The fate and transport of nitrate in shallow groundwater in northwestern Mississippi, USA

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Abstract Agricultural contamination of groundwater in northwestern Mississippi, USA, has not been studied extensively, and subsurface fluxes of agricultural chemicals have been presumed minimal. To determine the factors controlling transport of nitrate-N into the Mississippi River Valley alluvial aquifer, a study was conducted from 2006 to 2008 to estimate fluxes of water and solutes for a site in the Bogue Phalia basin (1,250 km^2). Water-quality data were collected from a shallow water-table well, a vertical profile of temporary sampling points, and a nearby irrigation well. Nitrate was detected within 4.4 m of the water table but was absent in deeper waters with evidence of reducing conditions and denitrification. Recharge estimates from 6.2 to 10.9 cm/year were quantified using water-table fluctuations, a Cl^- tracer method, and atmospheric age-tracers. A mathematical advection-reaction model predicted similar recharge to the aquifer, and also predicted that 15% of applied nitrogen is leached into the saturated zone. With current denitrification and application rates, the nitrate-N front is expected to remain in shallow groundwater, less than 6–9 m deep. Increasing application rates resulting from intensifying agricultural demands may advance the nitrate-N front to 16–23 m, within the zone of groundwater pumping.

Keywords Groundwater age · Nitrate · Recharge · Geochemical modeling · USA

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Introduction

Nitrate is the primary form of dissolved nitrogen in natural waters (Mueller and Helsel 1996) and is one of the largest contributors to groundwater and surface-water contamination in the world. High concentrations of nitrate in groundwater have potential health effects on drinking-water sources (Ward et al. 2005), can lead to eutrophication in streams where groundwater is a contributor to baseflow (Rabalais 2002), and can contribute to global warming (Galloway et al. 2003). Fertilizer use, livestock manure, soil mineralization, nitrogen fixation, and atmospheric deposition are the primary sources of N with farm fertilizer being one of the largest (Böhlke 2002). Increases in N fertilizer application have been significant since the late 1960s to 1970s as agricultural production has increased worldwide (Keeney 1986; Hallberg 1989). Between 1945 and 1985, the use of nitrogen fertilizer in the United States increased twenty-fold, from less than 1 million metric tons per year to more than 10 million metric tons (Mueller and Helsel 1996). As a result, several recent studies have noted concentrations above the drinking-water standards outlined by the World Health Organization (50 mg/L as NO_3^-; World Health Organization 2004) and the US Environmental Protection Agency (10 mg/L as N; USEPA 2006) in countries like India, China, Denmark, and the USA (Agrawal et al. 1999; Chen et al. 2005; Liu et al. 2005; Hansen et al. 2011; Puckett et al. 2011). Nutrients, including NO_3^- as N (nitrate-N), are naturally occurring in soils, rocks, and the atmosphere, and a national background concentration of 1 mg/L has been established for nitrate-N in shallow groundwater (well depths ≤30 m) of the United States (Dubrovsky et al. 2010). Concentrations higher than the national background can indicate influence from anthropogenic activities (Dubrovsky et al. 2010).

Due to the fertile soils in the Mississippi River alluvial plain, a region referred to locally as the Delta, the area is used extensively for agriculture. Although the primary land use is agricultural, there have been only low concentration detections of agricultural chemicals in water from pumping wells in the Mississippi River Valley alluvial (MRVA) aquifer, the irrigation source that underlies the region. Landreth (2008) sampled 705 aquaculture and irrigation wells screened in the MRVA aquifer. Nitrate

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was detected in water from 20% of the wells, with a maximum detection of 2 mg/L. Previous studies also show that water quality in the MRVA aquifer varies between two identified subunits. Twenty-five wells screened in Holocene alluvium and 29 wells screened in Pleistocene valley train deposits located in Arkansas, Louisiana, Mississippi, Missouri, and Tennessee were sampled as part of the US Geological Survey's National Water-Quality Assessment (NAWQA) program (Gonthier 2003). Nitrate-N was more frequently detected and at higher median concentrations in the valley train deposits than in the alluvium. When iron concentrations were greater than 50 μg/L (under anoxic conditions), nitrate-N was not detected or was present at concentrations less than 0.5 mg/L (Welch et al. 2009). These previous studies tended to focus on the deeper portions of the aquifer currently in use for irrigation. Although the shallowest portion of the aquifer is likely most strongly affected by modern water and chemical uses, the water quality of this resource remains uncharacterized.

The factors that dominate nitrate-N contamination of groundwater and how those factors interact with local conditions to contribute to groundwater concentrations remain poorly understood. In some cases, low concentrations have been attributed to high reaction rates at sites with high concentrations of organic carbon or other electron donors (Korom 1992). In other cases, low rates of vertical transport have been cited as a factor controlling nitrate-N fluxes in aquifers underlying fine-grained soils (National Research Council 1993). Because fine-grained soils are also commonly associated with high concentrations of electron donors, the low concentrations of nitrate-N in areas such as the Mississippi Delta could be controlled by either effect. Quantitative comparisons of fluxes from nitrate-N transport and reaction are needed to determine factors controlling water quality in areas such as the Mississippi Delta.

This report describes the results of a study designed to better understand the movement of nitrate-N through the unsaturated zone and groundwater in the delta environment at a site in Bolivar County, Mississippi (Fig. 1). Groundwater chemistry was analyzed for a shallow well screened near the top of the water-table, a co-located vertical profile of five temporary sampling points, and a deep, abandoned irrigation well screened near the bottom, most-productive part of the MRVA aquifer. Groundwater and nitrogen fluxes were estimated using geochemical characterization, recharge estimates from analyses of Cl^- mass balances, water-table fluctuations, and age-tracer profiles, as well as a mathematical model which was inversely fitted to multiple tracer profiles, including Cl^-, nitrate-N, and $[N_{2,denit}]$ (di-nitrogen gas produced by denitrification). To evaluate the future effects of intensifying agriculture, groundwater quality responses from various nitrogen input scenarios were modeled and prediction uncertainty was addressed.

Hydrogeology and study area description

The MRVA aquifer underlies an area of approximately 18,000 km^2 and 19 counties in northwestern Mississippi. The aquifer is composed of Quaternary age clay, silt, sand, and gravel deposited by the Mississippi River and its

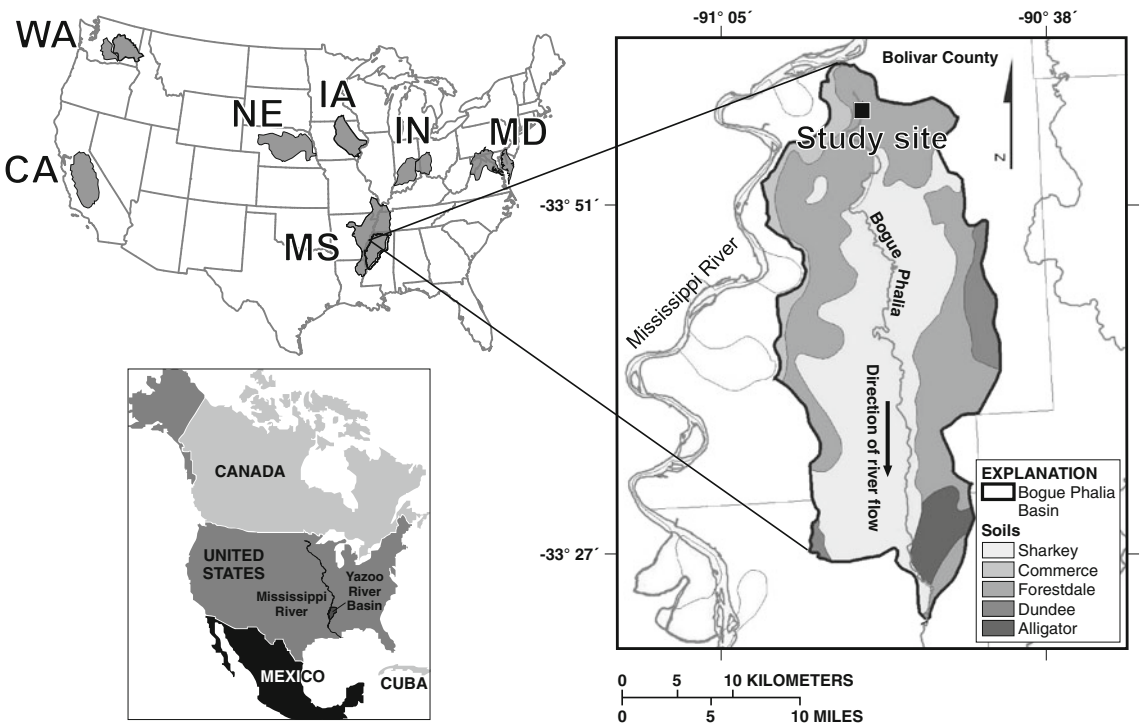

Fig. 1 Location of the study site in northwestern Mississippi (*MS*) and other agricultural study sites from the NAWQA program in the United States. *WA* Washington, *CA* California, *NE* Nebraska, *IA* Iowa, *IN* Indiana, *MD* Maryland

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tributaries (Arthur 1995). Average aquifer thickness is 43 m with the coarse gravel at the bottom fining upward into a layer of silts and clays which form an upper confining unit that ranges in thickness from less than 3 to 30 m thick (Arthur 1994). The two subunits of the MRVA aquifer differ in environmental setting and geologic age. The Pleistocene valley train deposits are geologically older and were deposited by high-energy braided streams. Sediments in the Pleistocene valley train deposits are coarser in grain size, and the sand and gravel layer in this portion of the aquifer is thicker and overlain by a thinner clay and silt surficial unit than the Holocene alluvium (Autin et al. 1991; Saucier 1994). The younger Holocene alluvium was deposited by meandering stream deposits and overlies the Pleistocene valley train deposits except in areas where the alluvium has been eroded exposing the valley train deposits.

Water-use data compiled in 2000 placed the MRVA aquifer as third largest in withdrawals of 66 large aquifers across the United States (Maupin and Barber 2005). Approximately 0.04 km^3/day is being withdrawn, mainly for irrigation purposes (Maupin and Barber 2005). Regional groundwater flow prior to pumping for irrigation was toward the Mississippi River and southward; however, modern pumping has reversed flow toward the inner parts of the Delta (Renken 1998). Transmissivity values from six pumping tests conducted from 1954 to 1971 at wells screened in the coarse gravel portion of the MRVA aquifer ranged from 1,100 to 4,700 m^2/day, and hydraulic conductivity values ranged from 40 to 120 m/day (Slack and Darden 1991). Precipitation likely is the primary source of recharge, but other contributors could be streams, lakes, upward movement from underlying aquifers, or downward seepage from irrigated lands, and lateral groundwater flow from the Bluff Hills which bound the aquifer on the east (Boswell et al. 1968). Krinitzsky and Wire (1964) stated that 5% of annual precipitation (approximately 6.6 cm) is recharged to the aquifer. A previous groundwater flow model by Arthur (2001) estimated that aerial recharge to the aquifer is 6.4 cm/year. A base-flow separation technique was used nationally to estimate values of natural groundwater recharge to the principal aquifers, which indicated that 12.7 to 25.4 cm is the mean annual recharge to the MRVA aquifer from precipitation and the interaction of groundwater with surface water (Reilly et al. 2008).

The Bogue Phalia basin (1,250 km^2) is a watershed in the Delta that lies within the larger Yazoo River basin (34,900 km^2; Fig. 1). Most of the Bogue Phalia basin is located in Bolivar County, MS. More than 90% of the county land use is for row-crop agriculture with the main crops being cotton, corn, rice, sorghum, and soybeans (Coupe 2002). Cotton and corn planting occurs on Dundee-type soils (fine-silty, mixed, active, thermic Typic Endoaqualfs) which compose 19% of the Delta land area and have better drainage than the Sharkey clay (very-fine, smectitic, thermic Chromic Epiaquerts that cover 26% of the Delta land area), which occurs in the interstream areas and is a dark, yellow waxy clay that tends to collect water for long periods of time (Fig. 1). Annual precipitation in the basin ranges from 114 to 150 cm, and about half of the precipitation returns to the stream as runoff from the fields, especially in the western part of the Delta where soils are much higher in clay content (Shaw et al. 2006). For the study period, annual precipitation ranged from a minimum of 92 cm in 2007 to a maximum of 132 cm in 2006.

The study site is located in northwestern Bolivar County just south of the headwaters of the Bogue Phalia near the Mississippi River, in the top portion of the Bogue Phalia basin (Fig. 1). The site was selected to investigate nitrate-N and water fluxes into the MRVA aquifer at a site in the Bogue Phalia basin with well-drained soils. Sediments in the shallow portion of the MRVA aquifer were characterized as well-sorted medium sands, and the thickness of the fine-grained unit overlying the aquifer was less than 3 m at the site (Arthur 1994). The local groundwater flow direction was established using water levels collected bimonthly at a network of five wells from June 2008 to May 2009 (Fig. 2). Moving eastward from the Mississippi River toward the Bogue Phalia at the study site, water levels decrease in elevation, on average, about 1.1 m/km. Hydrographs comparing rises and falls in the Mississippi River (located about 7.5 km away) show no influence on water levels in the MRVA aquifer at the study site. The sampled wells were located in a non-irrigated cotton field, while the rest of the land adjacent to and north of the field (which has historically been cotton) was planted with corn that was irrigated (Fig. 2). Although cotton and corn were the predominant crops at the site during the study period (2006–2008), the source area for the monitoring wells may be located in areas that were used for the cultivation of sorghum, rice, or soybeans.

Methods

In 2005, the Mississippi Embayment NAWQA study unit began collecting samples from air and rain, surface water, groundwater, and the unsaturated zone to investigate the sources, transport, and fate of agricultural chemicals in the Bogue Phalia basin of northwestern Mississippi. To assess the water quality of the MRVA aquifer at a site with relatively permeable soils, water samples were collected and analyzed for a variety of chemical constituents from a shallow water-table well, an irrigation well, and at a vertical profile of temporary sample points. The two wells were sampled nine times from 2006 to 2008 for major ion chemistry, nutrients, and field parameters (depth to water, pH, water temperature, specific conductance, dissolved O_2 (DO), and turbidity). In addition, the five temporary sample points were sampled during June 2008 for SF_6, CFCs, ^3H, dissolved gases (CH_4, N_2, Ar, CO_2, and O_2), and stable isotope ratios of O and N in nitrate.

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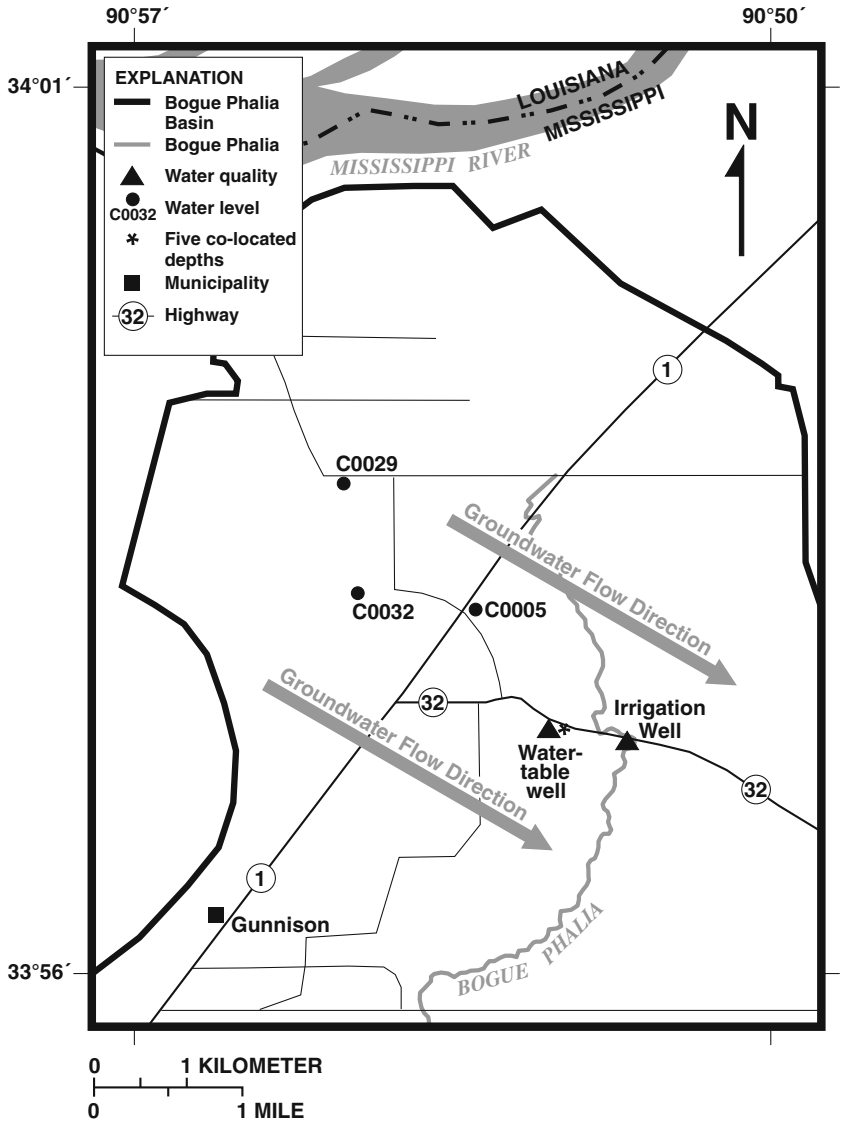

Fig. 2 Location of groundwater wells at the study site. The water-table well and five co-located depths are located at 33˚57'54"N latitude and 90˚54'11"W longitude. The irrigation well is located at 33˚57'46"N latitude and 90˚53'29"W longitude

Well installation

The study site in northwestern Bolivar County, MS, had an existing 40.6-cm diameter well—hereafter referred to as the "irrigation well"—which was located approximately 0.09 km west of the Bogue Phalia. The well has a stainless-steel casing and is screened from 21.3 to 36.6 m below the land surface in the most productive, coarse gravel part of the MRVA aquifer. In April 2006, to better understand the groundwater chemistry at the water table, a shallow 2.54-cm diameter PVC monitoring well—hereafter referred to as the "water-table well"—was installed with a screen from 8 to 10 m below the land surface using direct push methods. Once the PVC casing and screen were installed, the bottom 3 m of the hole was backfilled with sand and fine to coarse-grained bentonite up to the land surface. The well was later developed using a peristaltic-type pump until turbidity readings were less than 1 nephelometric turbidity unit (NTU). To characterize the shallow geochemical gradient, five temporary sampling points were installed in June 2008 using a direct push method at depths ranging from 11 to 18.3 m below the land surface (Table 1).

Groundwater sampling

Using a peristaltic-type pump at the water-table well and a portable, submersible pump at the irrigation well, sample collection began after purging three casing volumes and stabilizing field measurements according to USGS protocols (Koterba et al. 1995). Sample collection from the temporary sampling points differed in that Teflon tubing from the pump ran through the drill flights of the direct push equipment (the use of brand names in this report is for identification purposes only and does not constitute endorsement by the US Geological Survey). The same protocols for purging and field parameter stabilization were followed. All samples were shipped overnight on ice for analysis at the USGS National Water-Quality Labo-

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Table 1 Summary of data collected in June 2008 at two permanent wells and the five temporary sampling points located at the study site in northwestern Mississippi. All concentrations in mg/L unless otherwise noted. Cation–anion balances all differed less than 2%

Type of well	Screen interval (m)	Sample depth (m)	Depth to water table below land surface(m)	Depth below the water table (m)	Specific conductance (µS/cm)	Ca	Mg	K	Na	Cl	Fl	Si	SO_4^{2-}	TDS	NH_4^+	Nitrate–N	NO_2^-	P	Fe	Mn	CFC-12 apparent age in years	SF_6 apparent age in years	Tritium (pCi/L)
Water-table	8.3–9.8	9.5	7.5	2.0	822	121	32.6	1.50	12.0	9.19	0.40	21.1	31.4	504	ND	8.86	0.089	0.03	E0.006	0.362	34.5	30	8.62
Temporary sample point	9.9–11	10.7	7.5	3.2	884	120	33.4	1.83	13.5	11	0.34	21.7	35.5	529	0.087	5.9	0.049	0.04	5.42	0.916	46	NA	NA
Temporary sample point	11.1–12.2	11.9	7.5	4.4	897	128	36.9	2.25	15.1	9.95	0.30	17.3	36.3	524	0.030	ND	E0.001	0.08	4.8	0.959	30	9.5	NA
Temporary sample point	12.3–13.4	13.1	7.5	5.6	952	127	36.9	2.23	16.4	8.33	0.29	23.1	30.5	558	0.054	ND	E0.001	0.14	8.06	0.905	60	20	NA
Temporary sample point	14.8–15.8	15.5	7.5	8.1	974	134	40.4	2.14	11.9	4.50	0.26	30.4	ND	573	0.101	ND	0.003	0.20	13.6	0.680	46	41	NA
Temporary sample point	17.2–18.3	18	7.5	10.5	903	120	36.4	2.45	9.57	3.57	0.24	30.2	ND	546	0.103	ND	ND	0.17	17.4	0.634	60	39	NA
Irrigation	21.3–36.6	25.9	8.3	17.6	580	70	23.2	3.37	11.6	3.93	0.31	36.2	0.67	348	1.92	ND	ND	1.15	10.4	0.233	NA	NA	NA

ND not detected (<0.18 for SO_4^{2-}, <0.04 for nitrate-N, <0.002 for NO_2^-); *E* estimated; *NA* not available

ratory (NWQL) in Denver, CO. Major ions were measured using atomic absorption spectrometry, and nutrient concentrations were quantified using colorimetry (Fishman and Friedman 1989).

Stable isotope samples ($\delta^{15}N$ and $\delta^{18}O$ of nitrate) were collected in a 125-ml amber polyethylene bottle with a conical-insert polyseal cap after the collection of the environmental sample. After field rinsing and collection of the isotope samples, the bottles were stored on ice. Once collection at all depth intervals was completed, the isotope samples were filtered through a 0.2-µm filter, filling the bottle only three-fourths full. The bottles were then frozen to prevent any biological reaction of the nitrogen-bearing species. Once nitrate-N concentrations were measured by the NWQL, two samples containing nitrate-N>0.06 mg/L were shipped overnight on ice for analysis by the US Geological Survey Reston Stable Isotope Laboratory in Reston, VA, using mass spectrometry (Révész and Casciotti 2007).

Water samples were analyzed for dissolved gases, ^3H, chlorofluorocarbons $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), and $C_2F_3Cl_3$ (CFC-113), and SF_6 to estimate apparent ages of groundwater samples. Samples for ^3H analysis were unfiltered and collected in 1,000-ml polyethylene bottles with a polyseal cap after rinsing the bottle with sample water. Tritium samples were analyzed using the direct liquid-scintillation counting method described by Thatcher et al. (1977) at the US Geological Survey Tritium Laboratory in Menlo Park, CA.

Age-dating tracers were collected after the collection of water for the analysis of nutrients, major ions, ^3H, $\delta^{15}N$, and $\delta^{18}O$. All water samples were collected using nylon tubing with a 0.15-m length of Viton tubing in the peristaltic pumphead. CFCs were collected in 125-mL glass bottles with foil-lined caps following procedures outlined by the US Geological Survey CFC laboratory (US Geological Survey 2009) in Reston, VA. All bottles were stored and shipped upside down to the CFC laboratory for analysis (Busenberg and Plummer 1992). Methane was detected in some samples indicating conditions where CFCs have been known to degrade (Plummer et al. 1993). Concentrations of CFC-12, which is the most conservative CFC, were used for groundwater age estimation because CFC-11 and CFC-113 tend to degrade in anaerobic conditions. SF_6 samples were collected in two 1-L plastic-coated safety amber glass bottles according to established protocols (US Geological Survey 2010). Bottles were shipped overnight to the Reston CFC laboratory for analysis using the method described by Busenberg and Plummer (2000). Samples for analysis of dissolved gases (CH_4, N_2, CO_2, O_2, and Ar) were collected in serum bottles with no headspace and analyzed by gas chromatography after creation of low-pressure headspace in the laboratory (US Geological Survey 2006). Results of the analyses were corrected for solubility in sample water at laboratory temperatures and have typical uncertainties of ±1–2%. Dissolved gases were analyzed to estimate excess air

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concentrations which affect calculated apparent ages from CFC and SF_6 data (Plummer et al. 1993; Busenberg and Plummer 2000).

Dissolved gas calculations

In groundwater, dissolved gases originate from equilibrium exchange with the atmosphere at the water table, and dissolution of entrapped air bubbles. Air bubbles can become trapped in recharging water and entrained in the saturated zone. Similarly, denitrification produces N_2 that remains in solution in recharging groundwater. As long as the hydrostatic pressure remains greater than the total pressure of gases in solution, degassing is unlikely (Blicher-Mathiesen et al. 1998). In this report, the term "excess air" refers to atmospheric gases in excess of atmospheric solubility, often caused by bubble entrainment during recharge (Aeschbach-Hertig et al. 2008), and "excess N_2" refers to N_2 originating from denitrification.

Excess air and excess N_2 concentrations in groundwater were estimated using the concentration of N_2 and Ar, their solubility in water (Weiss 1970), the atmospheric pressure, and the recharge temperature. Calculation of excess air and assumptions associated with the calculation are documented by Green et al. (2008b). The recharge temperature used in the calculation was based on the annual average groundwater temperature in the water-table well (18.6°C).

Excess N_2 derived from denitrification was calculated using

$$[N_{2,bub}] = [air_{bub}] \cdot 34.8 \quad (1)$$

and

$$[N_{2,denit}] = [N_{2,meas}] - [N_{2,equil}](T, elev) - [N_{2,bub}], \quad (2)$$

where $[N_{2,bub}]$ is the N_2 from entrained bubbles (μmol/L), 34.8 is the conversion factor for the quantity of N_2 per volume of air (μmol/cm^3) at standard temperature and pressure, $[N_{2,denit}]$ is the N_2 from denitrification (μmol/L), $[N_{2,meas}]$ is the measured concentration of N_2 in the sample (μmol/L), and $[N_{2,equil}](T,elev)$ is the concentration of N_2 in air-saturated water as a function of temperature, T and elevation, elev.

Mathematical flux modeling

A mathematical model was developed to estimate recharge and mass flux parameters on the basis of a measured vertical profile of [nitrate-N], [Cl^-], and $[N_{2,denit}]$ (dinitrogen gas produced by denitrification). Similar approaches have been applied successfully to estimate water and solute fluxes on the basis of relationships between depth and chemistry at other agricultural sites that tend to have relatively uniform land use (see references in Böhlke 2002). The emphasis on a vertical profile is further justified by results from three-dimensional models of chemical transport in heterogeneous aquifers (Green et al. 2010) showing that vertical profiles of wells tend to have similar source areas and transport parameters. Vertical, advective transport was calculated for water and solutes, assuming steady-state water fluxes and time-varying inputs of nitrate-N and Cl^- (Fig. 3). Water and solute fluxes were assumed to be spatially uniform at the water table, which is consistent with the relatively uniform land use and geology at the site. The Bogue Phalia appeared not to affect hydrogeology or geochemistry substantially at this site on the basis of water-table gradients and chemistry, most likely because of large amounts of irrigation in upgradient areas and low conductivity clay layers in the streambed which inhibit downward flux. The solutes Cl^-, nitrate-N, and $N_{2,denit}$ were assumed to move advectively with water. The concentrations of the tracers at a particular depth and time were calculated from the fluxes of water and solute at the time of recharge

$$C_i(t,z) = \frac{M_i(t')f_i}{R}, \quad (3)$$

where $C_i(t,z)$ is the concentration of solute, 'i' (mg/L), at time, t, and depth, z (m), $M_i(t')$ is the mass flux, (ug/cm^2/yr), at the ground surface at a previous time, t', f_i is the fraction reaching the water table of the applied mass, and R is the recharge (cm/year).

For nitrate-N at agricultural sites, f_N values (leached fraction of N) are typically between 0.1 to 0.5 (Böhlke 2002) which includes effects of runoff, loss of applied mass to the atmosphere, uptake by plants, and chemical transformations. A larger fraction of Cl^- is expected to pass through the unsaturated zone because Cl^- is less reactive than N in the soil. Values of f_{Cl} less than one could result, however, from runoff of water and solutes and from export of harvested crops.

The sample time t and application time t' are related by

$$t' = t - \tau_u - \tau_s, \quad (4)$$

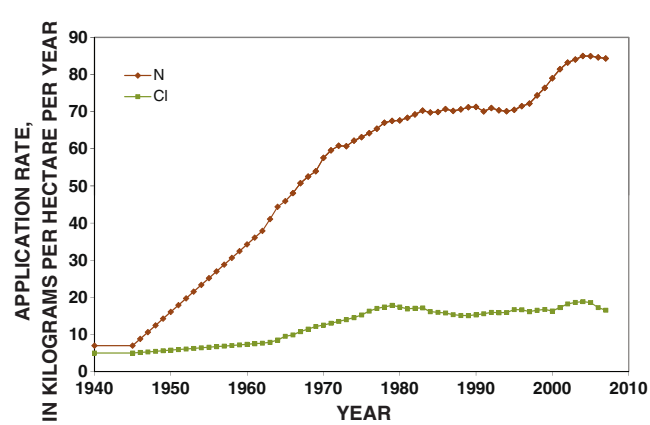

Fig. 3 Application rates of N and Cl^- used in the vertical transport model

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where τ_u is the unsaturated zone travel time and τ_s is the saturated zone travel time. The unsaturated zone travel time, in years, is estimated with

$$\tau_u = \frac{n_u H_u}{R}, \tag{5}$$

where n_u is the unsaturated zone mobile water content which is the specific volume through which the unsaturated zone water is transported and H_u is the unsaturated zone thickness, in meters. The saturated zone travel time, in years, is estimated with

$$\tau_s = \frac{n_s H_s}{R} \ln\left(\frac{H_s}{H_s - z}\right), \tag{6}$$

where n_s is the saturated mobile water content (assumed to be approximately equal to the effective porosity), H_s is the saturated zone thickness, in meters, and z is the depth of the sample point below the water table (Cook and Böhlke 2000) based on the assumption the aquifer system is homogeneous.

Values of M_i (kg/ha/year) were estimated for Cl^- and nitrate-N (Fig. 3) using records of county agricultural chemical use compiled from 1960–2008 (US Department of Agriculture 2010a, b). Modeled [nitrate-N] was estimated using zero-order kinetics,-

$$[\text{nitrate-N}] = \left[NO_3^-\right]_0 - \tau_s k \text{ for} \left[NO_3^-\right]_0 > \tau_s k, \tag{7a}$$

$$[\text{nitrate-N}] = 0 \text{ for} \left[NO_3^-\right]_0 \leq \tau_s k \tag{7b}$$

where $[NO_3^-]_0$ is the original nitrate-N concentration before denitrification, equal to [nitrate-N]+$[N_{2,denit}]$, and k is the zero order decay coefficient.

This parsimonious model of flow and transport was used to calibrate values of adjustable parameters (Table 2). Other field-verified parameters, such as H_s and H_u, were held constant at measured values. The calibrated parameters were changed to minimize the objective function, Φ, relating measured and modeled [nitrate-N], $[N_{2,denit}]$, and $[Cl^-]$.

$$\Phi = \sum_{i=1}^{m} \left[\omega_{N,i}\left(y_{N,i} - y'_{N,i}\right)\right]^2 + \sum_{i=1}^{m} \left[\omega_{N2,i}\left(y_{N2,i} - y'_{N2,i}\right)\right]^2 + \sum_{i=1}^{m} \left[\omega_{Cl,i}\left(y_{Cl,i} - y'_{Cl,i}\right)\right]^2, \tag{8}$$

where y is observed value, y' is a modeled value, m is the number of observations, i, the subscript N indicates a value of [nitrate-N], subscript N2 indicates $[N_{2,denit}]$, subscript Cl indicates $[Cl^-]$, and ω is a weight associated with each measurement, equal to the inverse of the standard error for that measurement (Doherty 2008). The objective function was minimized using a non-linear generalized reduced gradient solver (Lasdon et al. 1978) as implemented in the Risk Solver software 3 (Frontline Systems, Inc.).

Table 2 Parameter values specified in the flux model and calibrated values estimated with the inverse model

Specified parameter values	
Aquifer thickness, H_s	41.1 m
Unsaturated zone thickness, H_u	7.6 m
Adjustable parameter values	
Recharge rate, R	8.8 cm/year (2.9–22)[a]
Effective porosity, n_s	0.32 (0.16–0.46)[b]
Fraction N leached, f_N	0.15 (0.04–0.37)
Fraction Cl leached, f_{Cl}	0.55 (0.17–1.0)
Unsaturated zone mobile water content, n_u	0.20 (0.0–0.91)
Denitrification rate, k	0.53 mg/L/year (0.33–1.02)

[a] Values in parentheses are the upper and lower 95% nonlinear simultaneous confidence limits

[b] Porosity of saturated zone was defined using a prior distribution with expected value 0.32 and 95% confidence limits of 0.16 to 0.46 based on values from McWhorter and Sunada (1977). This range was included in prediction uncertainty analysis, but was not included in calibration to avoid non-uniqueness of solution

Uncertainty analysis was conducted to quantify the potential variability of adjustable parameter values and predicted profiles of nitrate-N at future times. In the uncertainty analysis, the objective function was allowed to vary by a factor, δ, defined by

$$\delta = \Phi_{min} \frac{nF(n, m-n)}{m-n}, \tag{9}$$

(Hill and Tiedeman 2007) where Φ_{min} is the minimized objective function from Eq. 8, n is the number of estimated parameters, m is the number of observations, and F is the F-distribution. Nonlinear simultaneous 95% confidence intervals of parameters were computed by consistently raising (for upper confidence intervals) or lowering (for lower confidence intervals) the parameter of interest while adjusting all other parameters to maintain the objective function at a value of $\Phi_{min}+\delta$. The confidence limit was set equal to the value of the parameter of interest at which the minimized objective function began to exceed $\Phi_{min}+\delta$. For predictions of future nitrate-N profiles, nonlinear simultaneous 95% confidence intervals were estimated by adjusting all parameters to minimize or maximize the total N in the profile, while maintaining the objective function at a value of $\Phi_{min}+\delta$. All solutions of confidence intervals for predictions and for parameters were validated by re-running multiple times using different starting values for the full set of parameters.

Recharge estimate methods

Estimates of recharge from the flux model were compared with those from the water-table fluctuation (WTF) method, the chloride-tracer method, and atmos-

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pheric age-tracer profiles. The WTF method looks at responses in groundwater levels over time to estimate recharge and is best used for short-term water-level rises that occur after individual storms (Healy and Cook 2002). The rises in water levels of an unconfined aquifer are attributed to recharge water arriving at the water table. Recharge (R) in cm/year was calculated using the equation

$$R = S_y \cdot \Delta h / \Delta t, \tag{10}$$

where S_y is specific yield, Δh is the change in water-table height which is the peak in the rise minus the low point of the extrapolated antecedent recession curve at the time of the peak, and Δt is the change in time (Fig. 4). Head values were from continuous water-level data collected at the water-table well during the non-irrigation season so that water levels were unaffected by pumpage in nearby wells. A specific yield value of 0.21 was used based on a site in California with similar aquifer materials (Fisher and Healy 2008) and on values in Fetter (1994) and Johnson (1967) for a fine-to-medium-grained sand. Uncertainty in the recharge estimate from this method can be introduced by the accuracy of the specific yield that is used, errors in determining the antecedent recession curve, and other effects such as entrapped air.

The rate of Cl^- deposition to the land surface by precipitation and dry deposition can be compared to the concentration in groundwater to calculate a recharge rate (Nolan et al. 2007) using the chloride-tracer method. The amount of Cl^- applied to the land surface for agricultural practices must also be taken into account. To test this standard method against the other methods of recharge estimation, recharge (cm/year) to the MRVA aquifer was calculated using the following equation

$$R = 1000 \cdot \left(Cl_{wetdep} + Cl_{drydep} + Cl_{applied}\right) / Cl_{water}, \tag{11}$$

where Cl_{wetdep} is the amount of Cl^- delivered to the land surface by wet atmospheric deposition, Cl_{drydep} is the amount of Cl^- deliver by dry deposition, $Cl_{applied}$ is the amount applied in agricultural chemicals, and Cl_{water} is the concentration of Cl^- in the saturated zone in mg/L. The long-term average Cl_{wetdep} (3.2 kg/ha/year) was calculated using data collected from 1984 to 2008 at a National Atmospheric Deposition Program (NADP) site located 165 km to the east of the study site (National Atmospheric Deposition Program 2009). The quantity of Cl_{drydep} was estimated as 8.7% of the wet rate (0.28 kg/ha; Nolan et al. 2007). A long-term rate for applied Cl^- ($Cl_{applied}$) in the form of muriate of potash was calculated from county-level agricultural chemical use from 1964 to 2007. For this time period, the average rate of $Cl_{applied}$ was 14 kg/ha. To account for Cl^- lost in runoff, which diverts an estimated 50% of water in this area (Rebich 2001), the value of $Cl_{applied}$ was reduced by one-half.

The apparent age of the groundwater is considered here to be the time that has lapsed from the moment that the water reached the phreatic surface to the time of sampling, with the assumption that the water sample has traveled as a discrete package and has not mixed with surrounding water, and that recharging water was in equilibrium with the atmosphere in the unsaturated zone. Recharge was calculated based on the apparent age profiles of CFC-12, SF_6, and ^3H (Fig. 5). Nonlinear least squares regression was used to find the optimal value of recharge to fit the theoretical ground-water age profile (Eq. 6) to the age-tracer data. The best-fit trend line intersects at zero because the estimate of age here is the time spent below the water-table surface (Fig. 5). For this estimation, aquifer thickness was set to the measured value of 41.1 m and aquifer porosity was 0.3, which is typical of fine-to-medium-grained sand (Freeze and Cherry 1979).

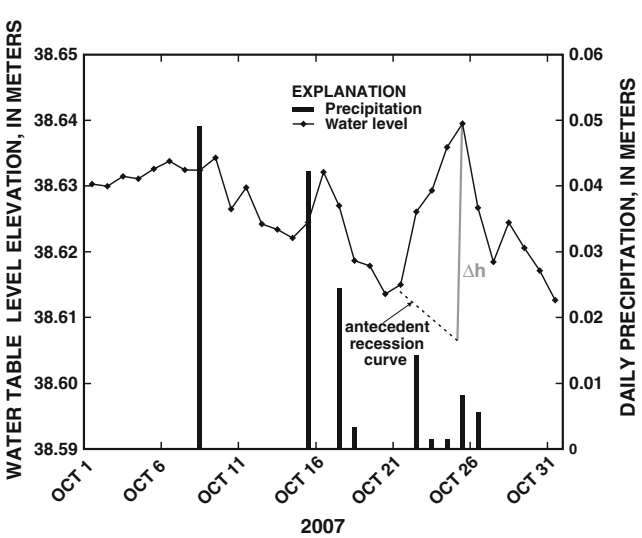

Fig. 4 Hydrograph showing a part of the water-table fluctuation analysis of the water-table well during October 2007

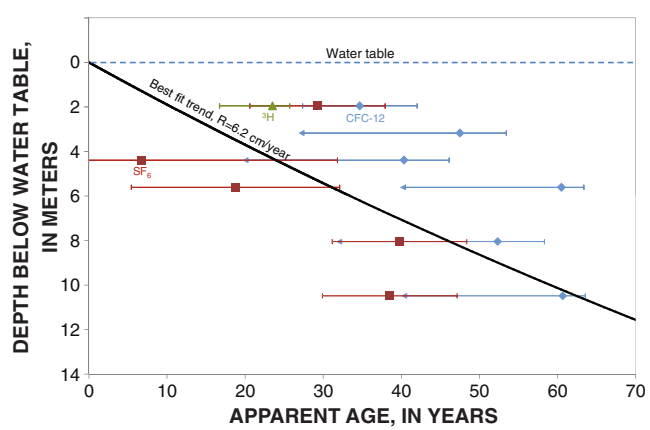

Fig. 5 Apparent age profiles for water samples collected during June 2008 at the study site. *Error bars* show two standard errors. Standard errors were estimated by propagating measurement errors (based on duplicate samples) through the functions of age versus atmospheric tracer concentrations (Meyer 1975). *Arrows on the left* of CFC samples indicate possible degradations of CFCs as indicated by presence of methane

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Results and discussion

Temporal sampling

Groundwater samples collected from 2006 to 2008 showed a surprising difference between the water-table and irrigation wells. Median values of DO, SC, Cl^-, Ca, Mg, SO_4^{2-}, Mn, nitrate-N, and NO_2^- are higher in the water-table well; whereas, for pH, K, Si, Fe, and NH_4^+, median values are higher in the irrigation well (data not shown). Water quality in the water-table well may reflect the influence of agricultural land use on shallow groundwater at this site because Cl^-, Ca, Mg, SO_4^{2-}, Mn, and nitrate-N are commonly applied to the land surface in fertilizer (Hamilton and Helsel 1995) and other soil amendments. The presence of these applied inorganic constituents at high concentrations near the water table suggests that there is downward infiltration through the unsaturated zone into the MRVA aquifer. Oxic conditions, high nitrate-N concentrations, and low Fe concentrations in the water-table well, and subsequent anoxic conditions, high Fe concentrations, and no nitrate-N in the irrigation well suggest reducing conditions in the deeper part of the MRVA aquifer.

Vertical profiles of geochemistry

Vertical depth profile sampling was conducted in June 2008 to better characterize the geochemical gradient within the aquifer. The vertical variability of groundwater chemistry at this site was consistent with influence of modern recharge on shallow groundwater (Table 1). The presence of nitrate-N with depth indicates downward transport into the MRVA aquifer (Fig. 6a). Oxidation-reduction (redox) conditions typically progress sequentially from an oxygen-reducing environment to nitrate-N-, Mn-, Fe-, SO_4^{2-}-reducing conditions, and finally to methanogenic conditions under which organic or inorganic carbon is reduced to form CH_4 (Chapelle 1993). The presence or absence of DO, nitrate-N, Fe, Mn, and SO_4^{2-} in groundwater can be used to characterize the redox conditions in the aquifer. High dissolved Fe concentrations, in addition to the generally low SO_4^{2-} concentrations, suggest Fe/ SO_4^{2-}-reducing conditions in the irrigation well. Concentrations of Fe are 200 times higher than 0.05 mg/L (Fig. 6a) which is the concentration at which nitrate-N was no longer detected in the two subunits of the MRVA aquifer (Welch et al. 2009). Redox indicators show anoxic conditions near the water table and changes in water chemistry with depth (Fig. 6a). Iron is not present at the shallowest interval, but concentrations increase with depth up to 10.5 m below the water table and then start to decrease (Fig. 6a). Sulfate concentrations are high in water collected from the four shallowest intervals; however, SO_4^{2-} is absent from the system below these intervals until it is detected at a very low level in water from the irrigation well. Manganese concentrations show an initial increase at 3.2 m below the water table, but concentrations then decrease with depth. In general, Fe concentrations increase and Mn and SO_4^{2-} concentrations decrease with increasing depth and increasingly reducing conditions in the aquifer.

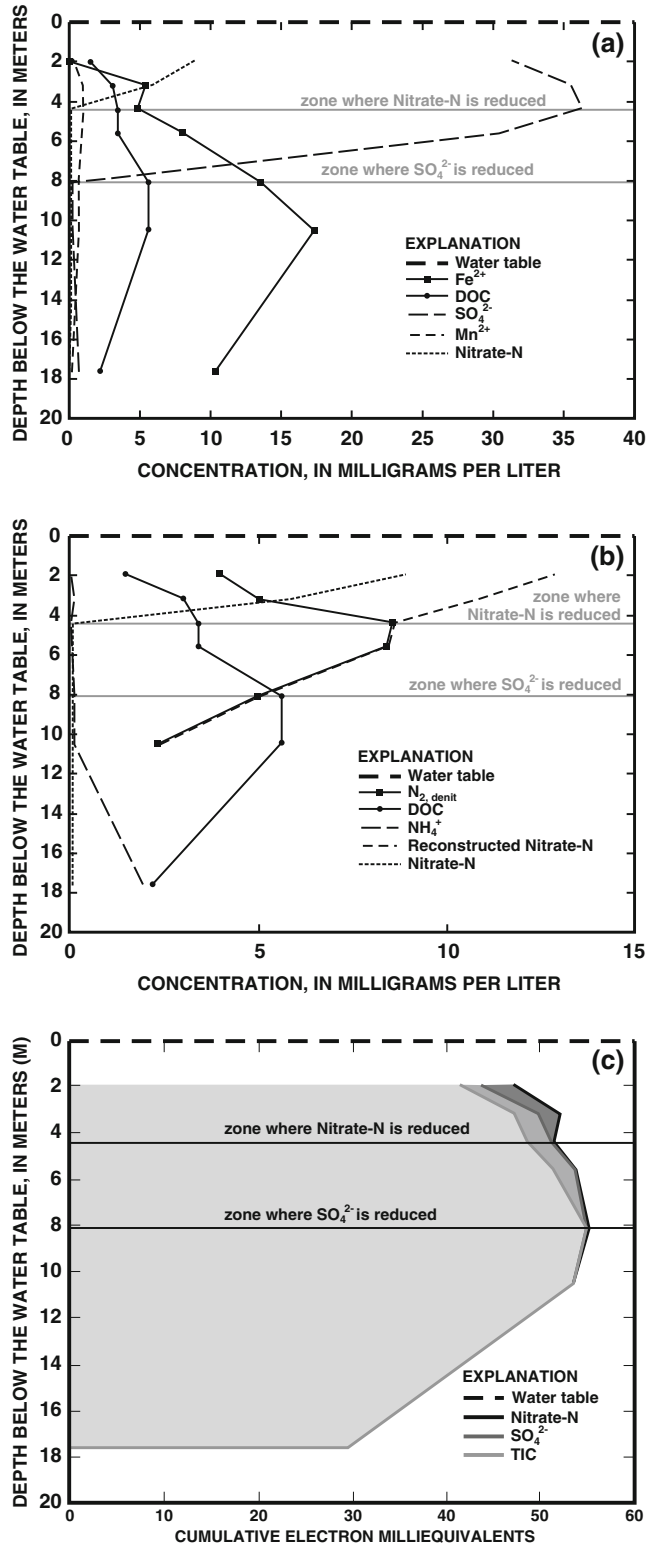

Fig. 6 Depth profile of **a** redox-sensitive indicators, **b** N species and DOC, and **c** cumulative electron milliequivalents of nitrate-N, SO_4^{2-} and TIC, for water samples collected June 2008. See Table 1 for screened intervals

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Vertical profiles of geochemistry confirm that nitrate-N is attenuated during downward transport by denitrification. Nitrate is present at concentrations greater than 1 mg/L in the MRVA aquifer in the upper part of the saturated zone indicating anthropogenic sources, but is completely absent within 4.4 m of the water table (Fig. 6a and b). Nitrate is thermodynamically unstable in a Mn/Fe or SO_4^{2-}-reducing zone and can undergo autotrophic denitrification where the electron donors are reduced inorganic species such as Mn^{2+}, Fe^{2+}, and HS^- (Korom 1992). At this site, the highest SO_4^{2-} concentrations observed are at or just below the depth where nitrate-N disappears from the system. In addition, Fe concentrations increase sharply below the depth where nitrate-N is depleted. Below the redox interface where nitrate-N has been depleted, decreases in SO_4^{2-} concentrations suggest that SO_4^{2-} reduction is occurring and increasing Fe concentrations indicate that Fe reduction is producing soluble Fe^{2+} in the system (Fig. 6a).

Further evidence that denitrification attenuates nitrate-N in the MRVA aquifer is the occurrence of reaction products and stable isotope enrichment in the shallow groundwater. In natural water systems, a complete loss of nitrate-N concurrent with an increase in excess N_2 is evidence for denitrification. Concentrations of excess N_2 produced by denitrification range from 2.4 to 8.6 mg/L (Fig. 6b); in the three samples collected at the shallowest depths, the ratio of $[N_{2,denit}]/[NO_3^-]_0$ increased with depth, indicating that denitrification progresses over a distance of approximately 3 m, and does not occur at a sharp interface. The depth profiles of water chemistry (Fig. 6a and b) show that most of the nitrate-N is lost from the system at 4.4 and 5.6 m below the water table, corresponding to the highest concentrations of excess N_2. Below these depths, all nitrate-N has been converted to excess N_2. Stable isotope data indicate that samples from 3.2 m below the water table with greater extent of denitrification ($[N_{2,denit}]/[NO_3^-]_0$) were associated with higher $\delta^{15}N$ and $\delta^{18}O$ values, 29.34 and 20.79‰ respectively, than samples from 2.0 m below the water table, with values of 16.18 and 14.61‰ respectively, as observed at other sites with active denitrification (Green et al. 2008b).

While the exact reactions driving reduction of O_2, nitrate-N, and SO_4^{2-} are not known, geochemical trends suggest involvement of organic carbon. Using a method from Postma et al. (1991), electron milliequivalents were calculated to assess the dominant electron donors and acceptors along the vertical depth profile. An increase in electron milliequivalents of total inorganic carbon (TIC) is similar to the loss of electron milliequivalents of nitrate-N and SO_4^{2-} with depth below the water table (Fig. 6c), which indicates that organic carbon oxidation is an important electron donor for reactions occurring at the redoxcline. Because recharging concentrations of DOC in the shallowest samples were too low to account for the extent of O_2 and nitrate-N reduction in deeper samples, denitrification below the water table likely is driven by organic C originating from solid phase material in the aquifer. Degradation of solid phase organic matter might also explain the general increase in NH_4^+ and DOC concentrations with depth (Fig. 6a and b).

Water and nitrogen fluxes

The calibrated advection-reaction transport model gives a reasonable match of predicted and observed profiles of nitrate-N, $N_{2,denit}$, and Cl^- (Fig. 7). Calibrated and specified parameter values for the inverse model are summarized in Table 2. The Nash-Sutcliffe model coefficient of efficiency for the nitrate-N, $N_{2,denit}$, and Cl^- data were 0.95, 0.89, and 0.99, respectively, indicating that the modeled concentrations are in close agreement with actual concentrations from the water samples. The Cl^- flux fraction of 0.55 implies that 45% of applied Cl^- does not percolate into groundwater, likely due to runoff to surface waters and uptake by harvested crops. The estimated fraction of mass loss of Cl^- is similar to an estimate of 50% runoff from an earlier study (Rebich 2001), so runoff may account for the majority of the difference between applied and recharged Cl^- at this site. A model estimate for the nitrate-N flux fraction (f_N) of 0.15 is consistent with a range of leached N fractions, from 0.1 to 0.5, observed at other agricultural sites (Green

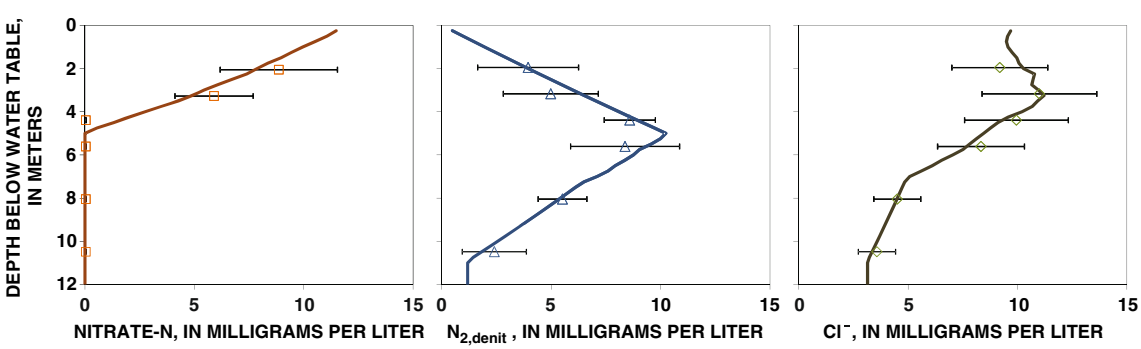

Fig. 7 Graphs showing results of the calibrated advection-reaction transport model of predicted (*solid line*) and observed (*squares, triangles, and diamonds*) profiles of nitrate-N, $N_{2,denit}$, and Cl^- concentrations. *Error bars* represent two standard errors including contributions from temporal variability (estimated from repeated samples at the water-table well) and errors during sampling or analysis (estimated from duplicate samples)

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et al. 2008a; Böhlke 2002). The estimated denitrification rate (k) of 0.53 mg/L/year was within the range of estimated rates of 0 to 0.82 mg/L/year for studies using similar methods in California, Maryland, Nebraska, and Washington (Green et al. 2008b).

Water-table fluctuation (WTF) analysis, atmospheric age-tracers, and the Cl^--tracer method were used to estimate recharge to the MRVA aquifer for comparison with the mathematical model (Table 3). Using WTF analysis, a total of 7.2 cm of recharge was calculated from 19 significant rainfall events that occurred over an 8-month period in the fall and winter 2007–2008 during the non-irrigation season. Murphree et al. (1976) and Murphree and Mutchler (1981) noted that 100% of infiltration of precipitation is lost to evapotranspiration when crops are present, usually May to August. Thus, we can assume that 7.2 cm of recharge that occurred during the non-irrigation season (September to April) is the yearly recharge using the WTF analysis. The ^3H concentration at the water-table well (8.62 pCi/L) indicates that some fraction of water was derived post-1953. Comparing this value to a decay-corrected tritium curve (Welch et al. 2009), suggests that water in the well is approximately 24 years old. The apparent groundwater age from each age-tracer was plotted versus depth along with the best fit trend from Eq. 6 for travel time of water (Fig. 5), which indicates that the recharge rate is approximately 6.2 cm/year which is an average rate over several decades of recharge. Noise and uncertainty in the travel time estimates result from issues such as contamination, degradation of CFCs under reducing conditions, and lag times for transported gas (affecting CFC and SF_6) and water (affecting ^3H) through the unsaturated zone. The full range of travel time estimates are bounded by recharge estimates of between 2 to 20 cm/year. An average recharge value of 10.9 cm/year was calculated from data collected over a 2-year period using the Cl^--tracer method at the water-table well and taking into account that approximately 50% of precipitation is lost to runoff (Rebich 2001). The recharge estimates of 6.2–10.9 cm/year are lower than similar sites located in California, Maryland, Nebraska, and Washington (Green et al. 2008a). However, estimates are consistent with the mathematical model prediction of 8.8 cm/year as well as estimates from most previous studies of recharge in this area (Reilly et al. 2008; Arthur 2001; Krinitzsky and Wire 1964).

Table 3 Summary of recharge estimates to the Mississippi River Valley alluvial aquifer at a site in northwestern Mississippi

Method/source	Recharge (cm/year)
Water-table fluctuation analysis	7.2
Atmospheric age-tracers	6.2
Cl- tracer method	10.9
Advection-reaction model	8.8
Arthur 2001	6.4
Krinitzky and Wire 1964	6.6

The mathematical model (Eqs. 3–7a and 7b) of nitrate-N and Cl^- transport indicated that fluxes of agricultural chemicals are low at this site due to low recharge and other factors, and that rates of denitrification are low, despite observations of strong reduction of Fe and SO_4^{2-} in deeper samples. An estimated 85% of the applied nitrogen is lost to runoff, denitrification in the unsaturated zone, volatilization of ammonia, storage in the unsaturated zone, and exported N in harvested crops. Geochemistry at the study site suggests more strongly reducing conditions than those found at the other agricultural sites in California, Maryland, Nebraska, and Washington (Green et al. 2008b). The similar denitrification rate of 0.53 mg/L/year is surprising but emphasizes the importance of including hydrogeological analysis along with geochemical characterization in vulnerability studies. The wider range of rates reported in previous literature may relate to the effects of scale (field vs. laboratory; Green et al. 2010) and differing methods such as short-term injection-extraction tests, which may not be able to detect slow reactions occurring over the course of decades, and nitrate gradient analyses, which can be affected by the history of N inputs at the water table (Green et al. 2008b). Studies at this site and the sites in California, Maryland, Nebraska, and Washington were conducted at similar scales and used consistent methods. Prediction uncertainties for the one-dimensional advection model are shown in Fig. 7 and only include uncertainty associated with the model; thus, the uncertainties do not account for changes that may occur in the future such as changes in irrigation practices with changing land use or variations in denitrification rates as solutes move into different geochemical zones of the aquifer. However, considering the close match of predictions and observations (Fig. 7), as well as the similarity of inversely estimated parameters with previously documented estimates, the one-dimensional advection model appears to be a viable tool for predicting the occurrence and fate of nitrate-N in the MRVA aquifer at this site.

Because the depth of leached nitrate-N was largely controlled by the slow vertical velocity of water, which is a function of soil properties, and annual fertilizer application rates to overlying fields, potential changes in nitrogen application rates as a result of intensifying agriculture have important implications for groundwater quality at this site. Three scenarios of future nitrate-N transport were evaluated using different input functions of N (Fig. 8). If nitrogen application rates remain at the same level as the 2007 rate (scenario 1), nitrate-N will be transported to a maximum depth of 7 m below the water table and reach equilibrium in about 42 years which means that the nitrate-N being lost to denitrification is balanced by the nitrate-N being input at the water table. Under this scenario, predicted nitrate-N concentrations exceed the US Environmental Protection Agency MCL of 10 mg-N/L (US Environmental Protection Agency 2006) in the upper 2 m of ground-

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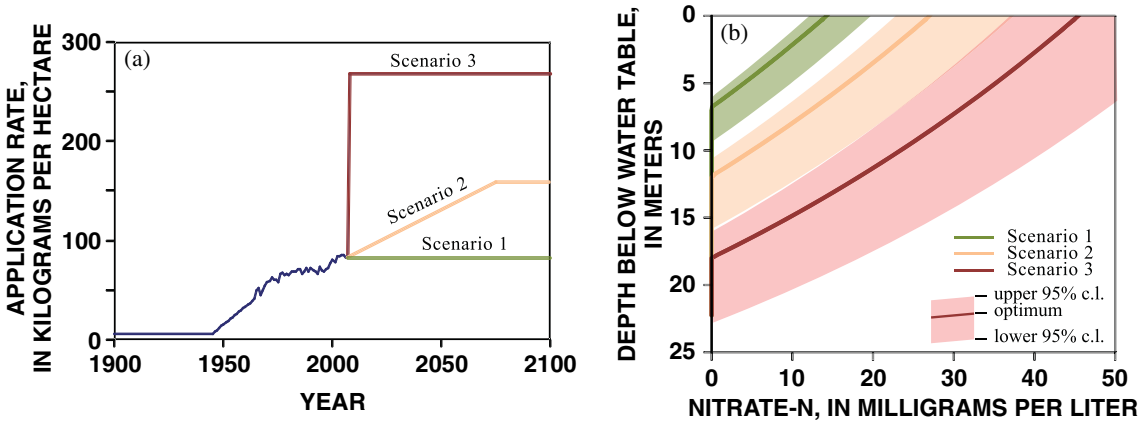

Fig. 8 **a** Input mass application rates and **b** model predictions for three model scenarios for future agricultural practices and resulting water quality. *Scenario 1* assumes fertilizer application remains at 2006 levels, *scenario 2* assumes an N application rate increase of 1.1 kg/ha/year^2 (the average rate of increase from 1990 to 2007), and *scenario 3* assumes an increase in fertilizer application rates to 269 kg/ha/year which is the recommended amount for corn cultivation. The *lines* show the prediction of the calibrated model. *Shaded areas* show the nonlinear simultaneous 95% confidence intervals on the predictions

water. Scenario 2 includes an N application rate increase of 1.1 kg/ha/year^2 (the average rate of increase from 1990 to 2007) until 2075 with a maximum of 160 kg-N/ha/year, which is comparable to current rates of application at other intensively cultivated sites (Green et al. 2008b). Under this scenario, equilibrium in the system will be reached in about 134 years, and nitrate-N will remain within 12 m of the water table. However, nitrate-N concentrations are higher than scenario 1, exceeding the MCL in the upper 6 m below the water table. This scenario takes the longest to come to equilibrium because the input function does not level off until 2075. Scenario 3 simulates an extreme hypothetical case to illustrate the upper limits of nitrate-N concentrations and fastest rate of migration of the nitrate-N front. In recent years, crop acreage in the Mississippi Delta has undergone a change from cotton to corn and/or soybeans, most noticeable was a 47% loss in cotton acreage, concurrent with a 288% gain in corn acreage in 2007 relative to 2006. More nitrogen fertilizer is recommended for corn cultivation than cotton, with recommended applications of 269 kg-N/ha/year (Mississippi State University 2009). In scenario 3, the N applications increase suddenly to this recommended level for corn. Under this scenario, predicted long-term nitrate-N concentrations in groundwater are higher than either scenario 1 or 2, exceeding the MCL in the upper 14 m below the water table, and the system comes to equilibrium in about 101 years. Nitrate-N reaches a maximum depth of 18 m, and migrates at a maximum rate of 0.16 m/year. While the timing of the N application rate increase is extreme, the maximum level of fertilization is feasible under the current trends of increasing intensification of agriculture to meet food and biofuel demands. Because the steady-state predicted profiles are controlled by the eventual N application rate, it is possible that N contamination will eventually penetrate to the zone being used for irrigation. These simple scenarios give a general idea of the sensitivity of the hydrogeochemical system to the influence of nitrogen inputs, and the upper limits of aquifer vulnerability to N inputs.

Summary and conclusions

Geochemical profiles and a mathematical model of vertical solute transport demonstrate that the MRVA aquifer underlying northwestern Mississippi at a site in Bolivar County is vulnerable to anthropogenic contamination. The flux of nitrate-N into the aquifer implies that other agricultural chemicals such as pesticides, could also migrate through the unsaturated zone into the shallow groundwater. Although conditions in the MRVA aquifer are reducing, the estimated rate of denitrification at this site, 0.53 mg/L/year, was surprisingly similar to rates that occur in aquifers with less reducing conditions. Oftentimes reducing conditions within an aquifer are seen as a sign of intrinsic invulnerability to nitrate-N contamination; however, the lack of nitrate-N detection in deeper portions of the MRVA aquifer may be a result of slow vertical travel time due to hydrogeological factors. This long time frame affords an opportunity to implement studies and balanced policies to mitigate loss of groundwater resources due to agricultural contamination.

The mathematical model of vertical movement of water and solutes was used to evaluate scenarios of the effects of increased N-applications as a result of intensifying agriculture. With current denitrification rates and current N-application rates, the nitrate-N front will reach an equilibrium depth of 7 m below the water table. Under scenarios of moderately increasing N-application rates, the migration of the nitrate-N front is affected by both the rate of increase of application, as well as, the maximum application rate. With a greater increase in N-applications, the nitrate-N front will advance as quickly as 0.16 m/year to an eventual maximum depth of 18 m below the water

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table which lies in the zone of pumpage from the alluvial aquifer. A great increase in N application rates is not unreasonable based on trends in use and intensifying agricultural demands. Policies for land-use management should consider that short-term and long-term vulnerability can differ greatly, and agricultural activities occurring today have far reaching implications on water-quality decades into the future. Additional study is needed to determine the sustainability of the electron donor pool and the effects of changing hydrology on the long-term vulnerability of deep groundwater in the MRVA aquifer to agricultural contamination.

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