



Simulated response of water quality in public supply wells to land use change

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[1] Understanding how changes in land use affect water quality of public supply wells (PSW) is important because of the strong influence of land use on water quality, the rapid pace at which changes in land use are occurring in some parts of the world, and the large contribution of groundwater to the global water supply. In this study, groundwater flow models incorporating particle tracking and reaction were used to analyze the response of water quality in PSW to land use change in four communities: Modesto, California (Central Valley aquifer); York, Nebraska (High Plains aquifer); Woodbury, Connecticut (Glacial aquifer); and Tampa, Florida (Floridan aquifer). The water quality response to measured and hypothetical land use change was dependent on age distributions of water captured by the wells and on the temporal and spatial variability of land use in the area contributing recharge to the wells. Age distributions of water captured by the PSW spanned about 20 years at Woodbury and >1,000 years at Modesto and York, and the amount of water <50 years old captured by the PSW ranged from 30% at York to 100% at Woodbury. Short-circuit pathways in some PSW contributing areas, such as long irrigation well screens that crossed multiple geologic layers (York) and karst conduits (Tampa), affected age distributions by allowing relatively rapid movement of young water to those well screens. The spatial component of land use change was important because the complex distribution of particle travel times within the contributing areas strongly influenced contaminant arrival times and degradation reaction progress. Results from this study show that timescales for change in the quality of water from PSW could be on the order of years to centuries for land use changes that occur over days to decades, which could have implications for source water protection strategies that rely on land use change to achieve water quality objectives.

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1. Introduction

[2] Agricultural and urban land uses are particularly important from the standpoint of water quality in public supply wells (PSW) because they are primary sources for some of the most commonly detected contaminants in groundwater. Studies in several countries have linked nitrate (NO_3^-) contamination in groundwater to agricultural and urban land use practices [Strebel *et al.*, 1989; Spalding and Exner, 1993; Appleyard, 1995; Wassenaar, 1995; Rivers *et al.*, 1996; Zhang *et al.*, 1996; Nolan and Hitt, 2003; Kass *et al.*, 2005; Zingoni *et al.*, 2005], and have linked volatile organic compound contamination in groundwater to urban land use practices [Benker *et al.*, 1996; Grischek *et al.*, 1996; Howard *et al.*, 1996; Lerner and Barrett, 1996; Zogorski *et al.*, 2006]. A national assessment of pesticides

in groundwaters of the United States found that 55 and 61% of shallow groundwater samples in urban and agricultural areas contained one or more pesticide compound detections, respectively, compared with 29 to 33% of the samples from undeveloped or mixed land use areas [Gilliom *et al.*, 2006]. Other contaminants of concern, such as microbial pathogens, pharmaceuticals, and personal care products, also have been linked to agricultural and urban settings [Holm *et al.*, 1995; Goss *et al.*, 1998; Macler and Merkle, 2000; Powell *et al.*, 2003; Focazio *et al.*, 2004].

[3] In some parts of the world, urban lands are rapidly expanding in response to population growth or redistribution [Auch *et al.*, 2004; Kaufmann *et al.*, 2007]. Nearly 70% of the world's population is projected to live in urban areas by 2050 (U.N. Economic and Social Development, World urbanization prospects—The 2007 revision (highlights), 2008, available at http://www.un.org/esa/population/publications/wup2007/2007WUP_Highlights_web.pdf). In other areas, agricultural lands are expanding because of a need for additional food production [Bruinsma, 2003; Scanlon *et al.*, 2007], or they are changing because of new demands such as biofuel production [U.S. Department of Agriculture, 2007]. The expansion of urban land often occurs at the

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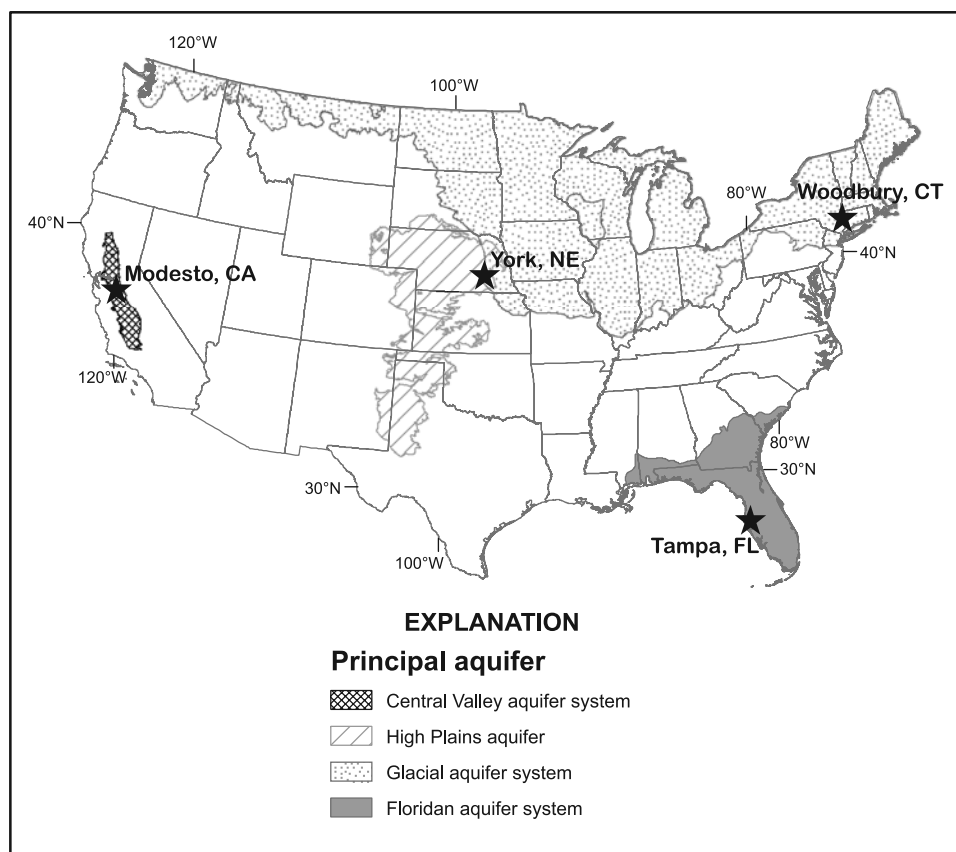


Figure 1. Location of the principal aquifers and communities where public supply wells were studied.

expense of agricultural land. The agriculturally important San Joaquin Valley experienced the largest farmland to urban conversion in California between 2002 and 2004 (California Department of Conservation, California farmland conversion report 2002–04, 2007, Farmland Mapping and Monitoring Program, available at http://redirect.conservation.ca.gov/DLRP/fmmp/product_page.asp). In addition to population and economic drivers of land use change, legislation such as the European Union’s Water Framework Directive and programs such as the U.S. Environmental Protection Agency’s Source Water Protection Program could lead to conversion of land from one type to another in an attempt to improve groundwater quality [Hiscock *et al.*, 2007]. Regardless of the reason for land use change, water quality in PSW could be expected to respond to that change.

[4] About 35% of the public water supply in the United States, England, and Wales comes from groundwater [Hutson *et al.*, 2004; Hiscock, 2005], and as many as 2 billion people worldwide may rely on groundwater as a source of drinking water [Alley, 2006]. Thus, understanding how changes in land use affect the water quality of PSW has practical implications with respect to human health. Understanding that response could be complicated by spatial and temporal variations in land use [Brawley *et al.*, 2000; Hiscock *et al.*, 2007] and by mixing waters of different age and source in long well screens such as are typical in PSW [Kauffman *et al.*, 2001; Böhlke, 2002; Weissmann *et al.*, 2002; Osenbrück *et al.*, 2006; Eberts *et al.*, 2006]. Age distributions of water captured by individual long-screen wells could span years to millennia or more [Kauffman *et al.*, 2001; Weissmann *et al.*, 2002; McMahon *et al.*, 2004; Plummer *et al.*, 2004; Sturchio

et al., 2004; Clark *et al.*, 2007]. These age distributions in captured water could have positive and negative consequences for the quality of water from PSW, such as dilution of contaminant concentrations and long lag times in responding to land use change or best management practices. An important implication of long lag times is that in spite of corrective management actions, contaminant concentrations in water from PSW could increase in the future (before eventually decreasing) as the fraction of already contaminated young recharge captured by wells increases [Fogg *et al.*, 1999; Böhlke, 2002; Fogg and LaBolle, 2006].

[5] The purpose of this paper is to examine the potential response of water quality in PSW to land use change in selected principal aquifers of the United States, with a focus on nonpoint sources of contamination. A single PSW in each of four communities across the United States was selected for 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 hydro-geologic conditions. In each area, groundwater was a major source, if not the sole source, of water supply.

2. Study Area Descriptions

2.1. Modesto, California

[6] Modesto, with a population of 188,856 (U.S. Census Bureau, Statistical abstract of the United States, 2000,

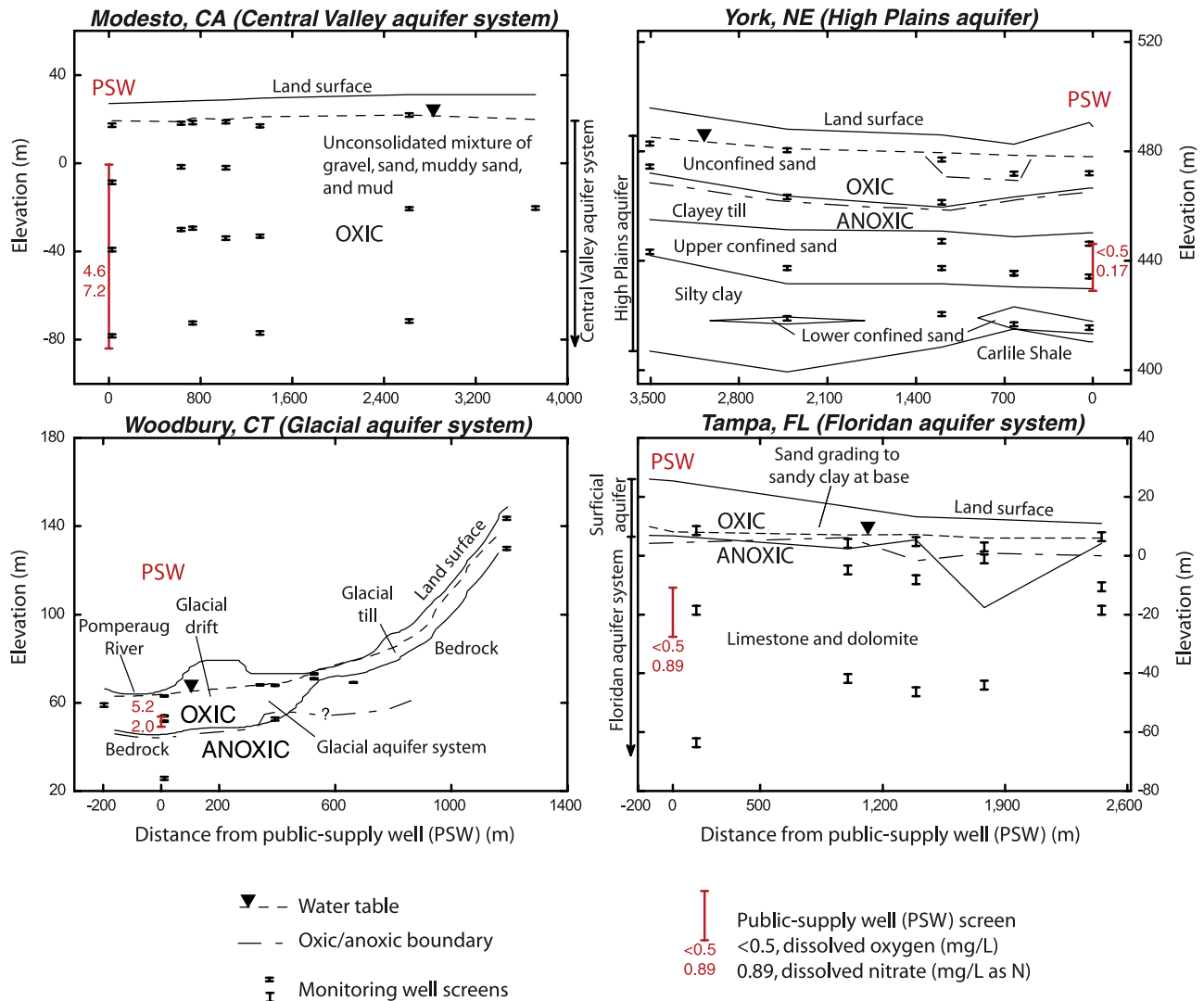


Figure 2. Hydrogeologic sections in the study areas. Oxidic waters are operationally defined by dissolved oxygen ≥ 0.5 mg/L. See Figure S2 for map location of the sections.

available a http://www.census.gov/prod/www/statistical-abstract-1995_2000.html), 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 San Joaquin Valley, comprising the southern two thirds of the Central Valley, is a northwest trending structural basin bounded on the west by the Coast Ranges and on the east by the Sierra Nevada. Unconsolidated sediments of Pliocene-Pleistocene age constitute the aquifer in the eastern San Joaquin Valley study area (Figure 2). The sediments comprise interlayered lenses of gravel, sand, silt, and clay deposited in a series of alluvial fan aggradation sequences linked to Pleistocene glacial episodes and the local base level of the San Joaquin River. The aquifer in the study area is unconfined in the shallow part of the system, becoming semiconfined with depth. The aquifer is at least 100 m thick, and the depth to water was about 10 m. Maps showing the extent of the modeled area and the contributing recharge area are presented in Figures S1 and S2 in the auxiliary material.¹

¹Auxiliary materials are available in the HTML. doi:10.1029/2007WR006731.

Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1.

2.2. York, Nebraska

[7] York, with a population of 8,081 (U.S. Census Bureau, http://www.census.gov/prod/www/statistical-abstract-1995_2000.html), 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 from lower confined fine sands of glaciofluvial origin in which the PSW is screened (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

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

Location	County	Year of Construction	Area Contributing Recharge (km ²)		Generalized Land Use in Area Contributing Recharge ^a (%)			Recharge Rate (mm/a)	Average Pumping Rate (m ³ /d)	Aquifer Thickness in Study Area (m)	Screened Interval (m Below Water Table)	Median Particle Age (years)	Median Particle Velocity (m/d)
			Forest	Rangeland	Urban	Wetland	Agriculture						
Modesto, California	Stanislaus	1961	4.2	<1	2.3	67	<1	400–700	3,750	>100	18–111	46	0.006
York, Nebraska	York	1977	6.3	39	3.7	45	<1	210	1,390	80	33–51	80	0.004
Woodbury, Connecticut	Litchfield	1967	0.5	4.8	1.3	75	6.9	Not applicable	390	23	10–14	7	0.03
Tampa, Florida	Hillsborough	1958	4.4	4.2	5.8	84	5.0	Not applicable	2,690	>100	33–50	13	0.02

^aBased on 1992 National Land Cover Data (NLCD) [Fogelmann *et al.*, 2001].

to water was about 10 m. The extent of the modeled area and contributing recharge area are presented in Figures S1 and S2. Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1.

2.3. Woodbury, Connecticut

[8] Woodbury, with a population of 9,198 (U.S. Census Bureau, http://www.census.gov/prod/www/statistical-abstract-1995_2000.html), is located within the glaciated New England Uplands in west-central Connecticut. The area has a humid continental climate and receives an average of 1,170 mm of precipitation each year. Near-surface sedimentary deposits in the Pomperaug River valley consist of stratified glacial deposits in the river valley (in which the PSW is screened) 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 unconfined, about 23 m thick, and the depth to water was about 4 m. The extent of the modeled area and contributing recharge area are presented in Figures S1 and S2. Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1.

2.4. Tampa, Florida

[9] Tampa, with a population of 303,447 (U.S. Census Bureau, http://www.census.gov/prod/www/statistical-abstract-1995_2000.html), 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 in which the PSW is screened. The upper Floridan aquifer varies from unconfined to confined conditions in the study area, but is mainly classified as unconfined or semiconfined. An intermediate confining unit separates the Floridan aquifer from the overlying surficial aquifer. The intermediate confining unit is 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 unconfined 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 100 m thick. The extent of the modeled area and contributing recharge area are presented in Figures S1 and S2. Characteristics of the PSW selected for study and land use in the area contributing recharge to the well are listed in Table 1.

3. Methods

3.1. Groundwater Flow Models

[10] Steady state, three-dimensional groundwater flow was simulated using MODFLOW-2000 [Harbaugh *et al.*,

2000] providing input to the particle-tracking software MODPATH [Pollack, 1994]. In each study area, regional models [Crandall, 2007; Landon and Turco, 2007; Lyford et al., 2007; Phillips et al., 2007] were used to provide stresses and boundary conditions for the more detailed local models (Figure S1) [Starn and Brown, 2007; Clark et al., 2007; Burow et al., 2008; C. Crandall, unpublished data, 2007]. The multinode well package for MODFLOW [Halford and Hanson, 2002] was used to track flow between specific model layers, and a combination of parameter estimation methods [Hill et al., 2000; Poeter et al., 2005] and systematic manual calibration was used to estimate hydraulic parameters. The models were calibrated to hydraulic data available in each study area and simulated concentrations of selected tracers (e.g., ^3H , SF_6 , CFC-11) were compared to measured concentrations in groundwater samples collected in each study area. In Modesto, York, and Tampa, flow measurements collected in the borehole of the PSW were also compared to simulated flow in the models.

[11] In Modesto, California, the flow model (Figure S1) was discretized into a uniform grid of finite difference cells consisting of 200 rows of 72-m-length cells and 100 columns of 34-m-length cells [Burow et al., 2008]. The grid has 200 layers of uniform 0.6 m thickness, representing the thickness of individual hydrofacies units. A mixture of specified head and specified flux boundaries were used to constrain the model using head and flux values from the surrounding regional model. The steady state flow model simulates conditions that existed in water year 2000, when the system was in quasi steady state. Stresses in the model include recharge and groundwater withdrawal from wells. Recharge from agricultural return flow was estimated using the calculated crop demand and estimated consumptive use of applied water. Recharge in the urban area was estimated by accounting for landscape irrigation, leakage from water distribution lines, and precipitation recharge. Pumping assigned to 22 public supply and irrigation wells was based on water use records for the public supply wells and on water budget analysis in the agricultural areas. The distribution of hydraulic properties in the model was estimated by model calibration. Sediments in the model domain were classified into four hydrofacies: gravel, sand, muddy sand, and mud. The spatial distribution of the four hydrofacies was determined using borehole lithologic data and by development of a three-dimensional spatial correlation model of hydrofacies using the program TProGS [Carle et al., 1998; Carle, 1999].

[12] In York, Nebraska, the flow model (Figure S1) was discretized into a uniform grid of finite difference cells consisting of 180 rows by 372 columns of uniform cells each 40.2 m on a side [Clark et al., 2007]. The grid has 14 layers of variable thicknesses representing the geologic layering. A mixture of specified head and specified flux boundaries were used to constrain the model using head and flux values from the surrounding regional model. A transient model was developed that simulates groundwater flow for a 60-year period from 1 September 1944 to 31 August 2004. A steady state model was derived from the calibrated transient model that represented average annual stresses for the period 1997–2001. This steady state model was used for the particle tracking simulations presented in this paper.

Stresses in the model include recharge and groundwater withdrawal from wells. Four recharge zones were assigned in the model: urban, nonirrigated, gravity irrigated, and sprinkler-irrigated areas. Recharge was assigned using precipitation-weighted estimates from the steady state regional model, which were modified during model calibration. Withdrawals from irrigation wells were assigned on the basis of reported irrigation withdrawal data and scaled during summer irrigation season using precipitation records. Withdrawals from industrial and public supply wells were based on water use records. Initial model simulations used hydraulic conductivity and vertical anisotropy values from the regional-scale model. These values were further refined during calibration by varying values uniformly within each model layer.

[13] In Woodbury, Connecticut, the flow model (Figure S1) was discretized into a uniform grid of finite difference cells consisting of 241 rows by 322 columns of 15.2-m-length cells [Starn and Brown, 2007]. The grid has 7 layers of variable thickness. Specified flux boundaries were used to constrain the model. The eastern zero-flux boundary corresponds to the watershed boundary; the specified fluxes for the other lateral boundaries were derived from the surrounding regional model. The steady state flow model simulates average annual conditions approximated during 1997–2001. Stresses in the model include recharge, seepage from streams, and groundwater withdrawal from wells. Average annual recharge for the period 1998–2004 was determined using a rainfall-runoff model, except in the commercial area where recharge was set to the annual rainfall at locations where all surface runoff flows into storm drains. Pumping rates for 5 public supply wells were assigned from available withdrawal data. The distribution of hydraulic properties in the model was estimated by parameter estimation methods for nine parameters in the model: five glacial hydrogeologic units, two bedrock hydrogeologic units, and the streambeds of the Pomperaug River and of tributary streams.

[14] In Tampa, Florida, the flow model (Figure S1) was discretized into a uniform grid of finite difference cells consisting of 80 rows and 69 columns of 125-m-length cells (Crandall, unpublished data, 2007). The grid has 13 layers of variable thickness. The model was constrained using specified flux boundaries. Zero-flux boundaries were applied in layers with very low permeability. Nonzero flux boundaries were derived from the surrounding regional model. The steady state flow model simulates average annual conditions for calendar year 2000. Stresses in the model include recharge from precipitation, seepage from streams, discharge to wetlands, and groundwater withdrawal from wells. Recharge from precipitation was applied uniformly over the model area, except with increased recharge in cells with closed-basin depressions. Pumping assigned to the 77 public supply, industrial, and agricultural wells were based on water use records. The distribution of hydraulic properties in the model was estimated by model calibration using parameter estimation methods. Karst features, such as closed-basin depressions, preferential flow along fractures, and conduit features were incorporated into the model by using large vertical hydraulic conductivity, higher recharge, and lower-porosity values where karst features were identified.

3.2. Particle Pathline Analysis

[15] Groundwater pathlines and advective travel times were simulated using MODPATH [Pollack, 1994] to delineate the areas contributing recharge to the PSW and to estimate age distributions of water captured by the PSW. The forward tracking option of MODPATH was used for pathline analysis. 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 travel times associated with those particles were used to estimate the age distribution of water captured by the PSW. The number of particles that defined the areas contributing recharge ranged from 2344 to 6832. 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.

3.3. Calculation of Flux-Weighted Average Contaminant Concentrations in the Public Supply Wells

[16] Flow and travel times associated with the particles that discharged at the PSW were used to estimate contaminant concentrations in the PSW. Contaminant concentration was assigned to each particle on the basis of the travel time and by assuming an input concentration history of the contaminant in the recharge area, as described below. Flux-weighted average contaminant concentrations for the PSW were determined by summing the product of concentrations assigned to each particle by the total flow associated with that particle and dividing by the total flow.

[17] Two approaches were used to define contaminant input functions in the areas contributing recharge to the PSW. In the first approach, a NO_3^- input function was developed for the Modesto study area to examine the effects of spatial and temporal variations in land use on NO_3^- concentrations in that PSW. The Modesto PSW was the focus of this effort because it had the best historical records of land use and N inputs among the study areas. In the second approach, slug inputs of hypothetical conservative and reactive contaminants lasting 25 years were used to illustrate the range in lag times, dilution, and degradation that may be expected given differences in hydrogeology and well characteristics between all four study areas.

3.4. Modesto Nitrate Input Function

[18] Three land use categories were considered in defining the Modesto NO_3^- input functions: urban land, rangeland, and agricultural land. They accounted for more than 99% of the land in the area contributing recharge to the PSW (Table 1). Nitrate concentrations in urban recharge were assigned a fixed value of 3.1 mg/L as N based on concentrations measured in water table monitoring wells located in that setting [Burow et al., 2008]. Nitrate concentrations in rangeland recharge were assigned a fixed value of 1.5 mg/L as N based on concentrations measured in groundwater that was >50 years old (<0.5 TU of tritium) [Burow et al., 2008], which presumably predated substantial use of fertilizer and irrigation water in the study area.

[19] Fertilizer N is interpreted to be the primary source of NO_3^- in Modesto agricultural recharge [McMahon et al., 2008], and its use in Stanislaus County increased from about 2×10^6 kg N in 1945 to 31×10^6 kg N in 2003 [Alexander and Smith, 1990; Ruddy et al., 2006]; thus NO_3^- concentrations in agricultural recharge (R_{ag-NO_3}) (in mg/L as

N) were calculated yearly between 1945 and 2003 using equation (1) [Böhlke, 2002]:

$$R_{ag-NO_3} = (F)(1/CA)(1/R)(LF)(100), \quad (1)$$

where F is the annual county-level fertilizer application (in kilograms of N) [Alexander and Smith, 1990; Ruddy et al., 2006], CA is the area of cropland in the county (in hectares) [California Department of Water Resources, 2000], R is the annual recharge (in millimeters) (Table 1), LF is the fraction of applied N that leaches to the water table, and 100 is a conversion factor. An LF value of 0.5 was determined on the basis of the fertilizer use records and NO_3^- concentrations in age-dated groundwater samples from the Modesto agricultural area [McMahon et al., 2008; Burow et al., 2008].

[20] The yearly NO_3^- input function for the area contributing recharge to the PSW was based on the input functions for the three individual land use categories and the spatial and temporal variability of those land uses in the capture zone. For this study, rangeland recharge was assumed to be the only source of NO_3^- in the contributing area prior to 1945. For the period 1945–1960, agricultural recharge was assumed to be the primary source of NO_3^- in the contributing area (increasing with time with increasing F , according to equation (1)). For the period 1960–2003, urban and agricultural recharge were assumed to be the primary sources of NO_3^- in the contributing area. The amount of urban land in the contributing area was assumed to increase at a mean annual rate of 2% (at the expense of agricultural land) starting in 1960. This urban growth rate of 2% is based on (1) the age of the PSW (Table 1), (2) the ages of subdivisions in the contributing area [Burow et al., 2008], and (3) time series land use data for California (California Department of Conservation, Download FMMP GIS data, 2007, Farmland Mapping and Monitoring Program, available at http://redirect.conservation.ca.gov/DLRP/fmmp/product_page.asp).

[21] Denitrification in the largely oxic aquifer at Modesto occurs very slowly [McMahon et al., 2008]. Therefore, for this part of the study, measured concentrations of NO_3^- in recharge were not corrected for minor denitrification effects produced in the aquifer.

4. Results and Discussion

4.1. Model Calibration

4.1.1. Modesto, California

[22] Estimates of hydraulic conductivity of individual hydrofacies were obtained by comparing simulated water levels to measured water levels in 18 monitoring wells screened at multiple depths (Figure S2). Water level data for each well were averaged between the summer low period and the winter high period to determine an annual water level observation. Hydraulic conductivity estimates (Table 2) were further refined by comparing fluxes in the regional model and comparing proportions of recharge in the urban and agricultural areas. The sum of weighted residuals between simulated and measured water levels was 4.4 m; the average weighted residual was 0.25 m. Simulated vertical gradients ranged from 0.04 to 0.07

Table 2. Hydraulic Parameters Used in Groundwater Flow and Particle Tracking Simulations

Location and Hydrogeologic Unit	Horizontal Hydraulic Conductivity (m/d)	Effective Porosity ^a
Modesto, California		
Gravel	800	0.2
Sand	98	0.25
Muddy sand	2.2	0.3
Mud	0.001	0.35
York, Nebraska		
Unconfined sand	12–55	0.2–0.25
Clayey till	0.03	0.35
Upper confined sand	6.1–15	0.15
Silty clay	0.03	0.35
Lower confined sand	5.8	0.15
Woodbury, Connecticut		
Glacial till	0.01–0.3	0.1
Glacial drift	6.2–18	0.3
Bedrock	0.035–14	0.001
Tampa, Florida		
Surficial aquifer	0.06–37	0.32
Intermediate confining unit	0.01	0.01–0.004
Upper Floridan aquifer	16–674	0.004–0.12

^aEffective porosity was estimated from previous modeling studies in Modesto and during model calibration in York, Woodbury, and Tampa.

between the water table and the deepest wells at each site, and measured vertical gradients ranged from 0.04 to 0.08.

[23] Simulated travel times and recharge rates for the public supply well and the monitoring wells were combined with estimated input concentrations for tritium (³H) and sulfur hexafluoride (SF₆) age tracers to calculate simulated flux-weighted concentrations reaching the wells. Measured ³H concentrations in 20 wells ranged from 0.02 to 17 TU. The sum of residuals between simulated and measured ³H concentrations was 32 TU; the average residual was 1.6 TU. Measured SF₆ concentrations in 8 wells ranged from 0.51 to 3.9 pptv. The sum of residuals between simulated and measured SF₆ concentrations was –3.3 pptv; the average residual was –0.41 pptv.

4.1.2. York, Nebraska

[24] Estimates of hydraulic conductivity, vertical anisotropy, specific yield, and specific storage were obtained by comparing simulated water levels to 470 water level measurements in 53 wells (Figure S2). These parameters were modified during the calibration process to accommodate a fining-downward sequence of sediment texture observed in lithologic descriptions, geophysical logs, and slug tests (Table 2). The sum of mean residuals for each year between simulated and measured water levels was –8.2 m; the average residual was –0.09 m.

[25] Simulated travel times and recharge rates for the public supply well and the monitoring wells were combined with estimated input concentrations for the age tracer chlorofluorocarbon-11 (CFC-11) to calculate simulated flux-weighted concentrations reaching the wells. Measured CFC-11 concentrations in 6 wells ranged from 0.07 to 2.86 pmol/kg. The sum of residuals between simulated and measured CFC-11 concentrations was –2.1 pmol/kg; the average residual was –0.35 pmol/kg.

4.1.3. Woodbury, Connecticut

[26] Estimates of hydraulic conductivity of individual hydrogeologic units (Table 2) were obtained by comparing simulated water levels to measured water levels in 34

monitoring wells screened at multiple depths (Figure S2) and by comparing simulated stream leakage to streamflow gain and/or loss estimates from streamflow data. The sum of weighted residuals between simulated and measured water levels was 28 m; the average residual was 0.3 m. The observed value of streamflow loss was the same as the simulated value.

[27] Simulated travel times were compared to ages interpreted from tritium-helium age dates in monitoring wells to calibrate effective porosity in the particle tracking simulations. Interpreted ages in the 10 wells ranged from 3.4 to 10 years. The sum of residuals between simulated and interpreted ages was 11 years; the average residual was 1.1 years.

4.1.4. Tampa, Florida

[28] Estimates of hydraulic conductivity of hydrogeologic units (Table 2) and recharge were obtained by comparing simulated water levels to measured water levels in 53 wells screened at multiple depths (Figure S2). The sum of weighted residuals between simulated and measured water levels was –1.6 m; the average residual was –0.03 m. The residuals of water level gradients from the surficial aquifer to the Upper Floridan aquifer ranged from –0.87 to –0.17 m.

[29] Simulated travel times and recharge rates for the public supply well and the monitoring wells were combined with estimated input concentrations for ³H and SF₆ age tracers to calculate simulated flux-weighted concentrations reaching the wells. The simulated concentrations were compared to measured concentrations in 18 wells to calibrate values of effective porosity. Measured ³H concentrations ranged from 0.02 to 2.6 TU. The sum of residuals between simulated and measured ³H concentrations was –23 TU; the average residual was –1.2 TU. Measured SF₆ concentrations ranged from 0.23 to 5.3 pptv. The sum of residuals between simulated and measured SF₆ concentrations was –7.8 pptv; the average residual was –0.41 pptv.

4.2. Simulated Groundwater Age Distributions in Public Supply Wells

[30] Simulated age distributions in water captured by the PSW differed substantially between aquifer systems in several respects. Age distributions spanned about 20 years at Woodbury and >1,000 years at Modesto and York (Figure 3). Moreover, the amount of <50-year-old water captured by the PSW ranged from 30% at York to 100% at Woodbury (Figure 3). This young fraction of water is important because presumably most anthropogenic contaminants are present in that age fraction. Water samples from each of the PSW contained detectable concentrations of several pesticide compounds and/or volatile organic compounds (Table 3). Young groundwater also is important because it could indicate limited natural attenuation capacity in flow systems where degradation processes are slow [Chapelle and Bradley, 1999; McMahon et al., 2008]. The old age fraction of water is important because that water could dilute anthropogenic contaminant concentrations when the waters of different age are mixed in the well screen [Osenbrück et al., 2006]. For natural contaminants such as arsenic, the older age fraction could contain larger concentrations than the younger age fraction [Stute et al., 2007; Thomas, 2007].

[31] Age distributions in the PSW are related to processes affecting contaminant fate and transport through the aquifer

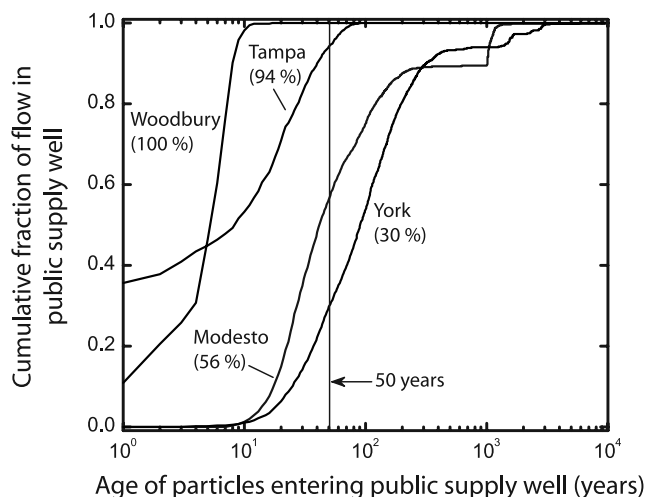


Figure 3. Fractions of flow in the public supply wells as a function of the simulated age of particles entering the wells. Numbers in parentheses indicate percentage of flow that is <50 years old.

and complex interactions between the wells and the flow systems [Weissmann *et al.*, 2002; Kauffman *et al.*, 2001; Clark *et al.*, 2007; Starn and Brown, 2007]. The relatively narrow age distribution and large fraction of water <50 years old in the PSW at Woodbury could be expected on the basis of the short well screen, shallow screen depth below the water table, small pumping rate and contributing area, high recharge rate, and high velocities through the aquifer at that site compared to the other sites (Table 1). In contrast, the PSW at York had the broadest age distribution and the smallest fraction of water <50 years old. That well and site had a moderate length screened interval, large screen depth below the water table, moderate pumping rate and large contributing area, low recharge rate, and low velocities through the aquifer (Table 1). Short-circuit pathways, such as long irrigation well screens that crossed multiple geologic layers in the contributing area at York [Clark *et al.*, 2007] and karst conduits in the contributing area at Tampa [Katz *et al.*, 2007], also affected age distributions in the PSW at those sites by allowing relatively rapid movement of young water to those well screens. Simulations suggest that the York PSW would not produce any water <50 years old if those short-circuit pathways were not present in the contributing area [Clark *et al.*, 2007]. Conceivably, age distributions in water captured by PSW could be manipulated

through well construction and operation decisions in order to achieve water quality objectives. For that endeavor to be successful, it would be necessary to understand the interactions between the PSW and the flow system.

4.3. Simulated Nitrate Concentrations in the Modesto Public Supply Well

[32] Simulated concentrations of NO_3^- in the Modesto PSW were sensitive to both the temporal and spatial variability in land use assigned in the contributing area. In simulation 1, it was assumed that agriculture was the only land use in the contributing area and that NO_3^- in recharge was proportional to fertilizer N loading. A fertilizer source for the agricultural NO_3^- is consistent with chemical, isotopic, and land use data for the study area [McMahon *et al.*, 2008]. Estimated NO_3^- concentrations in agricultural recharge increased with time because of the ~fifteenfold increase in fertilizer N use in Stanislaus County between 1945 and 2003 and subsequent leaching to the water table (Figure 4a, curve a). Simulated concentrations of NO_3^- in the PSW systematically increased with time in response to the increased fertilizer use (Figure 4b, curve a). Although the simulated NO_3^- concentrations were in general agreement with concentrations of NO_3^- measured in water samples collected from the PSW between 1983 and 2004, this land use scenario is not realistic for this particular well given the urban growth that occurred in the contributing area during at least the past 30 years. However, other PSW in this region with a large proportion of agricultural land use in the contributing area may resemble this simulation scenario, resulting in continued increases in nitrate concentrations over time.

[33] In simulation 2, it was assumed that agricultural land was converted randomly to urban land at a rate of 2% of the contributing area per year beginning in 1960. In this case, a composite NO_3^- input function was assigned to the entire contributing area that accounted for the agriculture-to-urban conversion over time (Figure 4a, curve b). This NO_3^- input function, however, did not account for systematic spatial variability in the land use change. The peak simulated NO_3^- concentrations for this scenario (Figure 4b, curve b) lagged behind the peak NO_3^- input by about 30 years (shaded bands in Figure 4), indicating that a large fraction of the NO_3^- in water pumped from the PSW in 2003–2004 could have been recharged in the late 1960s and early 1970s. Mixing with old groundwater that contained relatively small concentrations of NO_3^- diluted the simulated peak NO_3^- concentration in the PSW by about 45% compared to the peak input. The curve representing simulated NO_3^- concentra-

Table 3. Concentrations of Dissolved Oxygen and Nitrate and the Number of Pesticide and Volatile Organic Compounds Detected in Water Samples From the Public Supply Wells^a

Location	Oxygen (mg/L)	Nitrate (mg/L as N)	Number of Pesticide Compounds Detected ^b	Number of Volatile Organic Compounds Detected ^b
Modesto, California	4.6	6.1	3	3
York, Nebraska	<0.5	0.16	0	4
Woodbury, Connecticut	4.8	1.9	3	8
Tampa, Florida	<0.5	0.88	4	2

^aThe concentrations and number of detections are averages of three to six samples collected from each well from 2002 to 2005. Data from the U.S. Geological Survey (National water information system, 2007, available at <http://waterdata.usgs.gov/nwis/>).

^bNone of the concentrations exceeded a federal drinking water standard.

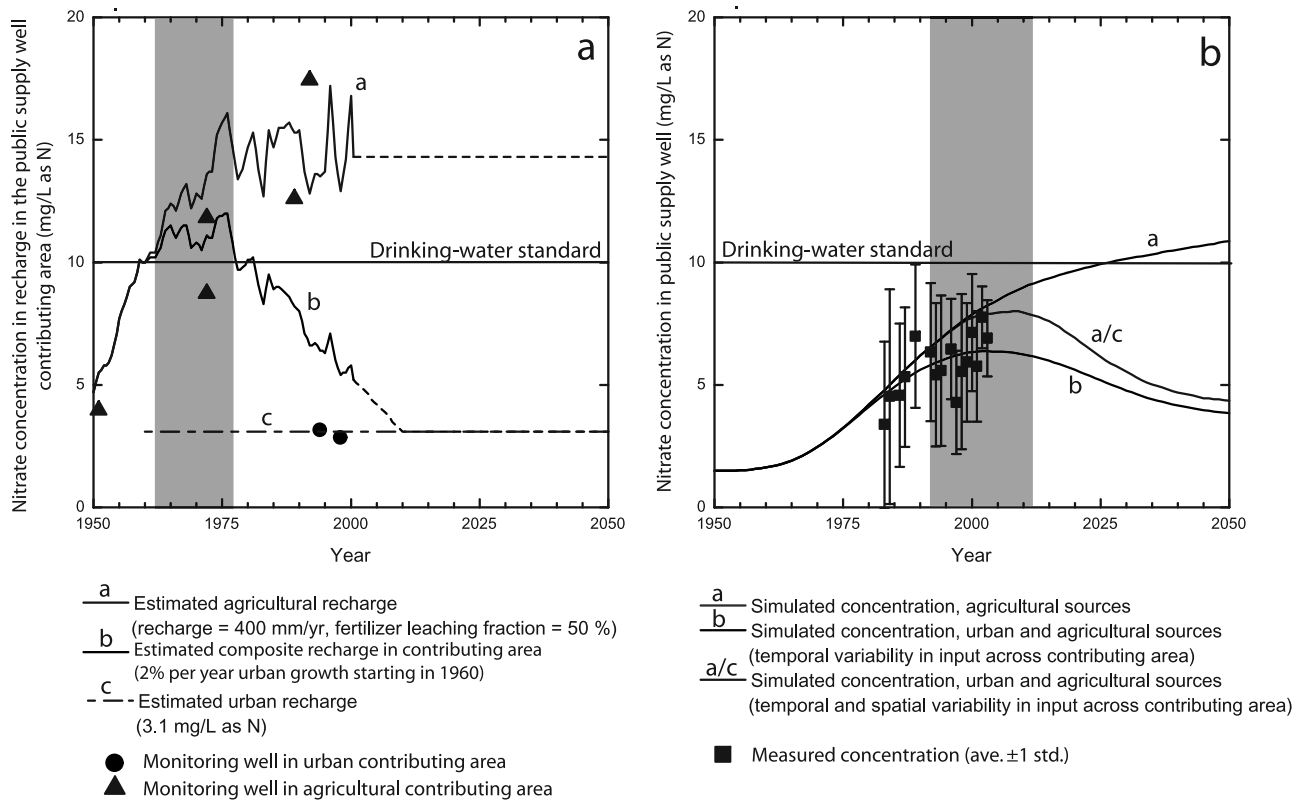


Figure 4. Concentration of nitrate in (a) urban and agricultural recharge and (b) the Modesto public supply well as a function of time. Shading represents the period of peak nitrate concentrations for curve b. Measured nitrate concentrations from *Burow et al.* [2008] and city of Modesto.

tions in the PSW for simulation 2 did not deviate from the curve for simulation 1 until about 1985 (Figure 4b, curves a and b), which is 25 years after urban development was assumed to have begun in the contributing area (Figure 4a, curves a and b).

[34] In reality, land use change can be heterogeneous in both time and space. Figure 5 provides an example of temporal and spatial variability in land use at Modesto. Between 1976 and 2005, the conversion of agricultural land to urban land in the area contributing recharge to the PSW generally progressed from south to north. Also shown in Figure 5 are starting points at the water table for particles captured by the PSW, color coded by travel time from the water table to the well. A key point illustrated in Figure 5 is that land use change and travel times to the PSW did not occur uniformly in space. Thus, the response of water quality in the PSW to land use change may depend on where the change occurs.

[35] Simulation 3 accounted for both temporal and spatial variability in land use by including a south-to-north conversion of agricultural land to urban land at the same rate of 2% of the contributing area per year. The curve representing simulated NO_3^- concentrations in the PSW for this scenario (Figure 4b, curve a/c) had a peak concentration that was 26% larger than the curve for simulation 2 (curve b). In simulation 3, the PSW also produced about 13% more NO_3^- mass than in simulation 2 during the period of urbanization from 1960 to 2010. A primary reason for the larger NO_3^- concentrations and mass in simulation 3 is that relatively large agricultural NO_3^- inputs were maintained for a longer

period of time in the north-northwest part of the contributing area where particles with some of the shortest transit times entered the aquifer (Figure 5). In simulation 2, the agriculture-to-urban conversion began uniformly across the study area in 1960. In simulation 3, the agriculture-to-urban conversion in the northern area did not begin until after 1980. This allowed high NO_3^- recharge to enter a vulnerable part of the contributing area (vulnerable in terms of short transit times to the PSW) for at least 20 more years than in simulation 2. Nitrate concentrations in the PSW from simulations 2 and 3 were in general agreement with the measured concentrations, given the large variability in measured concentrations (Figure 4b, curves b and a/c).

[36] At Modesto, understanding spatial variability in land use was important because of the broad range of transit times leading from different recharge areas to the PSW (Figure 5). The added effect of spatial variability in land use on simulated NO_3^- concentrations (Figure 4b, curve a/c), however, still was somewhat dampened by the diluting effect of old water. Spatial variability in land use relative to groundwater transit times could be even more important in PSW that capture water with broad age distributions that are shifted to younger ages, such as at the Tampa PSW. At the Modesto PSW, only about 1% of the captured water had modeled ages <10 years old. At the Tampa PSW, about 50% of the capture water had modeled ages <10 years old, but the age distribution still spanned about 90 years (Figure 3). Thus, at the Tampa PSW, transit times along the fastest and slowest flowpaths may still be substantially different from each other, but the large fraction of young water could

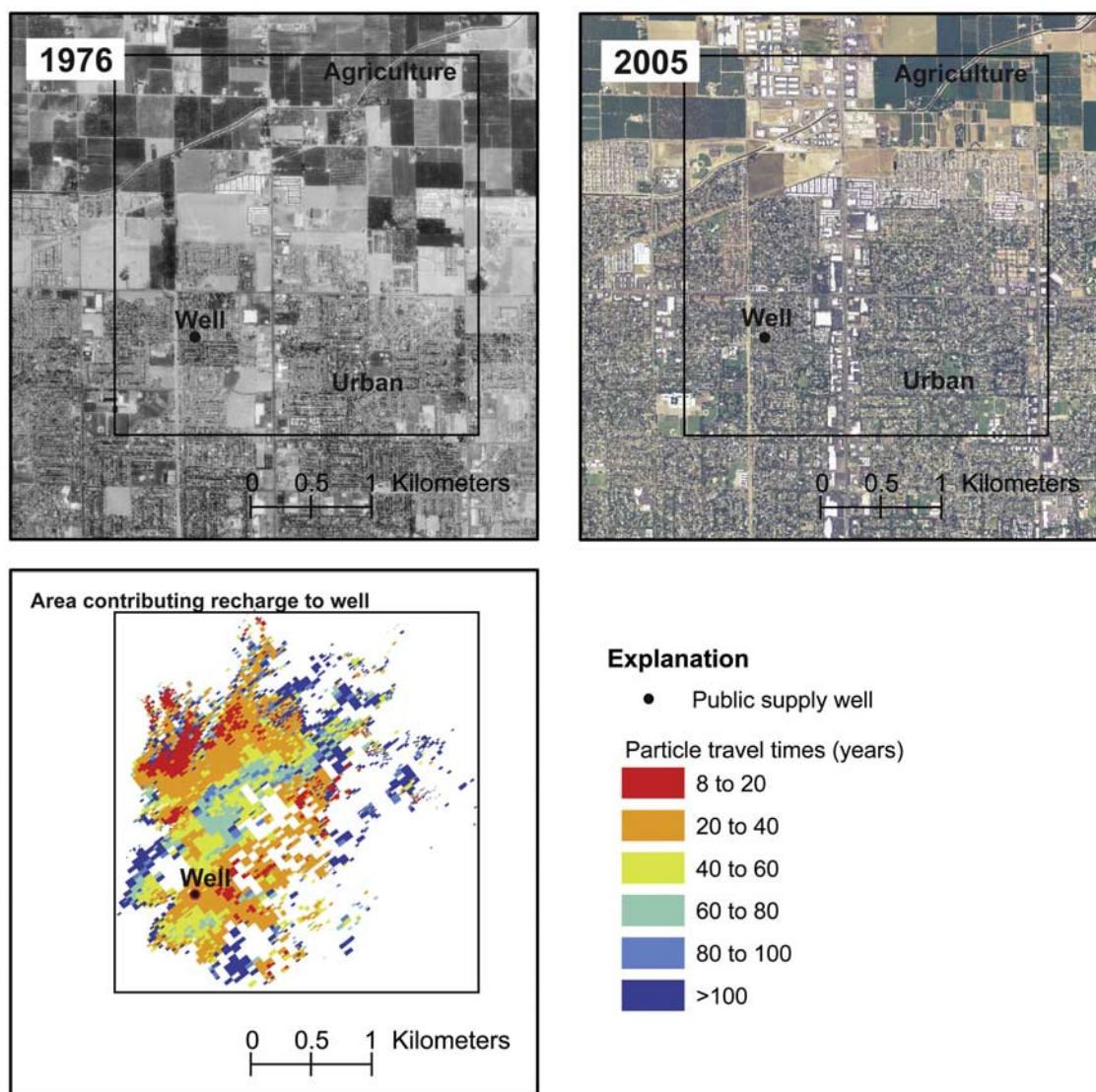


Figure 5. Aerial photographs of the Modesto study area in 1976 and 2005. Also shown are starting points at the water table for particles captured by the public supply well, color coded by steady state travel time from the water table to the well.

potentially dominate the water quality response to land use change in the PSW depending on where the change occurred in the contributing area.

4.4. Simulated Water Quality Response in Public Supply Wells to Hypothetical Land Use Change

4.4.1. Temporal Variability in Land Use

[37] The range of behaviors that may be expected among the four study areas, given differences in hydrogeology and well characteristics, was further explored by comparing simulated responses of water quality in the PSW to hypothetical land use change. Each PSW responded differently to contaminant input associated with the same hypothetical land use change. For the example shown in Figure 6a, which might be representative of rapid land use change in an area contributing recharge to a PSW, lag times in arrival of peak concentrations between the input and PSW ranged from 6 to 30 years (Table 4) and were shorter in the PSW with large fractions of young water (Woodbury and Tampa)

than in PSW with small fractions of young water (York and Modesto). Moreover, peak concentrations were substantially less diluted in the PSW with large fractions of young water (Table 4). Times required for arrival of the first 1% of contaminant mass and for flushing 99% of the contaminant mass from the PSW also were substantially less at the PSW with large fractions of young water (Figure 6a and Table 4). From a water quality management perspective, there could be benefits to PSW having large or small fractions of young water, depending on local issues and conditions. A benefit to having a large fraction of young water in a PSW (Woodbury and Tampa) would be a faster response to any land use change designed to reduce chemical fluxes to the water table. A benefit to having a small fraction of young water in a PSW (Modesto and York) would be greater dilution of anthropogenic contamination by old water [Osenbrück *et al.*, 2006]. However, the benefit of large or small fractions of water of a particular age group in a PSW also is dependent on the magnitude of the chemical input

concentrations and the duration of the chemical inputs at the water table.

[38] The effect of short-circuit pathways in the flow system on the movement of young water to PSW could greatly alter contaminant arrival times compared to what might be expected from advection in a system without short circuiting. This is particularly evident in the chemical breakthrough curve for Tampa. Chemical data and down-hole video from that PSW indicated that the well screen intersected a karst conduit that allowed young water to quickly reach the PSW [Katz *et al.*, 2007]. The simulated

concentrations for Tampa show rapid initial responses at the beginning and end of chemical input (Figure 6a), followed by more gradual responses in concentration as older water entered the well screen. Thus, short-circuit pathways such as these could lead to a relatively rapid water quality response to land use change in comparison to the response produced by more uniform advection-dominated parts of the flow system.

[39] The simulations in Figure 6a did not include degradation, but simulations that incorporated hypothetical degradation with first-order reaction kinetics illustrate the importance of groundwater age distributions with respect to degradation reaction progress. Compared to contaminant mass captured by the PSW in simulations without degradation (Figure 6a), the mass captured by PSW in simulations that applied a common degradation rate constant uniformly along each particle pathline was reduced by factors of 15 to 23 in the PSW with large fractions of old water (Modesto and York) and by a factor of only about 2 in the PSW with small fractions of old water (Woodbury and Tampa) (Figure 6b). Thus, for similar reaction kinetics, longer reaction times associated with old water would result in greater contaminant degradation than shorter reaction times associated with young water.

[40] Degradation reaction progress would depend on several other factors in addition to groundwater age, including reaction lag times and rates. This is illustrated using field data on denitrification in the aquifers. Nested monitoring wells installed along flowpaths leading to the PSW (Figure 2) were sampled for age tracers, redox constituents, N concentrations and isotopes, and other parameters to quantify denitrification lag times and reaction kinetics in each of the four study areas [McMahon *et al.*, 2008]. Reaction lag time refers to the time groundwater traveled through the O_2 reduction zone near the water table prior to the onset of denitrification. Typical lag times ranged from 5 years at Tampa to 40 years at York, and average denitrification rate constants ranged from 0 per year at Woodbury to 3 per year at York. Using the modeling approach of McMahon *et al.* [2008], in which site-specific denitrification rate constants varied with the spatial distribution of redox conditions along particle pathlines, resulted in simulated NO_3^- removal ranging from 0% at Woodbury to 100% at York (Figure 6c). Even though the Tampa PSW had a much larger fraction of young water than the Modesto

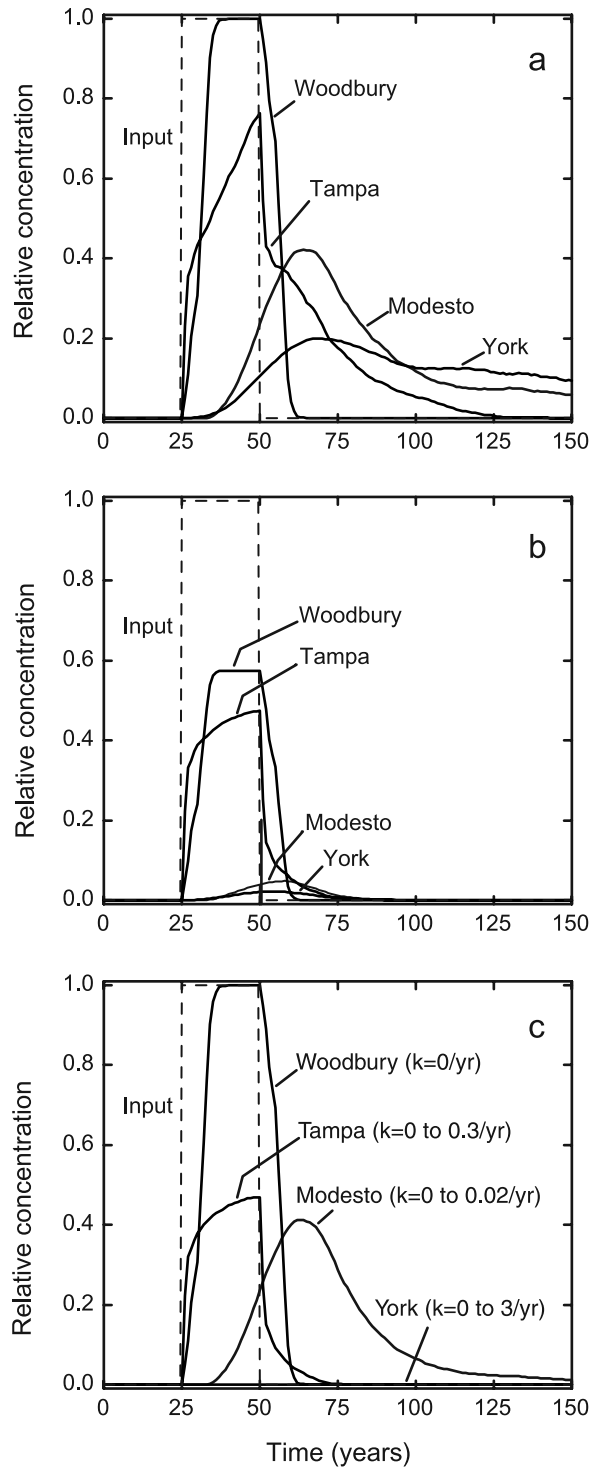


Figure 6. Relative concentration of a hypothetical contaminant in the public supply wells as a function of time for a slug input at the water table lasting 25 years. Uniform input across area contributing recharge to the wells (a) without and (b and c) with degradation. In Figure 6b, degradation with first-order reaction kinetics and a common rate constant of 0.1 per year was applied uniformly along each particle pathline using a post-MODPATH spreadsheet model. In Figure 6c, site-specific first-order denitrification rate constants (in parentheses) were used in the spreadsheet model and varied with the spatial distribution of redox conditions along particle pathlines (Figure 2) [McMahon *et al.*, 2008]. In Figure 6c, the relative concentration in the York PSW was equal to zero for the entire simulation period.

Table 4. Breakthrough Curve Characteristics at the Public Supply Wells for a Hypothetical Contaminant With a Slug Input at the Water Table Lasting 25 Years^a

Location	Peak Lag Time (years)	Dilution ^b (C/C ₀)	Arrival: 1% of Total Mass ^c (years)	Flush: 99% of Total Mass ^d (years)
<i>Uniform Input Across Area Contributing Recharge to Well, No Degradation</i>				
Modesto, California	26	0.43	17	216
York, Nebraska	30	0.20	18	359
Woodbury, Connecticut	6	1.0	3	8
Tampa, Florida	12	0.76	2	61
<i>Uniform Input Across Area Contributing Recharge to Well, Common Degradation Rate Constant</i>				
Modesto, California	20	0.05	13	38
York, Nebraska	16	0.02	8	43
Woodbury, Connecticut	6	0.58	3	8
Tampa, Florida	12	0.47	2	19
<i>Uniform Input Across Area Contributing Recharge to Well, Site-Specific Denitrification Rate Constants</i>				
Modesto, California	26	0.41	16	89
York, Nebraska	Not applicable	0	Not applicable	Not applicable
Woodbury, Connecticut	6	1.0	3	8
Tampa, Florida	12	0.47	2	14
<i>Input Across Fastest 25% of Area Contributing Recharge to Well, No Degradation</i>				
Modesto, California	18	0.28	14	24
York, Nebraska	30	0.20	13	43
Woodbury, Connecticut	2	0.25	2	2
Tampa, Florida	1	0.34	<1	1
<i>Input Across Slowest 25% of Area Contributing Recharge to Well, No Degradation</i>				
Modesto, California	118	0.05	111	307
York, Nebraska	238	0.03	233	>450
Woodbury, Connecticut	10	0.22	8	10
Tampa, Florida	40	0.16	30	75

^aCommon degradation rate constant is 0.1/a. Average site-specific denitrification rate constants range from 0 to 3/a [McMahon et al., 2008].

^bRelative to peak concentration.

^cRelative to start of input.

^dRelative to end of input.

PSW (Figure 3), the reduction in peak NO₃⁻ concentrations by denitrification at Tampa was about 8 times greater than at Modesto because of the larger rate constant at Tampa (Figures 6a and 6c). Nevertheless, a portion of flow in the Tampa PSW still contained relatively large NO₃⁻ concentrations because travel times along short-circuit pathways (karst conduits) to the PSW were shorter than the 5-year denitrification lag time (Figure 6c). This comparison illustrates how contaminant degradation is dependent on interactions between groundwater age, reaction lag times and kinetics, and flow processes.

4.4.2. Spatial Variability in Land Use

[41] The simulations of hypothetical land use change suggest that timescales for change in the quality of water from PSW could be on the order of years to centuries for land use changes that occur over days to decades. Although those simulations assumed uniform land use change across the area contributing recharge to the PSW, land use change can vary in time and space, as the previous discussion related to the Modesto PSW demonstrated. Two scenarios were simulated for each PSW to illustrate how the water quality response to spatial variability in land use might vary for the hydrogeologic settings and well characteristics represented by the four study areas. In the first scenario, land use change was assumed to occur only in 25% of the contributing area with the shortest transit times to the PSW, and in the second scenario land use change was assumed to occur in 25% of the contributing area with the longest

transit times to the PSW (Figure 7 and Table 4). These scenarios resulted in substantial shifts in arrival, lag, and flushing times relative to the uniform land use distribution case in Figure 6a. Peak dilution (C/C₀) also was substantially different between the scenarios (Table 4). At Modesto, for example, C/C₀ ranged from 0.05 to 0.28 for the scenarios in Figure 7. At York, flushing times ranged from 43 to >450 years. At Tampa, the lag time in arrival of peak concentrations was reduced from 12 years in the uniform distribution case (Table 4 and Figure 6a) to 1 year for the faster 25% of the contributing area (Table 4 and Figure 7a). These results demonstrate the importance of understanding the spatial distribution of land use change relative to groundwater transit times to more fully understand connections between land use and water quality in PSW.

4.5. Limitations of Analysis

[42] None of the analyses presented in this paper considered chemical storage and transit times in the unsaturated zone, dispersion/diffusion, or transient flow conditions in the aquifer, which could give substantially different results. Storage of large amounts of chemical mass in, and long transit times through, unsaturated zones could result in longer flushing times, as well as longer arrival and lag times, in the aquifer. On the other hand, even transit times through unsaturated zones probably are sensitive to land use change because of its potential effect on local recharge rates, with or without irrigation [Stonestrom et al.,

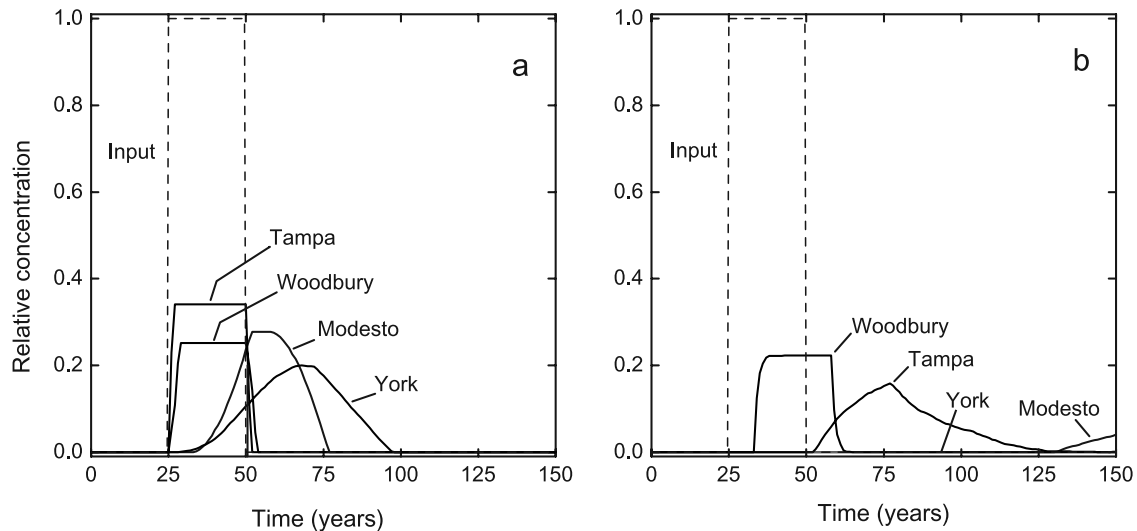


Figure 7. Relative concentration of a conservative contaminant in the public supply wells as a function of time for a hypothetical slug input at the water table lasting 25 years. Input across the (a) fastest and (b) slowest 25% of the areas contributing recharge to the wells (no degradation). In Figure 7b, the contaminant did not arrive at the York PSW within 150 years.

2003; McMahon *et al.*, 2006; Scanlon *et al.*, 2005]. An attempt was made to include as much heterogeneity as possible in the simulations of flow [Starn and Brown, 2007; Clark *et al.*, 2007; Burow *et al.*, 2008]; however there are small-scale heterogeneities that are not included. The impact of not using dispersion to represent spreading due to local heterogeneity is likely minimized because the focus is on large pumping wells and nonpoint sources of contamination. The major conclusions would not be expected to change if dispersion were included. Transient conditions in the flow system could result in more complex areas contributing recharge and groundwater age distributions than were assessed here and should be considered in future studies [Franke *et al.*, 1998; Rock and Kupfersberger, 2002].

[43] Another process that could be important in linking water quality in PSW with land use, but was not explicitly represented in the steady state flow model at Modesto, is flow down PSW wellbores with long open intervals during nonpumping periods [Reilly *et al.*, 1989]. This process occurred at the Modesto PSW during the winter [Burow *et al.*, 2008]. As a result, contaminants near the water table in the vicinity of the well entered the deeper formation around the well screen and were later pumped back out of the aquifer during the summer. Thus, depending on the duration of pumping in the summer and nonpumping in the winter, the net result of this process could be contamination of the deep production zone in the aquifer with much shorter contaminant arrival times and perhaps less dilution than would occur in the absence of wellbore flow.

5. Implications for Source Water Protection and Vulnerability Assessment

[44] Results from this and related studies [e.g., Barber *et al.*, 1996; Fogg *et al.*, 1999; Brawley *et al.*, 2000; Kauffman *et al.*, 2001; Böhlke, 2002; Weissmann *et al.*, 2002; Hiscock

et al., 2007] could have important implications for management strategies that rely on land use change to achieve water quality objectives [European Commission, 2007] (see also U.S. Environmental Protection Agency, Source water protection, 2007, available at <http://cfpub.epa.gov/safewater/sourcewater/>). Because of long lag times in the arrival of peak contaminant concentrations at some PSW, water produced now may have been recharged decades earlier under land use that no longer exists in the area contributing recharge to the well, making it harder to connect the quality of water in PSW to specific land uses that might be targeted for change. Moreover, because long times may be required to flush contaminants from contributing areas, the quality of water from PSW could actually deteriorate before responding to efforts designed to reduce contaminant loads to the water table. In the United States and Europe, source water protection strategies vary in their level of sophistication in terms of how PSW contributing areas are defined, from a simple fixed radius around the well to detailed numerical flow models [European Commission, 2007] (see also U.S. Environmental Protection Agency, Source water protection, 2007, available at <http://cfpub.epa.gov/safewater/sourcewater/>). Results from this study indicate that areas within PSW capture zones requiring the most protection (flow paths with short travel times and/or low degradation potential) may be spatially quite variable and not well delineated in the absence of additional information such as age tracers for model calibration/verification [Osenbrück *et al.*, 2006; Starn and Brown, 2007; Clark *et al.*, 2007; Burow *et al.*, 2008] and the distribution of redox processes along flow paths to PSW [McMahon *et al.*, 2008].

[45] The findings and methods outlined in this paper have larger implications for statistically based groundwater vulnerability models that are used to explore controls on nonpoint source contamination using simplistic assumptions of contributing areas and static land use inputs [Gurdak and Qi, 2006]. Furthermore, statistically based vulnerability

models of deeper flow systems in which PSW typically are screened [Nolan and Hitt, 2006] could overestimate the impact of land use on water quality if they do not account for mixing with old water in the well screens [Osenbrück et al., 2006; Burow et al., 2007].

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