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CHANGES IN SHALLOW GROUNDWATER QUALITY BENEATH RECENTLY URBANIZED AREAS IN THE MEMPHIS, TENNESSEE AREA[1]

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ABSTRACT: Memphis, the largest city in the state of Tennessee, and its surrounding suburbs depend on a confined aquifer, the Memphis aquifer, for drinking water. Concern over the potential for downward movement of water from an overlying shallow aquifer to the underlying Memphis aquifer provided impetus for monitoring groundwater quality within the shallow aquifer. The occurrence of volatile organic compounds (VOCs), nitrate, and pesticides in samples from the shallow well network indicate a widespread affect on water quality from the overlying urban land use. Total pesticide concentration was generally higher in more recently recharged groundwater indicating that as the proportion of recent water increases, the occurrence of pesticides related to the current urban land use also increases. Groundwater samples with nitrate concentrations greater than 1.5 mg/l and detectable concentrations of the pesticides atrazine and simazine also had higher concentrations of chloroform, a VOC primarily associated with urban land use, than in other samples. The age of the water from these wells indicates that these concentrations are most likely not representative of past agricultural use, but of more recent urban use of these chemicals. Given that the median age of water represented by the shallow well network was 21 years, a lag time likely exists between changes in land use and the occurrence of constituents related to urbanization in shallow groundwater.

(KEY TERMS: urbanization; land use/land cover change; nonpoint source pollution; organic chemicals; nutrients.)

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INTRODUCTION

In 2005, the United States (U.S.) relied on groundwater for 33% of public water supply and nearly 98% of self-supplied domestic water supply (Kenny *et al.*, 2009). Groundwater generally supplies high quality water for public use; however, it is susceptible to over-use (groundwater overdraft) and contamination (Reilly *et al.*, 2008). To ensure future sources of potable groundwater, it is important to monitor the quality of shallow groundwater as it is susceptible to contamination associated with overlying land use and provides the earliest indication that contaminants are moving into the groundwater system.

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Degradation of shallow groundwater quality has been widely documented in agricultural settings (Rasmussen, 1996; Spalding *et al.*, 2003; Ritter *et al.*, 2006; Burrow *et al.*, 2008; Dalton and Frick, 2008; Debrewer *et al.*, 2008; Frans, 2008). Estimates of the use of anthropogenic compounds, such as pesticides or nutrients, are readily available in agricultural settings and it is possible to relate the occurrence of contaminants in shallow groundwater to activities on the landscape. In contrast to agricultural settings, sources and use of anthropogenic compounds in urban settings are variable and diffuse. Urban contaminant sources are more difficult to estimate than agricultural sources due to the spatially and temporally heterogeneous landscape and use of chemicals (USGS, 1999).

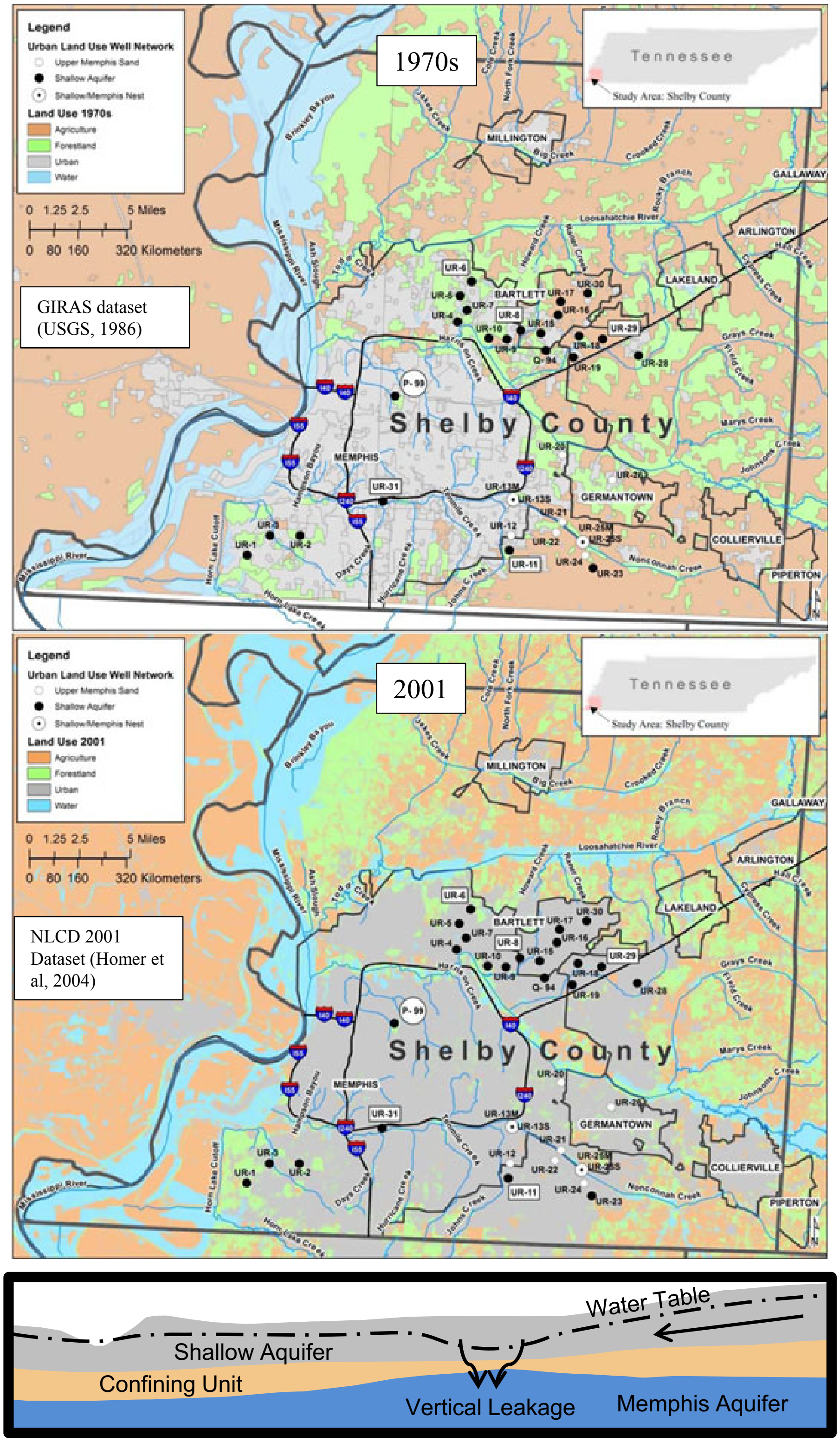
Several studies in other areas have documented groundwater and surface-water contamination in urban settings. In a study of shallow groundwater beneath the Denver, Colorado metropolitan area, Bruce and McMahon (1996) related sulfate and bicarbonate concentrations to a possible shift from oxidizing to reducing conditions in shallow groundwater beneath industrial areas of the city. However, they determined that the use of pesticides and volatile organic compounds (VOCs) was variable and widespread, thus making it difficult to relate the occurrence to one particular land use classification. Barbash *et al.* (2001) compared the occurrence of herbicides in groundwater in both agricultural and urban settings and showed that the detection of herbicides in shallow groundwater beneath urban areas was positively correlated with estimates of nationwide nonagricultural use. However, these authors also pointed to the lack of nonagricultural pesticide use data as a major limitation in understanding the factors that affect the occurrence of pesticides in shallow groundwater beneath urban settings. Blanchoud *et al.* (2007) showed that the pesticide transfer coefficients for the Marne River basin near Paris, France were higher in urban areas than in agricultural areas, the implication being that although pesticide input from agricultural areas were two orders of magnitude higher than urban pesticide inputs, total exports to surface water were almost equal between agricultural and urban areas. Although these and other studies (Flanagan *et al.*, 2001; Robinson, 2003; Blanchoud *et al.*, 2004) have documented the spatial occurrence of stream and shallow groundwater contamination within urban settings, there have been relatively few studies documenting the temporal changes in shallow groundwater quality underlying recently urbanized areas.

Memphis, the largest city in the state of Tennessee, and its surrounding suburbs rely solely on groundwater for public and domestic supply (Kenny *et al.*, 2009) (Figure 1). Most of this water is pumped from the underlying confined drinking water aquifer, locally referred to as the Memphis aquifer. The Memphis aquifer is overlain by a shallow water-table aquifer, hereafter referred to as the shallow aquifer. Although the Memphis aquifer and shallow aquifer are typically separated by a confining unit, previous studies have identified areas where this unit is thin or absent and the aquifers are in direct connection (Graham and Parks, 1986; Parks, 1990; Bradley, 1991; Parks *et al.*, 1995). In these areas, the potential exists for water and contaminants in the shallow aquifer to move downward to the Memphis aquifer (Figure 1).

A network of 31 shallow monitoring wells (Figure 1) was installed in 1996 as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program to characterize the quality of groundwater in the shallow aquifer beneath areas of recent urbanization (post-1970) (Gonthier, 2002). Several of these monitoring wells were installed in areas where the confining unit has been mapped as thin or absent. This shallow well network was sampled in 1997 and in 2006; a subset of five wells and one reference well representing background, or “reference” water-quality conditions in this area were sampled periodically between and after the 1997 and 2006 network-wide sampling events. The objectives of this article were to characterize the quality of shallow groundwater underlying recently urbanized areas around Memphis, Tennessee as well as the susceptibility of the shallow aquifer to contamination from the overlying land use. In addition, this article characterizes changes in shallow groundwater quality from 1997 through 2009.

STUDY SETTING

The near-surface geology in the Memphis urban area includes a surficial layer of fine-grained loess that generally thins from a maximum thickness of about 18 m at the bluffs along the Mississippi River to less than 3 m in eastern Shelby County. Predominantly unconsolidated fine sand to coarse gravel terrace deposits of Pleistocene to Pliocene age underlie the loess and contain the shallow aquifer. Maximum depth to the base of the shallow aquifer is about 52 m (Parks, 1990), and the saturated thickness ranges from less than 0.3 m to about 18 m. Sediments that make up this aquifer range from fine sand to coarse gravel. Locally, the clastic sediments of the aquifer are cemented to form ferruginous sandstone layers. Recharge to the shallow aquifer is predominantly



[Hydrogeology modified from Bradley, 1991]

FIGURE 1. Land Use in Memphis Study Area, Tennessee, 1970s and 2001, Shallow Groundwater Well Network Locations, and Conceptual Diagram of Hydrogeologic Setting for the Study Area. Subset of five wells sampled more frequently indicated by white squares; reference well indicated by white circle.

from infiltration of precipitation, but recharge also may occur along losing reaches of streams, particularly in the eastern part of the study area (Parks, 1990). The shallow aquifer is largely unconfined, but the overlying loess slows the downward movement of water, and locally, may be an upper confining unit. Depth to water in the shallow aquifer generally is about 4–9 m below land surface. There is only limited use of the shallow aquifer in the study area, and discharge from the shallow aquifer is to streams or locally to the Memphis aquifer.

A confining unit, composed primarily of clay, silt, sand, and lignite of Eocene age ranging in thickness from 0 to 106 m, underlies the shallow aquifer throughout most of Shelby County separating the shallow aquifer from the Memphis aquifer. However, locally and in the eastern part of the county, this confining unit is thin or absent, allowing for the downward movement of water from the shallow aquifer to the Memphis aquifer (Parks, 1990). The Memphis aquifer, composed predominantly of unconsolidated sand with minor lens of silt and clay of Eocene age ranging in thickness from 200 to 275 m, is the primary source of drinking water for much of western Tennessee and northern Mississippi, and supplies about 95% of the groundwater used by municipalities in the study area (Kingsbury, 1996).

URBAN SHALLOW WELL NETWORK AND LAND USE IN THE MEMPHIS AREA

Wells for the study were installed near the top of the water table to characterize the effect of urban land use on recently recharged groundwater. Wells were installed using a hollow stem auger drill rig and constructed with 5 cm diameter polyvinyl chloride (pvc) with 3 m screened intervals at the bottom of the well casing (Strom, 1997). As a consequence of the distribution of land use and local hydrogeology, 8 of the 31 wells were completed in the upper part of the Memphis aquifer in southeastern Shelby County because the terrace deposits that make up the shallow aquifer are virtually dry in these areas; 2 of these 8 wells were installed directly next to a well screened in the shallow aquifer as part of shallow/Memphis aquifer nests (Parks, 1990) (Figure 1). The confining unit separating the Memphis and shallow aquifers in these areas is relatively thin to absent, ranging from 0 to 10 m. In this study, samples from the Memphis aquifer and shallow aquifer are combined with respect to characterizing the effect of urban land use on shallow groundwater quality.

Land use was determined within a 500-m radius around each well in the network in 1997 and 2006. Land use was characterized using low-altitude aerial photography and was verified in the field, using a nationally consistent procedure (Koterba, 1998). Land use changed little between 1997 and 2006 (less than 2% for any category), with 1997 urban, forest, and agricultural land use ranging between 28 and 100% (median 86%), 0 and 70% (median 10%), and 0 and 25% (median 0%), respectively (Table 1).

County-level land use data from the 1970s and 2001 were assessed using the Geographic Information Retrieval and Analysis System (GIRAS) land use and land cover dataset (USGS, 1986) and the 2001 National Land Cover Database (NLCD) (Homer *et al.*, 2004), respectively (Figure 1). Because land use around each well changed little between 1997 and 2006, the NLCD 2001 was used to represent county-level land use during the sampling period. A comparison at the county level indicates substantial urbanization within the surrounding suburbs of Memphis. Overall, urban land use increased, whereas agricultural and forest/rangeland land use decreased between the 1970s and 2001. Land use within the city of Memphis did not change as much as the surrounding suburban areas because the city of Memphis was urbanized prior to the 1970s. Wells located in the suburban areas, especially near Germantown and Bartlett, are in areas where land use has changed considerably from agricultural and forest/rangeland to urban since the 1970s (Figure 1).

United States Census data also indicate an urbanization trend consistent with observed changes in land use. From 1990 through 2000, the population within the city of Memphis grew at a smaller rate than the surrounding cities and towns and from 2000 through 2008 the Memphis population decreased, whereas the population in many of the surrounding communities continued to grow. From 1990 through 2008, many of the surrounding cities, especially Bartlett, experienced large increases in population relative to the total areas of these cities (U.S. Census Bureau, 2008).

WATER-SAMPLE COLLECTION AND ANALYSIS

Throughout the study period (1997-2009), water samples collected from the shallow well network were analyzed for physical properties, major and minor inorganic constituents, nutrients, pesticides, and VOCs. Samples typically were collected in late April through late May. A subset of six wells was sampled generally biannually beginning in the spring of 2002 and ending the spring of 2009 (Figure 1). All groundwater samples

TABLE 1. Hydrogeologic, Land Use, and Chemical Data for Shallow Well Network in the Vicinity of Memphis, Tennessee.

	Hydrogeology			Land Use in 1997 (within 500 m radius around well)				Chloride		Nitrate		Atrazine		Simazine		Depth to Water	
								1997	2006	1997	2006	1997	2006	1997	2006	1997	2006
Well ID	Thickness of Overlying Loess (m)	Well Depth (m)	Apparent Ground-water Age (in years)	Urban (%)	Forest and Range-land (%)	Agricultural (%)	Other (%)	Concentration (mg/l)		Concentration (mg/l)		Concentration (μg/L)		Concentration (μg/L)		Distance Below Land Surface (m)	
UR-1†	10	21 (21)	26	28	70	3	0	3.0	3.1	0.89	0.87	E 0.001	<0.007	<0.005	E 0.004	6	8
UR-2	12	21	22	61	39	0	0	3.3	4.4	0.35	0.57	<0.001	E 0.005	<0.005	<0.005	8	10
UR-3	10	21	21	48	50	0	2	7.2	8.5	1.8	1.7	<0.001	<0.007	<0.005	E 0.006	5	6
UR-4†	6	12	12	84	15	0	1	9.9	15	<0.05	<0.06	<0.001	<0.007	<0.005	<0.005	7	6
UR-5	9	14	15	62	35	0	3	8.5	13	1.0	1.6	<0.001	<0.007	<0.005	<0.005	11	12
UR-6	7	12	22	73	27	0	0	30.5	16	1.6	1.5	<0.001	0.035	<0.005	0.038	9	10
UR-7	10	15	3	81	19	0	0	2.6	2.9	<0.05	<0.06	<0.001	<0.007	<0.005	<0.005	8	9
UR-8	8	13	15	46	22	25	8	8.7	5.9	0.66	3.1	0.005	0.008	0.006	E 0.007	3	4
UR-9	6	14	12	100	0	0	0	24	26	6.2	5.6	<0.001	<0.007	<0.005	<0.005	4	5
UR-10	8	15	30	86	14	0	0	2.8	2.7	<0.05	<0.06	<0.001	<0.007	<0.005	<0.005	5	6
UR-11	5	16	26	88	12	0	0	237	201	0.08	0.06	<0.001	<0.007	<0.005	E 0.004	4	5
UR-12*†	5	33 (38)	25	97	3	0	0	8.5	6.5	<0.05	<0.06	0.006	<0.007	<0.005	<0.005	30	30
UR-13S	9	10	19	68	28	0	3	11	14	<0.05	0.20	<0.001	E 0.005	0.058	0.01	4	5
UR-13M*	9	30		68	28	0	3	12	-	0.14	—	<0.001	—	0.01	—	20	—
UR-15	5	16	15	96	4	0	0	6.6	16	2.1	2.3	<0.001	0.053	<0.005	E 0.004	8	8
UR-16	7	27	18	100	0	0	0	26	19	1.9	3.4	0.015	0.015	0.008	0.016	19	20
UR-17	7	15	20	94	6	0	0	6.9	17	2.0	2.1	<0.001	0.066	0.007	0.07	6	7
UR-18	8	21	16	97	3	0	0	40	39	<0.05	0.37	0.072	0.035	0.23	0.10	19	20
UR-19	8	20	26	96	4	0	0	43	45	3.1	4.3	<0.001	0.017	<0.005	E 0.006	13	14
UR-20*	4	23	29	99	1	0	0	5.6	5.8	<0.05	<0.06	<0.001	<0.007	<0.005	<0.005	16	17
UR-21*	5	27	13	72	0	0	28	11	7.4	<0.05	0.04	<0.001	E 0.005	0.048	0.044	23	24
UR-22*	5	30	11	99	0	0	1	5.7	4.8	1.1	1.7	0.021	0.17	0.11	0.50	24	25
UR-23	4	13	24	96	1	0	4	10.0	6.2	0.30	3.7	<0.001	0.033	<0.005	0.02	10	10
UR-24*	5	30	20	86	14	0	0	4.2	9.2	<0.05	<0.06	—	—	—	—	20	21
UR-25S	4	13		71	18	3	8	8.5		<0.05	—	<0.005	—	<0.005	—	5	—
UR-25M*†	4	29 (32)	29	71	18	3	8	9.2	13	<0.05	<0.06	0.008	<0.007	<0.005	<0.005	22	19
UR-26*	5	33	25	100	0	0	0	4.6	4.5	<0.05	<0.06	0.007	<0.007	0.38	0.009	21	22
UR-28	2	12	27	100	0	0	0	167	98	0.80	1.3	0.07	0.023	0.009	0.032	6	6
UR-29	5	27	14	93	3	0	5	15	11	4.2	6.1	0.007	0.034	<0.005	0.024	21	23
UR-30†	5	24	23	99	1	0	0	5.9	4.2	0.51	1.6	<0.001	E 0.004	<0.005	E 0.004	22	23
UR-31	5	13	5	74	8	0	18	6.0	7.4	<0.05	<0.06	0.048	0.078	0.41	0.37	8	10
P-99‡	12	18	27	18	82	0	0	—	10	—	0.24	—	<0.007	—	<0.005	—	11
Q-094‡	6	27	25	82	18	0	0	13	14	2.7	3.1	<0.001	E 0.006	<0.005	0.018	22	21
Minimum	2	10	3	18	0	0	0	3	3	<0.05	<0.06	<0.001	<0.007	<0.005	<0.005	3	4

TABLE 1. (Continued)

	Hydrogeology			Land Use in 1997 (within 500 m radius around well)				Chloride		Nitrate		Atrazine		Simazine		Depth to Water	
								1997	2006	1997	2006	1997	2006	1997	2006	1997	2006
Well ID	Thickness of Overlying Loess (m)	Well Depth (m)	Apparent Ground-water Age (in years)	Urban (%)	Forest and Range-land (%)	Agricultural (%)	Other (%)	Concentration (mg/l)		Concentration (mg/l)		Concentration (μg/L)		Concentration (μg/L)		Distance Below Land Surface (m)	
Maximum	12	33	30	100	82	25	28	237	201	6.2	6.1	0.072	0.17	0.41	0.50	30	30
Median	6	20	21	86	12	0	0	9	10	0.33	0.87	0.001	0.01	0.00	0.01	9	10

Notes: -, no data available; E, estimated value.

*Well screened in upper part of Memphis aquifer.

†Well dry after 1997 sampling event and replaced with another well before 2006 samplinig event. Well depth shown as “1997 depth (2006 depth).”

‡Existing well added to network due to location within study area.

were collected using nationally consistent methods (Koterba *et al.*, 1995). Samples for inorganic and nutrient analysis were filtered through a 0.45-μm pore-size capsule filter, and cations were preserved with 7.5 N nitric acid; pesticide samples were filtered through a 0.7-μm pore-size glass fiber filter and collected in baked amber glass bottles. Samples collected for VOC analyses were preserved with 1:1 hydrochloric acid. Samples were chilled on ice and shipped for next-day delivery for analysis using approved analytical methods at the USGS National Water-Quality Laboratory (NWQL) in Denver. Dissolved inorganic constituents were determined at the NWQL using atomic absorption, inductively coupled plasma, ion-chromatography, ion specific electrode, and colorimetric methods, as described in Fishman and Friedman (1989) and Fishman (1993). Alkalinity was determined in the field at the time of sample collection using incremental titrations. Samples for analyses of pesticides were extracted at the NWQL on solid-phase extraction (SPE) cartridges to concentrate the analytes from the filtered samples. SPE cartridges then were eluted with a solvent, and the extracts were analyzed by either gas chromatography/mass spectrometry (GC/MS) or high-performance liquid chromatography/mass spectrometry (HPLC/MS) methods (Zaugg *et al.*, 1995, 2002; Lindley *et al.*, 1996; Furlong *et al.*, 2001; Sandstrom *et al.*, 2001; Madsen *et al.*, 2003). VOCs were analyzed by purge and trap GC/MS (Connor *et al.*, 1998). Age-dating samples were collected during the 2006 sampling event and sent to the USGS Chlorofluorocarbon Laboratory in Reston, Virginia for sulfur hexafluoride (SF6) analysis to determine an apparent groundwater age (Busenberg and Plummer, 2000). Samples for SF6 analysis were collected in 1 l glass bottles, capped with Polyseal screw-caps without headspace, and stored in coolers until shipment.

Quality-control data, including field blanks, replicate samples, and field-spiked samples, were collected along with routine samples to ensure that unintended contamination did not occur at any point in the sample collection and laboratory analysis. Quality-control results are presented in detail in Welch *et al.* (2009). Although the majority of the quality-control data indicated that unintended contamination did not occur, quality-control data associated with VOC samples collected in 1997 did indicate widespread occurrence of low-level (<0.2 μg/l) contamination. Quality-control data associated with VOC samples collected after 1997 did not indicate contamination. For this reason, only unaffected VOC data from samples collected after 1997 are presented in this study.

The Wilcoxon signed rank was used to determine whether the median value between matched pairs within two groups of data statistically differed from one another (Helsel and Hirsch, 1992). Differences were considered significant above the 95% or greater confidence level ($\rho < 0.05$). To account for changes in laboratory detection limits throughout the study period, all results that were not detected at the laboratory reporting limit (LRL) were assigned a rank less than the lowest detected concentration for each constituent (Helsel, 2005a,b; Bexfield., 2008).

RESULTS AND DISCUSSION

Natural Water Chemistry and Age of Shallow Groundwater

Shallow groundwater chemistry is variable throughout the study area but generally within the ranges of natural, uncontaminated water as determined by a previous study within the study area (Brahana *et al.*, 1987) (Table 2). Between 1997 and 2006, the major-ion chemistry of samples from each well did not differ significantly ($\rho < 0.05$ for all constituents shown in Figure 2). The chemical composition of groundwater samples ranged between calcium-magnesium-bicarbonate and sodium-bicarbonate waters and generally did not differ between samples from wells screened in the upper Memphis aquifer and wells screened in the shallow aquifer (Figure 2). Several physical properties and inorganic constituents were correlated ($\rho < 0.05$) with the thickness of the overlying loess and depth to water. For instance, pH, bicarbonate, calcium, and magnesium were positively correlated ($\rho < 0.05$) with the thickness of overlying loess suggesting greater mineralization of the water with increased residence time in the loess. Specific conductance, bicarbonate, calcium, and magnesium were negatively correlated ($\rho < 0.05$) with the depth to water as concentrations generally increase as the depth to water decreases. This negative correlation is possibly due to the correlation ($\rho < 0.05$) between depth to water and the thickness of overlying loess, with the depth to water decreasing generally as the thickness of overlying loess increases. Specific conductance, although not significantly correlated with the thickness of overlying loess, generally increased as the thickness of overlying loess increased. None of the physical properties or inorganic constituents were significantly ($\rho < 0.05$) related to well depth.

TABLE 2. Groundwater Chemistry Summary Statistics for the Shallow Well Network in the Memphis, Tennessee Area, Sampled in 1997 and 2006.

Year Sampled	**1997**	**2006**
Number of Wells	**31**	**32**
Constituent, Dissolved	**Median (range)**	**Median (range)**
Specific conductance, μs/cm at 25°C	235 (76-1,000)	229 (112-920)
Dissolved oxygen, mg/l	2.7 (0.1-5.8)	1.7 (0.2-6.2)
pH, standard units	6.1 (5.5-6.8)	5.8 (4.7-6.5)
Temperature, °C	19 (16.3-22.2)	20.4 (16.3-29.2)
Bicarbonate, mg/l	93 (23-350)	100 (21-610)
Calcium, mg/l	14 (2.4-54)	15 (2.7-84)
Magnesium, mg/l	6.8 (0.92-30)	7.7 (1-49)
Sodium, mg/l	18 (6.4-122)	17 (7.4-119)
Potassium, mg/l	1.1 (0.19-4.6)	0.85 (0.18-3.8)
Chloride, mg/l	8.6 (2.6-237)	10 (2.7-201)
Sulfate, mg/l	7.7 (0.43-44)	8.1 (0.79-65)
Silica, mg/l	28 (12-65)	28 (13-71)
Nitrate, mg/l	0.33 (<0.05-6.2)	0.87 (<0.06-6.1)
Iron, μg/l	19 (4-5,320)	72 (6-10,200)
Manganese, μg/l	58 (1.2-6,670)	27 (0.3-4,600)

Redox (reduction/oxidation) conditions varied in shallow groundwater with about half of the samples characterized as oxic (dissolved oxygen [DO] concentrations >0.5 mg/l) and seven samples as anoxic, following the classification scheme used by McMahon and Chapelle (2008). The remaining samples indicated mixed redox conditions with DO concentrations greater than 0.5 mg/l, but one or more of the redox sensitive constituents (for example manganese) greater than its threshold value for redox classification. Redox conditions and redox-sensitive constituents were not correlated ($\rho > 0.05$) to the thickness of the overlying loess, well depth, or depth to water; however, samples indicating oxic redox conditions generally were from wells completed closer to the top of the water table.

Estimates of groundwater ages for the network ranged from 3 to 33 years, indicating that assuming a piston flow model for recharge, groundwater samples collected in 2006 were recharged between 1976 and 2003 (Table 1). In reality, each groundwater sample consists of a mixture of waters, moving along different flow paths with varying lengths and time of travel. Therefore, groundwater age represents a composite residence time of groundwater from each well, and older groundwater ages indicate a larger component of water with longer residence times. Based on the range of ages and the time frame when the majority of urbanization occurred, the water quality of samples with residence times greater than 20 years (approximately 50% of all samples) could reflect both current and previous land use. Groundwater age was not significantly correlated ($\rho > 0.05$) with any of the above inorganic constituents or the thickness of overlying loess, depth to water, or well depth. The lack of correlation between apparent groundwater age and inorganic constituents and

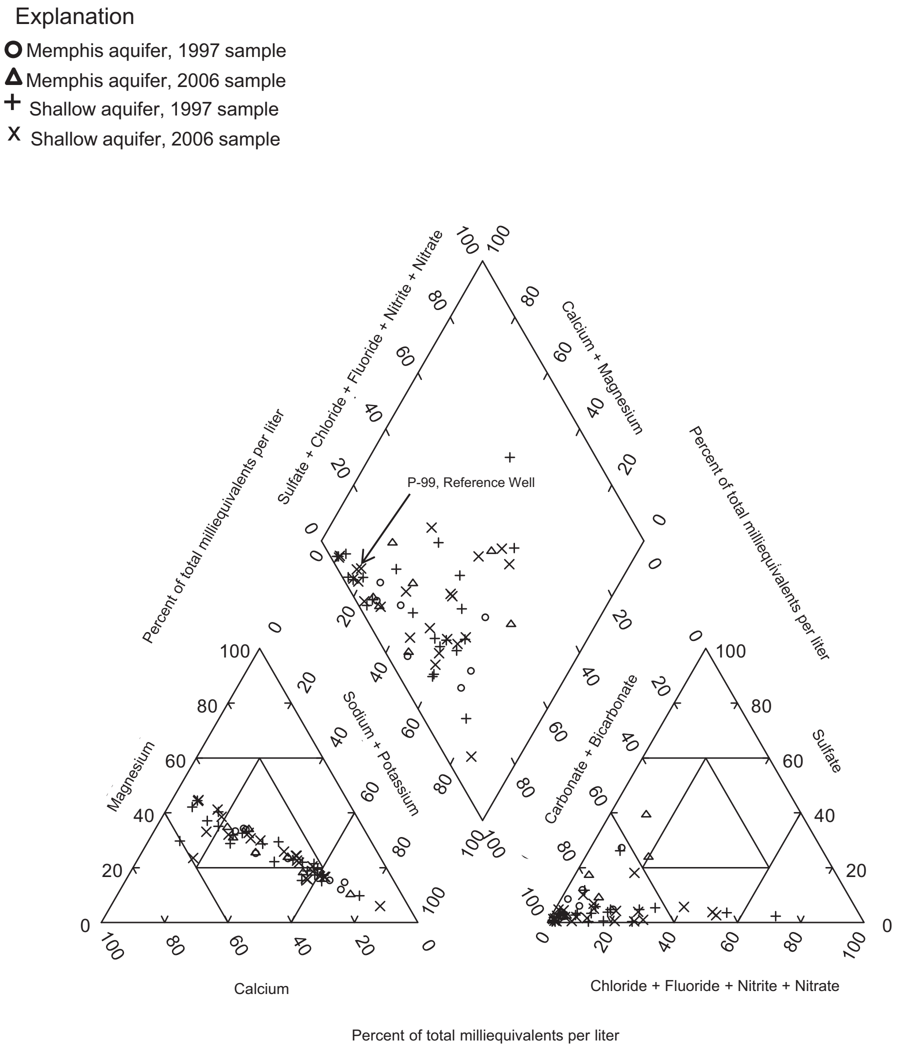


FIGURE 2. Chemical Composition of Groundwater Samples Collected in 1997 and 2006 From the Shallow Well Network. Eight wells were screened in the upper part of the Memphis aquifer, 25 wells were screened in the shallow water table aquifer. The chemical composition of the upper Memphis aquifer samples was similar to that of the shallow water table.

physical characteristics could be the result of heterogeneity of the aquifer sediments affecting the variability in water quality to a larger extent than groundwater residence time.

Occurrence of Anthropogenic Chemicals in Shallow Groundwater

Although inorganic constituent concentrations in samples from the shallow well network were generally not indicative of anthropogenic influence, elevated concentrations and the occurrence of certain chemicals did indicate anthropogenic influence on shallow groundwater. The median chloride concentration was 9.6 mg/l, and almost 80% of all samples had concentrations <20 mg/l (Table 2), which falls within previously reported ranges (1.2-22 mg/l) of chloride in areas of the shallow aquifer considered to be unaffected by surface contamination (Brahana *et al.*, 1987). Two sites had much greater concentrations than the other sites, UR-28 ($n = 2$, maximum concentration = 167 mg/l) and UR-11 ($n = 6$, maximum concentration = 237 mg/l), suggesting a local chloride source to the aquifer near these wells. In urban areas, elevated chloride concentrations in groundwater typically are indicative of anthropogenic sources, which can include septic systems or sewers, road salt use, fertilizer use, or waste disposal sites (Canter and Knox, 1985; Naftz and Spangler, 1994; USEPA, Office of Water, 2001; Panno *et al.*, 2006). Determining local sources of contamination was not an objective of this study and additional data collection and analysis would be needed to characterize the source(s) of chloride detected at these wells.

The widespread occurrence of VOCs, nitrate, and pesticides in samples from the shallow well network also indicate an effect on water quality from the overlying urban land use (Table 1). VOCs, in particular are most commonly associated with urban and industrial land use. Eleven VOCs were detected in samples from the shallow well network, with at least one VOC detected in samples from about two-thirds of the sites (Figure 3). All concentrations were below health-based screening levels and maximum contaminant levels. Trichloromethane (chloroform), a trihalomethane (THM), was the most commonly detected VOC in the study. Chloroform, a by-product of the drinking and wastewater chlorination/disinfection process, was also the most frequently detected VOC in a recent study of the occurrence of VOCs in aquifers of the U.S. (Carter

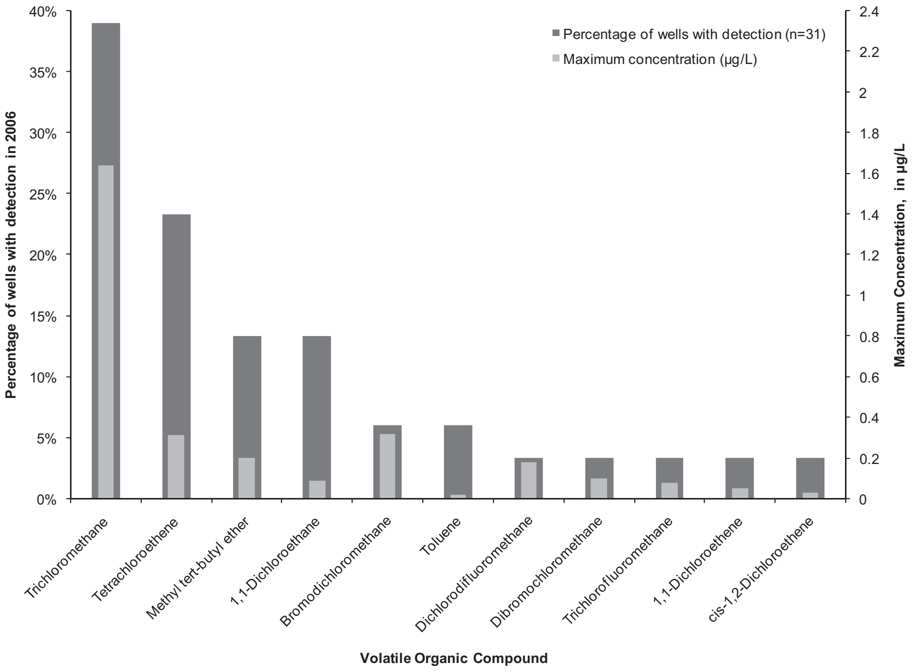


FIGURE 3. Volatile Organic Compounds Detected in Samples Collected in 2006 From the Shallow Well Network: Percentage of Samples With Detections and Maximum Concentration. All concentrations were below health-based screening levels and maximum contaminant levels (Toccalino *et al.*, 2008; USEPA, 2009).

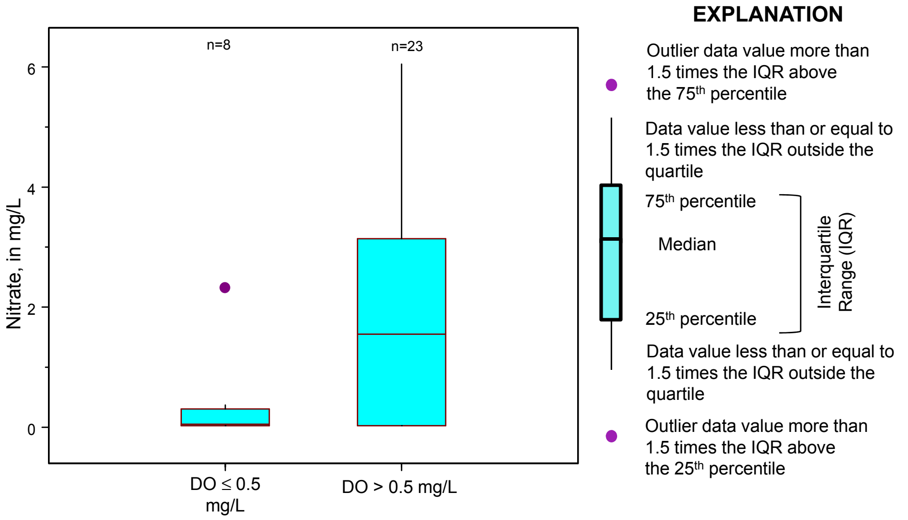


FIGURE 4. Distribution of Nitrate Concentrations Relative to Dissolved Oxygen (DO) Concentrations in Samples Collected in 2006 From the Shallow Well Network.

et al., 2008). Possible sources of chloroform to shallow groundwater include infiltration of chlorinated drinking water used for various irrigation purposes (lawns, gardens, golf courses), leaking water lines, septic system effluent, and wastewater sewer systems (Carter *et al.*, 2008). Tetrachloroethene, a solvent; methyl *tert*-butyl ether (MTBE), a gasoline oxygenate; and 1,1-dichloroethane, a solvent, were detected in more than 10% of samples analyzed in 2006. Concentrations of VOCs generally were less than 0.5 μg/l, with only two detections of chloroform at concentrations between 1 and 2 μg/l. The relatively widespread detections of low levels of VOCs, which are associated with urban and industrial land use, indicate that shallow groundwater has been affected by the recent conversion to urban land use in this area. For example, MTBE was detected in samples from four wells (UR-25M, UR-8, UR-15, UR-17), indicating that groundwa-

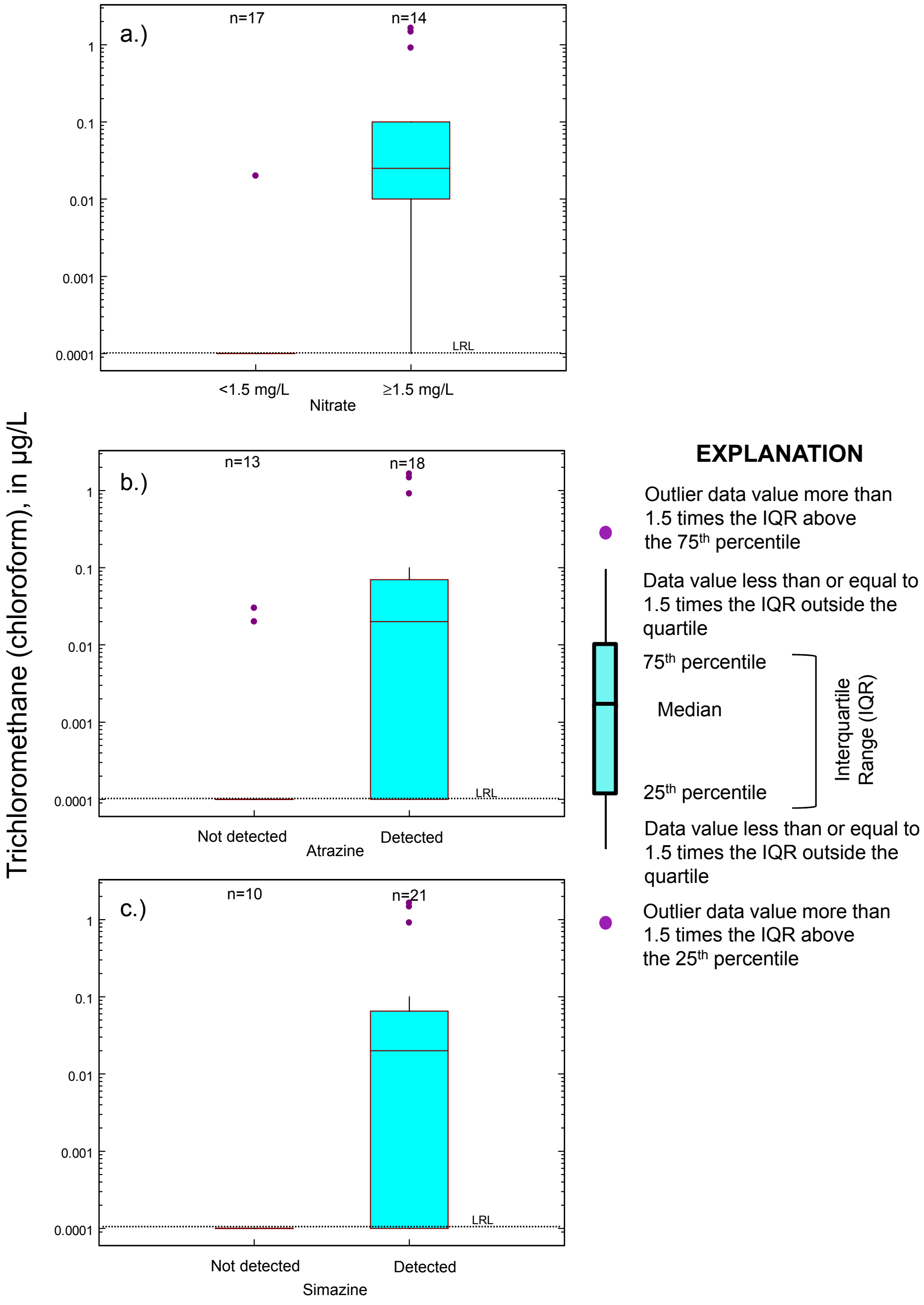
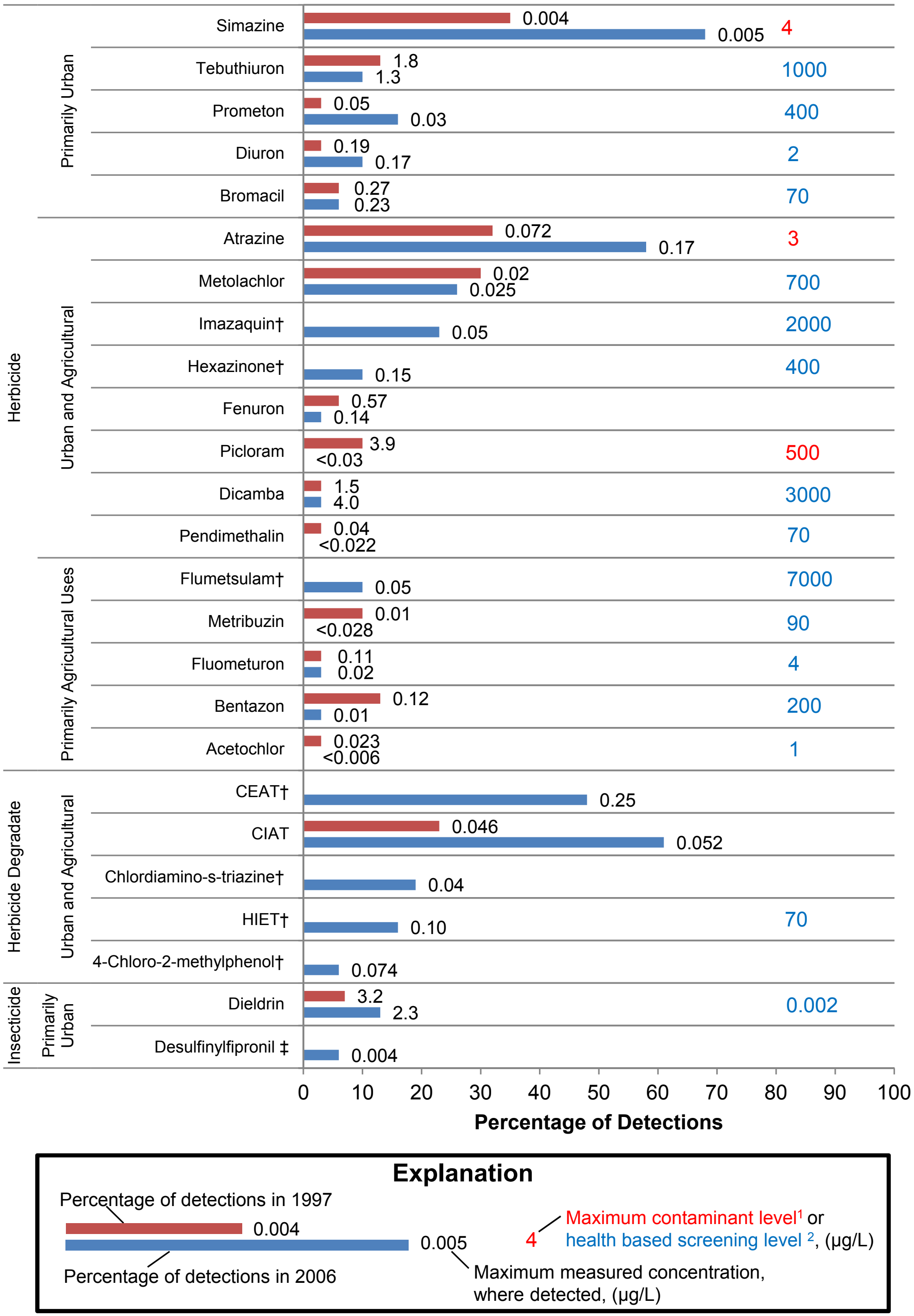


FIGURE 5. Distribution of Chloroform Concentrations with Respect to (A) Nitrate Concentrations Greater Than 1.5 mg/l, (B) Detectable Concentrations of Atrazine, and (C) Detectable Concentrations of Simazine for Samples Collected in 2006 from the Shallow Well Network. LRL, laboratory reporting limit.

ter from these wells has been affected by MTBE use subsequent to its initial introduction in 1979.

Nitrate concentrations in samples from the shallow well network ranged from <0.06 to 7.41 mg/l over the time period from 1997 through 2009, less than the U.S. Environmental Protection Agency (USEPA) maximum contaminant level for finished drinking water of 10 mg/l (Table 1). Potential sources of nitrogen in urban settings include fertilizer applications on lawns and gardens, golf courses, leaking sewer systems or septic systems, and atmospheric deposition (Wakida and Lerner, 2005). Another potential source of nitrate



[1] USEPA, 2009
[2] Toccalino and others, 2008

FIGURE 6. Summary of Pesticides Detected Two or More Times in Shallow Well Network, 1997 and 2006 Sampling Events (-, no data available; †, constituent not analyzed in samples from 1997 sampling event; ‡, insecticide degradate).

to groundwater in recently urbanized settings is storage of nitrogen in the unsaturated zone from fertilizer use or animal waste associated with the prior agricultural land use (Wilcox *et al.*, 2005; Showers *et al.*, 2008). Occurrence and concentrations of nitrate were correlated ($\rho < 0.05$) with DO concentrations suggesting that denitrification, in part, may be affecting nitrate concentrations in groundwater. The median concentration of nitrate in samples with DO concentrations >0.05 mg/l was 1.5 mg/l compared to a median concentration of 0.06 mg/l in samples with DO concentrations <0.5 mg/l (Figure 4). Concentrations of nitrate also were related to the occurrence of chloroform. Samples with nitrate concentrations at or above 1.5 mg/l had higher and detectable concentrations of chloroform, whereas samples with nitrate concentrations less than 1.5 mg/l generally did not have detectable concentrations of chloroform (Figure 5A). Chloroform, like nitrate, is more persistent in oxic than anoxic conditions (Zogorski *et al.*, 2006). In addition, nitrate and chloroform transported to shallow groundwater are potentially derived from a recent recharge that is primarily associated with more recent urban land use activities.

Thirty-eight pesticides and pesticide degradates were detected in samples collected in 1997 and 2006 from the shallow well network; 25 of these were detected more than once throughout the study period (Figure 6). With the exception of dieldrin, pesticide concentrations were below USEPA maximum contaminant levels and nonregulatory health-based screening levels (Toccalino *et al.*, 2008; USEPA, 2009) (Figure 6). Herbicides were the most frequently detected pesticides and, combined, were present in samples from almost 90% of the wells; concentrations typically were less than 1 μg/l. Some of the herbicides detected have both urban and agricultural uses such as atrazine and metolachlor, but several have predominantly urban, non-cropland use in the study area (for example simazine, tebuthiuron, prometon, diuron, and bromacil) (Figure 6). Herbicides used primarily for agricultural purposes occurred less frequently than those used primarily for urban or urban and agricultural purposes (Figure 6). Total pesticide concentration generally was higher in more recently recharged groundwater; that is as the proportion of recent water increases, the concentrations and occurrence of pesticides related to the current urban land use also tend to increase (Figure 7).

Atrazine and simazine were the most frequently detected herbicides in samples, occurring in more than half of the samples and almost twice as often as the next most frequently detected pesticide, metalochlor (Figure 6). Although the use of atrazine and simazine is not exclusively limited to urban or non-agricultural uses, they are frequently used in urban areas and are among the most frequently detected herbicides found in other shallow well networks in urban areas (Barbash and Resek, 1996; Braman *et al.*, 1997; Hoffman *et al.*, 2000; Gilliom *et al.*, 2006; Gilliom, 2007) (Table 3). Groundwater samples with detectable concentrations of atrazine and simazine also had higher concentrations of chloroform, similar to the relation between nitrate and chloroform (Figures 5B and 5C). The relation between chloroform and atrazine, and simazine does not exclude the possibility of non-urban sources of atrazine and simazine. However, when coupled with the relatively young age of groundwater sampled in the shallow network, the relation suggests that the increase in detection of atrazine and simazine between 1997 and 2006 is likely to be related to more recent urban land use activities. The lack of urban herbicide use data does not allow for a more rigorous assessment of the source of atrazine and simazine to shallow groundwater underlying the Memphis area.

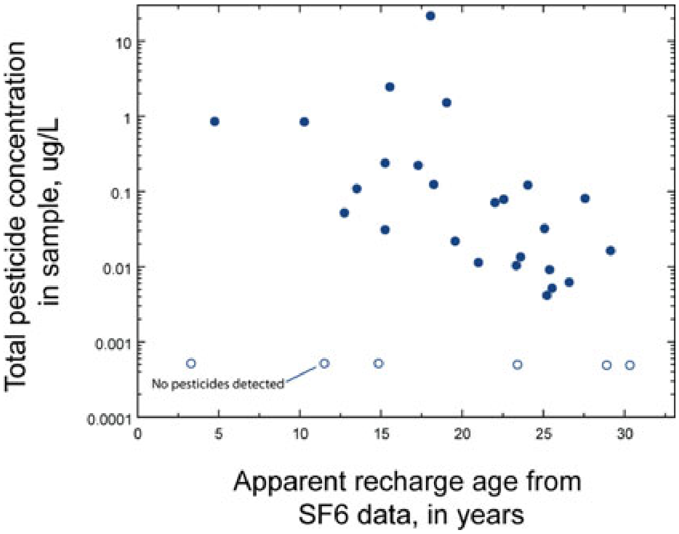


FIGURE 7. Total Pesticide Concentration and Apparent Age of Samples Collected From the Shallow Well Network in 2006 (age determined from sulfur hexafluoride [SF6] concentrations).

Temporal Changes in the Occurrence of Anthropogenic Chemicals

Water levels were generally lower in 2006 than in 1997 ($\rho < 0.05$) (Figure 8D), but systematic changes were not observed for most inorganic constituent concentrations between 1997 and 2006 (Table 2 and Figure 8B). Nitrate, atrazine, and simazine concentrations generally increased between 1997 and 2006 in water from about half of the wells; results from the Wilcoxon signed rank test indicate that these

TABLE 3. Summary of Nitrate, Atrazine, and Simazine Results From Studies Located in Urban Settings.

Constituent	Reference	Location	Study Result	Memphis, Tennessee Shallow Well Network Result
Nitrate	Robinson, 2003	Alabama	Nitrate was detected in both urban and agricultural settings with no statistical difference in concentrations between samples from agricultural and urban settings	Nitrate concentrations increased in samples collected from 1997 through 2009 in parts of shallow aquifer with oxic groundwater underlying the Memphis area
	Drake and Bauder, 2005	Helena, Montana	Increases in the magnitude and extent of nitrate concentrations in samples collected from shallow groundwater over a 32-year (1971-2003) period were coincident with rapid growth and urbanization of the Helena area	
	Xu *et al.*, 2007	Phoenix, Arizona	Changes in shallow groundwater nitrate concentrations attributed to changes in land use from the 1950s to the 1990s: desert to urban transistion resulted in increased nitrate concentrations; agricultural to urban transistion resulted in decreasing nitrate concentrations but concentrations remained above background concentrations	
	Bruce and McMahon, 1996	Denver, Colorado	Median concentration for nitrate (4.2 mg/l) found to be higher in shallow groundwater underlying residential land use settings than underlying commercial and industrial land use settings	
Atrazine	Bruce and McMahon, 1996	Denver, Colorado	Atrazine was the second most frequently detected pesticide in shallow groundwater underlying the Denver metropolitan area	Atrazine was the second most frequently detected herbicide in samples collected from shallow groundwater underlying the Memphis area from 1997 through 2009. During this time period, the occurrence and concentrations of atrazine also increased in shallow groundwater samples
	Ator and Ferrari, 1997	Mid-Atlantic Region, U.S.	Atrazine was the most frequently detected pesticide in shallow groundwater. However, detection frequencies were indistinguishable between urban and agricultural settings	
	Tesoriero *et al.*, 1998	Washington	Atrazine occurrence in shallow groundwater was positively correlated with urban land use within a 3.2 km radius of well and roadside application of atrazine	
	Barbash *et al.*, 2001	U.S.	Atrazine occurrence in shallow groundwater was positively correlated with nationwide non agricultural use	
	Robinson, 2003	Alabama	Atrazine was detected in shallow groundwater underlying urban and agricultural settings with no statistical difference in concentrations between samples from agricultural and urban settings	
	Gilliom *et al.*, 2006	U.S.	Atrazine was one of the most frequently detected herbicides in shallow groundwater underlying urban settings and agricultural settings	

TABLE 3. (Continued)

Constituent	Reference	Location	Study Result	Memphis, Tennessee Shallow Well Network Result
Simazine	Robinson, 2003	Alabama	Simazine was detected in shallow groundwater underlying urban settings but not in agricultural settings	Simazine was the most frequently detected herbicide in samples collected from shallow groundwater underlying the Memphis area from 1997 through 2009. During this time period, the occurrence and concentrations of simazine also increased in shallow groundwater samples
	Bruce and McMahon, 1996	Denver, Colorado	Simazine was the third most frequently detected pesticide in shallow groundwater underlying the Denver metropolitan area	
	Ator and Ferrari, 1997	Mid-Atlantic Region, U.S.	Simazine detection frequencies in shallow groundwater were indistinguishable between urban and agricultural settings	
	Barbash *et al.*, 2001	U.S.	Simazine occurrence in shallow groundwater was positively correlated with nationwide non agricultural use	
	Gilliom *et al.*, 2006	U.S.	Simazine was the most frequently detected herbicide in groundwater underlying urban settings and agricultural settings	

changes in concentration were statistically significant ($\rho < 0.05$) (Figure 8). In addition, between 1997 and 2006, the number of wells with detections for nitrate, atrazine, and simazine increased by an additional 4, 9, and 10 wells, respectively.

In samples from four wells (UR-1,UR-12,UR-25M, and UR-26), atrazine was detected at low concentrations (<0.01 μg/l) in 1997 but was not detected in 2006. Because of lower water levels throughout the area in 2006, three of these wells (UR-1, UR-12, and UR-25M) had to be replaced with wells drilled to a greater depth than the original well for the sample in 2006 (Table 1). The difference in sample depth could account for the difference in detections between 1997 and 2006. Analytical variability near or below the laboratory reporting level also could account for these differences. A few other pesticides were detected once or twice at concentrations between 2 and 16 μg/l in either 1997 or 2006 but not both. For example, 2,4-D was detected at a concentration of 14.8 μg/l in a sample collected in 1997 from UR-26 but was not detected in 2006. The occurrence of these compounds without a subsequent or previous corresponding detection may be a result of relatively rapid movement along preferential flow paths in contrast to recurring low-level concentrations of pesticides that move into groundwater with diffusely distributed recharge or could be the result of changes in pesticide use on the surface.

A subset of five wells was sampled six times from 1997 through 2009 to provide temporal water-quality data in addition to that of the 1997 and 2006 network samples. Daily water-level data from a reference well, P-99, located within a large park isolated from most urban activities are included to show the variability in hydrologic conditions from 1997 through 2009 (Figure 9). Well P-99 was sampled four times from 2002 through 2009 to document what are considered background, or "reference" water-quality conditions in this area. Nitrate concentrations were less than 1 mg/l and atrazine and simazine were not detected in any of the samples from P-99.

Groundwater age in samples from the subset of five wells ranged from 5 to 26 years. The youngest groundwater age was from UR-31, which is located in an area of Memphis where land use has been predominantly urban since at least the 1970s (Figure 1). Atrazine and simazine concentrations were the highest in samples from UR-31; however, between 1997 and 2009, these concentrations remained relatively stable (Figure 9). In contrast, samples from UR-11 had the oldest groundwater age and although land use within a 500-m radius of the well was more than 80% urban throughout the sampling period, simazine was detected in only one sample collected in 2006. The lack of atrazine and simazine detections could suggest either minimal use of these compounds in the contributing area to this well or a relatively small fraction of recent recharge at this sample depth such that these constituents are not detected. Samples from both UR-31 and UR-11 were anoxic, which could account for the lack of nitrate detected in UR-31 and the low nitrate concentrations (<0.1 mg/l) in UR-11 (Figure 9).

Water samples from UR-29, UR-6, and UR-8 were oxic, with ages between 13 and 18 years, and urban land use around each well composed of 93, 73, and 46%, respectively (Table 1). For all three wells, atrazine and simazine were detected in most of the water samples and nitrate concentrations were higher in

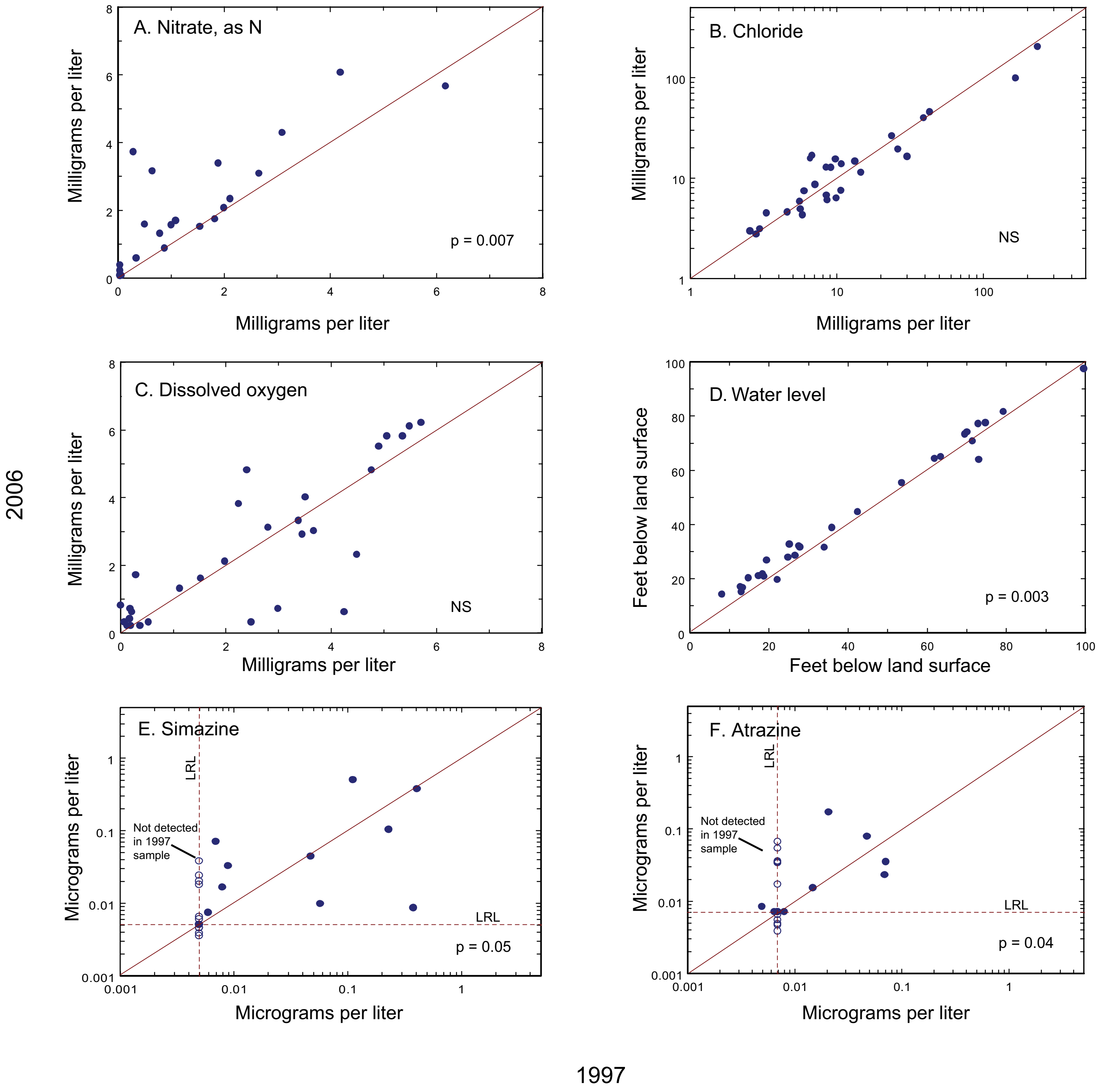


FIGURE 8. Graphs Showing the Changes in Select Constituents and Water Levels Between 1997 and 2006. The Wilcoxon signed rank significance value (ρ) was determined and is shown where statistically significant ($\rho < 0.05$) on each graph. (NS, not significant; LRL, laboratory reporting limit; $\rho > 0.05$).

samples collected in 2009 than when sampling began. Nitrate, atrazine, and simazine concentrations generally increased over time in samples from UR-29 and UR-6 (Figure 9). In 2006, concentrations of major inorganic constituents as well as nitrate, atrazine, and simazine in samples from UR-6 temporarily decreased. These decreases are most likely attributed to a nearby leaking potable water line as evidenced by a corresponding increase in chloroform concentrations from 0.008 to 3.3 µg/l and the additional detections of two drinking water disinfection by-products first detected in 2006. Chloroform was the only disin-

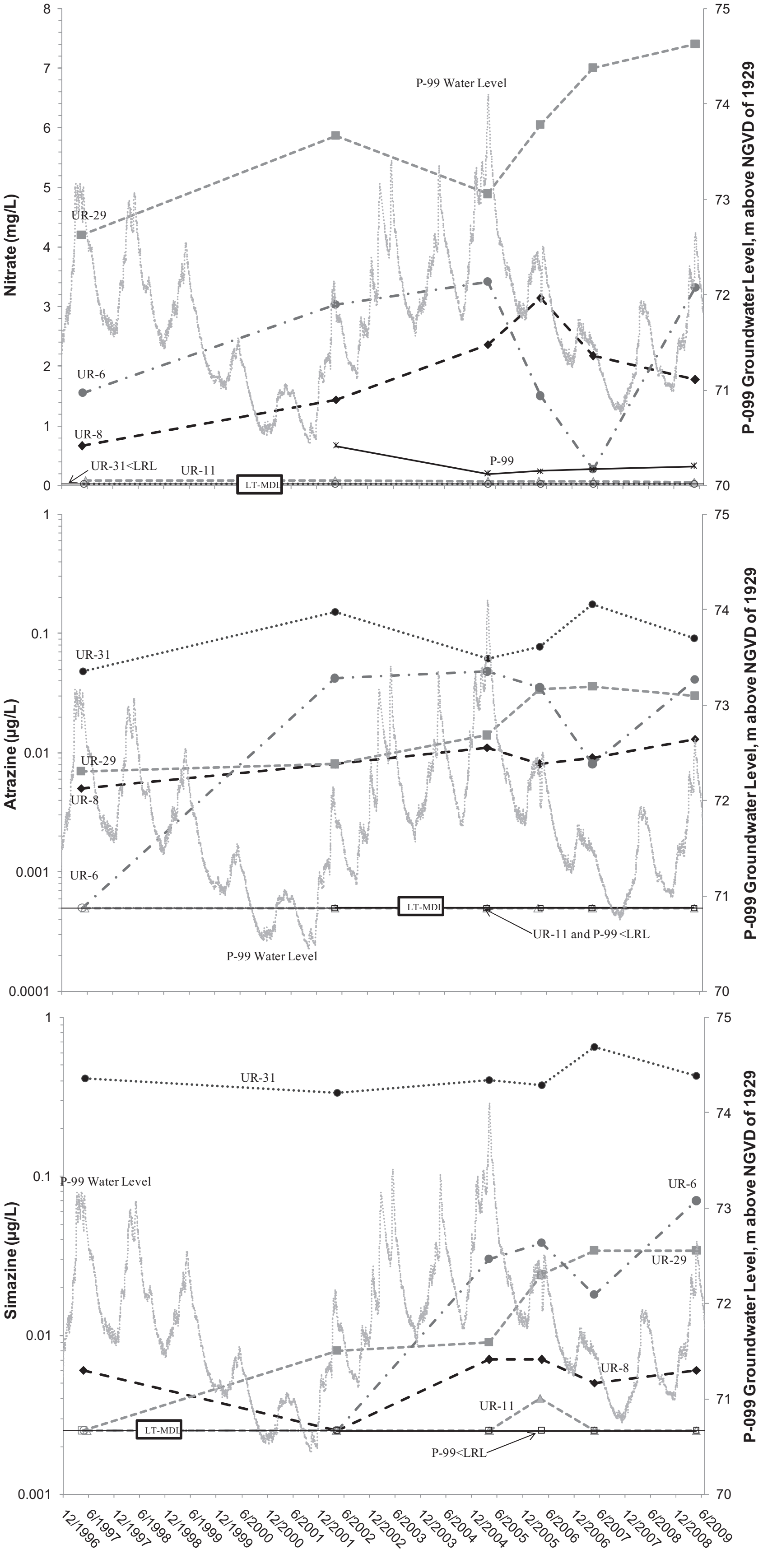


FIGURE 9. Nitrate, Atrazine, and Simazine Time Series Data for UR-6, UR-8, UR-11, UR-29, and UR-31 Along With Daily Water-Level Measurements From P-99, the Reference Well, Throughout the Study Period.

fection by-product detected in the sample collected in 2009, and all other constituent values returned to similar ranges as measured prior to 2006, suggesting that the apparent water-line leakage or the source of potable water had most likely ceased. For well UR-8, concentrations of nitrate, atrazine, and simazine were more variable; nitrate and atrazine generally increased over time but simazine concentrations did not increase (Figure 9).

Within the context of this sampling network, the analytical results of samples from UR-6, UR-8, and UR-29 show the temporal effects of urbanization on shallow groundwater quality with increasing concentrations of nitrate and generally increasing detections and concentrations of the herbicides atrazine and simazine. The recent age of the water sampled from these wells indicates that these concentrations likely are not related to prior agricultural land use within the study area, but are related to more recent urban land use. Sample results from UR-31 also are strongly indicative of the effect of recent urbanization on shallow groundwater quality as the concentrations of the herbicides at this location were highest and the groundwater age the youngest.

The pesticide results in this study are similar with respect to the occurrence of nitrate, atrazine, and simazine to other studies of shallow groundwater in urban settings (Table 3). Relating the occurrence of nitrate, atrazine, and simazine to a particular land use can be difficult because these constituents have both agricultural and urban uses and recently urbanized areas often previously were agricultural areas. Most of the shallow groundwater studies that have looked at nitrate, atrazine, or simazine, and were located in urban settings, have focused on the occurrence of these constituents at one particular time period. Outside of this study, few have assessed the temporal changes in the occurrence and concentrations of these constituents. The addition of a temporal dataset covering a period from 1997 through 2009 provides insight into whether or not the occurrence and concentrations are increasing, decreasing, or generally remaining stable over time.

CONCLUSIONS

Memphis, the largest city in the state of Tennessee, and its surrounding suburbs depend on a confined aquifer, referred to as the Memphis aquifer, for drinking water. Concern over the potential for downward movement of water from an overlying shallow aquifer to the underlying Memphis aquifer provided an impetus for monitoring groundwater quality within the shallow aquifer as part of the USGS NAWQA Program. A network of 31 shallow monitoring wells was installed to study the effects of recent urbanization (post-1970) on groundwater quality.

For this study, an overall increase in both the occurrence and concentrations of nitrate, atrazine, and simazine was observed in shallow groundwater samples. These increases coupled with the relatively recent age of most shallow groundwater samples and the occurrence of VOCs provide supporting evidence that the quality of shallow groundwater underlying the Memphis area has been affected by recent urbanization. Wells that make up the shallow well network in this study are located within and in surrounding parts of Memphis that have been urbanized as recently as the 1970s to the early 1990s. Shallow groundwater samples were estimated to have been recharged between 1976 and 2003 based on the ages determined from samples collected in 2006. Based on this range of recharge years and the history of urbanization, present day water quality could, to some extent, represent the effects of pre-urbanization land use. However, the overall increases in occurrence and concentrations of the noted constituents are more indicative to present urban land use and not a remnant of past land use. In addition, given that the median age of water for the entire network was 21 years, a lag time likely exists between changes in land use and the occurrence of constituents related to urbanization in shallow groundwater.

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