Influences of the unsaturated, saturated, and riparian zones on the transport of nitrate near the Merced River, California, USA

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Abstract Transport and transformation of nitrate was evaluated along a 1-km groundwater transect from an almond orchard to the Merced River, California, USA, within an irrigated agricultural setting. As indicated by measurements of pore-water nitrate and modeling using the root zone water quality model, about 63% of the applied nitrogen was transported through a 6.5-m unsaturated zone. Transport times from recharge locations to the edge of a riparian zone ranged from approximately 6 months to greater than 100 years. This allowed for partial denitrification in horizons having mildly reducing conditions, and essentially no denitrification in horizons with oxidizing conditions. Transport times across a 50–100-m-wide riparian zone of less than a year to over 6 years and more strongly reducing conditions resulted in greater rates of denitrification. Isotopic measurements and concentrations of excess N_2 in water were indicative of denitrification with the highest rates below the Merced River. Discharge of water and nitrate into the river was dependent on gradients driven by irrigation or river stage. The results suggest that the assimilative capacity for nitrate of the groundwater system, and particularly the riverbed, is limiting the nitrate load to the Merced River in the study area.

Résumé Le transport et la transformation des nitrates ont été étudiés le long d'un transect long d'un kilomètre dans un verger d'amandiers le long de la Merced River, en Californie (Etats-Unis), en environnement irrigué. Les dosages des nitrates dans l'eau des pores et les modélisations utilisant le modèle RZWQM (root zone water quality model) ont montré que près de 63% de l'azote utilisé était transporté à travers les 6.5 m de la zone non saturée. Les temps de transit depuis les lieux de réalimentation jusqu'à la bordure d'une zone ripicole étaient compris entre 6 mois environ et plus de 100 ans. Ceci a permis une dénitrification partielle dans les horizons relativement réducteurs, et quasiment aucune dénitrification dans les horizons à conditions oxydantes. Les temps de transit de moins d'un an à plus de 6 ans à travers une zone ripicole de 50 à 100 m de large, en conditions plus réductrices, ont généré des taux de dénitrification plus élevés. Les dosages isotopiques et les concentrations de N_2 en excès dans les eaux étaient indicatrices des taux de dénitrification les plus élevés à l'aval dans la Merced River. Le flux d'eau et de nitrates vers la rivière était dépendant des gradients générés par l'irrigation et du niveau de la rivière. Les résultats suggèrent que la capacité d'assimilation des nitrates du système aquifère, en particulier le lit de la rivière, limite la charge en nitrates de la Merced River sur le secteur d'étude.

Resumen Se ha evaluado el transporte y la transformación de los nitratos a lo largo de un transecto de 1 km desde un huerto de almendros hasta el Río Merced, California, USA, dentro de una zona de agricultura de regadío. Como indican las medidas de nitratos en el agua intersticial y la modelización utilizando el Modelo de Calidad del Agua en la Zona de la Raíz, alrededor de un 63% del nitrógeno aplicado se transporta a través de 6.5 m de zona no saturada. El tiempo de transporte desde los lugares de recarga hasta el límite de la zona ribereña oscila

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entre aproximadamente 6 meses hasta más de 100 años. Esto permite que exista denitrificación parcial en horizontes que tienen condiciones ligeramente reductoras, y esencialmente no exista denitrificación en horizontes con condiciones oxidantes. Los tiempos de transporte a lo largo de una zona ribereña de entre 50 a 100 m de ancho, de entre menos de un año a más de seis años y condiciones más fuertemente reductoras dan lugar a mayores rangos de denitrificación. Los resultados isotópicos y las concentraciones del exceso de N_2 en el agua fueron indicativos de denitrificación con los rangos más altos bajo el Río Merced. La descarga de agua y nitrato en el río dependieron de los gradientes producidos por el regadío o del estadio del río. Los resultados sugieren que la capacidad asimilativa del sistema de aguas subterráneas para el nitrato, y particularmente el lecho del río, está limitando la carga de nitrato al Río Merced en el área de estudio.

Keywords USA · Groundwater/surface-water relations · Solute transport · Unsaturated zone · Groundwater protection

Introduction

The use of agricultural chemicals such as nutrients and pesticides has greatly increased the ability of the world farming community to produce food for an expanding population. Agricultural chemical use significantly increased after the Second World War as farm management, driven by the so-called "green revolution", resulted in the introduction of new forms of cereal grains to combat problems of world hunger (Perkins 1997). The green revolution techniques also necessitated huge increases in nutrient (nitrogen and phosphorus) and pesticide applications, especially herbicides. Partially as a result of this, nitrate concentrations in groundwater, as well as nitrogen and phosphorus enrichment of rivers, streams, and coastal environments have increased. Certain areas of the United States, especially the northeast, mid-western, and West Coast, are especially prone to elevated levels of nitrate in groundwater (Mueller et al. 1995; Puckett 1995). Although wide-spread human exposure to levels of nitrate above the US Environmental Protection Agency standard within the United States are relatively rare, at least for communities on regulated systems, there is still considerable uncertainty about the risks of nitrate exposure from the use of privately owned wells (Manassaram et al. 2006). The current standard (maximum contaminant level or MCL) for drinking water is 10 mg/L as N, but is enforceable only for utilities supplying water to at least 25 people, or with 15 or more service connections (US Environmental Protection Agency 2003, 2007). Effective management of groundwater resources in agricultural areas requires information on the vulnerability of aquifers to nitrate.

Effective management of farm chemicals also requires an understanding of their fate or transformations in the environment. Nitrate, for example, may degrade to nitrogen gas under favorable geochemical conditions (Hiscock et al. 1991). Agricultural management practices (AMPs) are frequently designed to protect water quality or to prevent soil erosion (US Environmental Protection Agency 2006). One widely recommended practice, with assumed benefits for both soil erosion and water quality, is the use of riparian buffer strips (Lowrance et al. 2000). The typical riparian buffer is a section of natural vegetation, including trees, separating the agricultural field from the river or stream interface. Riparian buffer strips may create an interface along a groundwater flow path where geochemical conditions may change, and thereby affect the transformations, or rates of transformations, of fertilizers and pesticides (Naiman and Decamps 1997; Karr and Schlosser 1978; Mayer et al. 2007). Removal of nitrate by denitrification requires a geochemical condition of very low to zero dissolved oxygen, and sufficient organic matter to support a bacterial population (Knowles 1982). Riparian zones with woody vegetation may supply sufficient organic matter to support bacterial populations, such that dissolved oxygen is effectively removed from the groundwater and a population of denitrifying bacteria is supported. It has been hypothesized that riparian zones may be relatively rich in carbon for microbial denitrification as deep root systems, and associated fungal communities, become submerged seasonally (Haycock and Pinay 1993). It is then assumed that, in gaining reaches of rivers, the nitrate loading of groundwater discharging to the river through the riparian zone will be reduced. Nitrate may also be lost in the riparian zone through plant uptake (Lowrance et al. 1984, 1995).

Although the shallow groundwater within or adjacent to a riparian buffer may have low levels of dissolved oxygen and denitrification may be occurring, it is necessary to understand the groundwater flow paths and riparian processes fully to determine the effectiveness of a given riparian buffer to remove significant quantities of nitrate (Puckett and Hughes 2005). High rates of denitrification may be possible at shallow depths since groundwater migrates through zones of freshly decomposing organic matter where bacterial activity is assumed to be high. Deeper flow paths, which intersect aquifer materials identified as being associated with lower levels of bacterial activity, may be associated with slower rates of denitrification. If the rate of denitrification were slower than the time of travel, it would be possible for the nitrate to discharge to the stream interface (Burt et al. 1999).

Concentrations of nitrate in excess of the federal drinking water standard in the groundwater of the San Joaquin Valley of California have been documented, especially for the eastern San Joaquin Valley (Dubrovsky et al. 1998; Burow et al. 1998a). One land-use setting in the San Joaquin Valley identified as having elevated nitrate is the almond (*Prunus dulcis*) orchard (Burow et al. 1998b). Almond trees require nitrogenous fertilizers, and do well in regions of permeable or sandy soils. Almond orchards planted in these types of soils, with a shallow water table, increase the chance of transport of nitrate.

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In order to understand the processes controlling the distribution and fate of nitrate in a California orchard setting, a study was conducted with the intention of tracking the movement of water and associated agricultural chemicals along a transect from an orchard where chemicals were applied to a river discharge point. A gaining portion of the Merced River (Fig. 1) was identified in a reconnaissance and the direction of groundwater flow was determined from groundwater elevation data. Records of nitrate applications and amounts of irrigation water were supplied by individual growers. Monitoring wells, lysimeters, pressure transducers, soil-moisture, heat-dissipation, and temperature probes were used to collect information on chemical concentrations, measure water levels, and estimate water flux. This study is part of a larger effort by the US Geological Survey National Water Quality Assessment (NAWQA) Program to understand processes controlling the fate and transport of agricultural chemicals in multiple hydrologic compartments. The overall study is referred to as the Agricultural Chemicals: Sources, Transport, and Fate topical study (Lampe 2005). The overall study is being implemented in seven study units located in California, Washington, Nebraska, Iowa, Mississippi, Indiana, and Maryland. Additional papers will be available on various aspects of the study including comparative papers on the unsaturated zone, groundwater, riparian processes, and atmospheric processes. Information on those results, when available, will be listed on the Internet (see Lampe 2005).

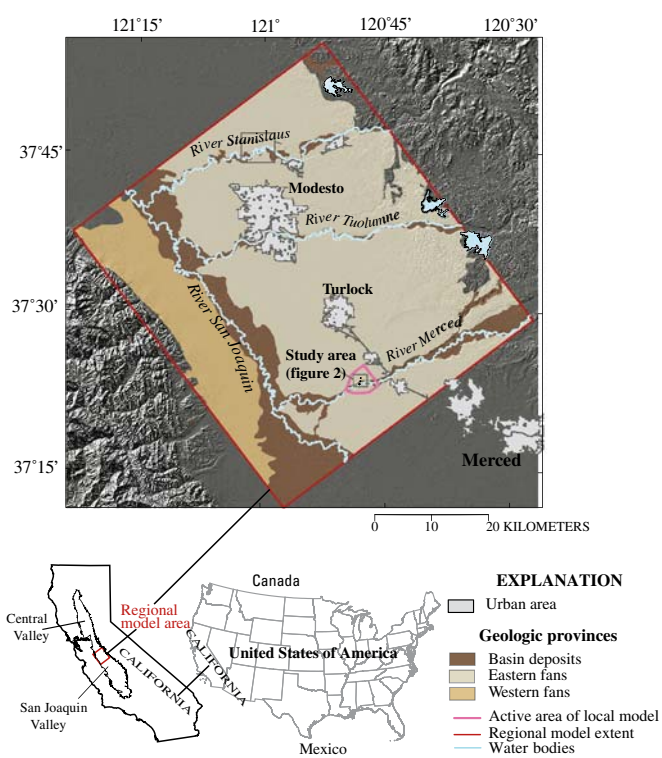

Fig. 1 Location of the regional and local groundwater model boundaries, study area, and geologic provinces

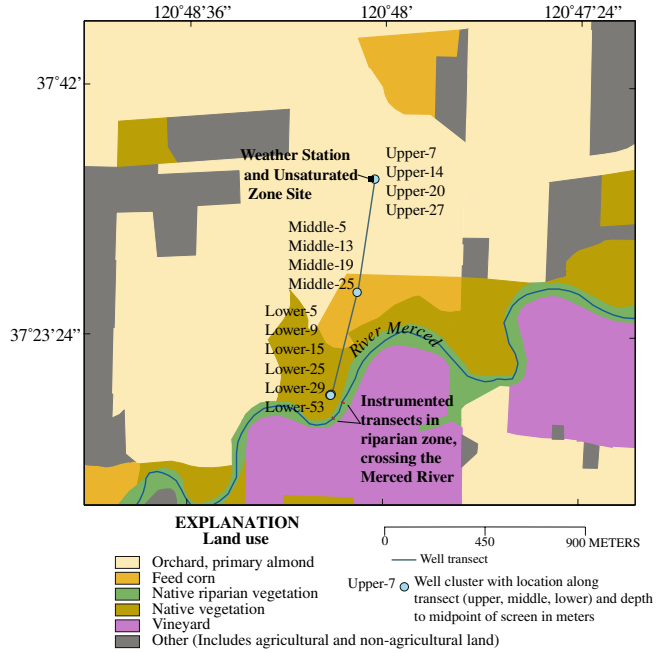

Fig. 2 Map of groundwater and river transects, location of weather station and unsaturated zone sites, depth of monitoring wells, and land-use (modified from Phillips et al. 2007)

Study area

The study area, about 6 km^2, is located south of Turlock, California, along a reach of the Merced River (Fig. 1). The Merced River is one of many that drain the Sierra Nevada, and has multiple reservoirs for irrigation and power generation along its length, which effectively delay discharge of large amounts of snowmelt runoff. An extensive network of canals is used to deliver surface water for irrigation. Although groundwater is also used for irrigation in parts of the San Joaquin Valley, groundwater is seldom used for irrigation in this study area. The land surface in the study area slopes westward toward the San Joaquin River and southward toward the Merced River; gradients range from about 1 to 4 m/km. The climate is semi-arid, characterized by hot summers and mild winters; the rainfall averaged 315 mm annually from 1931 to 1997 with most of the precipitation occurring during late fall through early spring (National Oceanic and Atmospheric Administration 2005). Land use in the study area is dominantly agricultural, with narrow strips of riparian vegetation along the river (Fig. 2). The dominant crops are deciduous orchards (primarily almonds) north of the river and vineyards to the south, followed by field crops, pasture, and various fruits and vegetables.

The aquifer system in the regional study area is composed of Tertiary and Quaternary alluvial deposits eroded from the surrounding Sierra Nevada and coastal mountain ranges. The basin-fill comprises coalescing alluvial fans, which tend to be coarse-grained near the mountains and finer grained toward the center of the basin. The Corcoran

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Clay Member of the Tulare Formation is a lacustrine clay deposit that separates the basin-fill deposits into an upper unconfined to semiconfined aquifer and a lower confined aquifer throughout much of the region (Burow et al. 2004). The study area is underlain entirely by the Corcoran Clay, which is encountered about 40 m below land surface and is about 18 m thick.

Recharge in the study area occurs primarily at the land surface, with secondary contributions from subsurface inflow from upgradient areas. About two thirds of areal recharge is attributed to irrigation return flow, and the remainder to precipitation. The estimated average rate of areal recharge in the study area is about 0.45 m/year (Phillips et al. 2007).

Groundwater flow in the study area generally is toward the Merced River, where most of the groundwater discharge occurs, and southwestward with the regional gradient. Vertically, the flow direction is downward farthest away from the river and upward near the river (Phillips et al. 2007).

Methodology

Weather station and unsaturated zone

An area of orchard within the study area was instrumented as follows. A weather station was installed (Fig. 2) to obtain the necessary measurements to calculate evapotranspiration. Weather station components consisted of an air temperature and relative humidity sensor, an anemometer for wind speed and direction, a pyranometer for solar radiation, a 20.3 cm tipping bucket rain gage, and a net radiometer for net radiation. The weather station also contained instrumentation to measure the surficial soil temperature and heat flux.

Unsaturated-zone instrumentation was installed in the orchard (Fig. 2) to collect data for estimating recharge and hydraulic properties, and water samples for chemical analysis. The unsaturated-zone monitoring station was equipped with instrumentation to measure surficial soil temperature, soil heat flux, and soil water matric potential and soil moisture at depth in order to estimate the flux of water out of the soil and the reservoir of water in the soil. Three types of soil instrumentation were installed. At 0.3, 0.6 and 1 m, soil water content probes were installed. Laboratory-calibrated heat dissipation matric-water-potential sensors were installed at six depths (0.3, 0.6, 1, 3, 4.6, and 6.1 m) in a hand-augured borehole. The sensors were set to obtain readings at 1–4-h intervals. Soil samples were obtained during placement of the instrumentation and analyzed for water content, organic matter content, grain size, anions, and bulk density. Ceramic porous-cup suction lysimeters were installed at various depths (1, 4.6, and 6.1 m) to quantify the movement of chemicals (nitrogen and phosphorus compounds, pesticides, major elements, pH, alkalinity, and specific conductance) through the soil over time. The shallowest lysimeter was located just below the tree root zone. The lysimeters were placed under vacuum for 3–24 h prior to sampling. The water was then pushed through the tube with a hand pump and collected into appropriate bottle types. Where applicable, samples were filtered with an in-line syringe filter (Pellman Supor filter with 0.45 μm pore size). The amount of water collected from a lysimeter varied from as low as less than 50 ml to as much as 300 ml. Sample handling was optimized to minimize loss of lysimeter water. Filtration was completed in the syringe and filter assembly using a pre-cleaned filter. The water was then collected into pre-cleaned bottles with instructions for the laboratory regarding the small sample size. A bromide tracer was added at the beginning of the irrigation season in the direct vicinity of the lysimeters. A 12 m section of land was treated with 180 g of KBr and enough water to move the tracer to just below the soil surface was added.

Groundwater

Clusters of monitoring wells were installed at three sites along a groundwater transect (Fig. 2) that was oriented in the general direction of groundwater flow toward the Merced River. The site at the upper end of the transect (northern, up-gradient end) was in an almond orchard. The middle site was between an upslope almond orchard and a cornfield (feed corn), and the site at the lower end was in native vegetation at the edge of the riparian zone of the Merced River. Four to six wells at each site were used for this study; mid-screen depths ranged from about 6 m below land surface near the water table to about 27 m below land surface for those screened above the Corcoran Clay. Screen lengths for this group of wells were 0.6 m except at the water table (1.5 m). One well at the lower end of the transect was screened below the Corcoran Clay at a depth of 53 m below land surface; the screen length was 3 m. Fourteen of these transect wells were instrumented using pressure transducers that recorded hourly water-level measurements for periods ranging from 1 to 1.6 years.

Groundwater/surface water interactions

Two river transects crossing the Merced River (Fig. 2) were established to gather information on the interaction of groundwater and surface water and other processes in the riverbed down-gradient of the lower end of the groundwater transect. The upstream and downstream river transects were separated by about 100 m. A total of 20 small-diameter (5 cm) polyvinylchloride (PVC) wells with 0.15–0.3 m screens were installed along each transect to house instrumentation for various measurements. Each transect was equipped with five pairs of wells: three pairs in the river and a pair on the right and left banks in the riparian zone. Well pairs consisted of shallow and deep wells screened at about 0.5 and 3 m below the streambed for the river wells, and about 3.5 and 5 m below land surface for the riparian zone wells. All wells on the river transects were equipped with high-precision temperature loggers, and subsets of wells included pressure transducers (10) and continuous water-quality loggers (2).

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Temperature loggers recorded temperature every 15 min in both the surface water and at three depths below the streambed (about 0.5, 1.0, and 2.0 m) and the banks (about 3.5, 4.0, and 5.0 m). Pressure transducers and continuous water-quality loggers located in the stream and aquifer recorded data hourly or every 15 min. Small stainless steel drive-point tips with 2-cm screens were installed within 0.5 m (laterally) of each well screen in order to collect water samples. Nylon tubing (6 mm) was attached to the drive-point tips and routed through pipe to a shelter on each bank. Water samples were collected in Teflon or glass bottles using Teflon tubing to minimize sampling artifacts.

Water sampling and analysis

Water samples were processed by filtering through glass fiber (0.7 μm) filters for organic compounds (pesticides) or through 0.45 μm capsule filters for inorganic constituents (nutrients, cations and anions, trace metals, alkalinity, etc.). Rain samples were collected through Teflon-lined funnels, and then processed in a similar manner. Nitrogenous nutrient species were analyzed by the method of Fishman (1993), and phosphorus species were analyzed by a colorimetric method of the US Environmental Protection Agency (1993). Nitrogen and phosphorus species are expressed in this paper as mg/L as N or P, respectively. Major common ions (Na, Ca, K, Mg, Cl, and SO_4) were analyzed by the methods of Fishman (1993), Fishman and Friedman (1989), and the American Public Health Association (1998).

Pesticide analysis was by gas chromatography/mass spectrometry (GC/MS) according to the method of Zaugg et al. (1995) with detection limits generally between 0.005 to 0.01 μg/L. Analysis of herbicidal degradation products was completed by the method of Lee and Strahan (2003) with detection limits of 0.005 to 0.02 μg/L. Samples for analysis of nitrogen (N_2) and argon (Ar) were collected and analyzed by methods described by Busenberg et al. (1998) and Sanford et al. (1996). Concentrations of N_2 and Ar gases were used to estimate the amount of nitrogen resulting from denitrification (Heaton and Vogel 1981; Vogel et al. 1981; Puckett et al. 2002). Further information on the calculation of denitrification from excess N_2 gas is given by Green et al. (2008b). Age dating of groundwater samples was completed using measurements of sulfur hexafluoride (Busenberg and Plummer 2000). The N and O isotopic composition of dissolved NO_3^- was determined by bacterial reduction to N_2O and continuous-flow isotope-ratio mass spectrometry (CFIRMS; Sigman et al. 2001; Casciotti et al. 2002; Coplen et al. 2004).

Quality assurance consisted of the collection of routine field and equipment blanks and replicates. Analysis of the blanks indicated that samples were either free of artifacts, cross-contamination, or carry-over, or, when detected, concentrations of nutrients in blank samples were far below those of the environmental samples while the analysis of replicates indicated that reproducibility was consistent with the analytical method.

Results and discussion

The transport and fate of water and agricultural chemicals in the study area was characterized using a combination of chemical analysis and modeling simulation of both groundwater flow and nitrate transport for the key hydrologic environments: the unsaturated, saturated, and riparian zones, and the riverbed.

Unsaturated zone

The root zone water quality model (RZWQM; Ahuja et al. 1999) was used to simulate the movement of water, bromide, and nutrients through the unsaturated zone underlying the almond orchard at the upper end of the groundwater transect. The RZWQM includes provisions to simulate most agricultural management practices, biological processes, preferential flow, seepage to the water table, unsaturated flow, and transport of agricultural chemicals and nutrients. In this study, climate, geology and farming information from the study site was used to build the models. Simulations of water and chemical transport were compared with measured bromide (an added tracer) and nitrate concentrations, and water-table elevation. RZWQM has had only limited use in simulating orchard management, and as a result, input parameters for the almond orchard were measured, acquired from the on-site farmer, supplied from the literature, or estimated by almond-cropping experts at University of California at Davis.

The simulated period was 1 January 2002 through 31 December 2004. Most measured data were available only for 2004, but a longer model period was required to generally equilibrate the hydrologic and chemical conditions. The upper boundary of the one-dimensional RZWQM model was land surface. Infiltration was simulated using the Green-Ampt equation (Green and Ampt 1911). The basal boundary of the model was a constant flux rate intended to simulate water movement in the saturated zone. The simulated column extended to the water table, 6.5 m below land surface. The soil profile was discretized into ten layers based on geologic descriptions from cores collected at the site. Layers were internally rediscretized by RZWQM into 140 cells with thicknesses ranging 1–5 cm. Model layers were parameterized with measured particle-size and organic-matter data, where available. Layers 1–6 and 8–10 contained more than 88% sand. Layer 7 was entirely composed of silt-sized material. Organic matter comprised less than 2% of the mass in all soil samples. Nitrogen content of the soil and sediments was low, about 0.1%. Soil water content—matric suction—unsaturated hydraulic conductivity functions were modeled using a slightly modified, non-hysteretic form of the Brooks-Corey relation and internally parameterized with values suggested by Rawls et al. (1982). While the texture of surficial deposits at the site was too coarse to use RZWQM's macropore-flow module, advective velocities computed from bromide-tracer data indicated that 'finger flow' may be occurring at this site and the use of higher hydraulic conductivity values was justified (DiCarlo et al. 1999).

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The hydraulic conductivity of sand layers was uniformly set to 0.02 cm/s and the silt-rich layer was set to 0.001 cm/s. The hydraulic conductivity value for sand layers was about ten times higher than the default value estimated by RZWQM from the particle-size distribution data but was still within the range of values commonly cited for this type of deposit. The final hydraulic conductivity used for silt was about 50 times higher than the value that RZWQM computed based on particle-size distribution, but was required for the model to match measured water-table elevations. This may indicate that the silt layer thinned or was locally discontinuous, fractured or contained variable quantities of sand beneath the study site. Initial values of soil tension were estimated to range from 0 at the base of the profile to −200 cm of H_2O in silt-rich layer 7. Initial soil-moisture values were intentionally estimated higher than expected actual values and the column was allowed to drain to a stable soil-moisture profile before the period of interest; simulations indicated that an equilibrated profile was rapidly achieved. Initial values of temperature were set to 15°C for all layers and were similarly expected to approach more natural conditions in advance of the simulated period of interest.

Climate data for the periods 23 January 2004–21 July 2004 and 28 October 2004–31 December 2004 were collected at the study site, and included hourly measurements of precipitation, temperature, wind speed, solar radiation and relative humidity. Climate data for the periods 1 January 2002–22 January 2004 and 22 July 2004–27 October 2004 were probabilistically generated from the RZWQM database of climate data collected over 44 years at the San Francisco WP AB site, 217 km from the study site. Evaporation and transpiration were computed using the measured and generated climate information and a revised form of the Shuttleworth-Wallace double-layer model (Shuttleworth and Wallace 1985).

Agricultural management information for 2004 was provided by the grower operating at the site. It was assumed for the three-year models that the 2004 farming practices were used throughout the simulation period; nutrient application data were essentially identical for the period 2002–2004. Agricultural management practices simulated in the RZWQM models included periods of almond tree production and dormancy, sprinkler irrigation, and applications of inorganic fertilizer. Almond trees were actively transpiring from early April through early September. Fertilizer was delivered to the orchard in irrigation water at a concentration of 14 kg/ha on approximately 2–4-week intervals. Ten irrigation events were simulated during the 2003 and 2004 growing seasons. A final simulation was completed for the last irrigation event, which followed the almond harvest during October. A potassium bromide tracer was applied to the land surface over the lysimeters on 24 March 2004 at a rate of 15 mg/m^2. Bromide concentrations in lysimeter samples were used to estimate the advective pore-water velocity. Agricultural practices were simulated to the extent that data were available from the farmer and within the allowable constraints of the RZWQM code. Parameters used to numerically characterize the almond orchards were measured on site, computed by RZWQM, acquired from the literature and the Internet, and communicated by California agricultural experts (Table 1).

The distribution of organic carbon and microbial activity was based on organic-matter measurements of core samples collected at the study site and estimates of the humus and residue reactivity, residue abundance, autotroph and heterotroph populations, and root distribution (Table 2). A warm-up period of 30 years was used to equilibrate the organic carbon and biological model components prior to executing the solute-transport simulations. In addition, nutrient-transport simulations used two implicit iterations of the simulation period to additionally generate reasonable initial distributions of organic carbon and microbiological populations prior to the modeled period of interest. Ratios of fast–slow–stable, etc. were coarsely adjusted to fit simulated to measured nitrate concentrations.

The model was initially calibrated to bromide concentrations in samples from lysimeters located at 1.0, 4.6 and 6.1 m depths. Simulated and measured bromide concentrations indicated that the advective flow component of the model was generally acceptable (Fig. 3). The simulated peak at 1 m (Fig. 3a) was noticeably higher than the maximum measured concentration; however, it is unlikely that discrete sampling captured the highest concentrations. At 4.6 m (Fig. 3b), a single sample on 5 August had a relatively high bromide concentration that could not be reproduced by the model; preferential flow may have caused this anomalous measurement. Simulated bromide concentrations at 6.1 m more closely resembled the relatively low concentrations in samples collected from a well screened across the water table (approximately 6.2–6.7 m below land surface). Concentrations in groundwater ranged 0.4–0.5 mg/L and 0.1–7.5 mg/L in pore water immediately above the water table. Dynamics in the capillary fringe and imprecision in the model parameterization made calibration at this depth difficult. Simulations indicated that at 4.6 m the bromide tracer penetrated the

Table 1 Almond orchard characteristics used for modeling nitrate transport near the Merced River, California

Characteristic	Value	Data source
Tree density	200/ha	Field measurement
Tree height	4.5–6 m	Field measurement
Total seasonal nitrogen uptake	120 kg/ha	P.H. Brown, University of California Davis, personal communication, 2006
Maximum daily nitrogen uptake	20 g/plant/day	Computed by RZWQM from above data
Maximum rooting depth	5.0 m	P.H. Brown, University of California Davis, personal communication, 2006

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Table 2 Initial distribution of residue, humus and microbiological organisms in the simulated profile

Model layer	Slow residue (μg C/g)	Fast residue (μg C/g)	Stable humus (μg C/g)	Transition humus (μg C/g)	Fast humus (μg C/g)	Aerobic heterotrophs (organisms/g)	Autotrophs (organisms/g)	Anaerobic heterotrophs (organisms/g)
1	271.7	0.0	2,408.1	568.7	181.3	531,441	11,774	187,681
2	0.6	0.0	1,914.7	220.4	122.8	38,668	457	1,165
3	0.7	0.0	1,913.1	215.2	104.2	30,585	416	708
4	0.7	0.0	2,390.0	258.6	79.1	21,438	454	396
5	0.7	0.0	2,868.5	304.7	68.0	19,626	536	363
6	0.8	0.0	2,862.8	309.2	51.9	4,623	432	348
7	0.3	0.0	9,651.2	827.7	76.0	36,489	3,158	6,861
8	0.8	0.0	1,907.6	207.1	35.3	3,844	273	208
9	0.4	0.0	888.8	0.0	0.0	0	0	0
10	0.0	0.0	904.9	0.0	0.0	0	0	0

silt layer in the profile; therefore, inhibited flow was likely not the cause of low concentrations at 6.1 m.

Simulated daily fluxes of water to the water table in 2004 ranged from −1.07 to +0.94 cm/d and were greatest from January through March and immediately following the October irrigation. Recharge rates were lowest during September and early October (Fig. 4). The mean daily recharge rate computed by RZWQM for 2004 was 0.13 cm/day or 47 cm/year. This rate agrees well with previous estimates of recharge at this site by Phillips et al. (2007; 0.12 cm/day; 45 cm/year), Green et al. (2008 a; 0.11 cm/day; 41 cm/year), and Fisher and Healy (2008; 0.11 cm/day; 42 cm/year). The previous estimates are based on responses of ground water that integrate recharge over a broad source area and the agreement with RZWQM results indicates that the hydrology at the local profile is similar to the hydrology of the larger area. This is to be expected given the lateral uniformity of surficial sediments at the site.

Nutrient-transport simulations were used to examine processes affecting the fate of inorganic fertilizer applications. Unlike bromide, concentrations of nitrate in groundwater prior to fertilizer application were unknown but assumed to be non-zero. Initial conditions were established by adjusting the distribution of various microorganism populations and the distribution of residue and humus into pools having various rates of reactivity. An internal 30-year warm-up period of the microbiological model was followed by multiple iterations of the 3-year simulation period to compute initial non-zero concentrations of nitrogen. The simulated nitrate concentrations approximated the measured concentrations reasonably well but underestimated a high concentration at 1.0 m below land surface on 15 June and underpredicted concentrations at 6.1 m below land surface (Fig. 5). The simulated concentrations of nitrate at 6.1 m below land surface averaged 8.2 mg/L less than measured concentrations and indicated that estimates of nitrate flux to the water table, approximately 6.5 m below land surface, could be less than the actual. Migration of groundwater with higher nitrate concentrations, from the saturated zone to the capillary fringe, may have increased the concentrations above the water table and could explain the presence of measured concentrations that are higher than those simulated.

During 2004, the simulated annual flux of nitrate to the saturated zone was 95 kg/ha, or 63% of the amount applied, and the simulated mean daily concentration of nitrate immediately above the water table was 17 mg/L. The mean nitrate concentration measured in samples from the 6.1 m lysimeter was 24 mg/L and from the shallowest

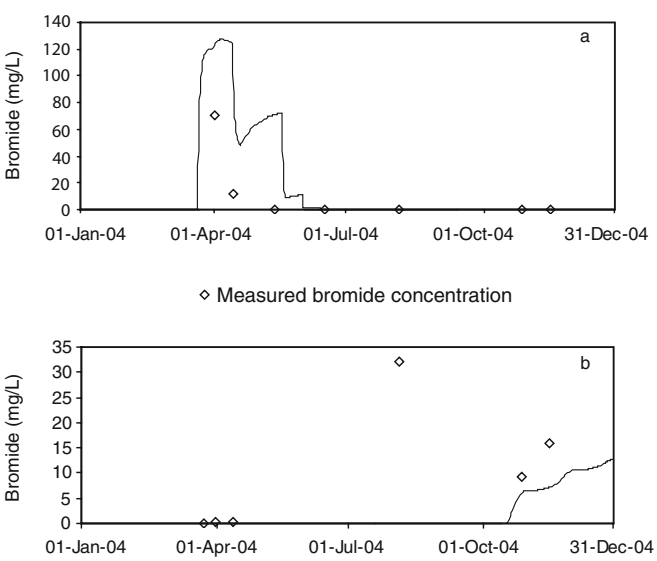

Fig. 3 Simulated and measured bromide concentrations at **a** 1.0 and **b** 4.6 m depths. The *curved line* is the simulated concentration and measured bromide concentrations are indicated by *diamonds*

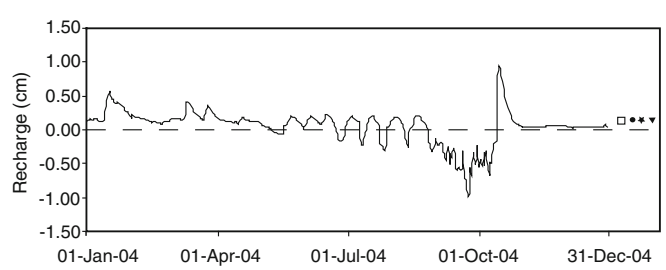

Fig. 4 Recharge to the water table for 2004 simulated with RZWQM, and estimated from other studies. The *curved line* is the simulated recharge from this study. *Negative values* indicate flow toward land surface. *Symbols* are from estimates of average recharge from this and other studies: *open square* Green et al. (2008a); *dot* Phillips et al. 2007; *star* Fisher and Healy (2008); *triangle* this study

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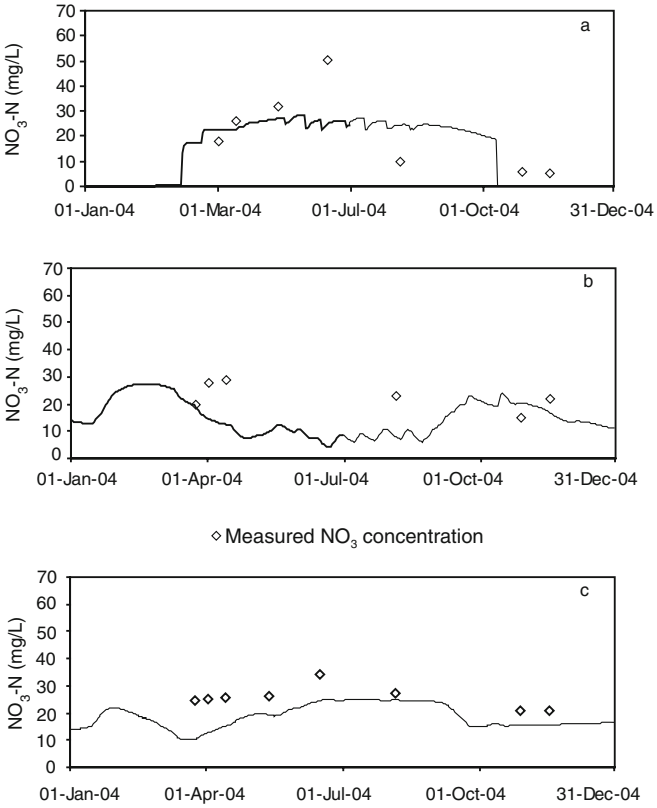

Fig. 5 Simulated and measured nitrate concentrations at **a** 1.0 m, **b** 4.6 m and **c** 6.1 m depths. The curved line is the simulated concentration and measured nitrate concentrations are indicated by *diamonds*

(water table) well was 27 mg/L. The simulations indicated that the processes most strongly affecting nitrate distribution in the subsurface were the application of inorganic fertilizer (140 kg/ha), nitrate from pre-amended irrigation and rain water (13 kg/ha), plant uptake (139 kg/ha), discharge to the water table (95 kg/ha), and mineralization (21 kg/ha). Other simulated processes that could potentially affect nitrate concentrations, including volatilization, nitrification, denitrification, fixation, and degradation of crop residue were determined to be insignificant at the study site. Nitrogen stored in various pools of the unsaturated zone provided the mass necessary to balance the system.

Saturated zone

Simulation of groundwater flow, interpretation of chemical analyses of samples from the groundwater transect wells, and age dating of these samples were used to characterize the transport of water and solutes along the transect. A local-scale, three-dimensional groundwater flow model of a 17 km^2 zone inclusive of the study area (Fig. 1; Phillips et al. 2007) was developed using MODFLOW (Harbaugh et al. 2000). The model was steady state, representing the year 2000, and included the aquifer system above the Corcoran Clay. Information for the lateral and lower boundary conditions was derived from a co-developed, steady-state (year 2000) regional-scale model of the surrounding area (Fig. 1; Phillips et al. 2007). The upper boundary of the local model was the water table, and the Merced River was a head-dependent boundary. The local model was finely discretized, with lateral dimensions of 40 m and 110 layers 0.5 m thick. Hydraulic conductivity was distributed by cell on the basis of sediment type, which was estimated using a geostatistical approach (Carle and Fogg 1996) that incorporates factors related to the depositional environments. Areal recharge was estimated on the basis of the water demand of crops or native vegetation (Burow et al. 2004), measured precipitation, and irrigation method. The model was calibrated to measured water levels in the groundwater transect wells (root mean square error of 0.08 m), and accurately simulated travel times estimated from concentrations of sulfur hexafluoride (a marker of groundwater age) measured in these wells (Phillips et al. 2007).

The calibrated local groundwater flow model suggests that 76% of total recharge was at the water table; two thirds of this was from irrigation. Groundwater inflow to the Merced River accounted for 65% of the total discharge; the reminder was through lateral boundaries (19%) and downward flow through the Corcoran Clay (16%). The resulting flow regime was primarily lateral, and downward, flow toward the Merced River over most of the model area, and upward flow in the immediate vicinity of the river, which is consistent with measured water levels (Phillips et al. 2007).

Concentrations of nitrate, specific conductance, dissolved oxygen concentrations, age of the groundwater in years, and flow directions in the groundwater transect are shown in Fig. 6. The youngest groundwater was detected in the shallow wells at the upper and middle sites on the groundwater transect because of downward flow driven by irrigation, whereas predominantly upward flow toward the Merced River near the lower end of the transect accounts for the older water at this site (Phillips et al. 2007). Specific conductance at the upper end of the groundwater transect was uniform with depth, suggesting similar sources

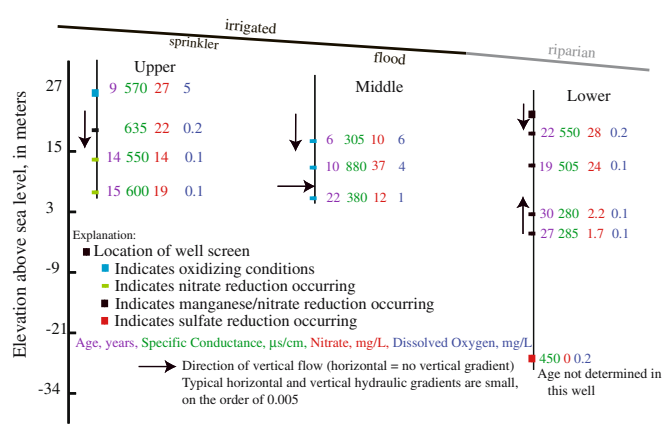

Fig. 6 Groundwater transect wells showing elevation relative to sea level, age of water in years, irrigation method, specific conductance, nitrate, dissolved oxygen, and general direction of groundwater flow

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of water up-gradient from the river. The middle site on the transect had a zone of higher conductance in-between zones of lower conductance above and below. It was not determined why that zone had a higher specific conductance, but it likely reflects variability in sources up-gradient from the site, which is in a direction oblique to the transect. Samples from most wells in the groundwater transect showed the effects of agricultural management practices on the basis of enrichment in calcium, sulfate, and chloride relative to the chemistry of the Merced River (Fig. 7). This enrichment is from soil amendments, which include calcium and sulfate applied in the form of gypsum, which shift the cation balance to the calcium and sulfate portions of the trilinear diagram. Specific conductances in the two shallow wells at the lower end of the groundwater transect were similar to those at the upper end of the transect, but conductances in the two deeper wells above the confining layer were the lowest in the transect because water sampled from those two wells was minimally impacted by agriculture as discussed below. Samples from those two wells were not enriched with respect to calcium and sulfate and are relatively old (27–30 years), suggesting they have had minimal impact from agriculture. These samples also had a lower specific conductance, lower nitrate concentrations, and no detectable pesticides, which are all consistent with the interpretation that they were minimally impacted by agriculture and represent what is most likely a natural geochemical signature. All other groundwater wells had detectable concentrations of pesticides, mostly simazine, metolachlor, degradates of metolachlor, and atrazine.

Samples collected from the groundwater transect wells in April, July, and October 2004 were analyzed for a number of constituents to help understand the transport and fate of nitrate along the transect. A key set of these constituents was the oxidation/reduction (redox) indicators because redox conditions largely limit the denitrification process. The measured concentrations of dissolved oxygen, nitrate, manganese (II), iron (II), and sulfide, when present, can be used to assign a redox state to the groundwater system. Concentrations of redox-sensitive constituents are controlled by a series of biogeochemical processes, referred to as "terminal electron-accepting processes" or TEAPs. TEAPs in aquifers proceed along a general path of beginning with the reduction of oxygen, followed by nitrate, manganese (IV), iron (III), and sulfate, with methanogenesis occurring in highly reducing environments (Chappelle et al. 1995). There is some overlap in the reduction of these constituents, and aquifer heterogeneity may facilitate the simultaneous operation of multiple TEAPs over short distances. However, nitrate reduction, dependent upon the presence of anaerobic, nitrate-reducing bacteria, will not occur if sufficient dissolved oxygen is present, while the presence of dissolved manganese (II) or dissolved iron (II) or sulfide indicates that nitrate reduction is possible if sufficient organic matter is present to support the bacterial population.

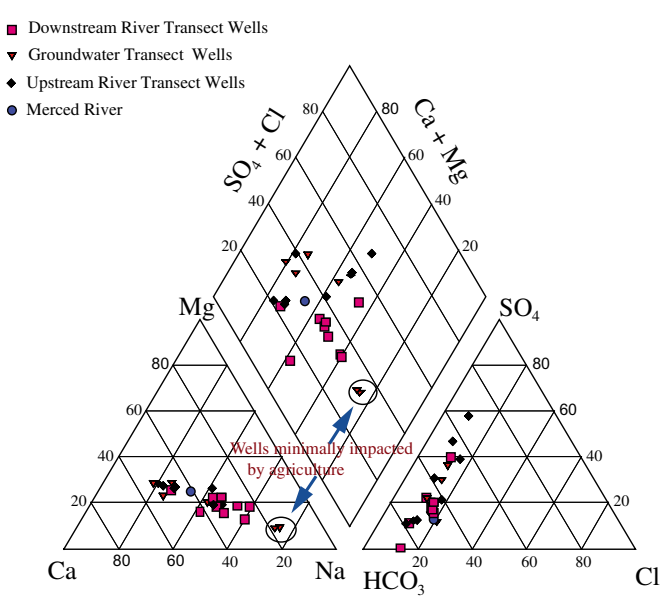

Fig. 7 Tri-linear plot of water samples from the groundwater transect wells, the Merced River, and the two sets of river transect wells

Threshold values of measured concentrations of these terminal electron acceptors can be used to categorize water as tending towards a particular stage of oxidation/reduction, although it is recognized that there will be overlap in most environments. For oxygen and nitrate, a threshold concentration of 0.5 mg/L was used, for manganese (II), 50 μg/L, and for iron (II), 100 μg/L. This analysis (Fig. 6) indicates that at the upper end of the groundwater transect, the shallow well has dissolved oxygen as the dominant terminal electron acceptor, with nitrate the dominant terminal electron acceptor at the deeper wells, except for one which has overlap with nitrate and manganese. The mid-transect wells all have dissolved oxygen as the dominant terminal electron acceptor, while the wells at the lower end of the groundwater transect, above the clay confining layer, have an overlap of nitrate and manganese as the dominant terminal electron acceptor. A different type of irrigation method is used in the immediate area of the mid-transect wells. Whereas sprinkler or drip irrigation is used upgradient, there is flood irrigation below the almond orchard to supply water for the corn crop. The flood irrigation may produce an excess of water recharging the site with saturated dissolved oxygen to account for the higher levels of dissolved oxygen in this part of the transect. Therefore, zones of denitrification are limited in the ground-transect to the deeper wells of the upper part of the transect and all wells in the lower part of the transect.

Concentrations of nitrate in groundwater measured during three sampling events did not vary much, and in many cases were above the drinking water standard of 10 mg/L as N (Fig. 6). Nitrate concentrations in the shallow well in an almond orchard at the upper end of the groundwater transect (mid-point of screened interval at 6.9 m below land surface) were 27–29 mg/L as N. Concentrations of nitrate about 7 m deeper in the system varied from 18 to 30 mg/L over the three sampling events.

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Concentrations of nitrate at the next deepest well (mid-point of screened interval at 20 m below land surface) varied from 14 to 22 mg/L. Finally, concentrations at the deepest well at the upper end of the transect (mid-point of screened interval at 26.8 m below land surface) were 19 mg/L with no variation over the three sampling events. Nitrate concentrations from the shallow well of the middle groundwater transect were 10 mg/L on each of the three sampling events, while those of the next deepest well varied between 36–38 mg/L and those of the deepest varied between 11–13 mg/L.

The wells at the lower end of the groundwater transect are on the landward side of a levee for the Merced River downgradient of the transition from an agricultural field planted in corn to native vegetation. Nitrate concentrations in the shallow well (mid-point of screened interval at 8.8 m below land surface) varied from 24–28 mg/L (Fig. 6). Nitrate concentrations 6.4 m deeper into the system varied from 22–24 mg/L. Nitrate concentrations in the next deepest well (mid-point of screened interval at 25 m below land surface were 2.2 mg/L, and the nitrate concentrations in the well screened just above the confining layer (mid-point of screened interval at 29 m below land surface) had nitrate concentrations of 1.7 mg/L. As discussed previously, the water sampled from the two deeper wells screened above the confining layer was minimally impacted by agriculture. The nitrate in that water may be from natural sources. Those wells did not have dissolved iron, although dissolved manganese was present. The well screened below the confining layer (mid-point of screened interval at 53 m below land surface) had no detectable nitrate, contained both dissolved iron and manganese, and also detectable sulfide. Because of the highly reducing conditions in that well, the denitrification process was complete.

Denitrification along the groundwater transect was further investigated by analysis of nitrogen gas (excess nitrogen present in the groundwater relative to amounts in recharge) and by an examination of the nitrogen and oxygen isotopes in nitrate. The isotope results are discussed later. Excess nitrogen gas in a groundwater sample is assumed to have been derived from denitrification (Heaton and Vogel 1981; Vogel et al. 1981). Therefore, a sum of the nitrate currently present and that attributable to excess nitrogen gas may be calculated. Although denitrification processes can also result in the production of other products such as ammonium or nitrite, all water samples had either very low to non-detectable concentrations. In most of the wells of the groundwater transect, the amount of nitrate was found to exceed the equivalent units of excess nitrogen in most of the wells of the groundwater transect (Fig. 8). At the upper end of the groundwater transect, denitrification was found to be minimal at the shallow well, consistent with high concentrations of dissolved oxygen. Denitrification generally increases with depth as reducing conditions prevail as evidenced by decreased dissolved oxygen, reduction of manganese, and increased concentrations of excess nitrogen gas. At the middle portion of the transect, there was very little evidence of any denitrification, which is consistent with the higher levels of dissolved oxygen. Denitrification was evident at the lower end of the transect near the riparian zone. The two shallow wells had about 25% of the total reconstructed nitrate present as excess nitrogen. The lower two wells above the confining layer were almost completely denitrified, with most of the total nitrate (measured nitrate plus calculated from excess nitrogen) present as nitrogen gas. As mentioned earlier, the geochemical signature of the groundwater sampled for these two wells indicated minimal impact or influence by agriculture, so the nitrate may be naturally occurring plus a small contribution from agriculture.

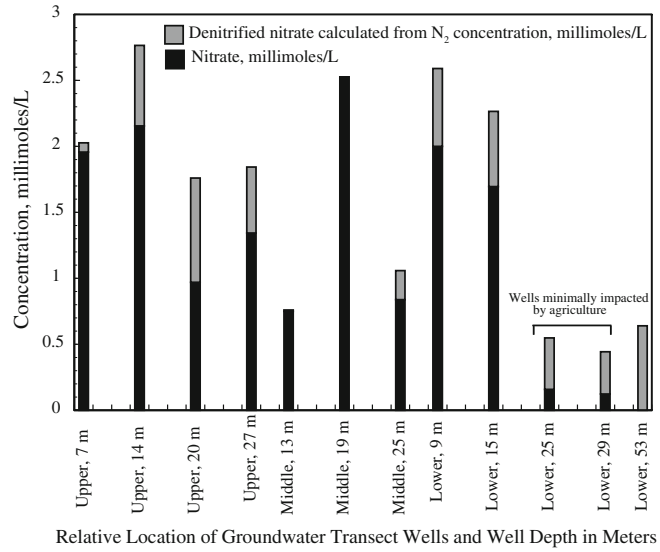

Fig. 8 Nitrate concentrations and reconstructed nitrate concentrations from water samples collected in the groundwater transect wells

Riparian zone and riverbed

The transport of water and chemicals through the riparian zone and riverbed into the Merced River was characterized through simulation of heat flow in the riverbed, particle tracking using the groundwater flow model, and interpretation of chemical analyses of samples from the riparian and riverbed wells along the upstream and downstream river transects.

One-dimensional models of heat and water flow were developed for sites on the downstream river transect to simulate groundwater interaction with the Merced River from March 2004 through October 2005 (Zamora 2006). The software used was the variably saturated two-dimensional heat flow model (VS2DH Healy and Ronan 1996) and its graphical interface VS2DI (Hsieh et al. 2000). Two instrumented sites were simulated, one in the middle of the river, and the other between that site and the right (north) bank.

The boundary conditions varied at 15-min intervals on the basis of measured temperature, and measured and

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estimated hydraulic head at the riverbed, and 2 m below the bed. High-precision measurements of river stage were unavailable for the upper boundary condition; therefore, the head at the riverbed was estimated by linear extrapolation of the hydraulic gradient between the deep and shallow river wells at each site. An arbitrary head of 0 was assigned at the riverbed (upper boundary) and the difference in head between that measured in the deep well and the extrapolated head at the riverbed was assigned to the lower boundary. Variability in head at the boundaries associated with changes in riverbed elevation and hydraulic conductivity were not accounted for. The temperatures assigned to the upper and lower boundaries were measured values above and 2 m below the riverbed, respectively.

The models were calibrated by varying the vertical hydraulic conductivity of the riverbed to best simulate the measured time-series of temperature at depths of 0.5 and 1 m. The vertical hydraulic conductivity of the riverbed was adjusted temporally, between 1 and 10 m/day, to account for increased conductivity from scouring of the bed during high stream-flow events and reduced conductivity from deposition of fines during low flows (Zamora 2006).

The average simulated vertical flux at the downstream river transect was upward at both sites, and varied from 2.2 cm/day (about 18 L/s per river km) at the mid-river site to 0.4 cm/day near the right bank (Zamora 2006). Although time-series data collected at the upstream transect were of insufficient duration to use this method, the data indicate that the average flux at this transect was upward, and greater than 2.2 cm/day.

The groundwater flow model described in the "saturated zone" section was used with MODPATH (Pollock 1994) to backtrack water particles from the riverbed to the water table in order to estimate travel times through the riparian zone and source areas of water discharging to the river. Simulated particles were placed on the bottom, northern, and southern faces of model cells representing the upper and lower river transects. The number of particles on each cell face was proportional to simulated flow across those faces. Each particle was tracked backward in time to the recharge location at the water table. Simulated particle paths for the upstream transect indicated that groundwater contributions from north and south of that reach were about equal, and that many of the particles from the north originated in the vicinity of the groundwater transect (Fig. 9). Simulated particle paths for the downstream transect, however, indicated that about 70% of the groundwater inflow to that reach was from south of the river, and that most particle paths from north of the river originated upgradient (north of) of the groundwater transect. Therefore, the following discussion of water chemistry will focus mainly on the upstream transect.

Indicators of TEAPs generally indicate more strongly reducing conditions along the river transects than along the groundwater transect. At the northern riparian well at the upstream transect, the shallow well chemistry was indicative of manganese reduction, and the deeper well of iron reducing conditions and possibly sulfate reduction. Water from the adjacent river well indicated manganese

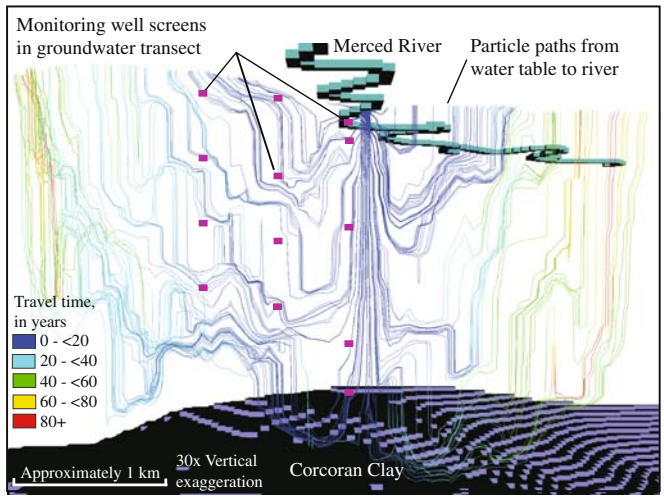

Fig. 9 Simulated paths of water particles backtracked from *Merced River* at the upstream transect to the water table (recharge location). View is eastward along the Merced River. Pathlines are *arc-shaped* in the horizontal dimension, *bowing westward* along the groundwater transect

reduction was occurring, and water from the bed in the center of the channel was indicative of iron reduction. Samples of water from river wells collected from near the southern bank were indicative of manganese reduction in the shallow well and oxygen reduction and slight manganese reduction in the deeper well. At the north bank riparian well of the downstream transect, shallow groundwater was indicative of oxygen and manganese reduction with strong iron reduction at the deeper well. Oxygen was the main terminal electron acceptor in water from the adjacent, northern river well. At the center of the channel, the shallow well was indicative of iron reducing conditions, but the deeper well was variable with iron reducing conditions during the June sampling and oxygen and manganese reduction during the March and November samplings. Water from the shallow river well near the south bank was indicative of iron reducing conditions, but of oxygen and manganese in the deeper well. Finally, water from the shallow riparian well on the south bank of the downstream transect was indicative of iron reducing conditions, and manganese reducing conditions in the deeper well. A further examination of the redox-active chemical species, oxygen, iron, and manganese, provides additional information on the redox conditions in the groundwater beneath the riverbed. River wells are generally low in dissolved oxygen (<1 mg/L), except for values of 1.8 mg/L in the shallow north bank-river well (T4-7B) and a value of 5.8 mg/L in the deeper north bank-river well (T4-7C) in March. Since specific conductance and head measurements are strongly indicative of hyporheic exchange (particularly at well T4-5B and T4-5C in the center of the river), these low dissolved oxygen values indicate that aerobic microbial respiration must be sufficiently rapid to generate the observed oxygen depletion. Low dissolved oxygen concentrations at well T4-5B (0.5 m depth) were accompanied by elevated concen-

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trations of dissolved manganese and iron, consistent with a shift in the terminal electron acceptor for microbial respiration. Dissolved metal concentrations at well T4-5B were higher in June than in March for both manganese (5,500 vs. 1,200 μg/L) and iron (7,500 vs. 3,000 μg/L), consistent with the expected response of microbial respiration rates to temperature.

Reconstructed nitrate concentrations from water and excess nitrogen for samples from the upstream transect across the Merced River are shown in Fig. 10. Some of the highest concentrations of nitrate, and total reconstructed nitrate, were measured in samples collected from the riparian well on the north bank of the river at the upstream transect (T4-9A). Denitrification is occurring at that well with about one third of the total reconstructed nitrate occurred as excess nitrogen. This well was screened about 0.5 m below the level of the riverbed. A sample from the deeper riparian well at this site (T4-9B) indicates more denitrification, with most of the total reconstructed nitrate present as excess nitrogen. Samples from each of these two wells had a specific conductance of 450–500 μS/cm, indicating that the water sampled was groundwater, and not substantially influenced by river water (specific conductance ~100 μS/cm). The specific conductance of samples from the lower end of the groundwater transect were essentially the same as these values (505–550 μS/cm). Water samples collected within the riverbed adjacent to the riparian-zone site discussed above (north bank, upstream transect) had some nitrate remaining in the deeper well (T4-7C, 3 m below river bottom), but no nitrate and mostly excess nitrogen present in the shallow well (T4-7B, 0.5 m below river bottom). The water collected from these wells also had specific conductance comparable to groundwater samples from the groundwater transect (400–700 μS/cm). Only excess nitrogen from denitrification was present at the remaining sites sampled along the upstream transect. Simulated travel times of water from the edge of the groundwater transect to the river are on the order of 2 months to 6 years. These measurements of nitrate and excess nitrogen gas provide evidence for nitrate inputs associated with high nitrate groundwater and for denitrification in the wells in the riparian zone (T4-9A and T4-9B) and north bank of the river (T4-7B and T4-7C). These wells would be expected to be uniformly low in dissolved manganese and iron due to the inhibition of microbial manganese and iron reduction by nitrate. As expected, low concentrations of both dissolved metals were observed in the north bank river wells (T4-7B and C) in June. The concentration of dissolved iron in well T4-7B was also low in March, but the concentration of dissolved manganese was elevated (900 μg/L). The patterns in the occurrence of nitrate and dissolved metals appear to reflect variations in the input of groundwater and the extent of hyporheic exchange across the river transect as well as the influence of in situ microbial processes. It is clear, however, that the conditions in the riparian and riverbed wells are substantially more reducing than in the upland wells located along the groundwater transect. In addition, because of the relatively low head gradients along the river transects, water residence time is sufficiently long to result in relatively high rates of denitrification (Puckett et al. 2008).

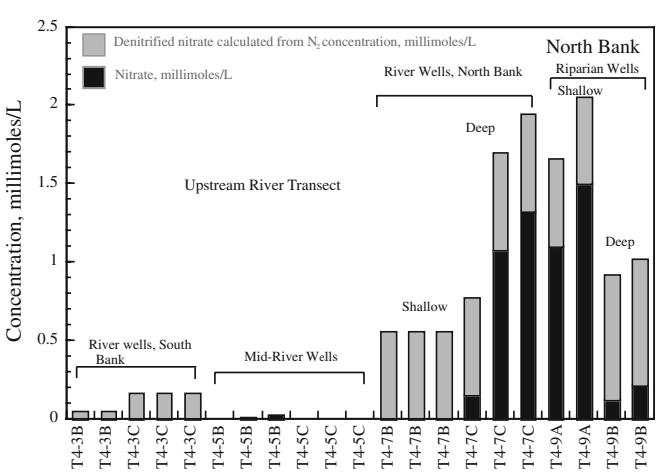

Fig. 10 Nitrate concentrations and reconstructed nitrate concentrations in wells of the upstream Merced River well transect

There are notable temporal variations in the sources of the water sampled. Water from well T4-5B, at 0.5 m below the river bottom, was always river water (specific conductance near 100 μS/cm, with low nitrate), whereas the water from T4-5C, at 3 m below the river bottom, was primarily river water during the March and June sampling, but was groundwater during the October sampling, indicating a dynamic flow regime. The shallow well at 0.5 m under the river bottom adjacent to the south bank of the river (T4-3B) was indicative of primarily river water during the March and June samplings, and groundwater during the October sampling. The deeper well (T4-3C), at 1.5 m below the riverbed, was primarily river water during the March sampling, a mixture in June, and primarily groundwater during the October sampling.

Nitrogen and oxygen isotopes in nitrate

Isotopes of nitrogen and oxygen in nitrate can be used to help quantify the relative degree of denitrification in water samples and to suggest sources of the nitrogen. The ratios of heavy isotopes of nitrogen (^{15}N) and oxygen (^{18}O) to their lighter isotopes increase with denitrification (Kendall 1998). A plot of ^{15}N and ^{18}O isotope ratios in nitrate from the rain, unsaturated zone, and the groundwater and river transects is shown in Fig. 11. The value of $\delta^{18}O$ in rain is 70‰ and the value of $\delta^{15}N$ was near zero. The rain was greatly enriched in the heavier isotope of oxygen relative to the other samples. If rain were a significant source of nitrate, it would be expected that the nitrate in the unsaturated zone water would be isotopically similar to the nitrate in rainwater, which it was not. Nitrogen and oxygen in nitrate from unsaturated zone samples had lower $\delta^{15}N$ and $\delta^{18}O$ values, and were more similar to what has been measured in chemical fertilizer. Chemical nitrogen fertilizers made from atmospheric nitrogen have a $\delta^{15}N$ value of 0–3‰ (Kendall 1998). The isotopic

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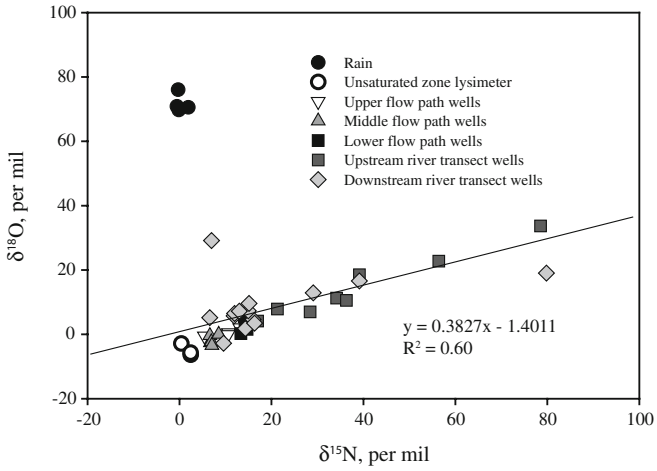

Fig. 11 Graph showing $\delta^{18}O$ and $\delta^{15}N$ in nitrate for rain, lysimeters, groundwater transect, and the upstream and downstream Merced River well transects

distribution of nitrate in the unsaturated zone is not unexpected because of the large amount of chemical fertilizer added to the orchard. There was a small increase in $\delta^{15}N$ and $\delta^{18}O$ values from the upper end to lower end of the groundwater transect, indicating that denitrification is occurring in the aquifer system up-gradient of the riparian zone (Fig. 11). However, denitrification had occurred to a greater degree within the riparian zone as indicated by a large increase in $\delta^{15}N$ and $\delta^{18}O$ values in nitrate in water sampled adjacent to and within the streambed. The slope of the line in Fig. 11 was calculated for all hydrologic compartments except the rain. The slope is 0.38, and the regression coefficient indicates that only 60% of the variability is accounted for. As mentioned previously, the sources of water to the upper and lower river transects is different, with the water of the upper transect originating mainly from the groundwater transect region. A plot of $\delta^{15}N$ and $\delta^{18}O$ for the unsaturated zone, groundwater transect wells and riparian and river wells (upper river transect only) is shown in Fig. 12. The slope of the line in Fig. 12 indicates that the ratio of $\delta^{15}N$ to $\delta^{18}O$ is very near 2:1 (slope=0.4967, r^2=0.96), which has been reported in other studies as being indicative of microbial induced denitrification (Bottcher et al. 1990; Aravena and Robertson 1998; Mengis et al. 1999). At sites in the riparian zone or riverbed where significant denitrification had occurred, the rates of denitrification are apparently faster than within the groundwater transect area, or geochemical conditions are more favorable. The geochemical condition of the water in the riparian zone and under the river tends to be more reducing than within the groundwater transect area. Alternatively, or in addition, more organic matter to support a bacterial population may be present within the riparian area or under the riverbed.

Water exchange across the riverbed

These spatial and temporal differences in nitrate concentrations and relative amounts of excess nitrogen associated with samples from the river transects, as well as their redox state, are probably attributable to transient flow conditions. Upward flow introduces groundwater to the river with generally high nitrate concentrations and low dissolved oxygen, whereas downward flow introduces river water low in nitrate (about 1 mg/L) and saturated with dissolved oxygen. Although model simulations (Phillips et al. 2007; Zamora 2006) and field data indicate that local groundwater predominantly discharges to the river, field data also indicate seasonal or higher-frequency reversals of flow at some sites. Flow directions are controlled by a combination of riverbed flow dynamics and changes in river stage, groundwater recharge, and groundwater discharge, which are, in turn, influenced by precipitation, irrigation, canal spills, reservoir operations, and groundwater pumping in the vicinity of the study area. Direct measurements of groundwater levels and chemistry were made at the river transects under different flow conditions. Measurements made in 2004 during April, early in the irrigation season, and October, after the irrigation season, for the upstream transect are shown in Fig. 13. Measurements made at the same transect in October of 2004, at the end of the irrigation season are shown in Fig. 14. Flow conditions and water chemistry clearly are variable in space and time, and although the modeling and field data indicated an overall upward flux of groundwater discharging to the Merced River, the observed variability across the channel, along with differences in denitrification rates across the channel, makes it difficult to quantify the amount of nitrate from groundwater entering the Merced River.

Conclusions

The combined results of flow and chemical analyses provide strong evidence for the processes controlling the transport and fate of nitrate in the study area. The flow analyses included multiple estimates of recharge at the

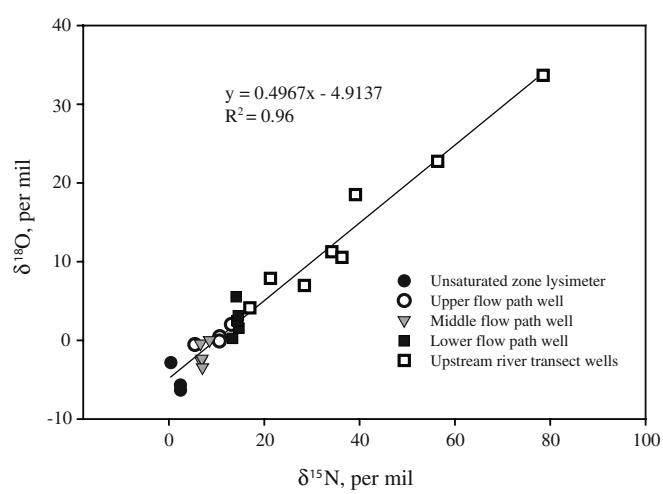

Fig. 12 Graph showing $\delta^{18}O$ and $\delta^{15}N$ in nitrate for lysimeters, groundwater, and the upstream Merced River well transect

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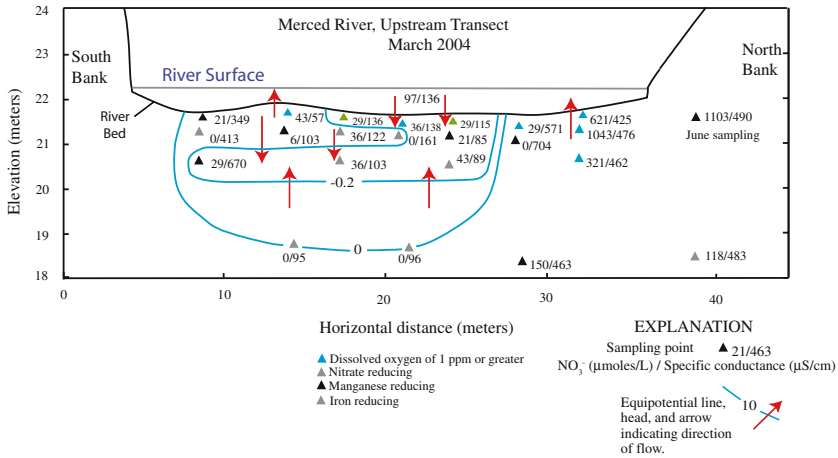

Fig. 13 Concentrations of NO_3 (mmol/L), specific conductance (µS/cm), and equipotential lines and flow directions at the upstream Merced River well transect, March 2004. Equipotential lines and flow directions are based on potentiometric heads (cm) measured at the time of sampling

water table and discharge to the Merced River, and comparison of simulated travel times with those estimated from concentrations of sulfur hexafluoride.

Water-table recharge was estimated for this study through simulation of the unsaturated zone at one site using the RZWQM, and areally through modification of a crop-based water budget (Burow and others 2004) using the study-area-specific distribution of irrigation methods. Related studies applied different methods to estimate recharge using data collected from the study area during this study. The average recharge-rate estimate from those various methods was 0.44 m/year with a range of 0.06 m/year across the methods.

The unsaturated zone at the top of the groundwater transect was relatively thin (6.5 m), and modeled and measured nitrate concentrations in lysimeters, along with a bromide tracer test, indicated that up to 63% of the yearly applied nitrate was transported to the water table during a typical growing season.

Groundwater discharge to the Merced River was estimated using the local groundwater flow model, and simulation of heat flow at two sites on the downstream river transect. Simulated discharge to the river in the cell of the local groundwater flow model that best represents the upstream river transect was about 4 cm/day (about 18 L/s per river km). Two sites on the downstream river transect were not adequate for estimating discharge to the river given the variability observed in the field, but results from heat flow simulations of the downstream transect and data from the upstream transect suggest that discharge at the upstream transect likely exceeded 2.2 cm/day. Although these discharge estimates are not as tightly constrained as are those for recharge, they are in general agreement.

Rates of flow through the aquifer system from the recharge location to the Merced River determine the residence time of water and associated solutes in the system, which can be an important control on denitrification potential. Simulated travel times from the water table to the well

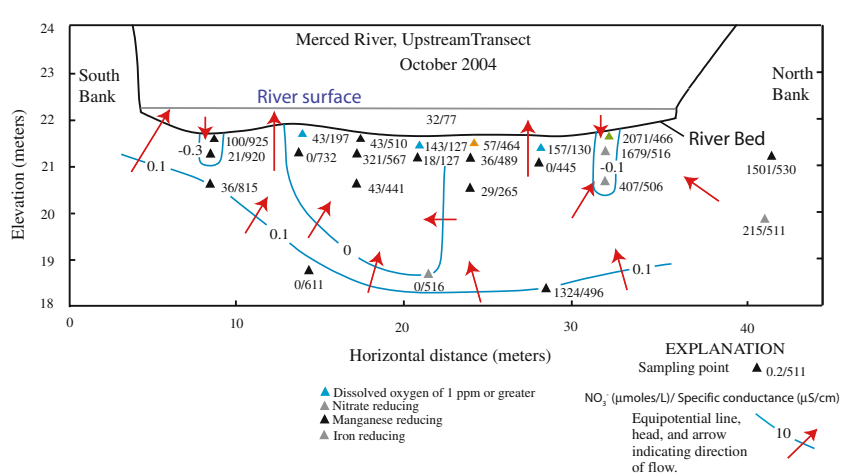

Fig. 14 Concentrations of NO_3^- (mmol/L), specific conductance (µS/cm), and equipotential lines and flow directions at the upstream Merced River well transect in October 2004. Equipotential lines and flow directions are based on potentiometric heads (cm) measured at the time of sampling

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screens along the groundwater transect compared well to those derived from concentrations of sulfur hexafluoride, suggesting that residence times are well estimated. The median simulated residence time for water discharging to the Merced River that originated north of the river was about 15 years, with a range of about <1 to 150 years.

Nitrate from fertilizer applications was detected in groundwater at well depths of up to 27 m below land surface below an almond orchard, and along a 1-km groundwater transect downgradient from the orchard. Analysis of stable isotopes of N and O in nitrate indicated that a principle source of this nitrate was chemical fertilizer applied to the orchard and cornfield. Mildly reducing conditions within the shallow aquifer resulted in a small amount of denitrification, but concentrations of nitrate above the federal drinking water standard were measured in most wells.

Subsequent transport of nitrate across a riparian zone and to a stream/groundwater interface resulted in higher levels of denitrification, especially under the riverbed because of changes in redox conditions that favored denitrification. Although some nitrate discharged into the Merced River along the banks, discharging groundwater near the center of the river channel and across to the adjacent bank contained either no nitrate or only excess nitrogen gas from denitrification.

Simulated transport times of water and nitrate generally ranged from a few years to three decades, with deeper flowpaths on the order of century or more along the 1-km groundwater transect. The transport time from the edge of the riparian zone to the bed of the Merced River ranged from a few months to 6 years. Direction of groundwater flow greatly influenced groundwater age, as the downward gradients found below the irrigated agricultural fields resulted in the presence of younger water. In turn, groundwater flow greatly influenced the amount of nitrate discharging into the Merced River. Older groundwater from deeper flow paths (older water) had either no nitrate because of sufficient time for denitrification to occur, or had less nitrate initially. Analysis of N and O isotopes in nitrate molecules suggest that, when present, nitrate discharging into the riverbed was part of an original assemblage that was subject to extensive denitrification.

Detections of pesticides of simazine and other herbicides or degradates in groundwater under the Merced River suggest that some groundwater with an age of 50 years or younger is present. This corresponds with the initial use of those pesticides in this location for agriculture.

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