Mn concentrations in the waters in the shallow aquifer are consistent throughout the year, although the values increase during the fall and winter months. These observations indicate that Fe and Mn concentrations are more related to reaction with aquifer materials and perhaps groundwater flux from dispersion than they are to interaction with creek water.

Water from well K-75 has the highest TDS, lowest temperature, and lowest Eh and D.O., and its constituents had the least amount of variability throughout the year. Chloride and SO_4^{2-} increase during the spring and summer and decrease into the fall and winter, whereas Ca^{2+} seems to show an opposite relationship during the year. Nitrate is generally near detection levels, although one anomalously high value (24 mg/L) was observed in the October sample. The principal source of most of these variations is interpreted to be infiltration of urban runoff; however, much of the consistency in composition likely lies in more long-term reactions with aquifer materials.

The water in well 96s shares some similarities to that in both 99s and in K-75, indicating that the waters in this well may reflect mixing of older and more chemically evolved modern water with that of infiltrated Nonconnah Creek water flowing along the paleovalley. This interpretation is consistent with well-log–based topography of the top of the upper Claiborne confining unit (Figure 7), which shows that well 96s is immediately down-gradient to the topographically higher well K-75.

Figure 12. Line plot of time-averaged values (2004 and early 2005) for selected oxidation-reduction measurements and constituents with depth at the NC cluster. Plotted depth is the middle of the screened interval for the wells and the water surface for Nonconnah Creek.

Inverse Geochemical Modeling

Inverse geochemical modeling along the flow path from Nonconnah Creek to the Sheahan well field provides a mechanism to test hypothesized geochemical reactions as well as to estimate mixing ratios among the waters concerned. Of primary interest is the chemical evolution of waters migrating from Nonconnah Creek along the paleovalley and recharging the upper Memphis aquifer through a window near the center of the well field (e.g., Parks, 1990; Ivey et al., 2008). PHREEQCi was used to model the equilibrium conditions in the input waters and to consider multiple chemical and mixing reactions with the inverse modeling option. In most cases, solutions were balanced with aquifer phases using Ca, Fe, Mg, Na, K, O, alkalinity, Cl, and S; however, S caused balance problems in models considering reactions from Nonconnah Creek to well 99s, and K was not included in models that excluded Nonconnah Creek. Mineral and gas phases included calcite, dolomite, siderite, pyrite, goethite, halite, Na-exchange, illite, Ca-montmorillonite, O_2 , H_2O , and CO_2 . A mineral was not allowed to precipitate in the models unless the saturation index in the input solution exceeded saturation. All of the listed minerals are known to be common in the loess, shallow aquifer, upper Claiborne confining unit, or Memphis aquifer (Larsen et al., 2003b; Gentry et al., 2006), except for halite. Halite is used in this case to represent the urban runoff component in the inverse models involving creek water and the shallow aquifer. Inverse modeling generally used a global uncertainty of 0.3.

Modeling of Nonconnah Creek water evolution to well 99s indicates minimal mineral transfers but reflects acquisition of dissolved NaCl (urban runoff or confining unit source), $CO₂$ gas, and water (Table 4). The water in 99s is estimated to contain as much as 31 percent urban runoff or dilute young water from sources other than Nonconnah Creek. Such waters could also contain the relatively high $NO₃⁻$ concentrations observed as well.

Modeling of the chemical evolution of Nonconnah Creek water and mixing with well K-75 waters to yield the water in well 96s indicates again minimal mineral transfers (Table 4). Iron could be lost from the mixed water by precipitation of siderite or goethite. Given that water in well 96s is oxygenated (mean D.O. of 4.7 mg/L), precipitation of goethite seems most reasonable and yields mixing percentages of 33 percent Nonconnah Creek water and 67 percent water from K-75. The chemical evolution and mixing of both Nonconnah Creek and shallow aquifer waters with water in the Memphis aquifer was modeled in a manner similar to that used by Larsen et al. (2003a) and Ivey et al. (2008). Water chemistry for Memphis aquifer waters affected by leakage is represented by production well 99 (Ivey et al., 2008), which is in an area in which a hydrologic window is present within the upper Claiborne confining unit (Gentry et al., 2005; Ivey et al., 2008). Unaffected water in the Memphis aquifer is represented by production well 78A (in the northeastern part of the well field), which consistently shows little or no 3 H and 3 He (Gentry et al., 2005; Ivey et al., 2008). The Memphis aquifer water chemistry is from 2002; however, comparison of data from Larsen et al. (2003a), Gentry et al.

Final Well	Water or Phase ^a	Mixing Fraction (by Mass) or Mass ^b (mol/kg H_2O)		
99 _s	Nonconnah Creek	0.693		
	Dilution	0.307		
	NaCl	0.00027		
	CO ₂	0.0033		
96s	$K-75$	0.331		
	Nonconnah Creek	0.669		
	Goethite	-0.00008		
99	78A	0.865		
	Nonconnah Creek	0.135		
	Goethite	-0.00002		
	Dolomite	0.00004		
	Pyrite	0.00001		
	NaCl	0.00004		
	CO ₂	0.0040		
99	78A	0.932		
	96s	0.068		
	Goethite	-0.00001		
	Pyrite	0.000004		
	NaCl	0.00004		
	CO ₂	0.0034		
99	78A	0.919		
	96s	0.081		
	Goethite	-0.000009		
	NaCl	0.00004		
	O ₂	-0.00002		
	CO ₂	0.0033		
99	78A	0.768		
	96s	0.232		
	Goethite	-0.00003		
	Dolomite	0.00004		
	Pyrite	0.00001		
	CO ₂	0.0036		

Table 4. Results of PHREEQCi modeling.

^aThe initial waters are from Nonconnah Creek or one or more shallow wells; the remainder are phases dissolved in or precipitated from the final water.

^bNumbers for the wells or creek are mixing fractions. For the phases, positive numbers indicate phase is dissolved in water and negative numbers indicate phase precipitates from water.

(2005), and Ivey et al. (2008) indicates little interannual variability in water chemistry. Considering Nonconnah Creek water, only one model satisfied the constraints and yielded dissolution of dolomite and pyrite, precipitation of goethite, and addition of NaCl and $CO₂$ (Table 4). The percentage of creek water in the final mixture is 14 percent. For leakage water from well 96s, the most reasonable models include precipitation of goethite, with or without concomitant dissolution of pyrite, and addition of NaCl and $CO₂$. Mixing percentages vary from 7 to 8 percent of shallow aquifer water derived from well 96s. For leakage from well 99s, only one model satisfied the constraints and yielded dissolution of dolomite and pyrite, precipitation of goethite, and addition of $CO₂$. The percentage of water from well 99s in the final mixture is 23 percent.

SUMMARY AND CONCLUSIONS

The stream discharge and hydraulic head measurements in the shallow aquifer near the Sheahan well field support the conclusions of previous studies that Nonconnah Creek loses water to the shallow aquifer (Nyman, 1965), which ultimately contributes to leakage to the Memphis aquifer (Graham and Parks, 1986; Larsen et al., 2003a; Gentry et al., 2005; and Ivey et al., 2008). Stream discharge measurements indicate a loss of at least 2,600 m³/d from Nonconnah Creek, and drawdown calculations and geochemical data support flow of creek water through the shallow aquifer toward the Sheahan well field, along with contributions of water from storage in the shallow aquifer. Although head decline in the shallow aquifer is shown to be asymmetrical about the center of the Sheahan well field in a north-south direction (Figure 7), this is in part an artifact of well control but may also reflect the geometry of the paleovalley in the shallow aquifer beneath the well field. Given the geochemistry of shallow aquifer water at the NC cluster and well K-75, little water from the shallow aquifer near these wells is argued to contribute to leakage in the Memphis aquifer, despite their proximity to the well field. Geologic and geochemical data indicate that much of the leakage follows a paleovalley that extends from Nonconnah Creek near the Mt. Moriah site to the Sheahan well field (Figure 7). The shallow aquifer strata in the paleovalley are coarser grained and likely to have high hydraulic conductivity, as indicated by ${}^{3}H/{}^{3}He$ derived plug-flow velocities for wells 96s and 99s. Water in the shallow aquifer flows along the paleovalley toward the window in the upper Claiborne confining unit near the Sheahan well field (Parks, 1990; Waldron et al., 2007; and Ivey et al., 2008), where it descends through the confining unit to recharge the Memphis aquifer.

Geochemical data and modeling indicate that several processes affect the shallow aquifer water as it passes from Nonconnah Creek to the well field. Mixing with older shallow aquifer water, as represented by that in well K-75, is likely to impact the water chemistry along the margins of the paleovalley. Water from well 96s in the paleovalley may contain as much as two-thirds of the more chemically evolved and older shallow aquifer water. Furthermore, a component of urban runoff that has infiltrated through the loess is interpreted to contribute to the flow in the shallow aquifer, adding $Na⁺$, $Cl⁻$, and $NO₃⁻$. The quantity of this component and its surface source cannot be resolved with the present tracer data; however, it may affect the accuracy of plug-flow velocity estimates using ³H/³He ages. Geochemical

processes affecting the creek water along the leakage pathway are primarily dissolution of soluble minerals, such as dolomite, and redox reactions. The redox reactions primarily involve oxidation of organic matter (yielding $CO₂$) and pyrite as well as precipitation of goethite. Bacterially mediated reduction of $NO₃⁻$ and $SO₄²⁻$ are important in areas where shallow aquifer waters are in contact with abundant organic matter and are slow moving (e.g., NC cluster and well K-75), but are of lesser importance along the paleovalley, where elevated D.O. levels are maintained and anaerobic respiration is suppressed. Cation exchange with clay minerals and silicate reactions are likely to be less important in the paleovalley because of limited residence time and lack of reactive phases (sediment is mainly quartz and chert); however, they become more important in the more mineralogically diverse upper Claiborne confining unit. The anomalously high noble gas concentrations in water from 99s as well as perhaps the S^{2-} are likely from older water diffusing from the finegrained strata in the confining unit (e.g., Bethke and Johnson, 2002). This may, in part, cause the resulting age estimate of water in 99s to be older (29 versus 14.9 years for 96s) and may again limit its use for hydraulic calculations.

The percentage of modern leakage water produced from production well 99 screened in the Memphis aquifer in the Sheahan well field varies depending on the contributing source. The lowest percentages were observed for models of leakage from well 96s, at 7 to 8 percent, and the highest percentages were from models using well 99s, at 23 percent. These percentages fall well within the range of values reported by Larsen et al. (2003a) and Ivey et al. (2008) for other affected wells in the Sheahan well field. The current work, in part, confirms the results of Larsen et al. (2003a), which used a Nonconnah Creek well distant from the study area for the modern water component.

The leakage pathway model presented herein is more complex and indirect compared to that which is typically modeled using wellhead protection models (e.g., WHPA). Similarly, use of more typical groundwater flow modeling approaches is difficult because of limited saturation in the shallow aquifer, irregular aquifer boundaries, and scarcity of data beyond the Sheahan well field (Waldron et al., 2007). Identification of the pathway required several investigative approaches, ranging from traditional observational methods (discharge and head measurements) to environmental tracer data and modeling. Several types of leakage pathways from shallow aquifer sources to the Memphis aquifer have been identified in the Memphis area, many clearly related to active well field production and proximity to one or more nearby streams (Parks et al., 1995; Larsen et al., 2003a; Bradshaw, 2011; and Koban et al., 2011) as well as more passive leakage sites that lack active nearby pumping, such as that at Shelby Farms Park (Figure 7) (Bradley, 1991; Parks and Mirecki, 1992; and Gentry et al., 2006). Application of an array of investigative tools is essential to clarifying connections between surface and subsurface waters and to better assessing groundwater vulnerability to environmental threats.

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