Source and transport controls on the movement of nitrate to public supply wells in selected principal aquifers of the United States

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[1] In 2003–2005, systematic studies in four contrasting hydrogeologic settings were undertaken to improve understanding of source and transport controls on nitrate movement to public supply wells (PSW) in principal aquifers of the United States. Chemical, isotopic, and age tracer data show that agricultural fertilizers and urban septic leachate were the primary sources of large nitrate concentrations in PSW capture zones at Modesto, California (Central Valley aquifer system) and York, Nebraska (High Plains aquifer). Urban septic leachate and fertilizer (possibly nonfarm) were the primary sources of large nitrate concentrations in PSW capture zones at Woodbury, Connecticut (glacial aquifer system), and Tampa, Florida (Floridan aquifer system), respectively. Nitrate fluxes to the water table were larger in agricultural settings than urban settings, indicating that it would be beneficial to reduce PSW capture zone areas in agricultural regions. Mixing calculations indicate that about 50 to 85% of the nitrate in water from the PSW could be from those modern anthropogenic sources, with the remainder coming from sources in old (>50 years) recharge or sources in young recharge in undisturbed settings such as forests. Excess N_2 concentrations and age tracers showed that denitrification at Modesto occurred gradually (first-order rate constant of 0.02/a) in a thick reaction zone following a ~30-year lag time after recharge. Denitrification generally was not an important nitrate sink at Woodbury. At York and Tampa, denitrification occurred rapidly (0.5 to 6/a) in thin reaction zones in fine-grained sediments that separated the anoxic PSW producing zones from overlying oxic, high-nitrate ground water. Particle tracking showed that a major pathway by which anthropogenic nitrate reached the York and Tampa PSW was by movement through long well screens crossing multiple hydrogeologic units (York) and by movement through karst features (Tampa), processes which reduced ground water residence times in the denitrifying zones. These results illustrate how PSW vulnerability to nitrate contamination depends on complex variations and interactions between contaminant sources, reaction rates, transit times, mixing, and perturbation of ground water flow in contrasting hydrogeologic settings.

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1. Introduction

[2] Nitrate (NO_3^-) is one of the most common ground water contaminants in the world and its presence in the environment at elevated concentrations poses well-known human health and ecological risks [*Fan and Steinberg*, 1996; *Galloway et al.*, 2003]. In 2000, about 37% of the public water supply in the United States came from ground water [*Hutson et al.*, 2004]. A nationwide survey of NO_3^-, pesticides, and volatile organic compounds in untreated water from domestic and public supply wells (PSW) in the United States showed that NO_3^- was the contaminant that most frequently exceeded a federal drinking water standard (10 mg/L as N for NO_3^-) [*Squillace et al.*, 2002]. Similarly, the U.S. Environmental Protection Agency reported that among organic and inorganic contaminants in all types of public water systems, NO_3^- was the one that most frequently exceeded a federal drinking water standard [*U.S. Environmental Protection Agency*, 2005]. In California, about 10% of the 38,000 water samples collected from PSW exceeded the NO_3^- drinking water standard in a 1975 to 1987 survey [*Franco et al.*, 1994]. Despite the importance of ground water to the nation's water supply and the relative impact of NO_3^- on the quality of that resource, detailed and systematic assessments of the processes re-

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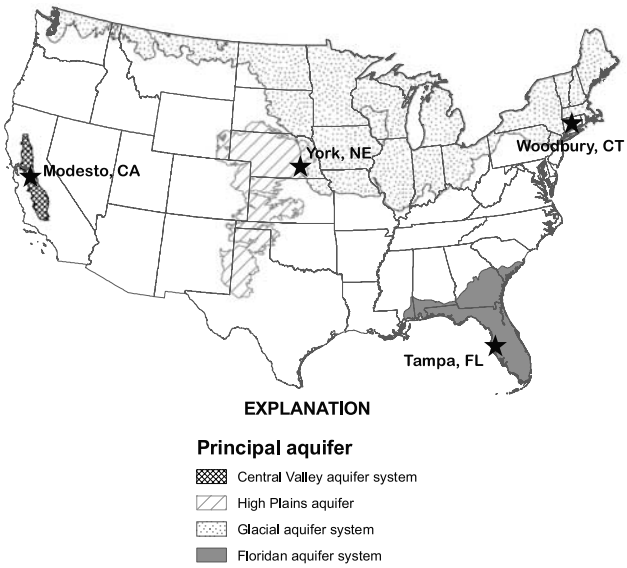


Figure 1. Location of the principal aquifers and communities where public supply wells were studied.

sponsible for NO_3^- contamination in PSW generally are lacking [*Kauffman et al.*, 2001].

[3] Understanding the origin, fate, and transport of NO_3^- and other contaminants to PSW is challenging for a number of reasons. Large-capacity pumping wells could have large and complex areas contributing recharge to the well screens [*Barlow*, 1997; *Kauffman et al.*, 2001], in which the land use (contaminant source) varies temporally and spatially. Under nonpumping conditions, water movement across long-screened intervals common in PSW could vertically redistribute contaminants in the flow system [*Reilly et al.*, 1989; *Shapiro*, 2002; *Konikow and Hornberger*, 2006]. Under pumping conditions, composite samples from long-screened intervals could consist of waters of varying ages and chemical compositions [*Reilly and LeBlanc*, 1998; *Weissmann et al.*, 2002], thus complicating interpretations of contaminant source and fate. Studies of contaminant movement to PSW that address these and other related issues could lead to better understanding of how to locate, construct, and operate PSW to minimize contamination. In 2001, the U.S. Geological Survey began a systematic assessment of processes affecting the transport of anthropogenic and natural contaminants, including NO_3^-, to PSW in the United States [*Eberts et al.*, 2005]. The purpose of this report is to examine source and transport controls on the movement of NO_3^- to PSW in selected principal aquifers of the United States.

[4] A single PSW in each of four communities across the United States was selected for detailed study. The communities and the principal aquifers in which the wells are screened are Modesto, California (Central Valley aquifer system); York, Nebraska (High Plains aquifer); Woodbury, Connecticut (Glacial aquifer system); and Tampa, Florida (Floridan aquifer system) (Figure 1). These four communities and principal aquifers were selected to represent a range of land uses, population sizes, and hydrogeologic conditions. In each area, ground water was a major source, if not the sole source, of water supply. Similar monitoring well network designs, sampling methodologies, broad suites of chemical and isotopic parameters, and analytical and modeling methods were used at all sites to enhance comparability of results between sites. Thus, this study represents one of the first to systematically evaluate source and transport controls on NO_3^- movement to PSW in diverse hydrogeologic settings.

2. Study Area Descriptions

2.1. Modesto, California

[5] Modesto, with a population of 188,856 (U.S. Census Bureau, 2000, U.S. Census 2000 American Fact Finder, accessed 13 April 2006, available at http://factfinder.census.gov/home/saff/main.html?_lang=en), is located in the Central Valley of California. The climate is semiarid and the area receives an average of 315 mm of precipitation each year. The Central Valley is a northwest trending structural basin bounded on the west by the Coast Range and on the east by the Sierra Nevada. Sediments in the study area largely consist of a series of overlapping terrace and alluvial fan deposits derived from the Sierra Nevada. Unconsolidated clay, sand, and gravels of the Pliocene-Pleistocene aged Laguna, Turlock Lake, and Riverbank Formations constitute the Central Valley aquifer in the study area (Figure 2). The aquifer in the study area is at least 100 m thick, and the depth to water was about 10 m. Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1. A map showing the area contributing recharge to the Modesto PSW is presented in Figure S1[1]. Recharge rates in the agricultural and urban areas were about 400–700 and 270 mm/a, respectively (Table 2). The primary sources of recharge are precipitation and irrigation return flow.

2.2. York, Nebraska

[6] York, with a population of 8081 (U.S. Census Bureau, 2000), is located within the High Plains in eastern Nebraska. The area has a humid, continental climate and receives an average of 711 mm of precipitation each year. The High Plains in eastern Nebraska is underlain by heterogeneous deposits of gravel, sand, silt, and clay of Quaternary age that form a layered sequence of coarse- and fine-grained units. A laterally continuous clayey till deposit 8 to 17 m in thickness separates upper unconfined coarse sands and lower confined fine sands of glaciofluvial origin (Figure 2). These units represent the High Plains aquifer in the study area. These unconsolidated sediments are underlain by the Carlile Shale, which is marine shale of Cretaceous age. The High Plains aquifer in the study area is about 80 m thick, and the depth to water was about 10 m. Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1. The area contributing recharge is shown in Figure S1. Recharge rates in the agricultural and urban areas were about 210 and 70 mm/a, respectively (Table 2). The primary sources of recharge are precipitation and irrigation return flow.

2.3. Woodbury, Connecticut

[7] Woodbury, with a population of 9198 (U.S. Census Bureau, 2000), is located within the glaciated New England

[1]Auxiliary materials are available in the HTML. doi:10.1029/2007WR006252.

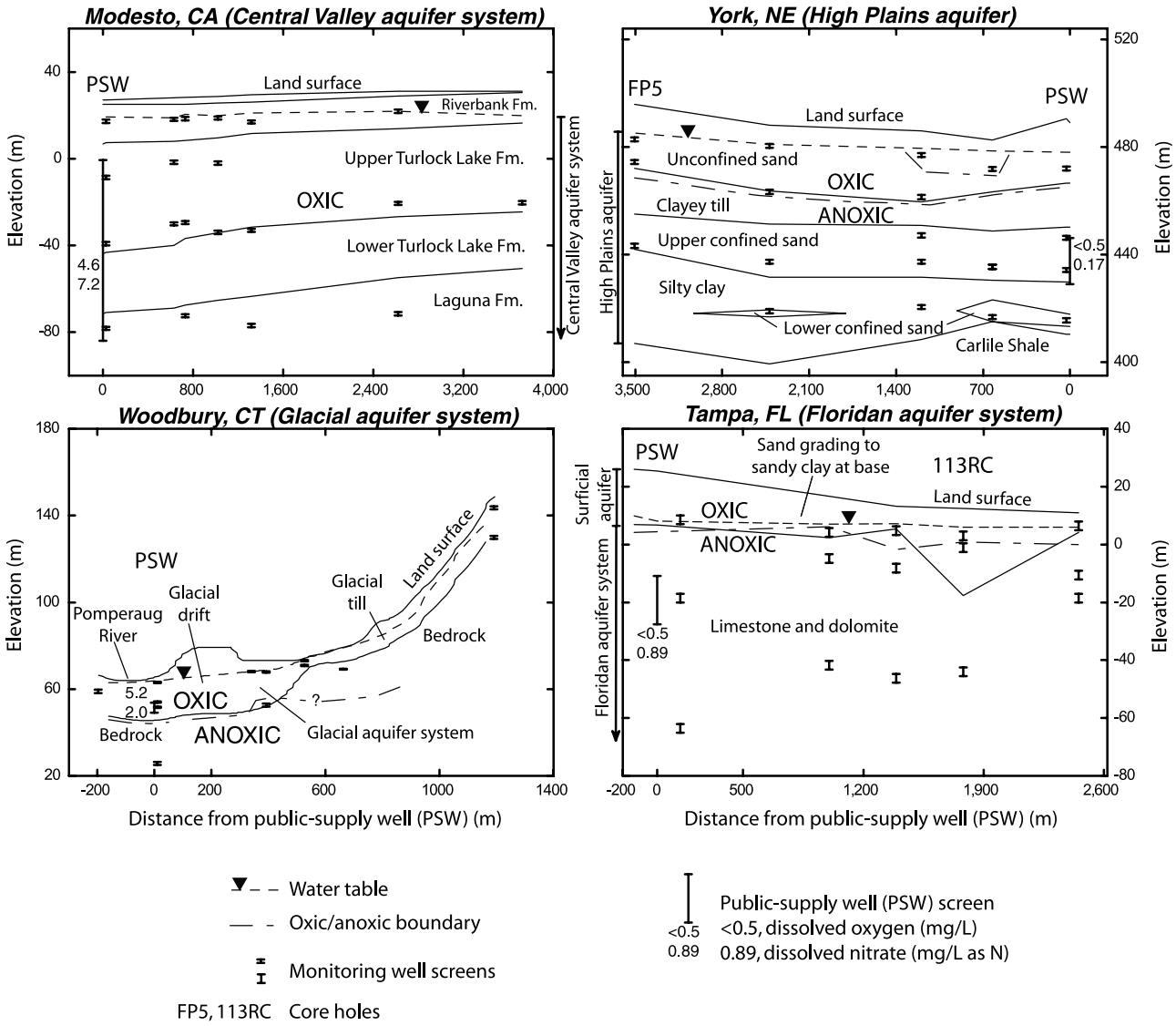


Figure 2. Hydrogeologic sections in the study areas. Oxic waters are operationally defined by dissolved oxygen $\geq$0.5 mg/L. See Figure S1 for map location of the sections.

Uplands in west central Connecticut. The area has a humid continental climate and receives an average of 1170 mm of precipitation each year. Near-surface sedimentary deposits in the Pomperaug River valley consist of stratified glacial drift in the river valley and glacial till deposits on the valley sides (Figure 2). These units are part of the Northeastern Glacial aquifer system. The valley is underlain by Mesozoic sedimentary and Paleozoic crystalline rocks. The valley sides and ridges are underlain by Paleozoic rocks that include granite, quartzite, schist, and gneiss. The Glacial aquifer in the study area is about 23 m thick, and the depth to water was about 4 m. Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1. The area contributing recharge is shown in Figure S1. The recharge rate in the study area was about 650 mm/a (Table 2). The primary sources of recharge are precipitation and infiltration of streamflow.

2.4. Tampa, Florida

[8] Tampa, with a population of 303,447 (U.S. Census Bureau, 2000), is located on Florida's Gulf Coast. The area has a subtropical climate and receives an average of 1,140 mm of precipitation each year. The study area is underlain by a thick sequence of limestone and dolomite of Eocene through Miocene age that is characterized by well-developed karst features such as springs, conduits, and sinkholes (Figure 2). These rocks constitute the Floridan aquifer in the study area. They are overlain by a discontinuous layer of late Miocene sediments composed of dense, plastic, green-gray clay, interbedded with varying amounts of chert, sand, clay, marl, shell, and phosphate. In places, this clay layer was breached by sinkholes associated with the underlying carbonate rocks. Overlying those sediments are unconsolidated sands, clays, and marls of Pliocene to Holocene age that constitute the Surficial aquifer. Depth to water in this aquifer generally was within 3 m of land surface. The Floridan aquifer in the study area is at least

Table 1. Characteristics of the Public Supply Wells Selected for Study

Location	County	Year of Construction	Average Pumping Rate (m^3/d)	Screened Interval (m below land surface)	Area Contributing Recharge (km^2)[b]	Generalized Land Use in Area Contributing Recharge (%)[a]				
						Agriculture	Urban	Forest	Wetland	Rangeland
Modesto, California	Stanislaus	1961	3750	28 to 111	4.2	30	67	<1	<1	2.3
York, Nebraska	York	1977	1390	43 to 61	6.3	39	45	11	<1	3.7
Woodbury, Connecticut	Litchfield	1967	390	14 to 18	0.5	4.8	75	13	6.9	<1
Tampa, Florida	Hillsborough	1958	2690	36 to 53	2.3	4.2	84	1	5.0	5.8

[a]On the basis of 1992 National Land Cover Data (NLCD) [*Vogelmann et al.*, 2001].
[b]Areas contributing recharge were derived from particle tracking models.

100 m thick. Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1. The area contributing recharge is shown in Figure S1. The recharge rate in the urban area was about 380 mm/a (Table 2). The primary sources of recharge are precipitation and infiltration of stream flow.

3. Methods

3.1. Particle Pathline Analysis

[9] Ground water pathlines and advective travel times were calculated using MODPATH [*Pollock*, 1994] to delineate the areas contributing recharge to the PSW, identify approximate flow paths to the PSW, and estimate age distributions of water captured by the PSW. Existing steady state, three-dimensional ground water flow models done using MODFLOW-2000 [*Harbaugh et al.*, 2000; *Starn and Brown*, 2007; *Clark et al.*, 2007; *Burow et al.*, 2008; U.S. Geological Survey, unpublished data, 2007] provided input into MODPATH. The forward tracking option of MODPATH was used for pathline analysis. From 2,344 to 47,008 particles were started at all inflow locations in the models and tracked to their discharge point. The particles were uniformly distributed on the face of the model cells associated with inflow to the model. Particles captured by the PSW were used to delineate areas contributing recharge and flow paths to those wells. The flow associated with each particle was computed by dividing the inflow at the source face by the number of particles started at that face. Effective porosity is required for pathline analysis and assigned values ranged from 0.2 to 0.45. Maps of the three-dimensional distribution of redox zones in the flow systems were superimposed on the pathlines to determine travel times in each zone.

3.2. Sampling

[10] Water table monitoring wells were installed under the major land uses in or near the contributing areas to characterize the chemical composition of recent recharge in each land use (Figure S1). Nested monitoring wells were installed along the MODPATH identified flow paths to the PSW to study the history, transport, and fate of NO_3^-. At the PSW, composite water samples were collected at the wellhead and depth-dependent samples were collected from discrete depth intervals in the well screen during pumping. Water samples were analyzed for over 100 chemical and isotopic parameters but only dissolved ammonium (NH_4^+), nitrite (NO_2^-), and NO_3^-; dissolved gases (Ne, Ar, O_2, N_2, CH_4); multiple isotopes (^3H, $\delta^{15}N[NO_3^-]$, $\delta^{18}O[NO_3^-]$, $\delta^{15}N[N_2]$); and age tracers (CFC-11, CFC-12, CFC-113, SF_6, $^3H/^3He$) are reported here. Further details on the collection and analysis of water samples are provided in Text S1.

3.3. Modeling Oxygen Reduction and Denitrification Rates

[11] Different approaches were used to estimate rates of O_2 reduction and denitrification (microbial reduction of NO_3^- to N_2), depending on the spatial and temporal scales

Table 2. Median NO_3^- Concentration in Recharge and Median NO_3^- Flux to the Water Table in Areas Contributing Recharge to the Public Supply Wells[a]

Location	Recharge Rate (mm/a)		NO_3^- Concentration in Recharge (mg/L as N)		NO_3^- Flux to Water Table (kg N/ha-year)		Probable Source of Large NO_3^- Concentrations in Ground Water	
	Agriculture	Urban	Agriculture	Urban	Agriculture	Urban	Agriculture	Urban
Modesto, California	400 to 700	270	12.5 (3.98 to 20.6)	3.48 (2.06 to 11.1)	69 (16 to 144)	9.4 (5.6 to 30)	Fertilizer	Septic Leachate, Fertilizer
York, Nebraska	210	70	15.7 (5.21 to 77.9)	22.5 (15.9 to 28.8)	33 (11 to 169)	16 (11 to 20)	Fertilizer, Manure spreading	Septic Leachate[b]
Woodbury, Connecticut	Not applicable	650	Not applicable	1.14 (<0.06 to 2.23)	Not applicable	7.4 (<0.4 to 14)	Not applicable	Septic Leachate, Fertilizer
Tampa, Florida	Not applicable	380	Not applicable	2.45 (0.21 to 4.56)	Not applicable	9.3 (0.8 to 17)	Not applicable	Fertilizer

[a]Ranges of values are reported in parentheses. Probable sources of large NO_3^- concentrations in ground water were selected on the basis of ^{15}N values, chemical data, and land use information.
[b]Septic leachate could include leaking sewer lines.

at which reactions occurred and on the density of sampling points in the reaction zones. *Groffman et al.* [2006] discuss in more detail scale issues associated with estimating in situ denitrification rates. In thick reaction zones where O_2 reduction and denitrification appeared to occur gradually, O_2 reduction and denitrification rates were estimated by comparing gradients in reaction progress and ground water age using the following models:

$$-R = \frac{\Delta(C - C_0)}{\Delta t} \quad (1)$$

$$-k = \frac{\Delta \ln(C/C_0)}{\Delta t} \quad (2)$$

where C is the measured O_2 or NO_3^- concentration, C_o is the initial O_2 or NO_3^- concentration in recharge [*Böhlke*, 2002], Δt is the difference between the ground water age of the sample and the age when it entered the relevant reaction zone, *R* is the rate (mg/L-year) for zero-order reaction kinetics, and *k* (1/a) is the rate constant for first-order reaction kinetics. For O_2 reduction, the water table was assumed to be the top of the reaction zone, and C_o was assigned the maximum measured O_2 concentration near the water table, which is likely to result in maximum estimates of *R* and *k*. For denitrification, C_o is equal to the sum of NO_3^--N + excess N_2-N, where excess N_2-N is the concentration of N_2 attributed to denitrification. The methods for calculating excess N_2-N and initial NO_3^- are presented in Text S1.

[12] In thin reaction zones where denitrification appeared to occur rapidly, denitrification rates were estimated by comparing analytical solutions to the one-dimensional advection-dispersion equation with decay to vertical NO_3^- concentration profiles using the following models:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - R \quad (3)$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - kC \quad (4)$$

where *D* is the coefficient of hydrodynamic dispersion, *z* is distance along the flow path, and *v* is ground water interstitial velocity in the denitrifying zone. Average ground water velocities in the denitrifying zones ranged from 0.7 (Tampa) to 1.6 m/a (York) and were obtained from the ground water flow models. Details of our 1-D modeling approach and the analytical solutions are presented in Text S1.

4. Results and Discussion

[13] The quality of water produced by PSW is complexly linked to the quality of water recharging and the effect of transport. By assessing relations between the quality of water recharging the aquifers (NO_3^- sources), the effect of transport through the hydrologic systems on NO_3^- (NO_3^- transport), and the quality of water produced by the PSW (NO_3^- receptors) in differing hydrogeological settings, insight can be gained into the factors controlling the occurrence of NO_3^- in water supplies.

4.1. Nitrate Sources

[14] Areas contributing recharge to the four PSW included a variety of land use settings such as agricultural, urban, and forest lands (Table 1). Thus, NO_3^- in water produced by the PSW could have been derived from numerous sources associated with those land uses. Nitrate under different land uses was characterized by its initial concentration and N isotope composition at the time of recharge (Figure 3), as well as its corresponding apparent ground water age (Figure 4). The NO_3^- source characterization is based on monitoring well samples. Samples from the PSW also are plotted in Figure 3, but they are discussed in the section "Nitrate Receptors."

4.1.1. Agricultural Sources of Nitrate

[15] Areas contributing recharge to the PSW in Modesto and York were the only ones to contain >5% agricultural lands (Table 1), so those were the only sites to have monitoring wells installed in agricultural areas. Median NO_3^- concentrations in agricultural recharge in Modesto and York were 12.5 and 15.7 mg/L as N, respectively (Table 2 and Figure 3). Median values of $\delta^{15}N[NO_3^-]$ in agricultural recharge in Modesto and York were 6.4 and 7.1‰, respectively.

[16] The values of $\delta^{15}N[NO_3^-]$ in agricultural recharge from both study areas could be consistent with NO_3^- derived from natural soil N or from fertilizer N that has undergone varying amounts of isotopic fractionation in the soil zone prior to recharge [*Kreitler*, 1979; *Gormly and Spalding*, 1979]. Fertilizer was the primary source of N applied to agricultural fields in both study areas. Furthermore, NO_3^- concentrations and $\delta^{15}N$ values in recent agricultural recharge were distinctly different from those in old recharge (>50 years) that may represent natural conditions (Figure 3). Thus, fertilizer is considered to be the most likely source of large NO_3^- concentrations in agricultural recharge in both study areas. The sample of York agricultural recharge with the largest NO_3^- concentration (well NWT1 in Figure 3), however, had a $\delta^{15}N$ value of 10.4‰, more characteristic of an animal waste source, and was located downgradient from a former manure-spreading area, so animal waste sources may be locally important in that agricultural area.

[17] On average, the dated ground water records indicate that NO_3^- concentrations in agricultural recharge at Modesto and York increased by about 11.5 and 14.5 mg/L as N, respectively, from before 1950 to 1995 (Figure 4). The increases in NO_3^- concentrations could be related to the temporal increase in farm fertilizer applications over the past ~50 years if the equivalent of about 40 to 50% of the applied N was nitrified and leached to the water table (Figure 4). Similar temporal trends and leaching fractions have been reported for agricultural recharge in other areas in the United States [*Hallberg*, 1986; *Böhlke and Denver*, 1995; *Böhlke et al.*, 2002, 2007; *Howarth et al.*, 2002; *McMahon et al.*, 2006].

4.1.2. Urban Sources of Nitrate

[18] Median NO_3^- concentrations in urban recharge at the four sites ranged from 1.14 mg/L as N at Woodbury to 22.5 mg/L as N at York (Table 2 and Figure 3). Excluding the York site, NO_3^- concentrations in urban recharge were

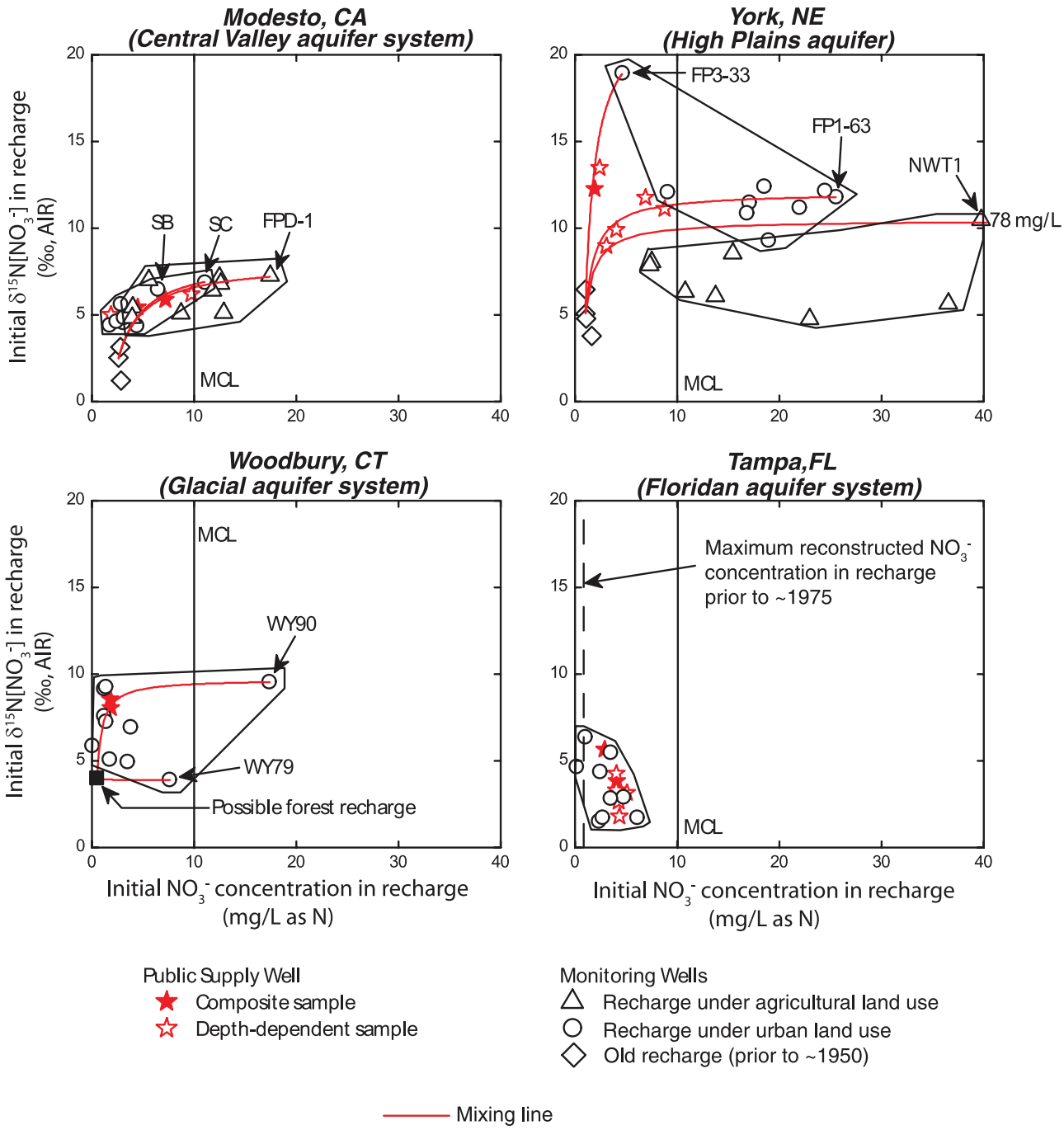


Figure 3. Initial nitrate concentrations and nitrogen isotope compositions in recharge to monitoring wells, by land use. Also shown are initial nitrate concentrations and nitrogen isotope compositions for public supply well (PSW) composite and depth-dependent samples. Where necessary, initial concentration and isotope compositions were obtained by correcting measured values for denitrification effects produced in the aquifer (see Text S1 for details). Mixing lines show some possible source contributions to nitrate in PSW samples. The forest end member for mixing in Woodbury is based on data from *Grady and Mullaney* [1998] and *Mayer et al.* [2002].

much smaller than the concentrations in agricultural recharge. This finding is consistent with a national survey of NO_3^- concentrations in shallow ground water in the United States that reported a larger median NO_3^- concentration under agricultural land than urban land [*Nolan and Stoner*, 2000]. Median values of $\delta^{15}N[NO_3^-]$ in urban recharge ranged from 2.9‰ at Tampa to 11.8‰ at York.

[19] The $\delta^{15}N$ values for York urban recharge generally were larger than 10‰, which could be characteristic of NO_3^- derived from animal waste sources [*Kreitler*, 1975; *Heaton*, 1986; *McMahon and Böhlke*, 1996]. The most likely sources of animal waste N at the York urban area are septic systems and perhaps leaking sanitary sewer lines. The $\delta^{15}N$ values for NO_3^- in urban recharge at Modesto and

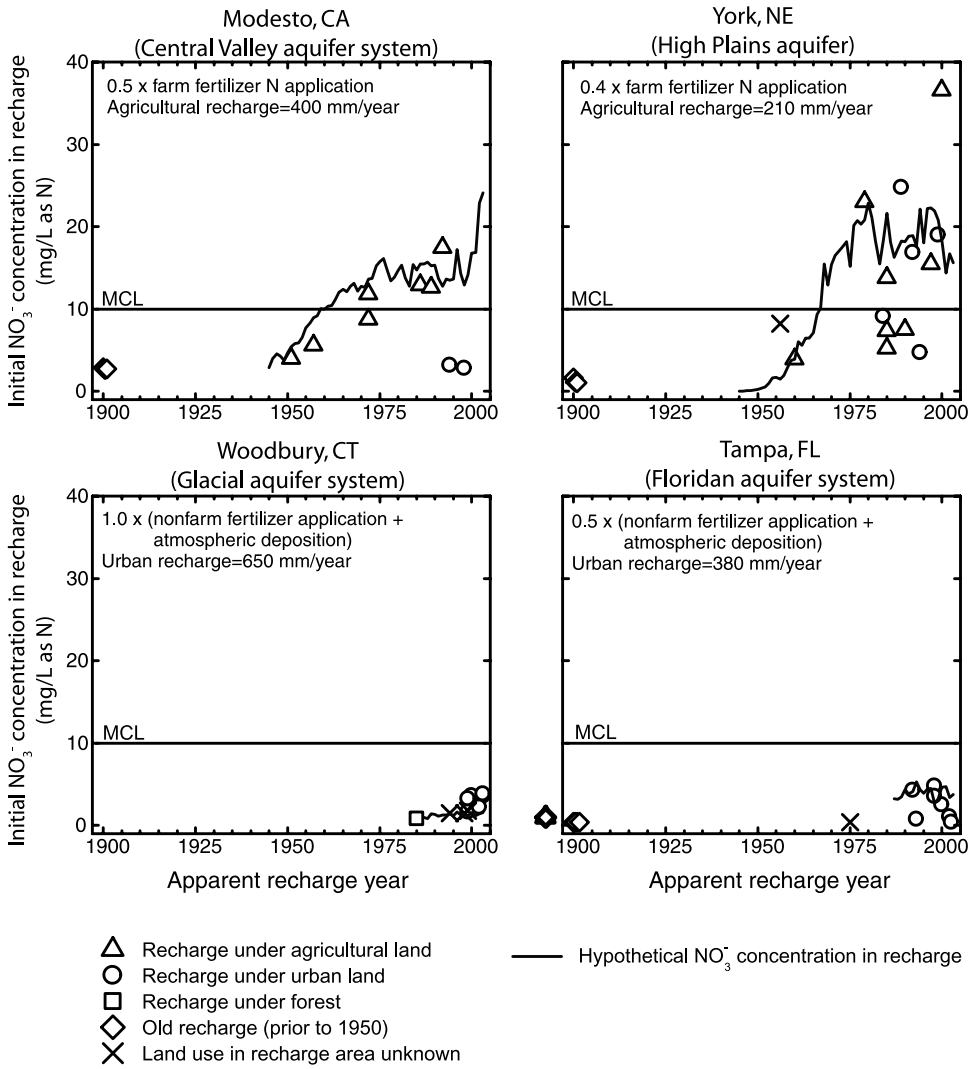


Figure 4. Initial nitrate concentrations in recharge in relation to recharge year. Where necessary, initial concentrations were obtained by correcting measured concentrations for denitrification effects produced in the aquifer (see Text S1 for details). Apparent groundwater ages were determined using CFC, SF_6, and (or) $^3H/^3He$ data. Samples containing <0.5 TU of ^3H were assigned recharge dates of ~1900; however, some samples could be older on the basis of particle ages and ^{14}C data, or slightly younger (but prior to ~1950). The solid lines represent nitrate concentrations that would occur in agricultural or urban recharge for the indicated recharge rates and fractions of applied nitrogen leached to the water table. Nitrogen applications were based on county-level data from *Ruddy et al.* [2006]. Farm fertilizer applications were normalized to total cropland in the county (U.S. Department of Agriculture, Census of agriculture: National Agricultural Statistics Service, variously dated, http://www.nass.usda.gov/Census_of_Agriculture/index.asp). Atmospheric nitrogen deposition is for wet deposition of nitrate and ammonium [*Ruddy et al.*, 2006]. MCL is Maximum Contaminant Level.

Tampa (Figure 3) are more consistent with NO_3^- derived from atmospheric deposition, natural soil N, or fertilizer N than with an animal waste source. It is not likely that atmospheric deposition in the absence of substantial evaporative concentration could produce NO_3^- concentrations larger than 1 to 2 mg/L as N in any of the study areas based on total inorganic N concentrations in wet deposition from nearby NADP sites (National Atmospheric Deposition Program, 2006, available at http://nadp.sws.uiuc.edu/sites/ntnmap.asp?), average values of which ranged from 0.21 to 0.83 mg/L as N. Likewise, the small NO_3^- concentrations in old recharge at Modesto and Tampa (Figures 3 and 4) indicate that soil N probably was not a source for the largest NO_3^- concentrations in urban recharge in those two areas. Hence, fertilizer probably was a more important source of large NO_3^- concentrations than soil N at Modesto and Tampa. The Modesto urban monitoring well with the largest NO_3^- concentrations (well SC in Figure 3), however, was located in an unsewered part of the city. Thus, it is possible that septic leachate also was an important source of large NO_3^- concentrations in Modesto urban recharge.

[20] At Woodbury, the $\delta^{15}N$ values for NO_3^- in urban recharge (Figure 3) indicate that fertilizer, soil, and animal waste all could have been possible sources of NO_3^- in that

area. Nitrate concentrations in forest recharge in Connecticut and other northeastern States typically are less than 1 mg/L as N (Figure 4) [*Grady and Mullaney*, 1998; *Mayer et al.*, 2002], so soil N was not a likely source of the large NO_3^- concentrations in recharge. The Woodbury sample with the largest NO_3^- concentration (well WY90 in Figure 3) was located downgradient from residential septic systems and had a $\delta^{15}N$ value (9.5‰) that is consistent with a septic source of N. The Woodbury sample with the second largest NO_3^- concentration (well WY79 in Figure 3) had a $\delta^{15}N$ value (3.9‰) that is more consistent with a fertilizer source of N.

[21] Nitrate concentrations in urban recharge at Tampa could be from nonfarm fertilizer applications and atmospheric N deposition if the equivalent of ~50% of that N was nitrified and leached to the water table (Figure 4). In the case of Woodbury, the available data indicate that nonfarm fertilizer and atmospheric N deposition could not account for most of the large NO_3^- concentrations in urban recharge, even if 100% of that N leached to the water table. This apparent discrepancy probably could be resolved if NO_3^- loading from septic systems in that area was accounted for. Septic systems are the primary waste disposal system used in that community.

4.1.3. Nitrate Recharge Fluxes

[22] Sources of NO_3^- in the areas contributing recharge to the PSW were diverse and appear to have included farm and nonfarm fertilizers, septic leachate or leaking sewer lines, manure spreading, atmospheric deposition, and natural soil N. Nitrate fluxes to the water table depended on the strength of those sources and recharge rates. Nitrate recharge fluxes were calculated using NO_3^- concentrations in recharge and water balance estimates of recharge (Table 2). Variability in the flux estimates probably represents spatial and temporal variations in NO_3^- inputs and recharge rates (Figures 3 and 4). Median NO_3^- recharge fluxes under agricultural land (33 to 69 kg N/ha-year) were larger than those under urban land (7.4 to 16 kg N/ha-year) (Table 2). The agricultural NO_3^- fluxes were similar to or larger than agricultural NO_3^- fluxes determined similarly in Minnesota, Maryland, and Nebraska (32 to 46 kg N/ha-year) [*Böhlke and Denver*, 1995; *Böhlke et al.*, 2002, 2007], and the largest urban NO_3^- flux was similar to the NO_3^- flux under Nottingham, England (21 kg N/ha-year) [*Wakida and Lerner*, 2005]. Although the NO_3^- recharge fluxes reported here are only approximations, they imply that agricultural sources produced larger NO_3^- loads to ground water than urban sources. From the standpoint of minimizing NO_3^- contamination in PSW, these findings indicate that it would be beneficial to reduce PSW capture zone areas in agricultural regions. In urban settings, consideration should be given to understanding the distribution of septic systems and leaking sewer lines in PSW capture zones.

4.2. Nitrate Transport

4.2.1. Terminal Electron-Accepting Processes

[23] Concentrations of O_2 in water from the aquifers at Modesto and Woodbury were mostly $\geq$0.5 mg/L, whereas waters containing <0.5 mg/L O_2 were more widespread in the aquifers at York and Tampa. For NO_3^- transport, the transition zone between oxic and anoxic conditions in an aquifer is important because that is generally where microbially mediated nitrate reduction begins [*Korom*, 1992]. *Chapelle et al.* [1995] proposed an O_2 concentration of 0.5 mg/L as the threshold at which NO_3^- reduction begins, but onset of NO_3^- reduction has been reported in aquifers where field measurements of O_2 concentrations were of the order of 1–2 mg/L [*Böhlke et al.*, 2002; *McMahon et al.*, 2004; *Böhlke et al.*, 2007]. In this study, oxic waters are operationally defined by $O_2 \geq 0.5$ mg/L. Data from all the sites show that excess N_2 concentrations were significantly smaller in samples containing $\geq$0.5 mg/L O_2 (average of 0.6 mg N/L) than in samples containing <0.5 mg/L O_2 (average of 1.7 mg N/L) ($p = 0.002$, Mann-Whitney test).

[24] The selected PSW at Modesto and Woodbury were screened in oxic zones (Figure 2). The general absence of anoxic conditions in the aquifers at Modesto and Woodbury indicates that NO_3^- was likely to persist as it was transported along flow paths from recharge areas to those PSW. At York, the transition zone between oxic and anoxic conditions was located in the clayey till confining unit between the base of the unconfined sand and the top of the upper confined sand (Figure 2). At Tampa, the transition zone was located near the top of the Floridan aquifer system, just a few meters below the water table, and probably is related to the downward fining of sediment texture in the surficial deposits. The selected PSW at York and Tampa were screened below the redox transition zones, indicating that NO_3^- was likely to be at least partially reduced as it was transported along flow paths from recharge areas to those PSW.

[25] Vertical profiles of redox-sensitive species at York and Tampa show that concentrations of excess N_2 increased with depth below the water table as concentrations of O_2 decreased (Figure 5), indicating that reduction of NO_3^- did occur along flow paths leading to the producing intervals in which those PSW were screened. Median denitrification reaction progress in the PWS production zones ranged from 0 to 94 percent (Figure 6), with the greatest progress occurring in the aquifers at York and Tampa. The presence of elevated Fe^{2+}, H_2S, and CH_4 concentrations indicate that anoxic zones at York and Tampa progressed beyond denitrification to Fe(III) reduction, SO_4^{2-} reduction, and methanogenesis (Figure 5).

4.2.2. Isotopic Evidence for Denitrification

[26] The N and O isotopes of NO_3^- in oxic water samples, which included almost all of the samples from Modesto and Woodbury, exhibited little or no evidence of fractionation (Figure 7). At York and Tampa, N and O isotopes in anoxic water are positively correlated and resemble fractionation trends that have been reported for denitrification [e.g., *Böttcher et al.*, 1990; *Aravena and Robertson*, 1998; *Mengis et al.*, 1999; *Fukada et al.*, 2003; *Sigman et al.*, 2005]. Least squares regressions yield apparent fractionation trends ($\Delta\delta^{18}O/\Delta\delta^{15}N$) of approximately 0.5 for York (near the low end of the reported range for denitrification) and 0.83 for Tampa (near the high end of the reported range). Scatter in these trends may be attributed in part to variations in the initial values of $\delta^{18}O$ and $\delta^{15}N$ for individual samples.

[27] The N isotope compositions of residual NO_3^- and excess N_2 plotted relative to denitrification reaction progress are qualitatively consistent with fractionations expected for denitrification (Figure 6). The apparent enrichment factors (ε) that would be consistent with the data are approximately −10 to −2‰. These apparent ε are variable

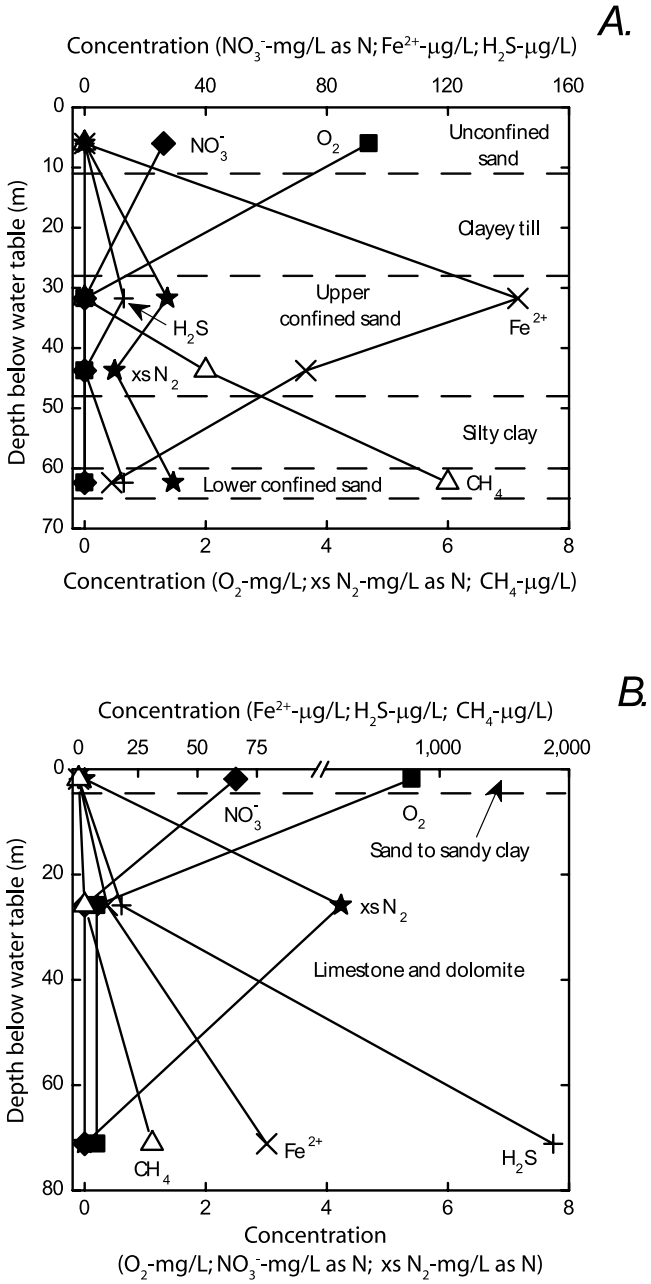


Figure 5. Concentration profiles for redox-sensitive species in ground water in relation to depth below the water table at selected monitoring well nests at (a) York, Nebraska, and (b) Tampa, Florida; xs N_2 refers to excess N_2 from denitrification.

and generally smaller than those determined experimentally for denitrification (about −30 to −20‰) but within the range of possibilities in heterogeneous ground water systems [e.g., *Mariotti et al.*, 1988].

4.2.3. Rates of Oxygen Reduction and Denitrification in Unconfined Sands

[28] The presence of relatively large O_2 concentrations in water from the Turlock Lake and Riverbank Formations in Modesto, unconfined sand in York, glacial drift in Woodbury, and surficial sand in Tampa (Figure 2) indicate that those coarse sediments could represent thick reaction zones where O_2 reduction and denitrification occur gradually. Thus, equations (1) and (2) were used to describe the reaction kinetics. Results for both kinetic models (zero-order and first-order) are presented in Table 3 for comparison with other data, although it is uncertain whether either of these is the correct model because of sparse data in the reaction zone. The following comparative discussion focuses on the first-order rate constants, *k*.

[29] Rate constants for O_2 reduction at York, Woodbury, and Tampa were roughly similar and ranged from 0.02 to 1/a (Figure 8). The values at those sites are similar to O_2 reduction rate constants reported for fluvial (0.1/a) and glaciofluvial (0.13/a) sands in Nebraska and Minnesota, respectively [*Böhlke et al.*, 2002, 2007]. The largest rate constant at Modesto, 0.03/a, was at the low end of values at the other sites. Rate constants for O_2 reduction in the study areas have important implications with respect to lag times for the start of denitrification.

[30] Excess N_2 was present in small concentrations (0.3 to 1.8 mg/L as N) in the aquifer at Modesto and the concentrations systematically increased with depth at multiple well nests, indicating that small amounts of denitrification occurred in the aquifer even though it was generally oxic. All of the samples with detectable excess N_2 had apparent ground water ages ≥40 years (Figure 8), indicating a lag time of possibly several decades before the onset of

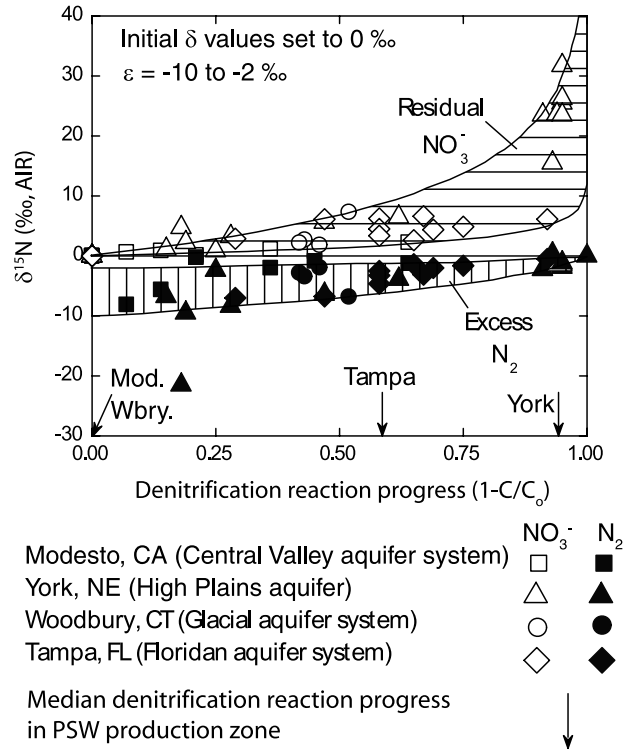


Figure 6. Nitrogen isotope compositions of residual nitrate and excess N_2 in relation to denitrification reaction progress. Initial (undenitrified) δ values for nitrate were set to 0‰ to facilitate comparisons between aquifers. Hatched areas represent Rayleigh-type fractionation trends with enrichment factors ranging from −10 to −2‰. The method for calculating denitrification reaction progress is presented in Text S1.

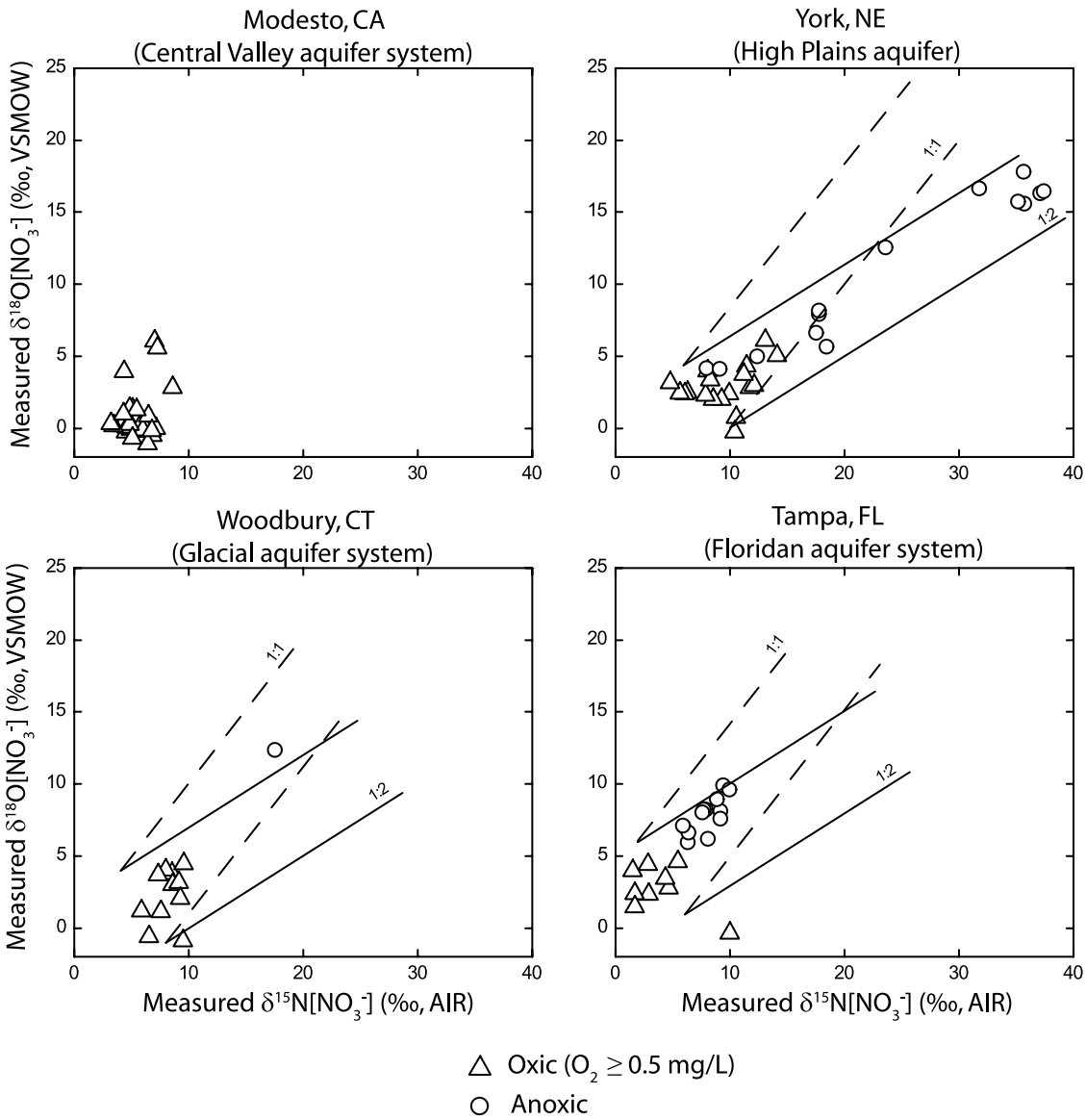


Figure 7. Measured nitrogen and oxygen isotope compositions of nitrate in ground water. The lines indicate the range of fractionation trends reported for nitrate reduction. ($\Delta\delta^{18}O/\Delta\delta^{15}N \approx 0.5$ to 1.0).

denitrification. Such a long lag time may be related to the relatively small rate constants for O_2 reduction at that site. Much longer lag times prior to denitrification have been reported elsewhere (e.g., ~3,000–10,000 years [*Vogel et al.*, 1981; *McMahon et al.*, 2004]). Values of $\ln(C/C_o)$ plotted in relation to ground water age correspond to a maximum k of 0.02/a at Modesto (Figure 8), assuming a lag time of ~30 years after recharge before the onset of denitrification. This lag time corresponds to the oldest sampled water at Modesto that did not contain detectable excess N_2 (Figure 8). This analysis is limited by the fact that the most denitrified samples, which were the deepest samples in their respective well nests, were too old to be dated with the available tracers and so were omitted from the analysis. One possible explanation for denitrification in this oxic flow system is that it occurred in association with abundant sand/clay contacts in the aquifer. Clay and silt comprise about 50% of the sediments in this aquifer. Despite the apparent occurrence of denitrification in the Central Valley aquifer, its rate was sufficiently slow to allow 95%, on average, of the NO_3^- originally present in modern recharge to persist along the sampled flow paths.

[31] For the most part, excess N_2 was not detected in the unconfined, sandy sediments at the other three sites (Figure 8), indicating a general lack of denitrification in those settings even though O_2 reduction rate constants were larger there than at Modesto (Table 3). Larger O_2 reduction rate constants presumably would produce anoxic conditions more quickly at those sites than at Modesto. At Woodbury and Tampa, the apparent lack of denitrification could result from the short residence time (roughly <10 years) of water in those sandy sediments (Figure 8). Ground water residence times in the unconfined sand in York were as long as

Table 3. Apparent Rates and Rate Constants for O_2 Reduction and Denitrification[a]

Variable	Modesto, California	York, Nebraska					Woodbury, Connecticut	Tampa, Florida		
		Unconfined Sand	Clayey Till	Upper Confined Sand	Silty Clay	Carlile Shale		Unconfined Sand	Sandy Clay/Clayey Sand	Carbonates
O_2 reduction rate, R (mg/L-year)	0.03 to 0.2	0.08 to 0.6	–	–[b]	–[b]	–	0.3 to 6	0.2 to 0.4	–	–[b]
O_2 reduction rate constant, k (1/a)	0.005 to 0.03	0.02 to 0.3	–	–[b]	–[b]	–	0.04 to 1	0.05 to 0.1	–	–[b]
Denitrification lag time[c] (years)	30	40	–	–	–	–	Not applicable	5 to 10	–	–
Denitrification rate, R (mg-N/L-year)	n.d.[d] to 0.07	n.d.[d] to 6	0.2 to 14	–[b]	–[b]	–	n.d.[d]	n.d.[d]	0.1 to 0.8	–[b]
Denitrification rate constant, k (1/a)	n.d.[d] to 0.02	n.d.[d] to 0.05	0.1 to 6	–[b]	–[b]	–	n.d[d]	n.d.[d]	0.1 to 0.5	–[b]

[a]Also listed are apparent denitrification lag times (–, not measured; n.d., no denitrification detected).
[b]Most sampled intervals in this hydrogeologic unit did not contain detectable NO_3^- (none contained detectable O_2).
[c]Lag time is the time of travel of a groundwater particle through the O_2 reduction zone prior to the onset of denitrification; lag time could be shorter than indicated where localized conditions support denitrification.
[d]O_2 concentration >3 mg/L in sampled interval.

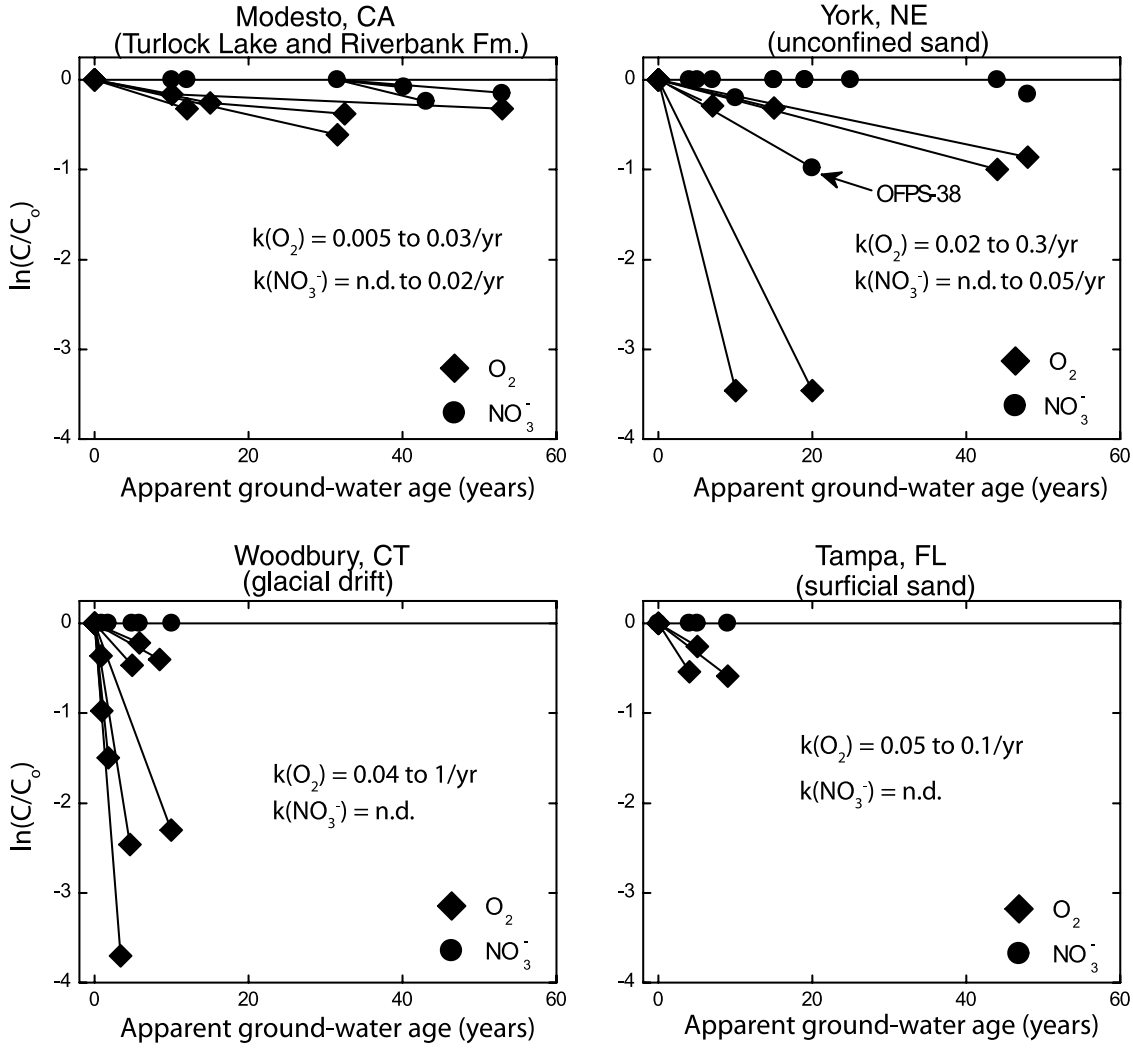


Figure 8. Range of apparent rate constants (k), assuming first-order kinetics (equation (2) in text), for oxygen reduction and denitrification in aquifer sediments. Samples are from monitoring wells; n.d. indicates "no denitrification" detected in samples on the basis of excess N_2 concentrations.

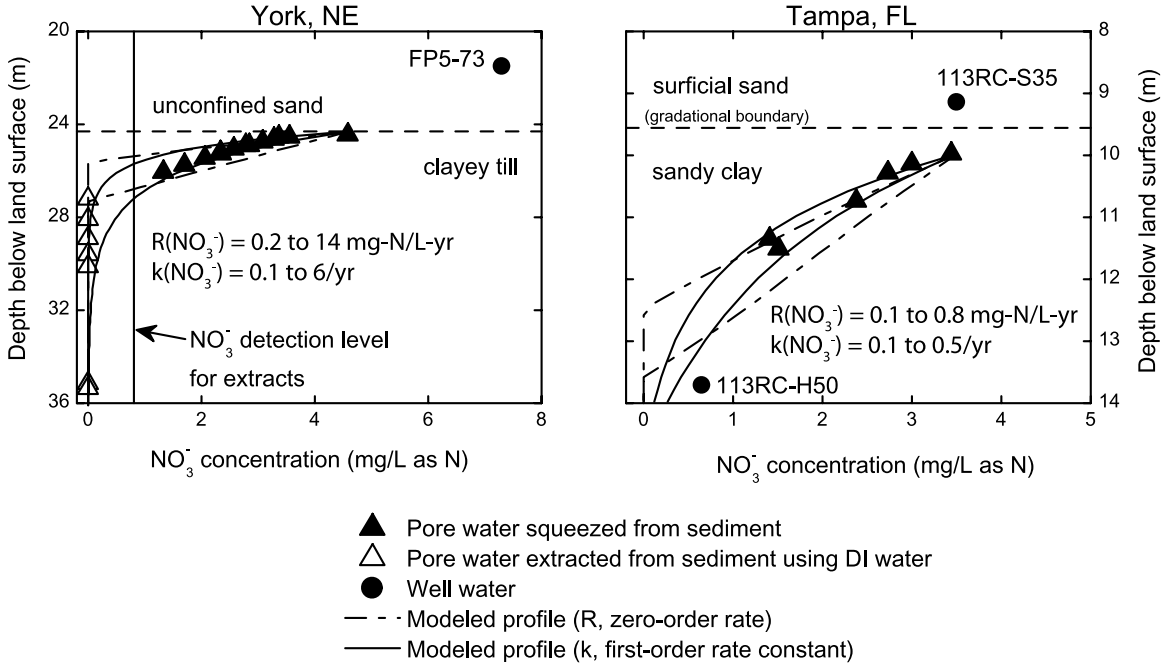


Figure 9. Range of apparent rates (R) and rate constants (k), assuming zero- and first-order kinetics, respectively, for denitrification in confining units in the High Plains and Floridan aquifer systems. Core was collected from site FP5 near York and from site 113RC near Tampa. Values of R and k were estimated by comparing analytical solutions to the one-dimensional advection-dispersion equation with degradation (equations (3) and (4) in text) to the vertical nitrate concentration profiles.

those at Modesto but systematic increases in excess N_2 with depth were not detected at York like they were at Modesto. The reason for this difference between the two sites is not clear, but it could be related to the smaller clay content in the sediment at York compared to Modesto if the clays contain more organic carbon to support denitrification than sands [*McMahon et al.*, 1999].

[32] Denitrification could be locally important in the unconfined sands at York, Woodbury, and Tampa, in places where lag times may be considerably shorter. For example, water from well OFPS-38 at York (Figure 8), which is located in the floodplain of a small stream, contained no detectable O_2, 5.7 mg/L of excess N_2-N and elevated concentrations of Fe^{2+} and CH_4. The apparent age of that water was about 20 years, but denitrification is likely to have begun soon after recharge in the anoxic floodplain sediments.

4.2.4. Rates of Oxygen Reduction and Denitrification in Clay Confining Units

[33] The presence of relatively small O_2 concentrations in the clayey till at York and sandy clay above limestone at Tampa (Figure 2) indicate that those sediments could represent thin reaction zones where O_2 reduction and denitrification occur rapidly. Thus, equations (3) and (4) were used to describe the reaction kinetics. At York, the modeled denitrification zone was the top of the clayey till confining unit at well site FP5, which was a transition zone from oxic to anoxic conditions at that site (Figure 2). At Tampa, the modeled zone was the top of the sandy clay at well site 113RC, which was the transition zone from oxic to anoxic conditions at that site (Figure 2).

[34] Nitrate concentrations in the sediment pore waters at both sites decreased with depth, implying that denitrification may have occurred (Figure 9). Other evidence for denitrification in those pore waters included fractionation of N and O isotopes in residual NO_3^-, accumulation of excess N_2, and (or) a decrease in NO_3^-/Cl^- ratios with depth. The decrease in NO_3^- concentrations with depth at both sites appears to be better represented by the models with first-order reaction kinetics than the ones with zero-order kinetics (Figure 9). In these instances, k ranged from 0.1 to 6/a at York and from 0.1 to 0.5/a at Tampa. These rate constants are considerably larger than those from the Modesto and Woodbury sandy sediments (Table 3), which lack laterally extensive confining layers. Thus, the confining layers at York and Tampa are considered to be more effective reactive barriers to NO_3^- transport than isolated denitrifying zones that might be present in the unconfined sands at Modesto and Woodbury. Furthermore, Fe(III)-reducing, SO_4^{2-}-reducing, and methanogenic conditions deeper in the aquifers at York and Tampa (Figure 5) imply that NO_3^- transported below the confining layers would not persist under natural conditions.

[35] The spatial distribution of denitrifying zones in the aquifers at York and Tampa differed markedly from the spatial distribution of denitrifying zones in a shallow sand aquifer at Cape Cod, Massachusetts. *Bowen et al.* [2007] reported that denitrification was focused near the shallow water table in that aquifer because the source of electrons for denitrification was DOC leached from the soil zone. At York and Tampa, the electron donors for denitrification had geologic sources deeper in the flow system. Thus, there was a ~5- to 40-year lag time prior to the onset of denitrification as ground water traveled through the O_2 reduction zone near the water table.

4.2.5. Nitrate Attenuation Efficiency

[36] The concentration of NO_3^- eventually entering PSW screens depends in part on denitrification rates and ground water velocities along all flow paths leading to the PSW.

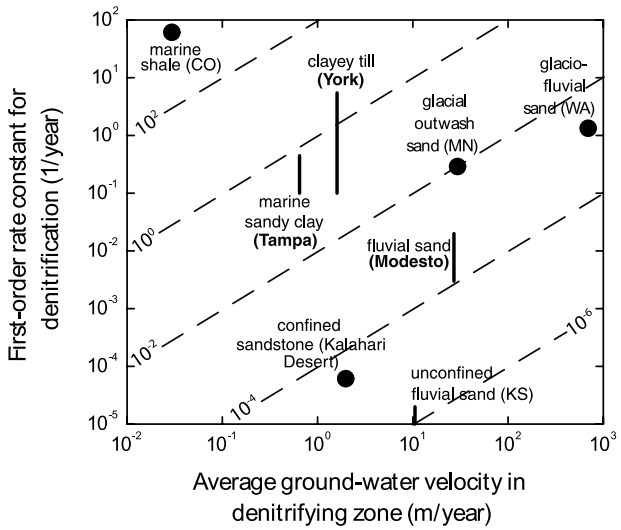


Figure 10. Nitrate attenuation efficiencies (1/m) represented by the ratio of first-order denitrification rate constant (k, 1/a) to average groundwater velocity (v, m/a). The attenuation efficiencies essentially represent fractional nitrate losses from denitrification per unit distance of transport within active denitrification zones. Data are from this study and from *Vogel et al.* [1981], *McMahon et al.* [1999, 2004], *Tesoriero et al.* [2000], and *Böhlke* [2002].

Nitrate concentrations should be relatively small where denitrification rates outpace velocities and relatively large where velocities outpace rates. Denitrification rate constants and average ground water velocities in denitrifying zones were used as a framework for comparing NO_3^- attenuation efficiency, defined as k/v, in the aquifers (Figure 10). The attenuation efficiencies essentially represent fractional NO_3^- losses from denitrification per unit distance of transport. General patterns in the NO_3^- attenuation efficiencies appear to be related to sedimentary depositional environment; attenuation efficiencies increased as follows: fluvial sand aquifers < glacial sand aquifers < glacial/marine clay < marine shale. Various uncertainties are associated with the NO_3^- attenuation efficiencies defined here, such as representative sampling of the reactive zone, ability to date ground water at appropriate timescales, and NO_3^- transport limitations on denitrification. Nevertheless, this approach could provide a useful framework for comparing aquifer susceptibility to NO_3^- contamination.

4.3. Nitrate Receptors

4.3.1. Nitrate Concentrations in Public Supply Wells

[37] Measured NO_3^- concentrations in the PSW composite (wellhead) and depth-dependent samples ranged from <0.06 to 9.7 mg/L as N (Figure 11). The largest measured NO_3^- concentrations (4.4 to 9.7 mg/L as N) occurred in samples from the Modesto PSW, and the smallest concentrations (<0.06 to 0.47 mg/L as N) occurred in samples from the York PSW. Denitrification apparently did not reduce any NO_3^- to N_2 in water captured by the Modesto and Woodbury PSW (Figure 11), whereas it reduced about 60 to 95%, on average, of the NO_3^- in water captured by the Tampa and York PSW, respectively.

[38] Reconstructed initial NO_3^- concentrations (indicated by the sum of NO_3^--N + excess N_2-N concentrations in Figure 11) exhibited substantial variability with depth in the well screens at Modesto and York. At Tampa, the lower third of the well intercepted a high-permeability conduit [*Katz et al.*, 2007] (represented by the 49-m sample) that may have dominated the chemistry of shallower depth-dependent samples. The short screen in the Woodbury PSW (Figure 2) precluded the collection of depth-dependent samples from that well. Initial NO_3^- concentrations in samples from the Modesto and York PSW were not consistently larger than those from the Tampa and Woodbury PSW even though NO_3^- fluxes to the water table at Modesto and York were larger than those at the other two sites (Table 2), indicating that water entering the PSW probably contained NO_3^- from multiple sources and (or) water of multiple ages.

4.3.2. Mixing in Public Supply Wells

[39] According to the MODPATH analysis, water from most of the PSW consisted of a broad distribution of ages–spanning <20 years at Woodbury to >1000 years at Modesto and York (Figure 12a). Contributions of <50-year-old water to flow in the PSW ranged from about 30% at York to 100% at Woodbury (Figure 12a). The <50-year-old fraction of these distributions is important because it contained the largest NO_3^- concentrations (Figure 4) and the >50-year-old fraction is important because it could dilute anthropogenic NO_3^- concentrations when waters of different age mixed in the PSW. Young ground water also is important because it could indicate limited denitrification potential in flow systems with long denitrification lag times (Table 3). For example, the single largest annual age fraction of water entering the Modesto PSW was about

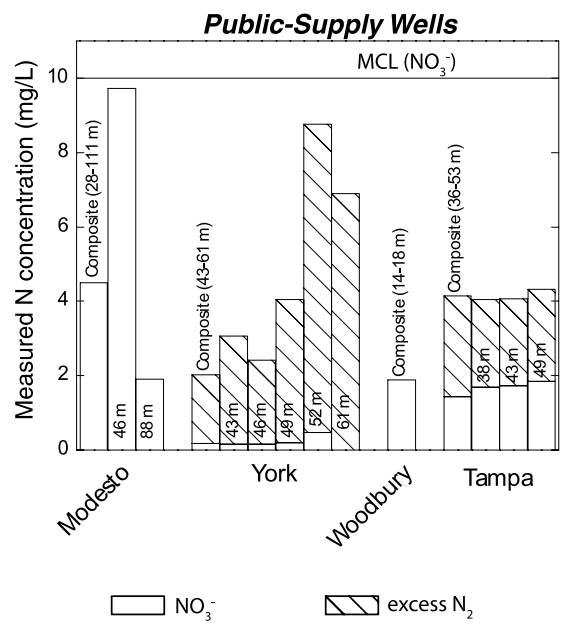
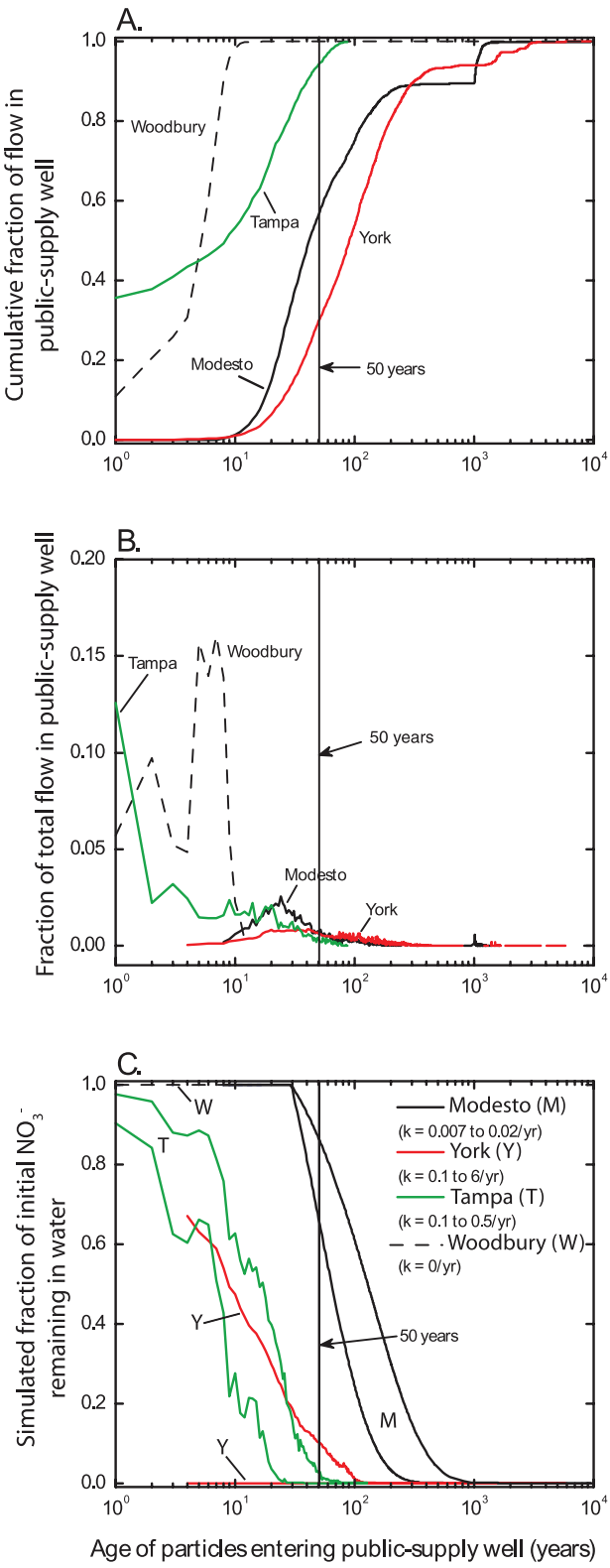


Figure 11. Concentrations of nitrate and excess N_2 in composite samples from the PSW wellhead and from depth-dependent samples in the PSW. The composite samples represent the entire screened interval, shown in parentheses. The depth-dependent samples are from specific depths, shown in parentheses, in the PSW well screen. MCL is Maximum Contaminant Level.



25 years old (Figure 12b), which is shorter than the 30-year denitrification lag time at that site (Table 3). Thus, NO_3^- in that young fraction of water is less likely to have been denitrified compared to NO_3^- in older fractions of water.

[40] All of the PSW samples contained some anthropogenic NO_3^- on the basis of mixing calculations in which initial NO_3^- concentrations and isotope compositions in recharge were used to define possible mixing end members (Figure 3). Most of the Modesto PSW samples plot along mixing lines defined by old recharge and contaminated modern urban (well SC) or agricultural (well FPD-1) recharge. Twenty to 55% of the water in the composite samples (and 55 to 85% of the NO_3^-) may have been derived from urban sources such as septic leachate (as represented by SC). Alternatively, 15 to 30% of the water in the composite samples (50 to 75% of the NO_3^-) may have been derived from agricultural sources such as irrigation return flow containing fertilizer N (as represented by FPD-1). It also is possible that the composite samples contained NO_3^- from both anthropogenic sources. The remaining NO_3^- presumably was from old, possibly natural, sources. These fractions of modern anthropogenic recharge in the Modesto PSW samples are roughly consistent with the simulated fraction of <50-year-old water entering the Modesto PSW (Figure 12a).

[41] Old recharge (>50 years) apparently was not present in the aquifer at Woodbury, but recharge through forest soils in New England generally contains small NO_3^- concentrations (<1 mg/L as N) [*Grady and Mullaney*, 1998; *Mayer et al.*, 2002]. The Woodbury PSW samples plot along a mixing line defined by hypothetical forest recharge and contaminated urban recharge (WY90) (Figure 3), indicating that only about 10% of the water in those composite samples (but 75% of the NO_3^-) may have been derived from urban sources such as septic leachate (as represented by WY90). The composite samples do not plot near the mixing line defined by well WY79 (Figure 3), which may contain NO_3^- from a fertilizer source.

[42] The York PSW samples generally plot along mixing lines defined by old recharge and two urban end members (wells FP1-63 and FP3-33 in Figure 3), such that 25% of the water in the composite sample (60% of the NO_3^-) may have been derived from urban sources such as septic leachate (as defined by FP1-63). These results are consistent with particle-tracking simulations for the York PSW, which showed that about 30% of the water entering the well was <50 years old (Figure 12a).

[43] At Tampa, the most likely recharge end members containing small NO_3^- concentrations were old recharge and

Figure 12. (a and b) Fractions of flow in the PSW. (c) Simulated fractions of initial nitrate remaining in water captured by the PSW as a function of the simulated age of particles entering the PSW. In Figure 12c, *k* refers to the first-order denitrification rate constant within a zone of active denitrification (ranges of values indicate uncertainty of the estimations). Along each flow path, the value of *k* was zero before the onset of denitrification. It was assumed that the rate constants measured in the overlying confining layers were representative of the rate constants in the underlying sediments.

modern recharge from wetlands/rivers. The ^{15}N composition of those types of waters could not be analyzed because of their small NO_3^- concentrations and (or) small amounts of excess N_2. Nevertheless, the initial NO_3^- concentrations and isotopic compositions in Tampa PSW samples indicate that a substantial fraction of NO_3^- in those samples probably was derived from urban sources like fertilizer (Figure 3).

4.3.3. Short-Circuiting Pathways at York and Tampa

[44] The York PSW produced waters that were recharged with 2.0 to 8.8 mg/L NO_3^- as N (Figure 11), whereas four of seven monitoring wells in that interval produced water that was recharged with <2 mg/L NO_3^- as N and 6 of 8 wells contained <1 TU ^3H. Such data indicate that much of the confined part of the High Plains aquifer may have contained old water that was recharged with substantially less NO_3^- than water captured by the PSW. The youngest particle age for water moving downward through the confining unit by advection was about 60 years, further suggesting that under natural flow conditions the confined aquifer should not have contained modern, high-NO_3^- water. *Clark et al.* [2007] proposed that the occurrence of modern recharge in the confined aquifer resulted from downward leakage of water through wells screened in multiple geologic layers and through the annular space of well bores that penetrated the confining layer, essentially bypassing the confining unit. If that interpretation is correct, the leakage probably did not occur at the PSW itself because the deepest depth-dependent samples contained the largest initial NO_3^- concentrations (Figure 11). It is more likely that leakage between aquifers occurred at upgradient locations in the PSW capture zone through high-permeability features such as irrigation wells. Even though NO_3^--rich water may have either partially or fully bypassed the denitrifying zone in the confining unit, about 95% of the initial NO_3^- in water captured by the PSW was removed by denitrification (Figure 11). Thus, it appears that denitrification must have occurred within the confined sand where highly reducing conditions naturally existed (Figure 5a).

[45] As at York, waters from the Tampa PSW contained substantially larger initial NO_3^- concentrations than several monitoring wells screened in the same producing interval. The PSW samples were recharged with about 4 mg/L NO_3^- (Figure 11), whereas 7 of 12 monitoring wells in that interval produced water that was recharged with <1 mg/L NO_3^- as N, and 6 of 10 wells contained <1 TU ^3H. The high-permeability conduit at a depth of about 49 m that was intercepted by the PSW apparently was connected to the surficial aquifer allowing for the rapid movement of modern recharge to the PSW. *Katz et al.* [2007] estimated that 50 to 70% of the water produced from the PSW was from the surficial sand aquifer, rather than the Floridan aquifer, on the basis of chemical mass balance calculations. Those chemical results are consistent with the particle-tracking results (which accounted for conduit flow) that showed the PSW capturing a large fraction of very recent recharge (Figures 12a and 12b). Conduit flow such as this could bypass the denitrifying zone at the top of the Floridan aquifer and also reduce reaction time in the underlying carbonate sediments which were highly reducing (Figure 5b). All of these factors may explain why the PSW contained detectable NO_3^- but most monitoring wells in the same interval did not (Figure 3).

4.3.4. Nitrate Age Distributions in Public Supply Wells

[46] Denitrification rates, spatial distribution of redox conditions, and time spent by water in different redox zones strongly influenced the fractions of initial NO_3^- remaining in different age fractions of water captured by the PSW. The combined effect of these factors resulted in very different relations between NO_3^- losses and particle ages in the different study areas (Figure 12c). Because first-order reaction kinetics was assumed, the fractional NO_3^- concentrations in Figure 12c are independent of specific NO_3^- input histories. At all of the sites except for Woodbury, denitrification had the potential to substantially reduce initial NO_3^- concentrations if there was sufficient ground water residence time in the denitrifying zones. Well construction or management practices that reduce water residence time in those zones, such as screening across confining layers, do not take full advantage of the natural NO_3^- attenuation capacity of the aquifer system. Sites like Woodbury do not have substantial NO_3^- attenuation capacity, but the short ground water residence times indicate that those types of systems would be relatively responsive to land use changes designed to reduce NO_3^- fluxes to the water table. These results illustrate that PSW vulnerability to NO_3^- contamination depends on complex variations and interactions between contaminant sources, reaction rates, transit times, mixing and perturbation of ground water flow in contrasting hydrogeologic settings.

5. Conclusions

[47] Understanding factors controlling the source and transport of NO_3^- to public supply wells (PSW) is challenging because of complex areas contributing recharge to the wells, spatial and temporal variability in NO_3^- sources within the contributing areas, spatially variable denitrification rates along flow paths leading to the wells, mixing, and possible perturbations in the flow system caused by well construction and (or) operation. Systematic studies of NO_3^- movement to PSW in four diverse hydrogeologic environments showed that NO_3^- in PSW was derived from varying proportions of agricultural (fertilizer, manure spreading), urban (septic leachate, fertilizer), and natural sources. Nitrate fluxes to the water table were larger in agricultural settings than in urban settings, indicating the PSW capture zones should be designed to limit inputs from agricultural sources. Denitrification in the aquifers was characterized by either slow rates in broad reaction zones within sandy fluvial and alluvial fan deposits or by fast rates in thin reaction zones at clay/sand contacts of glacial and marine deposits. In undisturbed flow systems, denitrification in the thin reaction zones provided more protection against NO_3^- contamination than the broad reaction zones. However, well construction and (or) operational features caused high-NO_3^- water in two study areas to partially bypass or move more quickly through the denitrifying zones. In one sand aquifer, shallow NO_3^--contaminated water bypassed the thin reaction zone and entered the producing interval of the PSW by moving down in local high-permeability features such as long well screens of nearby irrigation wells. In one carbonate aquifer, shallow NO_3^--contaminated water bypassed the thin reaction zone and entered the producing interval of the PSW by moving through a high-permeability conduit. Consideration should be given to constructing and manag-

ing PSW to minimize bypass of denitrifying zones to take full advantage of the natural NO_3^- attenuation capacity of aquifer sediments.

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