ELSEVIER

Resolving aquifer behavior near a focused recharge feature based upon synoptic wellfield hydrogeochemical tracer results

Randall W. Gentry [a,*], Teh-Lung Ku [b,a], Shangde Luo [b,c],
Vincent Todd [b,c], Daniel Larsen [d,b], John McCarthy [e,d]

[a] *Department of Civil and Environmental Engineering, The University of Tennessee, 62 Perkins Hall, Knoxville, TN 37996, USA*
[b] *Department of Earth Sciences, The University of Southern California, Los Angeles, California 90089-0740, USA*
[c] *Department of Earth Sciences, National Cheng Kung University, Tainan 701, Taiwan, ROC*
[d] *Department of Earth Sciences, The University of Memphis, Memphis, TN 38152, USA*
[e] *Department of Earth and Planetary Sciences, The University of Tennessee,*
306 Earth and Planetary Sciences Building, Knoxville, TN 37996-1410

Abstract

Aquitard windows are known to occur in unconsolidated aquifer systems and represent areas of focused recharge to otherwise confined underlying aquifers. The study herein focused on a known window site affecting the Memphis aquifer located in the Sheahan wellfield in Shelby County, Tennessee. Uranium- and thorium-series radioisotopes were evaluated from production wells sampled in the wellfield and compared to other geochemical characteristics of the system. From the research, a conceptual model was realized whereby higher uranium concentrations from near-surface waters flow through a redox barrier in the aquitard window and become depleted in uranium. Further, $^{234}U/^{238}U$ activity ratio increased downgradient of the recharge source by alpha-recoil mobilization of ^{234}U via ^{234}Th, and possibly leaching of uranium bound by iron hydroxides via dissolution and subsequent precipitation by reducing waters flowing to downgradient wells. The behavior of the hydrogeochemical tracers could be best described in the conceptual model by normalizing uranium to Fe^{2+} throughout the system. The use of the $[U]$–$[Fe^{2+}]$ pair provides a useful tool for understanding of the mixing behavior near focused recharge sites with redox barriers and may be useful for developing aquifer behavior models.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Environmental tracers; Hydrogeochemical tracers; Aquitard leakage; Mississippi embayment

1. Introduction

Accurate conceptual models are needed to understand the complex relationship between groundwater reservoirs and other hydrologic interfaces. These conceptual models will by necessity be used by the broad community of decision makers to address risk and

---

* Corresponding author. Tel: (865) 974-7718; fax: (865) 974-2669.

E-mail addresses: rgentry@utk.edu (R.W. Gentry), rku@usc.edu (T.-L. Ku), sluo@mail.ncku.edu.tw (S. Luo), vtodd@usc.edu (V. Todd), dlarsen@memphis.edu (D. Larsen), jmccart1@utk.edu (J. McCarthy).

sustainable yields from groundwater reservoirs. The development and verification of a conceptual model is complicated by temporal and spatial uncertainty and scaling issues. Many of the core scientific issues regarding groundwater fluxes were identified recently by the Committee on Hydrologic Sciences (US National Research Council), specifically recognizing the importance of better understanding of diffuse versus focused recharge mechanisms as they relate to potential aquifer vulnerability (Fogg et al., 1999; Bohlke, 2002; NRC 2004).

The purpose of this study was to investigate the hypothesis that environmental and hydrogeochemical tracers (e.g. uranium-, thorium-series radioactive isotopes, and $^3H/^3He$) could be used to establish a new conceptual model for aquifer behavior near a focused recharge site where the hydrologic interface is affected by local pumping from the groundwater reservoir. The setting for the study was an aquitard window, a localized opening in an otherwise confined aquifer setting, located near the Sheahan wellfield in the Memphis Tennessee, USA area. The location of the study area is shown in Fig. 1 and the site specific layout of the Sheahan wellfield area is shown in Fig. 2.

2. Hydrogeologic setting for the study

2.1. Hydrogeology

The Memphis aquifer, defined regionally as a part of the Claiborne group sequence, is the major drinking water resource for western Tennessee (Parks and
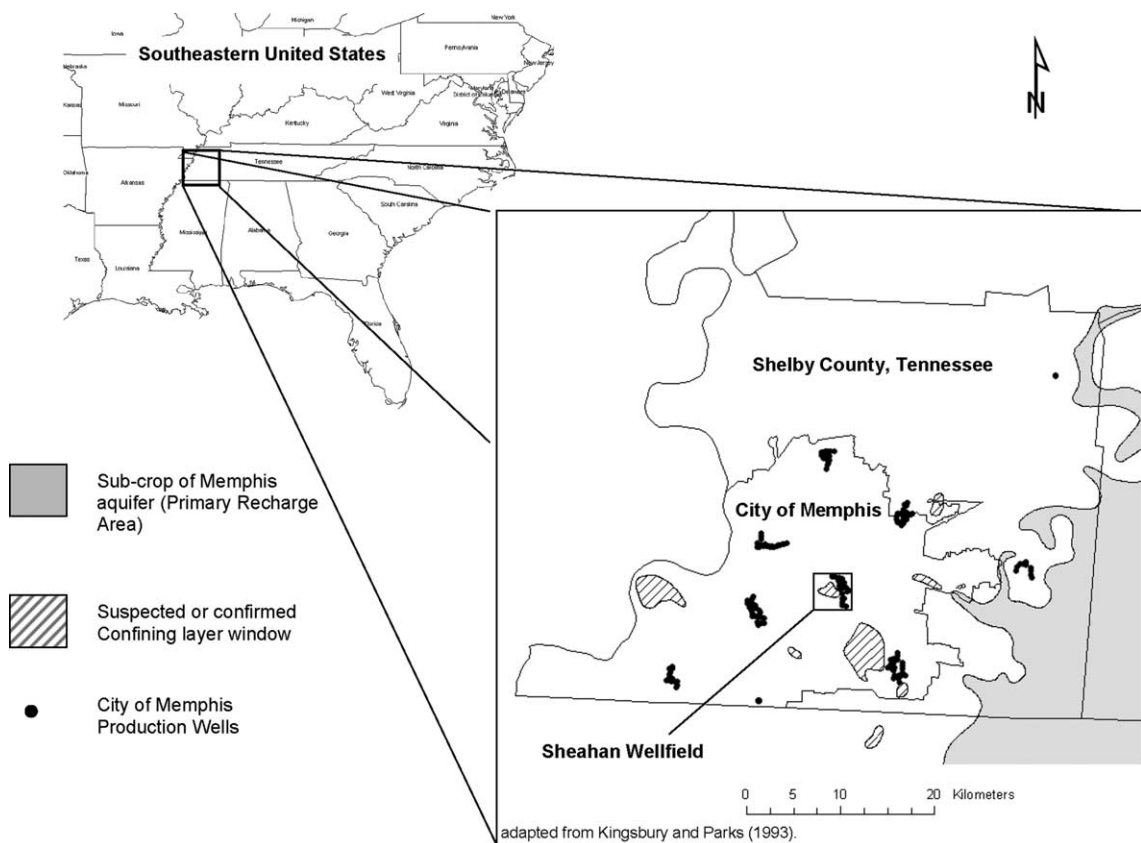

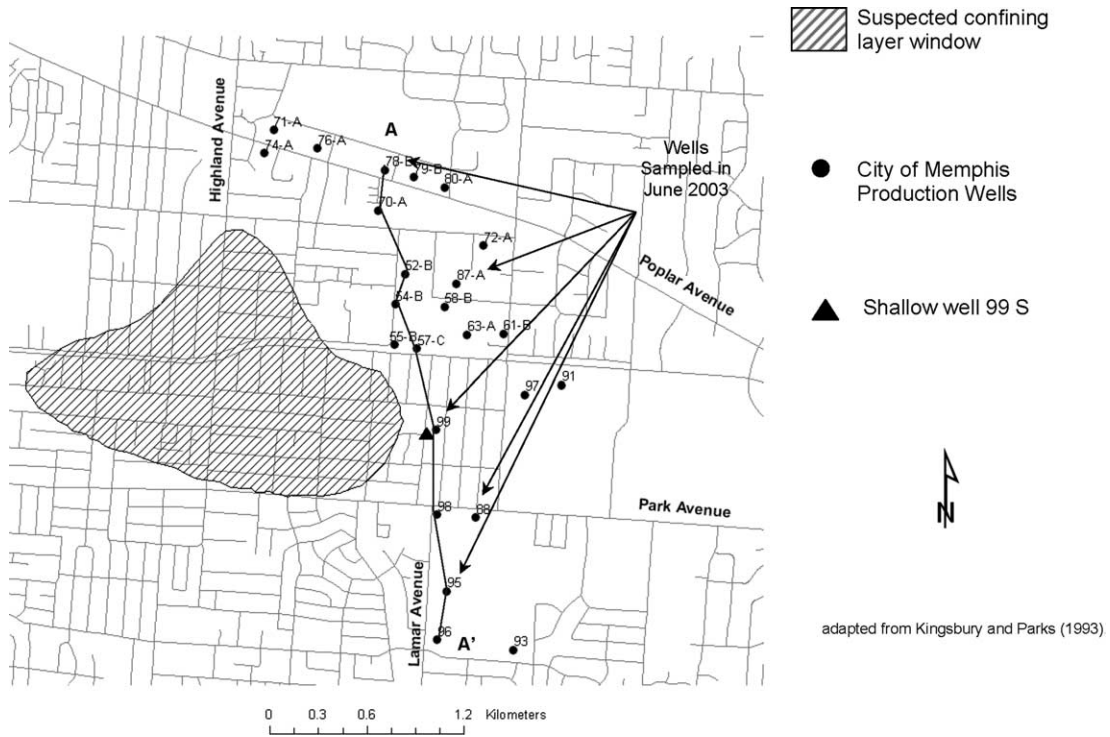Fig. 1. Geographical study area site location.

Fig. 2. Sheahan wellfield production well locations.

Carmichael, 1990) and is part of the Mississippi Embayment aquifer system, which extends from southwestern Kentucky to the Gulf of Mexico (Grubb, 1998) and 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 unconformably overlie the mid-Tertiary units (Krinitsky, 1949; Saucier, 1987). Excluding the present-day tributary valleys, 3 to 20 m of loess (windblown silt and clay) overlie the fluvial deposits and mantle the underlying topography. 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 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. 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.

Locally in southwestern Tennessee, the Memphis aquifer outcrops, or sub-crops, in eastern and southeastern Shelby County, but the aquifer is confined by the overlying upper Claiborne aquitard throughout most of the remainder of the county (see Fig. 1). 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), see Fig. 1. 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.

2.2. Recharge through Aquitard Windows

Over the past decade or so, a number of studies have shown that recharge and contamination are entering the Memphis aquifer through hydraulic pathways in the upper Claiborne aquitard (Bradley, 1988; 1991; Parks, 1990; Parks and Mirecki, 1992; Kingsbury and Parks, 1993; Parks et al., 1995; Larsen et al., 2003), which allow direct hydraulic contact between the shallow unconfined aquifer and the deeper Memphis aquifer. 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 (^{14}C and tritium), and geochemical studies (Graham and Parks, 1986; Parks, 1990; Bradley, 1991; Parks and Mirecki, 1992; Mirecki and Parks, 1994; Parks et al., 1995). The suspected locations of aquitard windows in the Shelby County, Tennessee area are shown in Fig. 1.

Aquitard windows can be formed by depositional or erosional processes, as well as by earthquake activity, and are common in many layered aquifer systems (Flavin and Joseph, 1983; Miller, 1986; Fortin et al., 1991; Castle and Miller, 2000). Historically, locations of aquitard windows were inferred from observed depressions in the water table or from geochemical evidence of mixing between waters of the upper unconfined aquifer and the Memphis aquifer (Graham and Parks, 1986; Parks and Mirecki, 1992; Parks et al., 1995). The goal of recent research in the Memphis aquifer setting has been to quantify, to the extent possible, the recharge flux through window features using a variety of inverse modeling and geochemical techniques (Gentry et al., 2001; 2003; Larsen et al., 2003).

2.3. Sheahan Wellfield

The Sheahan wellfield is one of 10 wellfields operated by the City of Memphis, Tennessee and has been active since 1932, see Fig. 2. The wellfield consists of 24 turbine shaft production wells emplaced at various depths in the Memphis aquifer ranging from approximately 95 to 237 m below ground surface. The wells produce feed water to a central treatment facility with typical pumping capacities near the magnitude of 3000 l/min. The capacity of the central treatment plant is 132.5×10^7 l/day (35 MGD).

In the 1980 s, analyses of groundwater from the wellfield for tritium demonstrated that modern water was being produced from the Memphis aquifer (Graham and Parks, 1986). Parks (1990) later demonstrated that by evaluating geologic data and shallow aquifer saturated thickness that a suspected window site may exist just west of the wellfield. Kingsbury and Parks (1993) estimated the location of the window by mapping the area of the shallow aquifer in the vicinity that has lost significant saturated thickness, as delineated in Fig. 2. More
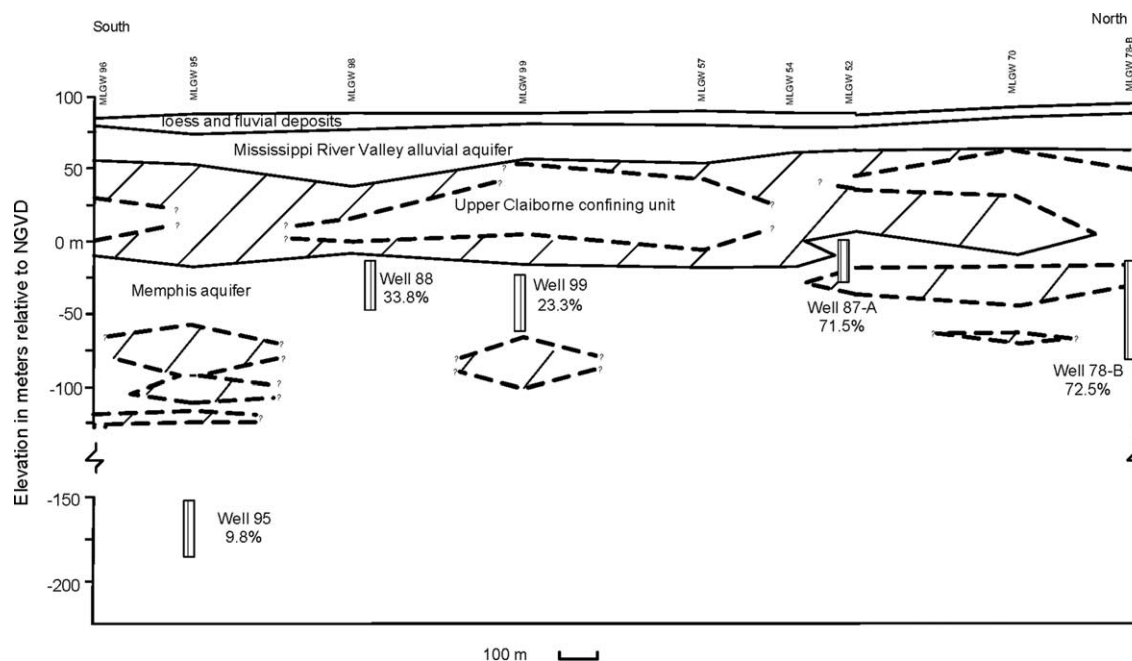
Note: Percentages are based upon the number of hours that the well was active during the 2003 calendar year.
       Hatched areas in the figure represent clay lenses.

Fig. 3. North–South stratigraphic cross-section *A–A'* (shown in Fig. 2) of Sheahan Wellfield (Larsen et al., 2003). Note, well screen intervals are shown for the wells sampled in 2003.

recent research has focused on identifying mixing relationships and discrete flowpaths in the Sheahan wellfield. Using geophysical log information from select wells, a north to south stratigraphic cross-section has been constructed and is shown in Fig. 3. Note in Fig. 3, that clay lenses exist at depth near Well 99, but it is not known how the clay and sand are interconnected spatially. In 2001, rotasonic drilling implaced a shallow well (Well 99S) in the central part of the wellfield, see Fig. 2. The drilling results indicated little to no clay where the top of the confining layer should have been encountered at Well 99S located immediately east of the estimated location of the window (Fig. 2), and provides further detail in regard to the localized leakage. The Tennessee district of the United States Geological Survey (USGS) performed a natural gamma log of Well 99S and the result of the log is shown in Fig. 4. The natural gamma log (Fig. 4) indicates a typical response observed in the region, with the loess

deposits providing a positive signal to a depth of 8 m below ground surface. Also, the natural gamma log demonstrates a lack of response in the natural gamma that would be consistent with the lack of clay rich deposits in the vicinity of Well 99S, from the 10 to 45 m below land surface depth. As shown in Fig. 3, clay lenses were noted deeper in the vicinity of Well 99, but the interconnection of those lenses is unclear. In further research, Larsen et al. (2003) using geochemical modeling, demonstrated that mixing of between 6 and 32% of shallow aquifer water with deep Memphis aquifer water accounts for geochemical variability in waters pumped from the upper part of the Memphis aquifer in the Sheahan wellfield. Ivey (2003) modeled geochemical, environmental tracer, and window geometry data using a coupled inverse code and lumped parameter model to identify a probable location for leakage near Well 99 in the central part of the Sheahan well. Her results independently confirm the hydrostratigraphy-based
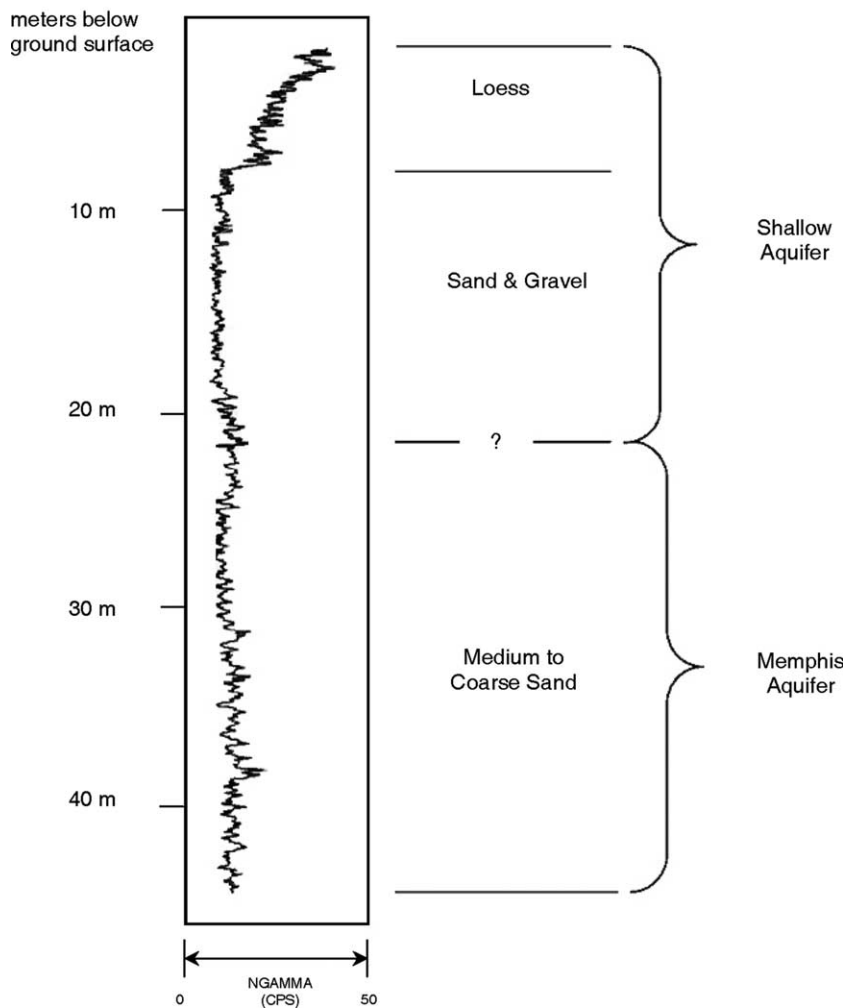
Fig. 4. Natural gamma log performed by USGS from shallow well in the vicinity of production well MLGW 99.

interpretations of window locations inferred by Parks (1990) (Fig. 2) and Larsen et al. (2002) (Fig. 3).

3. Sampling and Analytical Techniques

In June 2003, samples were collected from five wells with bottom screen intervals ranging in elevation from 21 to 181 m, see Fig. 3. Water samples were collected from a spigot located on the discharge penstock of the turbine pump. The wells were in operation for at least 24 h prior to the collection of samples. Pressure in the discharge penstock was

increased (>200 kPa gauge) by adjusting discharge valves in order to avoid degassing and bubble generation in the sampling lines.

3.1. Water Chemistry Analyses

A YSI 6600 SONDE flow-through cell was used to collect data for pH, temperature, conductivity and oxidation-reduction potential (ORP). A factory-calibrated Hach 2000 spectrophotometer and Hach colorimetric field kit methods were used to measure dissolved oxygen, Fe^{2+}, and total iron.

3.2. Radiochemical Sample Collection and Assay

The radiochemical sampling methodology used for the study was designed and used by Luo et al. (1995, 2000) for evaluating preferential groundwater flow at the Idaho National Engineering and Environmental Laboratory (INEEL). The groundwater samples were pumped through a set of serial filters consisting of: (1) a prefilter (Ametek[TM] polypropylene filter, 0.5 µm nominal pore size), and (2) a primary and secondary MnO_2-impregnated polypropylene-fiber filter. The prefilter was used to remove suspended particles and the MnO_2 filters were used to capture and concentrate dissolved Th and Ra from the water. The preparation of the MnO_2 filters followed the procedure outlined by Luo et al. (1995, 2000). Radiochemical analyses followed the procedures described in Luo et al. (1995) with minor modifications.

In addition to the filtered samples, 1 and 3.8 l groundwater samples were collected for ^{222}Rn and uranium analysis, respectively. For the ^{222}Rn analysis, a Tygon tube was connected to the sampling spigot and water was drawn into the bottom of a glass bottle, while keeping bubbles from forming in the water stream. The bottle was allowed to overflow for several minutes, and sealed for later laboratory analyses.

3.3. $^3H/^3He$ Sampling and Analysis

The ground water age tracers, tritium (^3H) and helium-3 (^3He), were used to support interpretation of the data by better defining the presence of young waters (e.g. Solomon et al., 1992). ^3H samples were collected in one-liter amber glass bottles and shipped to the Nobel Gas Laboratory at the University of Utah for analysis. The ^3H activity was determined using the He in-growth method with a practical detection limit of 0.05 tritium units (TU) (Clarke et al., 1976; Bayer et al., 1989; Solomon and Cook, 2000). ^3He was collected using dissolved gas sample containers consisting of two copper tubes connected by a gas permeable silicon tube. The containers were placed in a flow-through cell connected to the sampling spigot. After equilibrating for approximately 24 h, the tubes were cut, sealed and shipped to the Nobel Gas Laboratory at the University of Utah for analysis using a magnetic sector-field mass spectrometer.

3.4. Geochemical Speciation Modeling

The water chemistry data were used to evaluate speciation and mineral solubility controls on iron and uranium concentrations. The geochemical speciation modeling was performed using Geochemist's Work-bench[®] version 5.0. For both iron and uranium, the temperature was assumed to be 18 °C and at a pressure of 1.013 bars, which is consistent with field observations. For speciation, hematite, magnetite, wustite, FeO(c), and geothite were suppressed leaving ferrihydrite as the only precipitating iron phase, which is consistent with the phase of iron in the Memphis aquifer. Total iron and inorganic dissolved carbonate activities are based on typical concentrations observed in the Sheahan well field (Larsen et al., 2003 and unpublished data).

4. Results

Chemical parameters monitored during sample collection are summarized in Table 1. The results of the ^3H and ^3He, and trace nitrogen and neon gas analyses in addition to the apparent age determination for samples from the Sheahan wellfield are summarized in Table 2. The U, Th, Ra, and Rn results are provided in Table 3. Activity ratios for certain parent–daughter and isotope pairs are summarized in Table 4.

4.1. Chemical Parameters

The data show a range of redox, pH and iron concentration values throughout the wellfield. Temperature ranged from 17.4 to 20.2 °C with the central part of the wellfield at 18.0 °C. pH varied from 5.83 to 6.69 and ORP (relative to the hydrogen electrode), from 51.4 to 575 mV. Conductivity showed a range of 0.099 to 0.281 ms/cm and dissolved oxygen, 2.78 to 252 µg/l. Reduced iron (Fe^{2+}) ranged from 0.09 to 1.3 mg/l and total iron concentrations ranged from 0.12 to 1.33 mg/l.

4.2. $^3H/^3He$

The data indicate the presence of modern water (<50 years) in the upper strata of the Memphis aquifer. The apparent ages of 14.9, 24.9 and 48.8

Table 1
Water chemistry from Sheahan wells

Well ID	Top of screen (elevation (m))[a]	Temperature (°C)	pH	Conductivity (ms/cm)	ORP (mV)	DO (µg/l)	Fe^{2+} (mg/l)	Total Fe (mg/l)	U (g/l)
MLGW 87-A	−3.35	17.43	5.83	0.127	473	178	0.69	0.71	5.83×10^{-8}
MLGW 88	−13.41	18.00	5.88	0.146	421	2.78	0.12	0.19	4.16×10^{-8}
MLGW 99	−23.47	18.00	5.88	0.123	475	45	0.09	0.12	3.98×10^{-8}
MLGW 78-B	−35.05	17.70	5.94	0.099	462	57	0.29	0.29	1.28×10^{-8}
MLGW 95	−149.05	20.17	6.69	0.281	51.4	252	1.3	1.33	1.63×0^{-8}

[a] National Geodetic Vertical Datum (NGVD) 1929.

Table 2
^3H and ^3He sample analysis results

Well ID	Top of Screen (elevation (m))[a]	N_2 (ccSTP/g)	^{20}Ne (ccSTP/g)	^4He (ccSTP/g)	^3H (TU)	^3He_t (TU)[b]	$^3H+^3He_t$ (TU)	R/R_a[c]	Apparent age (yr)
MLGW 87-A	−3.35	0.0149	1.95×10^{-7}	5.66×10^{-8}	1.6	4.7	6.3	1.111	24.9
MLGW 88	−13.41	0.0149	2.01×10^{-7}	5.38×10^{-8}	1.1	1.4	2.5	1.045	14.9
MLGW 99	−23.47	n.a.[d]	n.a.	n.a.	0.2	n.a.	n.a.	n.a.	n.a.
MLGW 78-B	−35.05	0.0143	1.97×10^{-7}	5.91×10^{-8}	0.1	1.4	1.5	0.952	48.8
MLGW 95	−149.05	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[a] National Geodetic Vertical Datum (NGVD) 1929.
[b] Tritogenic ^3He.
[c] R is the $^3He/^4He$ ratio of the sample; R_a is the $^3He/^4He$ ratio of air (1.384×10^{-6}).
[d] Data not available due to loss of sample.

years for the upper strata of the Memphis aquifer, at elevations −3 to −72 m National Geodetic Vertical Datum (NGVD), showed a south-to-north increase. Trace gas analyses of nitrogen determined a range of concentrations from 0.0143 to 0.0149 cc, at standard temperature and pressure, per gram of sample (ccSTP/g). Neon concentrations ranged from 1.95×10^{-7} to 2.01×10^{-7} ccSTP/g and ^4He ranged from 5.38×10^{-8} to 5.91×10^{-8} ccSTP/g. The samples from nearest the window feature and the southernmost well were unfortunately lost during sampling due to poor sealing of the sample tubes.

Table 3
U, Th, Ra and Rn isotope sample analysis results

Well ID	Top of screen (elevation (m))[a]	^{238}U (dpm/m³)	^{234}Th (dpm/m³)	^{230}Th (dpm/m³)	^{232}Th (dpm/m³)	^{228}Th (dpm/m³)
MLGW 87-A	−3.35	43.5±4.3	1.46±0.08	0.137±0.0051	0.104±0.010	1.448±0.105
MLGW 88	−13.41	31.0±3.4	9.31±0.09	0.062±0.003	0.030±0.004	n.d.[b]
MLGW 99	−23.47	29.7±3.9	1.04±0.10	0.284±0.018	0.189±0.020	n.d.
MLGW 78-B	−35.05	9.6±1.4	1.63±0.08	0.091±0.004	0.038±0.005	0.861±0.065
MLGW 95	−149.05	12.1±1.3	8.90±0.10	0.072±0.004	0.042±0.006	3.673±0.237
Well ID	^{222}Rn (dpm/l)	^{226}Ra (dpm/m³)	^{228}Ra (dpm/m³)	^{224}Ra (dpm/m³)	^{223}Ra (dpm/m³)	
MLGW 87-A	66.3±2.0	109.6±0.3	190.1±2.1	298.2±6.5	5.7±3.9	
MLGW 88	110.8±2.6	323.9±1.3	526.8±3.1	1115±15	39.2±5.1	
MLGW 99	75.6±2.1	484.1±1.9	557.0±4.2	653±12	30.8±8.5	
MLGW 78-B	78.2±2.4	136.0±0.7	186.7±1.6	251.9±6.5	< 8.4	
MLGW 95	67.6±2.2	73.5±0.7	85.7±1.5	124.5±5.3	<3.7	

[a] NGVD 1929.
[b] Non-detectable.

Table 4
U, Th, Ra, and Rn isotopic activity ratios

Well ID	Top of screen (elevation (m))[a]	$^{234}U/^{238}U$	$^{234}Th/^{238}U$	$^{234}Th/^{230}Th$	$^{230}Th/^{232}Th$	$^{228}Th/^{232}Th$
MLGW 87-A	−3.35	1.32 ± 0.06	0.034 ± 0.004	10.7 ± 0.7	1.3 ± 0.1	13.9 ± 1.2
MLGW 88	−13.41	1.02 ± 0.04	0.300 ± 0.033	149.5 ± 10.3	2.1 ± 0.2	n.a.[b]
MLGW 99	−23.47	1.11 ± 0.06	0.035 ± 0.006	3.7 ± 0.3	1.5 ± 0.1	n.a.
MLGW 78-B	−35.05	1.43 ± 0.09	0.171 ± 0.026	18.0 ± 1.2	2.4 ± 0.3	22.4 ± 2.5
MLGW 95	−149.05	1.08 ± 0.05	0.734 ± 0.077	123.5 ± 9.5	1.7 ± 0.2	87.1 ± 8.7
Well ID	$^{228}Ra/^{226}Ra$	$^{224}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$			
MLGW 87-A	1.73 ± 0.024	1.57 ± 0.029	0.052 ± 0.035			
MLGW 88	1.63 ± 0.012	2.12 ± 0.025	0.121 ± 0.016			
MLGW 99	1.15 ± 0.010	1.17 ± 0.020	0.064 ± 0.017			
MLGW 78-B	1.37 ± 0.014	1.35 ± 0.033	<0.06			
MLGW 95	1.17 ± 0.023	1.45 ± 0.056	<0.05			

[a] NGVD 1929.
[b] Not available due to non-detectable activity of parent or daughter isotope.

4.3. Decay-series radioisotopes

The $^{234}U/^{238}U$ activity ratio from the sampled wells ranged from 1.02 to 1.43 and indicates an increasing trend from Well 95 in the south to Well 78 north (Table 4, Fig. 2). Data analyses indicate higher activities of ^{238}U in the more shallow strata of the Memphis aquifer with the highest activities (29.7 to 43.5 dmp/m^3) being associated with wells in the central part of the wellfield (Table 3). The activity ratio of $^{234}U/^{238}U$ versus $1/^{238}U$ was plotted to discern mixing behavior (Fig. 5). Note that that the activity ratios for $^{234}U/^{238}U$ are shown with error bars and the arrows shown in Fig. 5 demonstrate the effects of leaching, sorption, precipitation and alpha recoil. The plot indicates non-conservative behavior of uranium with two possible trends associated with the northern and southern part of the wellfield.

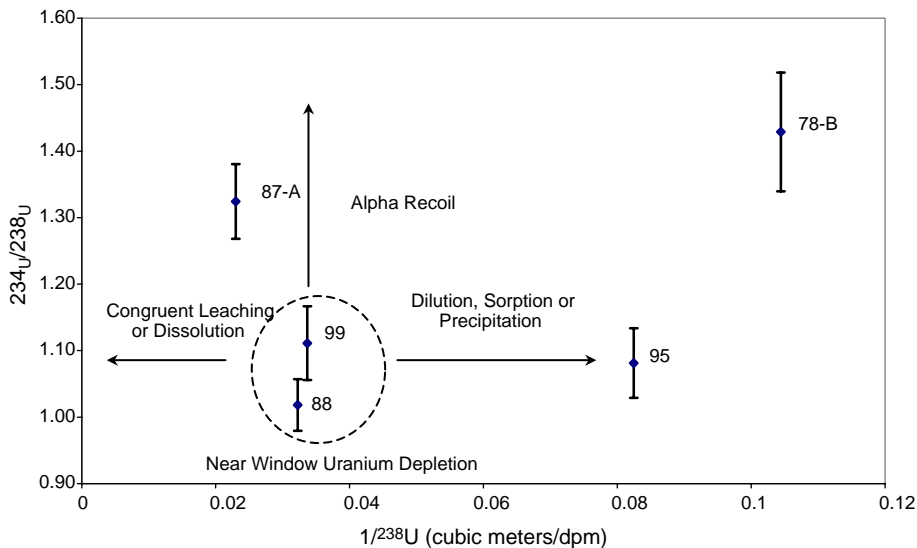The activity ratio of $^{234}Th/^{230}Th$ ranged from 3.7 to 149.5 with the highest ratios being associated with the

Fig. 5. Plot of $1/^{238}U$ and $^{234}U/^{238}U$ AR for sampled wells.

southern part of the wellfield, e.g. in Well 88 and 95 (Table 4). In contrast, the highest ^{234}Th activities occurred in the central portion of the wellfield, with Well 88 and 95 containing activities of 9.31 and 8.9 dpm/m^3, respectively.

The highest radium activities for each of the analyzed isotopes occurred in the shallow strata of the central portion of the wellfield. For example, ^{224}Ra activities ranged from 124.5 to 1115 dpm/m^3 with the highest activities, 653 and 1115 dpm/m^3 being associated with Well 99 and Well 88, respectively (Table 3).

^{222}Rn activities ranged from 66.3 to 110.8 dpm/l throughout the wellfield with no discernable spatial pattern (Table 3).

5. Discussion

5.1. Evidence of aquitard window from hydrogeochemical tracers

As shown in Fig. 3, of the sampled wells in the Sheahan wellfield, the highest pumping activity occurs in the northern part of the wellfield at Wells 78 and 87. These wells have ^{3}H/^{3}He apparent ages of 48.8 and 24.9 years, respectively (Table 2). The ^{3}H/^{3}He data show that the youngest fraction of water in the system, with an averaged transit time of 14.9 years, may occur near the shallow strata of the central portion of the wellfield (Well 88). The general age trend is similar to Larsen et al. (2003), although their data indicate younger apparent ages at Wells 87 (19 years), 78 (28 years) and a somewhat older (by 1.1 years) apparent age at Well 88 (16 years). These results indicate that an aquitard window may likely exist near Well 88 in the central portion of the wellfield.

Trace gas analyses summarized in Table 2, have provided some quality control for the determination of the apparent ages by the ^{3}H/^{3}He method (Solomon and Cook, 2000). A determination of tritiogenic ^{3}He requires the measurement of the ^{3}He/^{4}He ratio, total ^{4}He and total Ne (Solomon and Cook, 2000). The measurement of nitrogen and noble gases also provides information regarding the reliability of the apparent ages due to excess air, or supersaturation of atmospherically derived gases (Solomon and Cook, 2000). The range of values for the trace gases indicate

that the samples were not affected by air entrainment during sampling or air loss during the sealing of the sampling tubes.

In addition to providing apparent ages for Wells 87, 78 and 88, Larsen et al. (2003) described two distinct water zones in the Memphis aquifer at the Sheahan wellfield: a shallow Na–SO$_4$–Cl rich zone, and a deeper Ca–Mg–HCO$_3$ rich zone. They also modeled the leakage to the Memphis aquifer using NETPATH and found that the most meaningful model results required a substantial input of dissolved CO$_2$ gas and precipitation of ferrihydrite. These findings are consistent with the water chemistry data presented in Table 1, which suggests that the shallow Memphis aquifer wells sampled in this study are near a redox zone boundary. The dissolved Fe^{2+} and total iron concentrations are lowest at Wells 99 and 88, which are near the proposed window, whereas wells further away or deeper (Well 95) have higher concentrations. Although the ORP values for Wells 78, 87, 88, and 99 are essentially the same, discrepancies between ORP and measured redox couples have often been noted and attributed either to various sources of disequilibrium and is exacerbated at low specific conductance in Wells 78, 87, 88, and 99 (Grundl and Macalady, 1989). The only Well that shows good agreement between ORP and the ferric–ferrous couple is Well 95, which has a much higher specific conductance and is screened in a significantly deeper and more geochemically stable part of the aquifer. When discrepancies exist, the use of the Fe^{2+}/Fe^{3+} redox couple is generally taken to be a more accurate representation of the redox status of a system. Thus, the vertical gradients in redox appear to be more significant than the lateral variations, consistent with data in Larsen et al. (2003). The source of reducing conditions is not known, but could be related to oxidation of labile organic matter known to exist in the aquifer.

5.2. Behavior of decay-series radioisotopes near the window area

As demonstrated by Luo et al. (2000), the ^{234}U/^{238}U, ^{234}Th/^{230}Th, and ^{224}Ra/^{228}Ra activity ratios exhibit a strong correlation with aquifer

recharge and flow paths. In systems with active groundwater exchange, the movement of radio-nuclides can be retarded by multiple chemical and physical processes (Nereknieks, 1980). Luo et al. (2000) noted in the study at INEEL that ^{238}U was not entirely free of interactions with the aquifer solids. Implicit in the literature is that redox conditions can strongly influence the phase or pool in which the isotopes preferentially reside (Osmond and Cowart, 1992; Ku et al. 1998). The principal mechanisms for radionuclide transfer are dissolution, (co-) precipitation, and/or alpha-recoil (Luo et al., 2000). For short-lived radionuclides, sorption and desorption also play an important role (Krisnaswami et al., 1982). In this study, we observed that the Th isotope activities in the semi-confined Memphis aquifer are all similar to those observed from the unconfined (oxygenated) basaltic aquifer at INEEL, Idaho (Luo et al., 2000) as well as other sandy unconfined aquifers (Tricca et al., 2001). It appears that the concentrations of Th isotopes in groundwater are not significantly affected by the chemistry of groundwater, nor by the chemical/mineralogical compositions of the aquifer rocks. Tricca et al. (2001) hypothesized that the concentration of Th in groundwater is controlled by

the solubility of Th minerals. If so, one would expect the concentration to increase with decreasing pH. However, this hypothesis is not supported by our observations that the activities of ^{232}Th in Wells 88 and 99 (Table 3) vary by a factor of >6, while these wells have the same pH and temperature. We suggest that the large variation of Th concentration in groundwater reflects mainly the occurrence of colloids in groundwater (Luo et al., 2000).

Another important feature of Th isotopes in groundwater is the negative correlation in activities between short-lived ^{234}Th and long-lived ^{232}Th and ^{230}Th (Fig. 6), with high ^{234}Th and low ^{232}Th and ^{230}Th activities occurring mainly in the southern portion of wellfield (Wells 95 and 88). As ^{234}Th has activities about one order of magnitude higher than those of ^{232}Th and ^{230}Th, its concentration is less affected by the occurrence of colloids in the groundwater. Therefore the high ^{234}Th activities in the southern portion of wellfield are likely to reflect the lower scavenging or higher desorption rates of Th from solution to aquifer rocks. A higher input rate by alpha recoil in Well 88, as shown by high radon activities in this Well (Table 3), may also contribute to higher ^{234}Th activity.
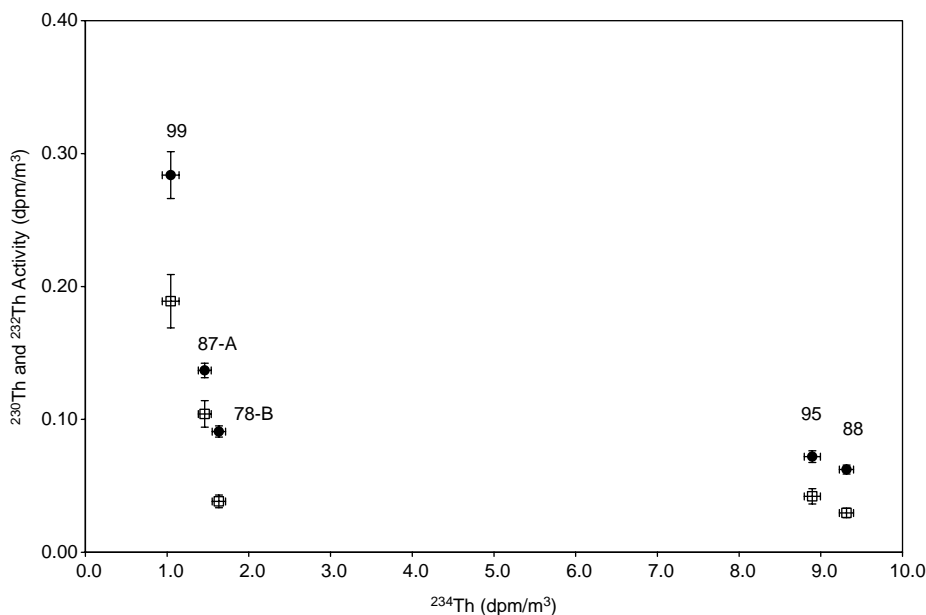

Fig. 6. Plots of ^{230}Th (solid circles) and ^{232}Th (hollow squares) versus ^{234}Th activities. Error bars are shown for each isotope.

Redox gradients exist across the wellfield, which can impact the behavior and transport of radionuclide isotopes. For example, our results show that ^{238}U activity decreases with aquifer depth from ∼44 dpm/m^3 to ∼10 dpm/m^3 (Table 3). These values are generally within the ranges of Tricca et al. (2001); Reynolds et al. (2003) from other confined and unconfined sandy aquifers. However, they are more than two orders of magnitude lower than those in the unconfined and oxygenated basaltic aquifer at INEEL, Idaho (Luo et al., 2000). The low U concentrations are consistent with the observed high Fe^{2+} concentrations in Memphis aquifer, compared to INEEL, reflect a low redox potential and pH in the ground water. It can be seen from Table 3 that there is progressive drop in ^{238}U activity with aquifer depth. Speciation modeling of Fe and U (Fig. 9) suggests different mechanisms of immobilization of U in different regions of the aquifer. The deep aquifer (Well 95) has highly reducing conditions that favor

reduction dissolution of iron to soluble Fe^{2+}, and reductive precipitation of U to insoluble uraninite. In contrast, U forms soluble carbonate complexes under conditions at Wells 99, 88, 87 and 78, but the low levels of U are consistent with increased U sorption by Fe-oxyhydroxides (Langmuir, 1997).

The $^{234}U/^{238}U$ activity ratio (AR) in Well 88, being close to the secular equilibrium ratio of the aquifer rocks, is the lowest among the five wells sampled (Table 4). This may reflect rapid desorption and re-precipitation of U in the window area. Coincidently, as shown earlier, the high ^{234}Th activity in this Well also indicates higher thorium desorption rate than in wells at the northern portion of the wellfield. This is consistent with the expected similarity in the behavior of the particle-reactive Th and reduced U in the suboxic ground waters at the window source.

A plot of $^{234}U/^{238}U$ AR against $1/^{238}U$ indicates non-conservative behavior of uranium in the system (Fig. 5). The non-conservative behavior can be
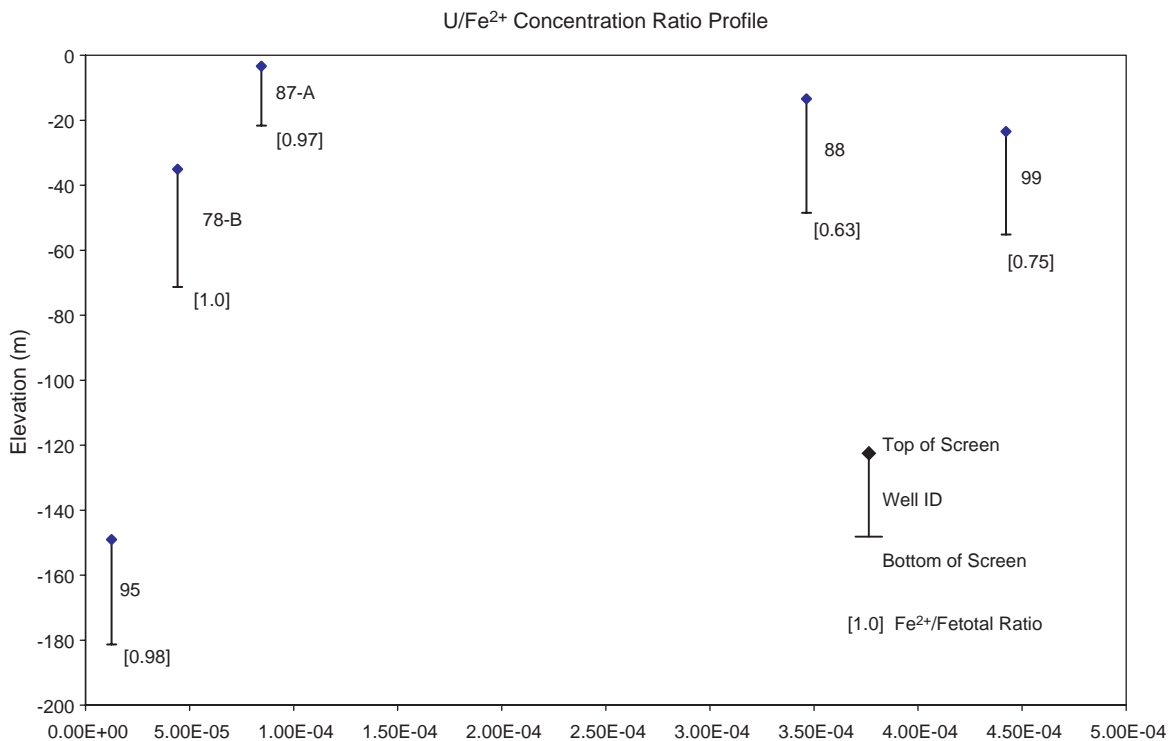

Fig. 7. U/Fe^{2+} concentration ratio profiles.

represented schematically by the mechanisms of leaching, recoil, and dilution processes, as shown in Fig. 5. The observed relationship between uranium concentration and the $^{234}U/^{238}U$ ratio is similar in Wells 88 and 99; in other wells it is modified by dilution (Wells 95 and 78), dissolution (Well 87)

and alpha-recoil (Wells 78 and 87). We interpret the data to indicate that Wells 99 and 88 are located in or near the aquitard window and associated with a redox barrier. The radium isotope data support this conceptualization, with the highest radium concentrations being associated with Wells 88 and 99 (Table 4).
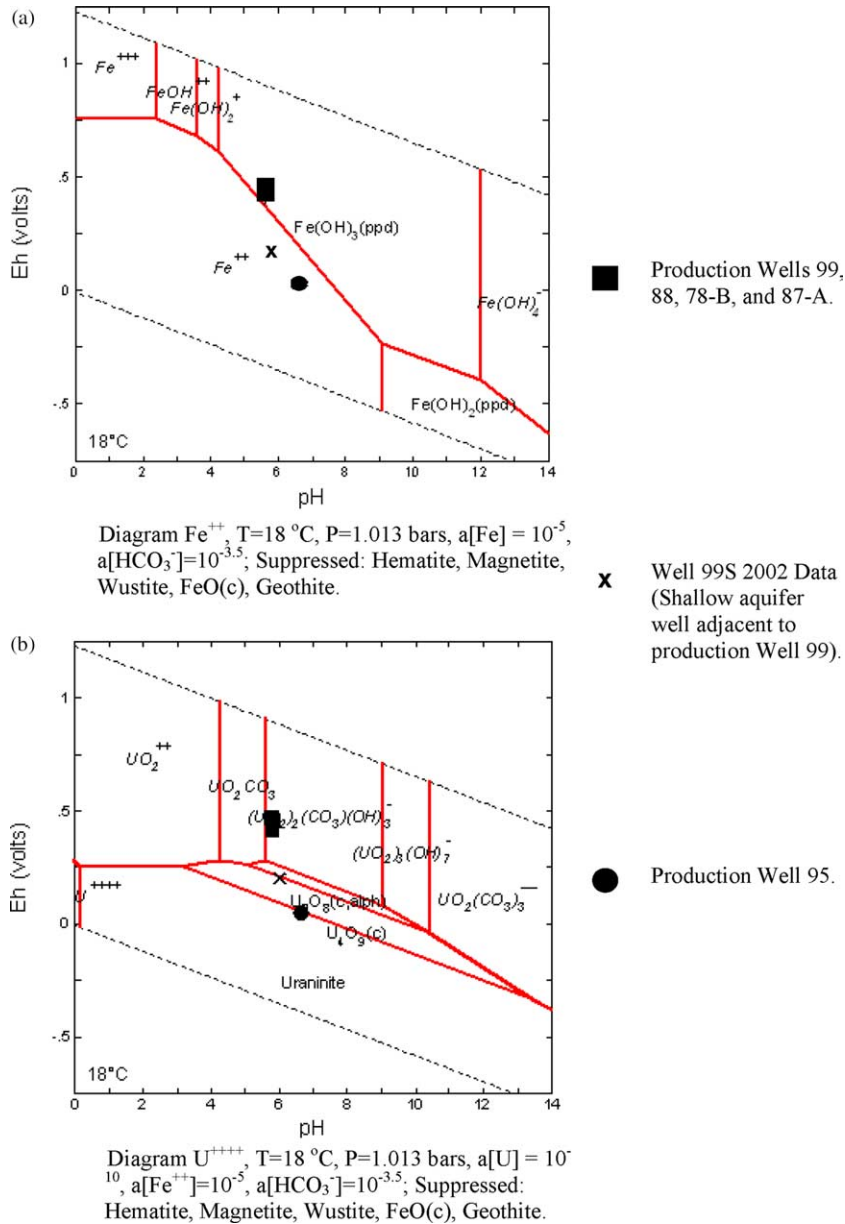

Fig. 8. Eh–pH phase diagrams for (a) Fe^{2+} and (b) U^{4+}

The conceptual model that emerges from the data indicates that U is being depleted in the redox-mixing zone due to U sorption to Fe-hydroxide in the shallower horizons, and U precipitation to uraninite in deeper zones. The high dissolved CO_2 required by Larsen et al. (2003) in order to develop a meaningful model points to possible oxidation of organic material and iron in the mixing zone between the aquifer systems. The data were evaluated by normalizing the uranium concentration to Fe^{2+} iron concentrations $[U/Fe^{2+}]$, and are plotted in Fig. 7. As seen in Fig. 7, Wells 99 and 88 had the highest ratio of U/Fe^{2+}. The normalization serves to accentuate the understood conceptual model at the wellfield. In addition to a better understanding of the aquifer behavior, these techniques may prove useful in future management of the resource and assessment of vulnerability of production wells based upon these naturally occurring hydrogeochemical signals.

Evaluation of an Eh–pH phase diagram for U^{4+} and Fe^{2+} indicates that uranium likely exists in a bound state, such as uraninite, or sorbed on an appropriate Fe-oxide material, see Fig. 8. Although uranium is considered to be more soluble and mobile under oxidizing conditions it is likely that the uranium is being sorbed in the iron hydroxide phase being formed in the redox barrier in and near the window site.

The analysis has demonstrated that a redox and pH control of uranium behavior can be used to explain the source and mixing behavior in and near an aquitard window. A conceptual model is proposed, as shown in Fig. 9, where high uranium concentration near-surface waters enter the Memphis aquifer through an aquitard window. Due to redox reactions and changes in pH occurring within the redox barrier, uranium is depleted. Downgradient flow paths gain ^{234}U through alpha-recoil mobilization from ^{234}Th, and possible

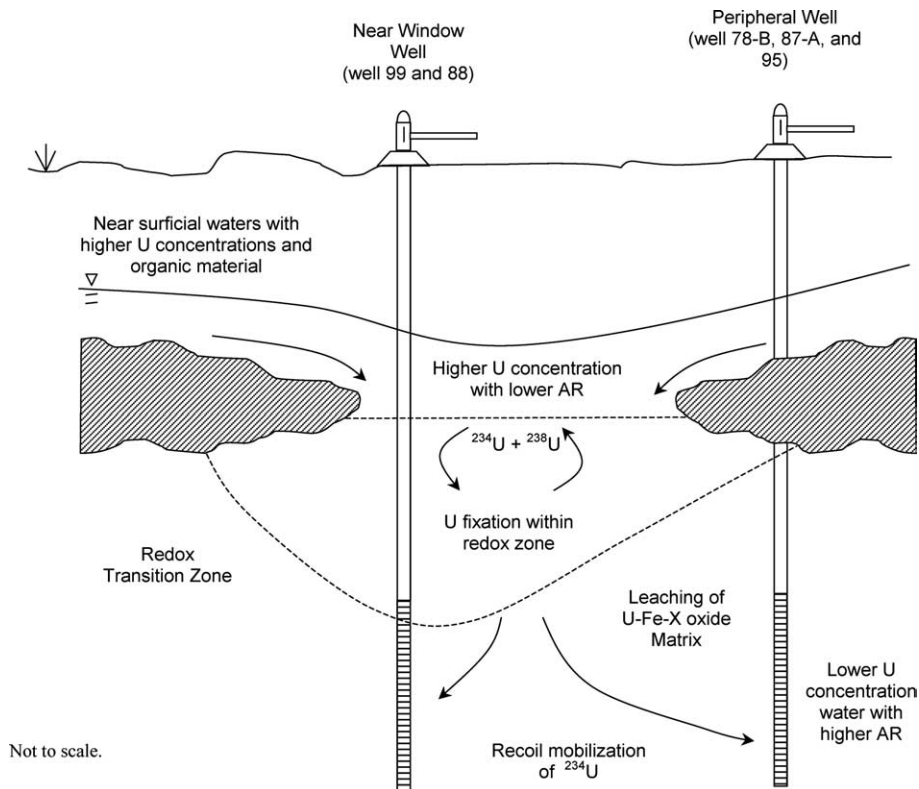Fig. 9. Sheahan wellfield conceptual model based upon hydrogeochemical tracer results. AR = activity ratio of $^{234}U/^{238}U$.

dissolution and precipitation of uranium along reducing flow paths from the aquitard window.

6. Conclusions

The combined use of hydrogeochemical tracers (U, Th, Ra, and Rn) and ground water age tracers, such as ^3H and ^3He is useful in determining aquifer behavior in and near focused accretion sites. Redox conditions within the aquitard window are complex and require a careful evaluation of the $^{234}U/^{238}U$ AR as a recharge source indicator. In this study, total iron and Fe^{2+} concentrations were found to be important in describing the behavior of uranium. The Fe^{2+}-normalized uranium concentrations have indicated the wells with the highest aquitard window recharge are Wells 99 and 88 within the Sheahan wellfield. This conclusion is in agreement with other lines of hydrologic and geochemical data (Ivey, 2003; Kingsbury and Parks, 1993; Larsen, 2003), and helps further interpret the possible lateral heterogeneities, and the resulting aquifer vulnerability that exist in the aquitard in the near wellfield vicinity. The conceptual model formulated from the research demonstrates higher uranium concentrations from near-surface waters flow through a redox barrier in the aquitard window and become depleted in uranium along flow paths to the Memphis aquifer. The $^{234}U/^{238}U$ activity ratio increased downgradient of the recharge source by alpha-recoil mobilization of ^{234}U via ^{234}Th, and leaching of uranium bound by iron hydroxides via dissolution and possibly subsequent precipitation by reducing waters flowing to downgradient wells. The behavior of the hydrogeochemical tracers could be best described in the conceptual model by normalizing uranium to Fe^{2+} throughout the system. The use of the [U]–[Fe^{2+}] pair provides a useful tool for understanding of the mixing behavior near focused recharge sites with redox barriers and may be useful for developing aquifer behavior models and better tools for vulnerability assessment in similar systems.

Acknowledgements

References

Bayer, R., Schlosser, P., Bonisch, G., Rupp, H., Zaucker, R., 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.

Bohlke, J.K., 2002. Groundwater recharge and agricultural contamination (vol 10, pg 153, 2002). Hydrogeol. J. 10 (3), 438–439.

Bradley, M.W., 1988. Construction, geology, and ground-water data for observation wells near the Shelby County Landfill, Memphis, Tennessee. US Geological Survey Water Resources Investigation Report 88-186, 32 p.

Bradley, M.W., 1991. Ground-water hydrology and the effects of vertical leakage and leachate migration on ground-water quality near the Shelby County Landfill, Memphis, Tennessee. US Geological Survey Water Resources Investigation Report 90-4075, 42 p.

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 Geological Survey Water Resources Investigation 89-4131.

Castle, J.W., Miller, R.B., 2000. Recognition and hydrologic significance of passive-margin updip sequences: an example from Eocene coastal-plain deposits, USA. J. Sediment. Res. 70 (6), 1290–1301.

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 Geological Survey Circular 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 Geological Survey Water Resources Investigation 76-67.

Criner, J.H., Sun, P.-C.P., Nyman, D.J., 1964. Hydrology of the aquifer systems in the Memphis area, Tennessee. US Geological Survey Water-Supply Paper 1779-O.

Flavin, R.J., Joseph, J.B., 1983. The hydrogeology of the Lee Valley and some effects of artificial recharge. Quart. J. Eng. Geol. (London)16, 65–82.

Fogg, G.E., LaBolle, E.M., Weissmann, G.S., 1999. Groundwater vulnerability assessment; hydrogeologic perspective and example from Salinas Valley, California. In: Corwin Dennis, L., Loague, K., Ellsworth Timothy, R. (Eds.), Assessment of Non-point Source Pollution in the Vadose Zone. American Geophysical Union, Washington, DC, pp. 45–61.

Fortin, G., van der Kamp, G., Cherry, J.A., 1991. Hydrogeology and hydrochemistry of an aquifer-aquitard system within glacial deposits, Saskatchewan. J. Hydrol. 126, 265–292.

Gentry, R.W., Camp, C.V., Anderson, J.L., 2001. Use of GA to determine areas of accretion to semiconfined aquifer. ASCE J. Hydr. Eng. 127 (9), 738–746.

Gentry, R.W., Larsen, D., Ivey, S.S., 2003. Efficacy of genetic algorithm to investigate small scale aquitard leakage. ASCE J. Hydr. Eng. 129 (7), 527–535.

Graham, D.D., Parks, W.S., 1986. Potential for leakage among principal aquifers in the Memphis area, Tennessee. US Geological Survey Water-Resources Investigations Report 85-4295, 46 p.

Grubb, H.F., 1998. Summary of hydrology of the regional aquifer systems, Gulf Coastal Plain, south-central United States. US Geological Survey Professional Paper 1416-A, United States Government Printing Office, Washington, DC, Ivey, S.S., 2003. The development of a combined age distribution and inverse technique to identify wellhead protection zones for a semi-confined aquifer, PhD dissertation, University of Memphis, 122 p.

Grundl, T.J., Macalady, D.L., 1989. Electrode measurement of redox potential in anaerobic ferric/ferrous chloride systems. J. Contam. Hydrol. 5, 97–117.

Hosman, R.L., Long, A.T., Lambert, T.W., Jeffery, H.G., 1968. Tertiary aquifers in the Mississippi embayment. US Geological Survey Professional Paper 448-D.

Ivey, S.S. 2003. Use of lumped parameter models in wellhead protection area delineation for semi-confined aquifers. PhD dissertation University of Memphis, Memphis, TN.

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 Geological Survey Water-Resources Investigations Report 93-4075, 18 p.

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.

Krisnaswami, S., Graustein, W.C., Turekian, K.K., Dowd, J.F., 1982. Radium, thorium and radioactive lead isotopes in groundwater: application to the in-situ determination of adsorption–desorption rate constants and retardation factors. Water Resour. Res. 18, 1663–1675.

Ku, T.L., Luo, S., Leslie, B.W., Hammond, D.E., 1996. Assessing in-situ radionuclide migration from natural analog studies: Response to McKinley and Alexander (1996). Radiochim. Acta 80, 219–223.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice Hall, Upper Saddle River, NJ. 600 p..

Larsen, D., Gentry, R.W., Ivey, S.S., Solomon, D.K., Harris, J., 2002. Groundwater leakage through a leaky confining unit beneath a municipal well field, Memphis, Tennessee, USA. In: Schulz, H.D., Hadeler, A. (Eds.), Geochemical Processes in Soil and Groundwater. Wiley-VCH, Berlin, pp. 51–64.

Larsen, D., Gentry, R.W., Solomon, D.K., 2003. The geochemistry and mixing of leakage in a semi-confined aquifer at a municipal well field, Memphis, Tennessee USA. Appl. Geochem. 18 (7), 1043–1063.

Luo, S., Ku, T.L., Kusakabe, M., Bishop, J.K.B., Yang, Y.L., 1995. Tracing particle cycling in the upper ocean with ^{230}Th and ^{228}Th: an investigation in the equatorial Pacific along 140 °W. Deep-Sea Res. II 42, 805–829.

Luo, S., Ku, T.L., Roback, R., Murrell, M., McLing, T.L., 2000. In-situ radionuclide transport and preferential groundwater flows at INEEL (Idaho): Decay-series disequilibrium studies. Geochim. Cosmochim. Acta 64, 867–881.

Miller, J.A. 1986. Hydrogeology framework of the Floridan aquifer system in Florida and in parts of Georgia, South Carolina, and Alabama. US Geological Survey Professional Paper 1403-B, 91 p.

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.

National Research Council, 2004. Groundwater Fluxes Across Interfaces. National Academy Press, Washington, DC. 85 p.

Nereknieks, I., 1980. Diffusion in rock matrix: an important factor in radionuclide retardation? J. Geophys. Res. 85, 4379–4397.

Nyman, D.J., 1965. Predicted hydrologic effects of pumping from the Lichterman well field in the Memphis area, Tennessee. US Geological Survey Water-Supply Paper 1819-B.

Osmond, J.K., Cowart, J.B., 1992. Groundwater. In: Ivanovich, M., Harmon, R.S. (Eds.), Uranium-Series Disequilibrium. Oxford Science Publication, Oxford.

Parks, W.S. 1990. Hydrogeology and preliminary assessment of the potential for contamination of the Memphis aquifer in the Memphis area, Tennessee: US Geological Survey Water-Resources Investigations Report 90-4092, 39 p.

Parks, W.S., Carmichael, J.K., 1990, Geology and ground-water resources of the Memphis Sand in western Tennessee: US Geological Survey Water-Resources Investigations Report 88-4182, 30 p.

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 Geological Survey Water-Resources Investigations Report 91-4173, 79 p.

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 Geological Survey Water Resources Investigations Report 94-4212, 58 p.

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 Geological Survey Water-Resources Investigations Report 97-4228.

Reynolds, B.C., Wasserburg, G.J., Baskaran, M., 2003. The transport of U- and Th-series nuclides in sandy confined aquifers. Geochim. Cosmochim. Acta 67 (11), 1955–1972.

Saucier, R.T., 1987. Geomorphological interpretation of Late Quaternary in western Tennessee and their regional tectonic implications. US Geological Survey Professional Paper 1336-A.

Solomon, D.K., Cook, P.G., 2000. ^{3}H and ^{3}He. 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.

Tricca, A., Wasserburg, G.J., Porcelli, D., Baskaran, M., 2001. Transport of U- and Th-series nuclides in a sandy unconfined aquifer. Geochim. Cosmochim. Acta 65, 1187–1210.