

Regional Nitrate and Pesticide Trends in Ground Water in the Eastern San Joaquin Valley, California

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Protection of ground water for present and future use requires monitoring and understanding of the mechanisms controlling long-term quality of ground water. In this study, spatial and temporal trends in concentrations of nitrate and pesticides in ground water in the eastern San Joaquin Valley, California, were evaluated to determine the long-term effects of agricultural and urban development on regional ground-water quality. Trends in concentrations of nitrate, the nematocide 1,2-dibromo-3-chloropropane, and the herbicide simazine during the last two decades are generally consistent with known nitrogen fertilizer and pesticide use and with the position of the well networks in the regional ground-water flow system. Concentrations of nitrate and pesticides are higher in the shallow part of the aquifer system where domestic wells are typically screened, whereas concentrations are lower in the deep part of the aquifer system where public-supply wells are typically screened. Attenuation processes do not seem to significantly affect concentrations. Historical data indicate that concentrations of nitrate have increased since the 1950s in the shallow and deep parts of the aquifer system. Concentrations of nitrate and detection of pesticides in the deep part of the aquifer system will likely increase as the proportion of highly affected water contributed to these wells increases with time. Because of the time of travel between the water table and the deep part of the aquifer system, current concentrations in public-supply wells likely reflect the effects of 40- to 50-yr-old management practices.

IN 2000, ground water provided 37% of the public drinking water supplies used by 242 million people in the USA (Hutson et al., 2004). Dependence on ground water for public supply has increased fivefold over the last 50 yr, causing increased concern about the sustainability of the quality of water pumped by public-supply wells. Ground-water withdrawals from the Central Valley Principal aquifer are the second largest in the USA, accounting for 13% of total withdrawals (Maupin and Barber, 2005). Irrigation is the dominant water use, and most of the population and ground-water use in the Central Valley is in the eastern San Joaquin Valley, where intensive farming and rapid population growth are expected to increase reliance on ground water.

Widespread occurrence of nitrate and pesticides in ground water at concentrations of concern affects rural and public drinking water supplies in the eastern San Joaquin Valley (Schmidt, 1972; Miller and Smith, 1976; Nightingale and Bianchi, 1974; Schmidt, 1986, 1987; Burow et al., 1998a; Harter et al., 1998; Loague et al., 1998a, 1998b; Loague and Abrams, 1999). In shallow ground water, concentrations of nitrate exceeded the U.S. Environmental Protection Agency's maximum contaminant level (MCL) of 10 mg L⁻¹ in 24% of wells sampled during 1993–95 (Dubrovsky et al., 1998), and the Central Valley is one of the top three regions in the state in the number of public drinking water wells in which the MCL for nitrate is exceeded (California State Water Resources Control Board, 2002b). Elevated concentrations of nitrate in ground water in the eastern San Joaquin Valley are expected to persist over the long term, owing to continued anthropogenic nitrogen inputs and generally oxic geochemical conditions. Pesticides were detected in 61% of wells sampled during 1993–95 in shallow ground water in the eastern San Joaquin Valley. Two of the most frequently detected pesticides, simazine and 1,2-dibromo-3-chloropropane (DBCP), were detected in 35 and 24% of the wells, respectively (Dubrovsky et al., 1998). Although concentrations of simazine were generally low (<1 µg L⁻¹), DBCP persists in ground water in this region at concentrations above the MCL of 0.2 µg L⁻¹, posing a threat to drinking water supplies more than 25 yr after it was banned from use (California State Water Resources Control Board, 2002a).

Protection of ground water for present and future use requires monitoring and understanding of the mechanisms controlling long-term quality of ground water. Some studies have analyzed data on temporal trends in concentration of nitrate and pesticides in the eastern San Joaquin Valley (Nightingale, 1970; Schmidt, 1972; California State University Fresno Foundation, 1994; Kloos, 1996; Burow et al.,

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Abbreviations: USGS, United States Geological Survey; NAWQA, National Water-Quality Assessment; MCL, U.S. Environmental Protection Agency Maximum Contaminant Level; DBCP, 1,2-dibromo-3-chloropropane; DHS, California Department of Health Services.

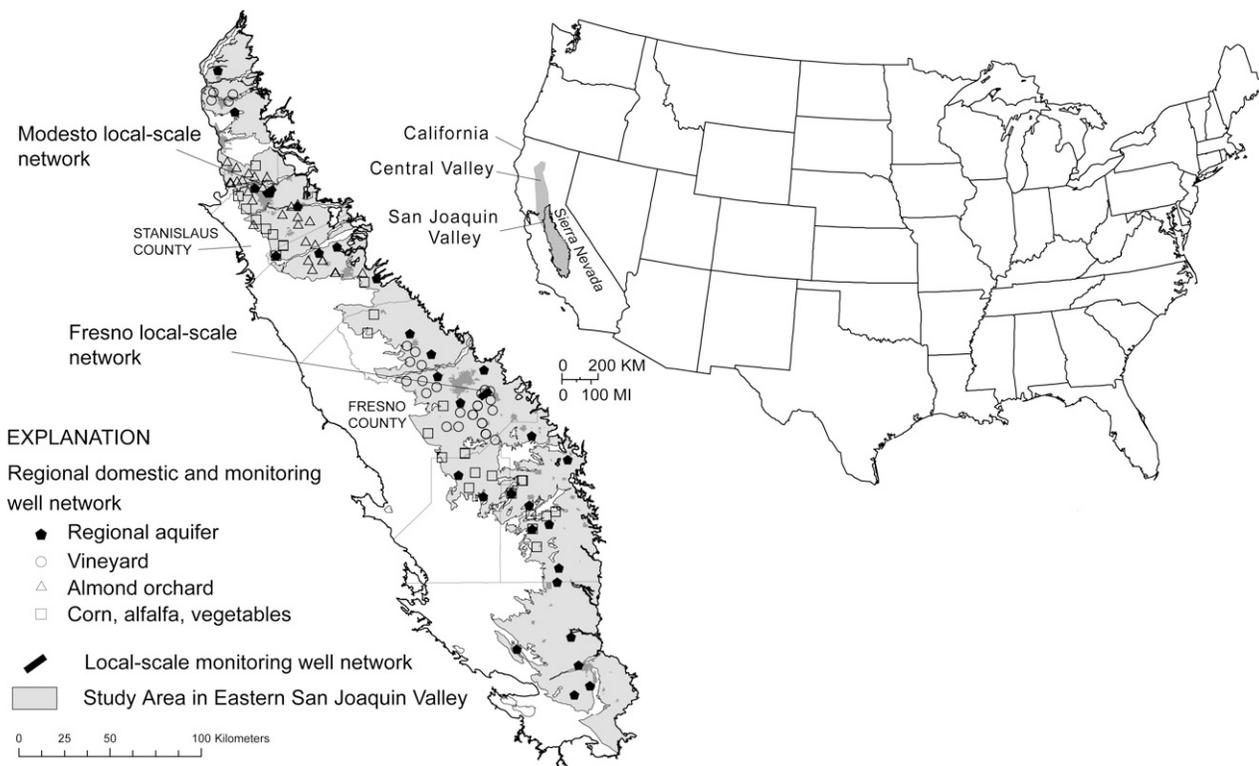


Fig. 1. Study area and U.S. Geological Survey National Water-Quality Assessment program networks in the eastern San Joaquin Valley, California.

1998b; Burow et al., 1999). However, few wells have been sampled over time spans long enough to assess the relation between regional management practices and potential long-term degradation of water quality in the eastern San Joaquin Valley aquifer system.

To assess spatial and temporal trends in ground-water quality in the eastern San Joaquin Valley and to evaluate the long-term effects of development on ground-water quality in this region, concentrations of nitrate, DBCP, and simazine in ground water were evaluated at multiple spatial scales. At the local scale, mean ground-water ages from analysis of age-dating tracers were combined with concentrations of nitrate and pesticides to reconstruct inputs through time and to compare with estimated applications. Data from regional-scale networks were evaluated to determine whether shallow ground water containing nitrate, DBCP, and/or simazine is migrating to deeper parts of the aquifer system. The local- and regional-scale networks were designed and sampled as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program. Nitrate data from the NAWQA regional-scale networks were then combined with historical data from shallow and deep parts of the aquifer system to evaluate changes in concentrations of nitrate since the 1950s and to determine the response of the regional aquifer to long-term management practices. Predicting the long-term fate of nitrate and pesticides in ground water in this region is difficult owing to intensive ground-water pumping, mixed sources of recharge water, and complex flow paths through heterogeneous alluvial fan sediments. However, understanding the behavior of nonpoint source constituents such as nitrate and pesticides can assist in characterizing dominant aquifer processes controlling the fate

and transport of a wide range of possible chemicals of potential concern in the subsurface.

Materials and Methods

Study Area

The San Joaquin Valley, a 26,000-km² level depression, comprises the southern two thirds of the Central Valley of California (Fig. 1), a large, northwest-trending, asymmetrical structural trough filled with marine and continental sediments up to 10 km thick (Page, 1986). The study area is in the eastern San Joaquin Valley, where the primary aquifer comprises a series of overlapping, stacked alluvial fan sequences deposited by streams draining the Sierra Nevada. The unconsolidated to semi-consolidated alluvial fan sediments were derived primarily from the weathering of granitic intrusive rocks of the Sierra Nevada and have a low organic content. Near the axis of the valley, the Sierra Nevada sediments interfinger with the sediments derived from the Coast Ranges.

The primary aquifer in the study area is unconfined, although sand and gravel layers are locally confined by discontinuous fine-grained layers. A confined aquifer also exists beneath the Corcoran Clay, an areally extensive diatomaceous lake clay (Frink and Kues, 1954) that underlies the distal portions of the alluvial fans of the eastern San Joaquin Valley. All of the wells sampled by the NAWQA program were screened at depths above or outside the areal extent of the Corcoran Clay. Some of the wells in the historical data network may be screened across or below the Corcoran Clay, although the confined aquifer below the Corcoran Clay is generally more saline, and it is expected that few wells in the dataset represent the confined part of the aquifer.

The movement of water and solutes in the eastern San Joaquin Valley aquifer system is complex due to the heterogeneous distribution of alluvial fan sediments and the modification of the natural hydrologic system. Under natural conditions, recharge occurred at the mountain fronts and ground water moved laterally until it discharged at streams near the center of the basin (Bertoldi et al., 1991). However, diversion of surface water from streams and development of ground-water supplies significantly altered the natural flow system. Development of the ground-water basin began in the late 1800s. Ground-water pumping increased slowly until the 1940s and 1950s, when pumping increased significantly (Bertoldi et al., 1991). Irrigation water (supplied from both surface and ground water) became the primary form of ground-water recharge, and irrigation pumpage became the primary form of ground-water discharge (Davis et al., 1959), causing water and solutes to move vertically downward through the system.

Ground-water quality in the study area is influenced by recharge from irrigated fields and by regional ground-water flow from the upper parts of the alluvial fans toward the axial trough (Davis et al., 1959; Bertoldi et al., 1991). Ground water in the eastern San Joaquin Valley is largely oxic, although geochemically reduced conditions commonly occur in discharge zones along the axial trough or near streams where long flow paths terminate and residence time and organic matter increase (Gronberg et al., 1998).

Abundant water, combined with the long growing season, results in an exceptionally productive agricultural setting in the San Joaquin Valley, where in 1987 about half of the total value of agricultural production in California was generated (Gronberg et al., 1998). Major products include livestock and livestock products, fruit and nuts, cotton, vegetables, hay and grains, and other crops. The distribution of crops generally reflects the distribution of soil texture and chemistry. In the eastern San Joaquin Valley, grapes and almonds, which are intolerant of some trace elements, are typically grown in the coarse-grained, upper and middle parts of the alluvial fans, whereas corn, alfalfa, and vegetables are typically grown in the distal parts of the fans near the basin region where sediments are more variable and commonly more fine grained (Burow et al., 1998a).

Well Networks

Data for analysis were compiled from three sources: the USGS National Water Information System database, the U.S. Environmental Protection Agency Storage and Retrieval database, and the California Department of Health Services (DHS) database. The dataset was grouped by network into three components that vary with respect to the spatial distribution of wells, well depth, and period of record. Two local-scale networks of monitoring wells near Fresno and Modesto (Fig. 1) designed as part of the NAWQA program consist of 20 monitoring wells in a vineyard land-use setting near Fresno (Burow et al., 1999) and 23 monitoring wells in the zone of contribution of a public-supply well in Modesto (Jurgens et al., unpublished data, 2007). The local-scale networks were installed along the approximate horizontal ground-water flow direction and are designed to characterize the spatial and temporal distribution of water quality in relation to ground-water flow.

Five regional-scale well networks were evaluated in this study: three agricultural land-use networks, one regional aquifer network, and one historical data network. The agricultural land-use networks consist of 75 domestic and 15 monitoring wells located in areas representing vineyards, almond orchards, and a crop grouping of corn, alfalfa, and vegetables (Fig. 1). Together, these three crop groups represent 47% of the agricultural land and account for 67% of the total ground-water use in the eastern San Joaquin Valley (Burow et al., 1998a) (Table 1). The agricultural land-use networks were designed and sampled as part of the NAWQA program to characterize shallow ground-water quality in each agricultural setting. The 25 domestic wells are spatially distributed throughout each agricultural land-use setting; in addition, the 15 monitoring wells screened near the water table were co-located near five domestic wells from each network. The regional aquifer network consists of 30 domestic wells located throughout the eastern San Joaquin Valley without regard to land-use setting. This network was designed and sampled as part of the NAWQA program to provide a broad assessment of water-quality conditions, and likely reflects the influence of multiple land-use settings (Burow et al., 1998b). Because domestic wells are typically screened in the shallow part of the aquifer, this network generally represents shallow ground-water quality. The historical data network (Table 1; Fig. 2) contains analyses of nitrate from 1437 domestic, irrigation, public-supply, and other well types from the USGS National Water Information System database; 3216 domestic, irrigation, public-supply, and other well types from the U.S. Environmental Protection Agency Storage and Retrieval database; and 1689 public-supply wells from the DHS database. Median concentrations of nitrate were calculated for each well for each decade from 1950 through 2004, and the dataset was grouped into shallow and deep well depths. Because well depths in the dataset ranged from about 15 m to more than 1000 m, and the depth to water ranged from 1 m to nearly 200 m, well depths were grouped according to depth below water table to group wells with similar distances from the water table to the well screens (as a proxy for travel times). Well depths ≤ 36 m below the water table were included in the shallow dataset, and wells >36 m were included in the deep dataset. The depth of 36 m was selected because nitrate concentrations were significantly lower in domestic wells screened more than 36 m below the water table. Public-supply wells from the DHS database did not contain well depth information; however, public-supply wells are typically screened in the deep parts of the aquifer system, so these wells were included in the deep dataset.

To maximize the use of available water quality data, this analysis combines results from monitoring, domestic, irrigation, public supply, and other well types. Because of differences in screen lengths and pumping rates, water quality results might be expected to be different among the well types. Water quality samples from public-supply and irrigation wells with high pumping rates and long-screened intervals integrate over a larger part of the aquifer, representing a wide range of ages and a large contributing recharge area. Domestic wells are pumped at much lower rates, and monitoring wells are not pumped at all; therefore, water quality samples from these wells are more discrete, representing a narrower range of ages and a localized contributing recharge area.

Table 1. Characteristics of well networks used in data analysis in the eastern San Joaquin Valley, California.

Well networks	Years sampled	Median well depth below water table (meters)	Well type					Total
			Monitoring	Domestic	Public-supply	Irrigation	Other	
<u>Local-scale monitoring well networks</u>								
Fresno local study	1994–95	varied	20	0	0	0	0	20
	2003	varied	20	0	0	0	0	20
Modesto local study	2003–05	varied	23	0	1	0	0	24
<u>Regional domestic and monitoring well networks</u>								
Regional aquifer	1986–87	20	0	23	0	0	0	23
	1995		0	30†	0	0	0	30
	2002		0	30†	0	0	0	30
Vineyard	1993–94	23	5	20	0	0	0	25
	2001		5	25	0	0	0	30
Almond orchard	1994	28	5	20	0	0	0	25
	2001		5	25	0	0	0	30
Corn, alfalfa, vegetable	1995	29	5	20†	0	0	0	25
	2002		5	25†	0	0	0	30
<u>Regional historical data network</u>								
Historic shallow	1950–59	20	0	55	55	77	49	236
	1960–69	23	0	67	76	101	40	284
	1970–79	24	0	147	99	68	28	342
	1980–89	26	0	70	74	28	11	183
	1990–99	23	0	58	0	0	0	58
	2000–04	25	0	68	17	0	0	85
Historic deep	1950–59	130	0	123	98	494	299	1014
	1960–69	90	0	94	156	391	130	771
	1970–79	100	0	88	375	255	142	860
	1980–89	100	0	71	355	102	141	669
	1990–99	no data	0	31	1689	0	0	1720
	2000–04	65	0	35	83	0	0	118

† Two wells were shared between the regional aquifer and corn, alfalfa, vegetable agricultural land-use networks in 1995 and 2002.

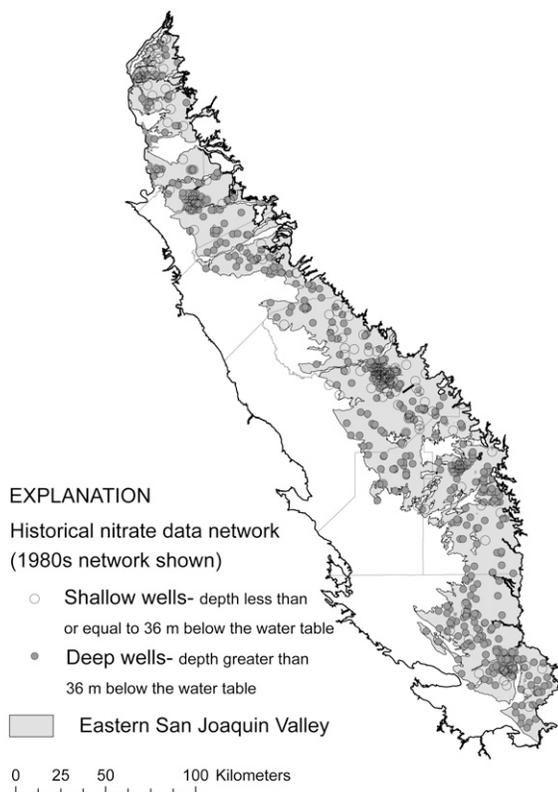


Fig. 2. Historical nitrate data network in the eastern San Joaquin Valley, California. Well locations shown for 1980s dataset.

In spite of inherent differences among the well types, the results are consistent among the different well networks. Because of the large number of densely spaced irrigation and public supply wells, the age of ground water in the aquifer is vertically stratified. Well depth is likely an overriding factor in characterizing ground-water quality regardless of well type.

Sample Collecting and Data Analysis Methods

Samples were collected from wells in the NAWQA local- and regional-scale networks following a nationally consistent set of protocols (Koterba et al., 1995) and were analyzed at the USGS National Water Quality Laboratory. Nitrate samples were filtered using a 0.45- μm pleated capsule filter and analyzed using standard methods of analysis (Fishman and Friedman, 1985). The DBCP samples were collected by filling 40-mL vials with unfiltered water and analyzed by liquid/liquid extraction followed by gas chromatography/electron-capture detection (Fishman, 1993). The detection limit for DBCP using this method was 0.03 $\mu\text{g L}^{-1}$. Simazine samples were filtered using a 0.7- μm baked glass-fiber filter and analyzed by C-18 solid-phase extraction and capillary column gas chromatography mass spectrometry (Zaugg et al., 1995). Although changes in laboratory recovery during the last two decades may influence simazine detection frequencies (Bexfield, 2008), the interpreted results presented in this manuscript were unaffected by recovery corrections.

Concentrations below the laboratory reporting limit and above the long-term method detection limit were reported as

estimated, and concentrations below the long-term method detection limit were reported as nondetects (Childress et al., 1999; Bexfield, 2008). Rank-based nonparametric methods were used for statistical analysis. The significance level (or α) used for hypothesis testing was 5% ($\alpha = 0.05$). The Kruskal–Wallis test was used to test differences among groups of data (Conover, 1980). If the Kruskal–Wallis test indicated a significant difference among the groups, the multiple-stage Kruskal–Wallis test was used (Helsel and Hirsch, 2002) to determine whether a significant difference exists between successive groups. The significance level used for the multiple-stage Kruskal–Wallis test was $\alpha_p = 0.02$. Tukey’s multiple comparison test was also performed on the ranks of the data in the case of unequal sample sizes among groups (Helsel and Hirsch, 2002); however, the results were unaffected by the use of different methods. The signed rank test was used to evaluate the differences in matched pairs of data, and the chi-square statistic was used to evaluate contingency tables for categorical variables (Conover, 1980). For the purpose of ranking concentrations, nondetects for nitrate and pesticides were assigned half of the lowest concentration detected of a given compound (Helsel, 2005; Rupert, 2008; Bexfield, 2008).

Samples from the regional historical data set were collected by different agencies using different methods. The potential bias introduced by mixing different sources of data is difficult to determine. Analysis of nitrate concentrations is not typically subject to contamination and analytical recovery issues common to organic compounds, and differences in concentration between filtered and unfiltered samples from production wells are not expected to significantly affect concentrations. Therefore, it is expected that the combined dataset is adequate for assessment of broad, regional trends. The median concentration of nitrate was calculated for wells sampled more than once in a given decade, and nitrate concentrations were not censored. A method described by Paschke et al. (2007) was used to classify ground waters as geochemically oxidized or reduced. Reduced samples were removed for statistical analysis of paired data and when comparing nitrate concentrations to fertilizer applications.

Results

Local-Scale Networks: Vertical Distribution of Ground-Water Age

Mean ground-water ages estimated from age-dating tracers sampled from the local-scale network of monitoring wells near Fresno and Modesto (Burow et al., 2007; Jurgens et al., unpublished data, 2007) indicate that ground-water age increases with depth below land surface (Fig. 3a and 3b). The vertical stratification of ages reflects the downward movement of ground water in response to intensive irrigation pumping and recharge. In both study areas, water in the shallow aquifer (<10 m below the water table) was generally <15 yr old. Water at depths of >60 m below the water table was >45 yr old. The ground-water ages discussed in this manuscript are derived from age-dating tracers and do not necessarily reflect the full

distribution of ages in a sample. Further discussion of ground-water age interpretations in the local-scale network near Fresno is included in Weissmann et al. (2002) and Burow et al. (2007). In Modesto, samples collected from deep monitoring wells indicate that water at depths of >85 m below the water table is >100 yr and perhaps as much as 5000 yr old, representing background conditions before significant development (Jurgens et al., unpublished data, 2007). The water chemistry in deep production wells is expected to be dominated by contributions of ground-water recharged under pre-development conditions, although these wells likely receive water representing a wide range of ages due to their long screened intervals and increased mixing with depth in the aquifer.

Local-Scale Networks: Vertical Distribution of Nitrate and Pesticides

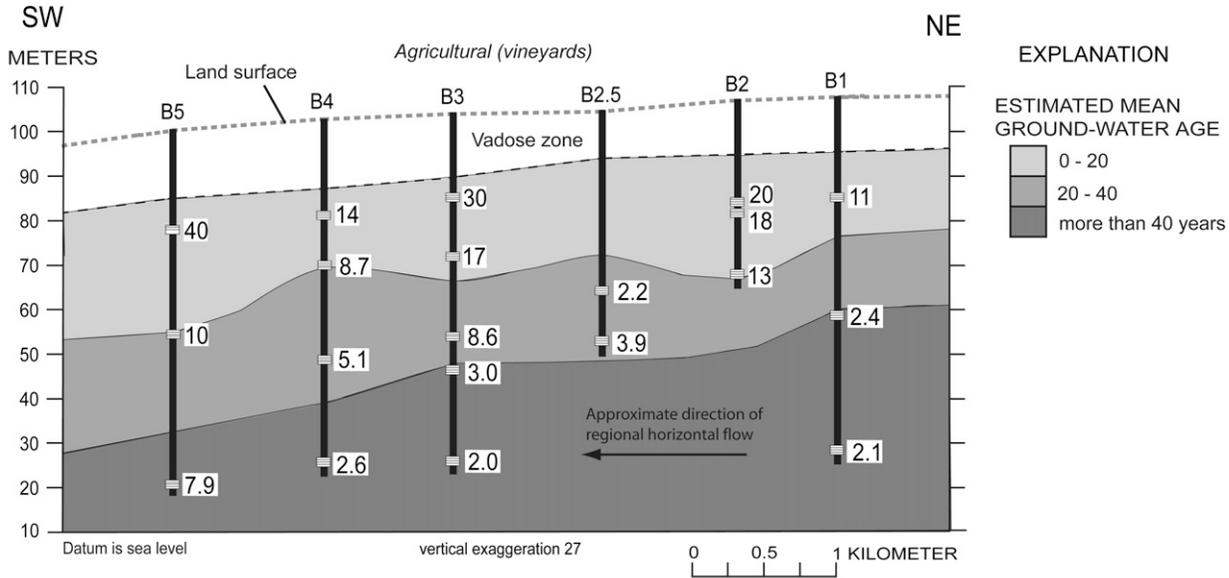
Concentrations of nitrate in samples from monitoring wells near Fresno in 2003 and in Modesto in 2003–05 were generally highest near the water table and decreased with depth (Fig. 3a and 3b). Concentrations above the MCL reached depths of about 25 m below the water table. Concentrations of nitrate were highest beneath the agricultural setting, with concentrations near the water table as high as 40 mg L⁻¹ near Fresno and 17 mg L⁻¹ in Modesto (Burow et al., 2007; Jurgens et al., unpublished data, 2007). Concentrations of nitrate near the water table beneath the urban setting in Modesto were generally low (median, 3 mg L⁻¹). Concentrations in the deepest wells (in Modesto) were generally less than background concentrations of about 2 mg L⁻¹ (USGS, 1999).

The concentration of nitrate in ground-water samples with mean recharge dates from about 1940 to 2001, coupled with an estimate of the amount of nitrate in recharge through this time period, indicate increasing concentrations of nitrate in recharge (Fig. 4a and 4b). Expected concentrations of nitrate in recharge water from nitrogen fertilizer applications were estimated using a method outlined by Böhlke (2002) using ground-water recharge dates and county-level nitrogen fertilizer application data (Alexander and Smith, 1990; Ruddy et al., 2006). The number of dairies and other confined-animal feedlots, and hence manure production, also has increased greatly during this period. However, estimates indicate that nitrogen fertilizer is the largest source of nitrate in the eastern San Joaquin Valley (Alexander and Smith, 1990; Gronberg et al., 1998; Ruddy et al., 2006). Based on the mean ground-water age from age-dating tracers, a linear ground-water age gradient with depth was characterized, indicating a constant vertical velocity with depth for ground water younger than about 60 yr (Cook and Böhlke, 1999). The estimated recharge rate, r (m yr⁻¹), was calculated using Eq. [1]:

$$r = nZ/\tau \quad [1]$$

where n is the effective porosity (dimensionless), Z is the saturated thickness of the aquifer (m), and τ is the mean age of water in the aquifer (yr) (Cook and Böhlke, 1999; Böhlke, 2002). An effective porosity of 0.3 was assumed for both networks. A saturated thickness of 50 m was assumed for Fresno and 55 m was assumed for Modesto. A mean ground-

a. Local-scale network near Fresno



b. Local-scale network near Modesto

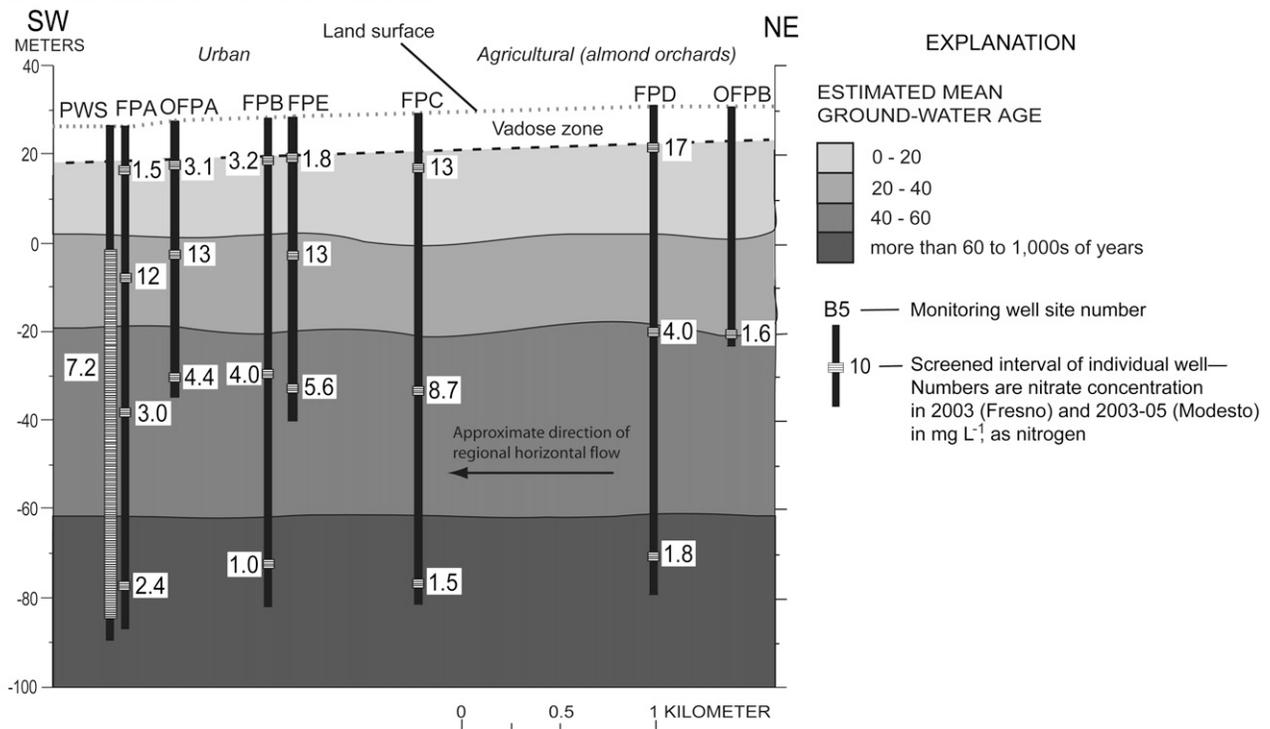


Fig. 3. Estimated ground-water age and median concentrations of nitrate in monitoring wells near (a) Fresno, California (figure modified from Burow et al., 2007) and (b) Modesto, California (figure modified from Jurgens et al. (unpublished data, 2007)). SW, southwest; NE, northeast; PWS, public-supply well. Letter designations above monitoring wells are site numbers.

water age of 24 yr was calculated for Fresno and 37 yr was calculated for Modesto by averaging the apparent mean ages from the age-dating tracers. The resulting estimated recharge rate was 0.6 m yr^{-1} for the Fresno network and was 0.4 m yr^{-1} for Modesto. The nitrogen application was estimated by dividing the reported annual nitrogen fertilizer application for each county (Ruddy et al., 2006) by the area of fertilized land

in that county and assuming that 50% of the nitrogen fertilizer applied reached the water table.

An increase in concentrations of nitrate over time in both networks near Fresno and Modesto generally corresponds to increasing nitrogen fertilizer applications over time (Fig. 4a and 4b). The axes representing initial nitrate concentration and nitrogen fertilizer application are quantitatively related through the

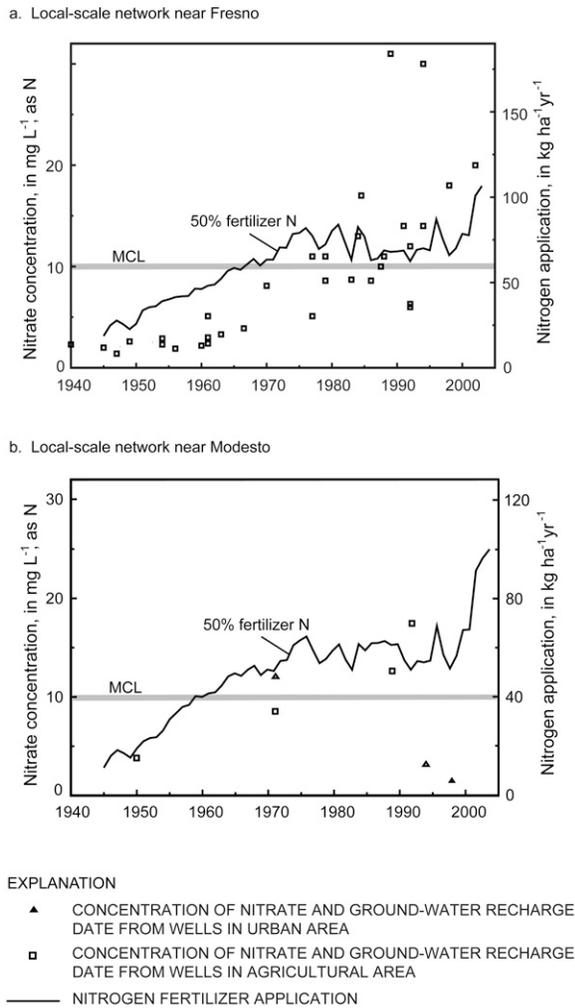


Fig. 4. Estimated concentrations of nitrate in recharge and observed concentrations of nitrate in monitoring wells in (a) Fresno, California (figure modified from Burow et al., 2007) and (b) Modesto, California. Observed concentrations of nitrate from ground water sampled in 1994–95 and 2003 (Fresno) and 2003–05 (Modesto) are plotted against corresponding dates of ground-water recharge. Estimated concentrations of nitrate from nitrogen fertilizer applications represent 50% of the nitrogen fertilizer applications divided by the area of fertilized land, dissolved in 0.6 m yr^{-1} of recharge in Fresno and 0.4 m yr^{-1} of recharge in Modesto. MCL, maximum contaminant level.

recharge rate, such that the application amount on one axis corresponds to the expected concentration in recharge on the other axis (Fig. 4a and 4b). In the network near Fresno, the concentrations of nitrate expected from nitrogen fertilizer applications were higher than observed concentrations of nitrate before about 1980 (Fig. 4a), whereas after about 1980 observed concentrations in several wells were higher than expected from nitrogen fertilizer applications. In the network near Modesto, observed concentrations in a few wells were also higher than expected from nitrogen fertilizer applications, although there were significantly fewer data points than in the network near Fresno. The low concentrations of nitrate in recently recharged (1990s) water in Modesto are from wells screened at the water table beneath the urban land-use setting and are not expected to receive agricultural fertilizer

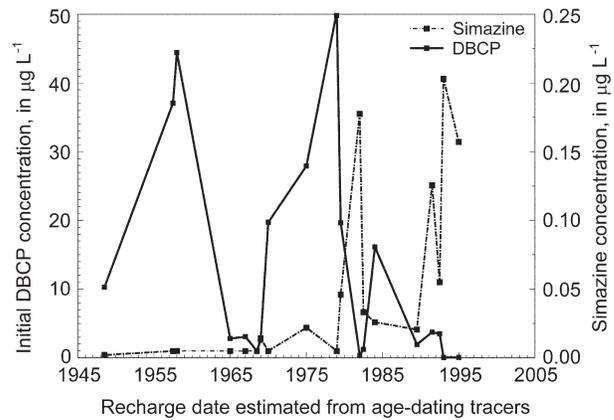


Fig. 5. Initial concentrations of 1,2-dibromo-3-chloropropane (DBCP) and simazine and estimated ground-water recharge dates from water samples collected during 1994–95 and 2003 at the local-scale network near Fresno. Initial concentrations for DBCP were calculated assuming a 6-yr half-life. Initial simazine concentrations are assumed to be equal to observed concentrations.

inputs. Other possible factors affecting observed concentrations of nitrate include local variability in fertilizer management practices near the monitoring wells, other sources of nitrate such as manure or septic, and the mixing of water of different ages in the ground-water samples. Manure is not expected to be a significant source of nitrate in either network near Fresno or Modesto because of the absence of confined animal operations in the vicinity of the wells. Septic inputs are expected to be minor in comparison to fertilizer applications. The method used to compute estimated nitrogen fertilizer applications may also overestimate nitrate concentrations because of dispersion and mixing of ages in ground-water samples (Burow et al., 2007).

Evaluation of trends in concentrations of pesticides corroborates the results of the nitrate trends in the local-scale studies and indicates that anthropogenic constituents in shallow water are moving deeper in the flow system. The soil fumigant DBCP was applied to crops beginning in the 1950s; the most intensive use was between about 1960 and 1977 (California Department of Food and Agriculture, 1973; Domagalski, 1997). Used intermittently to treat nematode problems, DBCP was used only once at many locations (California State University Fresno Foundation, 1994). In 1977, agricultural use of DBCP was suspended in California in response to concern about the potential hazardous effects of DBCP on human health. In the network near Fresno, DBCP persists at concentrations above the MCL at depths of nearly 40 m below the water table (Burow et al., 2007). Recent analysis indicates that the in situ half-life for DBCP is on the order of 4 to 6 yr (Deeley et al., 1991; Burow et al., 1999; Burow et al., 2007), although it was inconclusive whether observed regional decreases in concentrations were due to chemical transformation or physical processes, such as dispersion or recycling of ground water through pumping and reapplication of irrigation water (Burow et al., 1999). Initial concentrations of DBCP in recharge over time were estimated using a first-order decay equation (Domenico and Schwartz, 1998), assuming a half-life of 6 yr (Burow et al., 1999), and using mean ground-water ages from the age-dating tracers (Burow et al., 2007). Initial concentrations of DBCP in recharge and estimated ground-

Local-scale network near Fresno

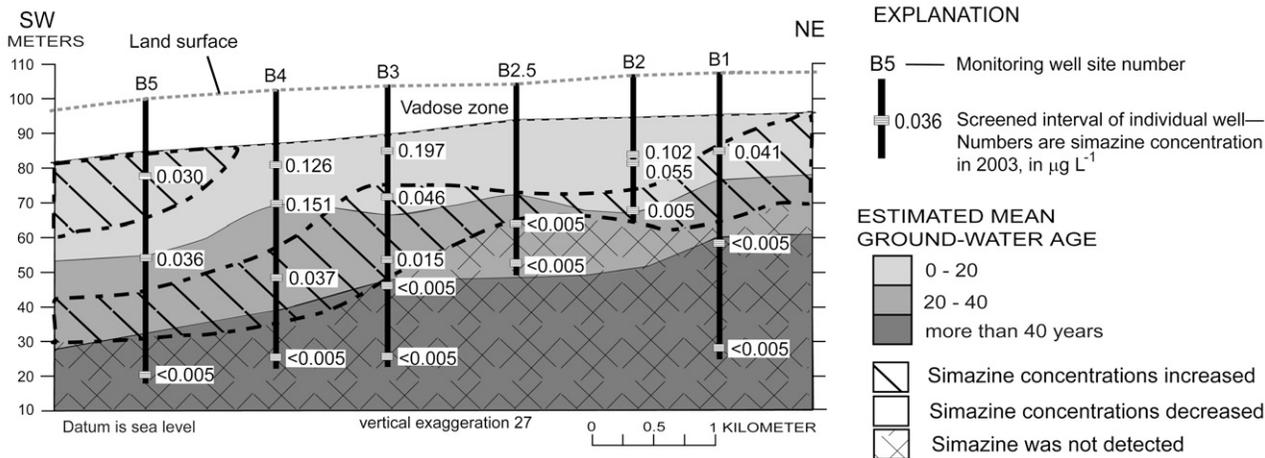


Fig. 6. Simazine concentrations in ground-water samples collected from wells in 2003 and change in simazine concentrations between 1994–95 and 2003 along the monitoring well transect near Fresno in the eastern San Joaquin Valley, California.

water recharge dates are consistent with variable inputs and a decrease in use after the late 1970s (Fig. 5).

Monitoring wells in the local-scale network near Fresno were also sampled for analysis of simazine in 1994–95 and 2003. Simazine, a widely used herbicide in the San Joaquin Valley for agricultural and nonagricultural use, was detected at the water table and to depths of nearly 40 m below the water table at very low concentrations (Fig. 6). Simazine was not detected in samples from the deepest wells along the transect. The extent of vertical movement of simazine in the transect is similar to the extent of anthropogenic nitrate concentrations, which is generally consistent with the beginning of simazine use in the late 1950s (USEPA, 1994). On the basis of simazine concentrations in samples collected during 1994–95 and in 2003 and corresponding ground-water recharge dates from the age-dating tracers (Burow et al., 2007), concentrations of simazine in recharge seem to have increased overall since about the 1970s (Fig. 5), although concentrations decreased near the water table during the last decade (Fig. 6). The lack of long-term simazine application data precludes further analysis of the causes of observed changes in simazine concentrations.

Results from the analysis of nitrate and pesticides in the local-scale monitoring networks demonstrate the predominantly downward movement of water and solutes over time as a response to pumping, irrigation recharge, and nonpoint source inputs of these constituents. Physical and chemical attenuation processes, such as geochemically reducing conditions and dispersion and mixing, do not seem to prevent constituents in the shallow system from moving to deeper parts of the aquifer. Aside from differences in chemical use between the networks near Fresno and Modesto, both study areas seem to be affected by similar processes.

Link between Local-Scale and Regional Networks

The results of the local-scale studies near Fresno and Modesto provide evidence of shallow, affected water moving to deeper parts of the ground-water flow system. However, without additional data it is difficult to determine whether the results of the local studies reflect regional spatial and temporal

trends. Therefore, nitrate and pesticide data from wells in the regional aquifer and agricultural land-use networks were evaluated to link the regional spatial and temporal trends in nitrate and pesticides to processes observed in the local-scale studies.

Concentrations of nitrate ranged from below the detection limit of 0.05 mg L^{-1} to 75 mg L^{-1} in 102 domestic wells from the regional aquifer and agricultural land-use networks sampled throughout the eastern San Joaquin Valley in 2001–02 (Table 2). The median concentration was 6.4 mg L^{-1} , which is higher than the median of 2.4 mg L^{-1} for ground water in similar alluvial settings with agricultural land use nationwide (Mueller et al., 1995). Concentrations of nitrate were above the MCL in 29% of the wells sampled in 2001–02.

Nitrate concentrations from the regional agricultural land-use monitoring and domestic well networks were compared with median concentrations at different depths from the local-scale networks of monitoring wells near Fresno and Modesto. The regional aquifer network of domestic wells was not included in the analysis because the local-scale networks reflect primarily agricultural land use. In the eastern San Joaquin Valley, domestic wells are generally screened in the shallow part of the aquifer, whereas public-supply wells tend to be screened in the deeper part of the aquifer. Monitoring wells from the agricultural land-use networks were screened near the water table. Boxplots indicating the distribution of nitrate concentrations in selected regional networks were grouped by well type and plotted by the depth of the screen midpoint below the water table (Fig. 7) to characterize concentrations of nitrate at different depths in the aquifer. A boxplot of screen depths for each well type is also plotted, indicating the distribution of screen depths associated with each well type. Although the public-supply wells included in Fig. 7 are located in an urban land-use setting (Wright et al., 2004), public-supply wells are likely to be influenced by agriculturally affected water because recharge is higher in the agricultural areas, and the deep, high-production wells may capture water recharged at greater distances. Additionally, many public-supply wells in the eastern San Joaquin Valley are drilled on former agricultural land because

urbanization has spread into agricultural areas.

Because the dominant movement of ground water is downward, the decrease in concentrations of nitrate with age likely is a result of increased concentrations of nitrate in recharge over time combined with nitrate attenuation processes. In some ground-water systems, attenuation processes such as nitrate reduction in geochemically reducing environments could be expected to lower concentrations of nitrate over time; however, ground water in the eastern San Joaquin Valley aquifer system is predominantly oxic, and nitrate is expected to be transported conservatively through the system (Burow et al., 1999; Jurgens et al., unpublished data, 2007; Burow et al., 2007). Concentrations of nitrate may also seem to be attenuated by increased mixing and dispersion as water moves deeper in the system (Burow et al., 1999; Weissmann et al., 2002).

The spatial trend of decreasing concentrations of nitrate with depth observed in the local-scale studies was similarly reflected in the regional networks. Concentrations of nitrate were highest and most variable in the monitoring wells screened near the water table, and concentrations and variability decreased with depth (Fig. 7). Mean ground-water ages estimated from age-dating tracers in the local studies were used to infer the approximate ages of water containing nitrate at different depths and in different well types in the regional studies (Burow et al., 2007). Water in samples from monitoring wells screened near the water table was inferred to be generally less than 10 yr old. Water at depths of the domestic wells was inferred to have a mean age of about 20 yr, and water at depths of the public-supply wells was inferred to have a mean age of 40 to 50 yr. These estimates of mean age are based on age-dating tracers and do not reflect the full distribution of ages of ground water at these depths (Burow et al., 2007). Weissmann et al. (2002) indicated that water samples from short-screened monitoring wells in the eastern San Joaquin Valley can contain mixtures of ages ranging from tens to hundreds of years old; therefore, it would be expected that wells with long screened intervals (such as public-supply wells) could contain water with ages ranging from hundreds to thousands of years. A mean ground-water age of about 6 yr was determined from sampling 18 domestic wells for age-dating tracers in the southeastern San Joaquin

Table 2. Summary of nitrate concentrations in the 1980s-2000s in the regional well networks in the eastern San Joaquin Valley, California.

Regional well network	Well type	Decade sampled	n	Nitrate concentration, in mg L ⁻¹ as N			Percent samples above MCL†
				Minimum	Median	Maximum	
Regional aquifer	domestic	1980s	23	<0.1	2.4	31	9
	domestic	1990s	30	<0.05	4.6	34	17
	domestic	2000s	29	<0.05	5.4	32	10
Vineyard	monitoring	1990s	5	2.4	7.0	20	20
	monitoring	2000s	5	0.04	13.0	29	60
	domestic	1990s	20	0.058	4.6	14	15
Almond orchard	domestic	2000s	25	E 0.045	4.9	18	28
	monitoring	1990s	5	4.3	17.0	53	80
	monitoring	2000s	5	3.9	16.3	34	80
Corn, alfalfa, vegetables	domestic	1990s	20	1.3	10.0	55	40
	domestic	2000s	25	1.4	10.1	75	44
	monitoring	1990s	5	1.2	18.0	33	60
All networks	monitoring	2000s	5	1.0	16.0	26	60
	domestic	1990s	20	<0.05	6.2	29	35
	domestic	2000s	25	E 0.027	8.5	26	36
All networks	monitoring	1990s	15	1.2	14.0	53	53
	monitoring	2000s	15	0.04	16.0	34	67
	domestic	1980s	23	<0.1	2.4	31	9
All networks	domestic	1990s	88	<0.05	5.6	55	26
	domestic	2000s	102	<0.05	6.4	75	29

† E, estimated; MCL, maximum contaminant level; (reporting limit for nitrate is 0.05 mg L⁻¹, except in the 1980s, where it is 0.1 mg L⁻¹); <, less than reporting limit.

Valley (Spurlock et al., 2000). However, results of recent sampling (2006) for age-dating tracers in nine of the domestic wells in this network indicate a mean age of about 19 years (Shelton, unpublished data, 2007).

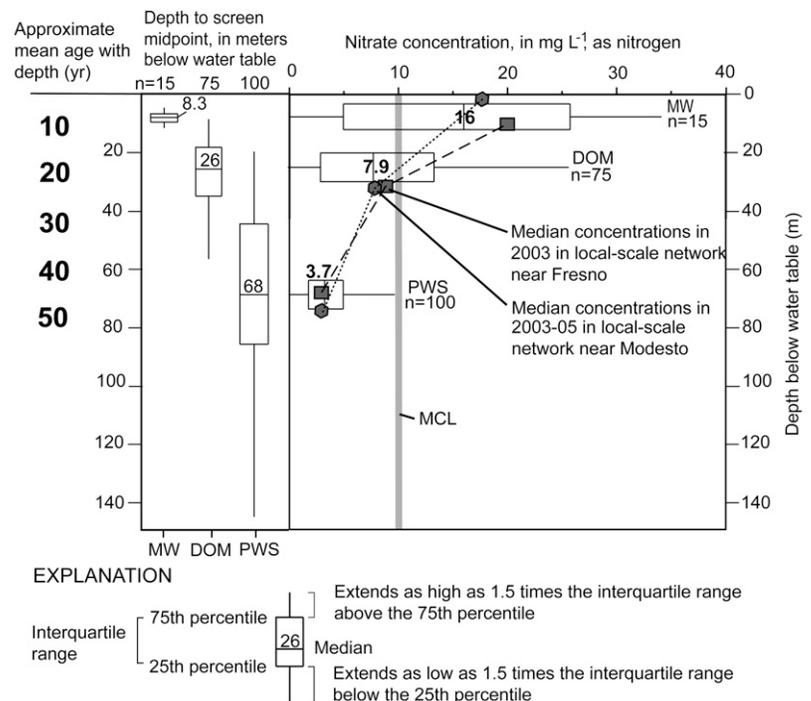


Fig. 7. Relation among nitrate concentration, well type, well screen depth below water table, and ground-water age in the eastern San Joaquin Valley, California. Concentrations of nitrate are grouped by well type and well depth. Boxplots are concentration of nitrate sampled in 2001–02 from agricultural land-use networks. Boxplot of concentrations in public-supply wells from Wright et al. (2004). DOM, domestic well; MCL, maximum contaminant level; MW, monitoring well; n, number of samples; PWS, public-supply well. Figure modified from Burow et al. (2007).

Table 3. Summary of 1,2-dibromo-3-chloropropane (DBCP) detections in the 1990s–2000s in the agricultural land-use networks in the eastern San Joaquin Valley, California.

Regional well network	Well type	Decade sampled	No. of samples	No. of detections	Median concentration	Percent of total
					of detections	samples above MCL†
					$\mu\text{g L}^{-1}$	
Vineyard	monitoring	1990s	5	1	0.4	20
	monitoring	2000s	5	2	0.06	0
Almond orchard	domestic	1990s	20	12	2	50
	domestic	2000s	25	18	0.7	44
	monitoring	1990s	5	3	0.6	60
	monitoring	2000s	5	1	0.5	20
Both networks	domestic	1990s	19	6	1	26
	domestic	2000s	25	7	0.4	20
	monitoring	1990s	10	4	0.4	40
	monitoring	2000s	10	3	0.08	10
	domestic	1990s	39	18	1	38
	domestic	2000s	50	25	0.7	32

† MCL, maximum contaminant level (MCL for DBCP is $0.2 \mu\text{g L}^{-1}$).

In 2001–02, DBCP was detected in 50% of the domestic wells in the vineyard and almond orchard land-use networks sampled (Table 3). Samples for DBCP were not collected from the corn, alfalfa, and vegetable land-use or regional aquifer networks in 2001–02 because DBCP was used primarily on orchards and vineyards. Concentrations in both agricultural land-use networks ranged from below the detection limit of 0.03 to $3.1 \mu\text{g L}^{-1}$. Concentrations were above the MCL of $0.2 \mu\text{g L}^{-1}$ in 32% of the wells. The spatial trends in the occurrence and concentrations of DBCP with depth observed in the local-scale study near Fresno were reflected in the regional networks. Concentrations of DBCP in water sampled from wells in the local-scale study are low near the water table, increase at the depths of the domestic wells, and decrease at the depths of the public-supply wells (Fig. 8a). Similarly, the detection frequency of DBCP in the regional network of monitoring wells screened near the water table is lower than in the domestic wells.

Between 1994–95 and 2003, concentrations of DBCP decreased in the local-scale network monitoring wells screened near the water table because recently recharged water with no DBCP replaced or mixed with the high-DBCP water. The decrease in occurrence and concentration at the water table is consistent with the ban on DBCP use in the late 1970s. In the deep part of the

system, DBCP occurrence and concentrations have increased as water containing DBCP has moved deeper in the system (Burow et al., 2007). Similar to the local-scale study near Fresno, concentrations in the regional network of monitoring wells screened near the water table also seemed to decrease. Ten of the 15 monitoring wells were sampled for DBCP in both decades. Concentrations of DBCP were lower in 2001–02 than in 1993–95 in the four wells where it was detected (Table 3). However, DBCP was detected in 2001–02 in an additional well where it was not detected in 1993–95; concentrations of nitrate and simazine also increased in this monitoring well. In the regional agricultural land-use networks of domestic wells, the detection frequency of DBCP increased from 46% in 1993–95 to 50% in 2001–02 (Table 3). However, concentrations of DBCP were lower in 2001–02 in 76% of the wells where it was detected in 1993–95; DBCP concentrations decreased by 46% in the vineyard land-use network wells and by 4% in almond orchard land-use network wells (Table 4). The number of wells with DBCP concentrations above the MCL decreased from 38% in 1993–95 to 32% in 2001–02.

Simazine was detected in 43% of the agricultural land-use network domestic wells and 43% of the regional aquifer network wells sampled in 2001–02 (Table 5). Concentrations ranged from below the detection limit of $0.005 \mu\text{g L}^{-1}$ to $0.16 \mu\text{g L}^{-1}$. More than 70%

Table 4. Summary of 1,2-dibromo-3-chloropropane (DBCP) and simazine detections in paired samples from the 1980s–2000s in the regional domestic well networks in the eastern San Joaquin Valley, California.

Regional well network	Decades sampled	DBCP			Simazine		
		No. of paired samples	No. of detections in each decade	Median increase or decrease in concentrations, in percent	No. of paired samples	No. of detections in each decade	Median increase or decrease in concentrations, in percent
Regional aquifer	1980s–1990s				19	6	–1000
	1990s–2000s				28	9	63
Vineyard	1990s–2000s	17	10	–46	17	8	82
			11			9	
Almond orchard	1990s–2000s	18	6	–4.2	19	6	–5.3
			6			9	
Corn, alfalfa, vegetables All networks	1990s–2000s				18	6	–17
	1990s–2000s	35	16	–14	82	29	19
			17			36	

of the simazine used in the San Joaquin Valley since 1991 was applied to vineyard and citrus crops (about 35% each) (California Department of Pesticide Regulation, 2003); therefore, simazine was further evaluated in the vineyard land-use network. In contrast to DBCP, the detection frequencies and concentrations of simazine in the vineyard land-use network and in the local-scale study near Fresno are highest in wells screened near the water table and decrease with depth (Fig. 8b).

In the local-scale study near Fresno, concentrations of simazine decreased near the water table from 1994–95 to 2003, although concentrations were still higher at the water table than at depth (Fig. 6). Simazine concentrations increased at intermediate depths, similar to observed changes in DBCP concentrations. Also similar to DBCP, the detection frequency of simazine in all regional-scale domestic well networks increased from 35% in 1993–95 to 43% in 2001–02, although the change was not statistically significant ($p = 0.3$; Chi-squared test). Concentrations of simazine increased by 63% in the regional aquifer network and by 82% in the vineyard land-use network from 1993–95 to 2001–02 in wells samples in both decades (Table 4). In contrast, concentrations decreased by 5 and 17% in the almond orchard and corn, alfalfa, and vegetables land-use networks, respectively. In 1986–87, simazine was detected in 6 of 19 domestic wells sampled in 1986–87 and 1993–95. Simazine was detected in only 2 of those 19 wells in 1993–95 above detection limits in 1986–87; however, concentrations of simazine decreased by an order of magnitude in the six wells where it was detected in 1986–87 (Burow et al., 1998b).

The amount of simazine applied was generally constant from 1991 to 2003 (California Department of Pesticide Regulation, 2003), consistent with generally similar concentrations between the 1994 and 2001 samples from monitoring wells screened near the water table in the regional vineyard land-use network (Table 5). Lack of data on the application of simazine during the time that water reaching the domestic wells was recharged makes it difficult to establish any relation to pesticide use. However, concentrations of simazine and ground-water recharge dates in the local-scale monitoring well network in vineyards near Fresno (Fig. 5) indicate that concentrations of simazine increased in recharge during the 1970s to 1990s, which may correspond to approximate recharge dates for water reaching domestic wells. The increase in concentrations of simazine in the domestic wells in the vineyard land-use network is consistent with increased simazine use between the 1970s and 1990s, to the extent that management practices at the local-scale vineyard network represent the larger vineyard land-use practices.

The results of the analysis of DBCP and simazine sug-

Table 5. Summary of simazine detections in the 1980s–2000s in the regional well networks in the eastern San Joaquin Valley, California.

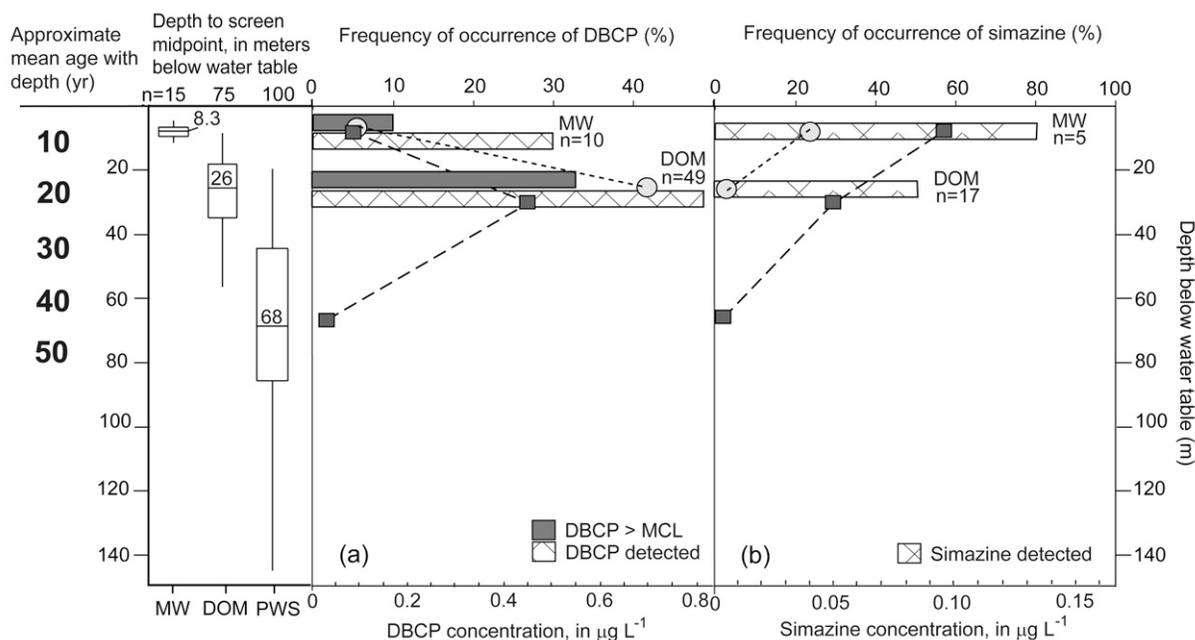
Regional well network	Well types	Decade sampled	No. of samples	No. of detections	Median concentration of detections
Regional aquifer	domestic	1980s	23	6	0.2
	domestic	1990s	30	10	0.03
	domestic	2000s	30	13	0.01
Vineyard	monitoring	1990s	4	4	0.03
	monitoring	2000s	5	5	0.02
	domestic	1990s	20	10	0.04
	domestic	2000s	25	14	0.05
Almond orchard	monitoring	1990s	5	2	0.2
	monitoring	2000s	5	3	0.007
	domestic	1990s	20	6	0.02
	domestic	2000s	25	10	0.009
Corn, alfalfa, vegetables	monitoring	1990s	5	2	0.03
	monitoring	2000s	5	3	0.01
	domestic	1990s	20	6	0.05
	domestic	2000s	25	8	0.02
All networks	monitoring	1990s	14	8	0.02
	monitoring	2000s	15	11	0.02
	domestic	1980s	23	6	0.2
	domestic	1990s	88	31	0.02
	domestic	2000s	103	44	0.02

gest that whereas detections and concentrations of DBCP will likely decrease in domestic wells during the next decade, detections and concentrations of simazine will likely increase over the next decade and then level off as ground water recharged after the early 1990s reaches these wells.

The regional spatial and temporal trends in nitrate and pesticides have been shown to be related to well depth in the flow system and regional land-use management practices. A mean age for ground water on the order of 40 to 50 yr or greater at depths of the public-supply wells indicates that most of the impacts of nitrate and pesticide use are likely not reflected in current sampling data. Low concentrations in wells screened in the deep part of the aquifer will likely increase as the proportion of young (<50 yr old) water contributed to these wells increases with time. The length of time for public-supply wells to be affected by 50-yr-old management practices, however, is difficult to estimate. Ground water becomes increasingly mixed with depth and travel time, and public-supply wells typically have long screened intervals representing a wide range of ground-water ages. Additional data and analysis are needed to characterize the distribution of ages in the deeper aquifer and to predict long-term impacts of current management strategies on drinking-water supplies.

Long-Term Concentrations of Nitrate at Regional Scale Using Historical Data

The results of the analysis of regional- and local-scale nitrate concentration data indicate that widespread high concentrations of nitrate in the shallow part of the eastern San Joaquin Valley aquifer system are likely to move to deeper parts of the ground-water flow system. Concentrations of nitrate in the regional networks were



EXPLANATION

- Median concentration of samples collected in 2001-02 from regional agricultural land-use networks
- Median concentration of samples collected in 2003 from local-scale network near Fresno

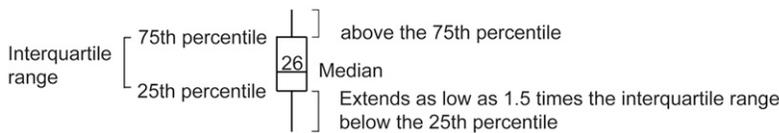


Fig. 8. Relation among concentration, detection frequency, well type, well screen depth below water table, and ground-water age for (a) 1,2-dibromo-3-chloropropane (DBCP) and (b) simazine. Concentrations are grouped by well type and well depth. Bar charts correspond to frequency of detection of DBCP from samples collected in 2001-02 from the vineyard and almond orchard land-use networks and the frequency of detection of simazine from samples collected in 2001 from the vineyard land-use network. DOM, domestic well; MCL, maximum contaminant level; MW, monitoring well; n, number of samples; PWS, public-supply well. Figure modified from Burow et al. (2007).

combined with historical data from a large number of wells to evaluate long-term concentrations in the aquifer and further demonstrate the link between the shallow and deep parts of the aquifer. Results indicate that concentrations of nitrate have increased during the last 50 yr in both the shallow and deep parts of the aquifer and that concentrations have not been significantly attenuated as ground water has moved downward through the flow system.

Nitrate concentrations increased by more than 1 mg L^{-1} between 1994-95 and 2003 in 12 of 20 wells in the local-scale network near Fresno (Burow et al., 2007). Increases in concentrations of nitrate were greatest near the water table and increased to a lesser degree with depth, indicating that water is moving deeper in the system and suggesting some damping of input concentrations with depth. Nitrate concentrations increased during the last two decades in domestic wells in the regional aquifer and agricultural land-use networks. Nitrate concentrations increased significantly from 1986-87 to 1995 ($p = 0.05$; Wilcoxon signed-rank test) in 23 wells sampled in both decades (Burow et al., 1998b). Nitrate concentrations were higher in 1993-95 than in 1986-87 in 56% of the wells, and overall median concentrations increased from 2.4 to 5.6 mg L^{-1} . Concentrations also increased significantly from

1993-95 to 2001-02 ($p = 0.04$; Wilcoxon signed-rank test) in 79 wells sampled in both decades. Nitrate concentrations were higher in 2001-02 than in 1993-95 in 58% of the wells, and overall median concentrations increased from 5.6 to 6.4 mg L^{-1} (Table 2). Wells in the regional aquifer and agricultural land-use networks were grouped for this analysis because the domestic wells generally represent the same depth horizon in the aquifer system. The statistical significance was close to the threshold value ($\alpha = 0.05$), suggesting a generally weak indication of change. The number of wells with concentrations of nitrate above the MCL increased from 9% in 1986-87 to 26% in 1993-95 to 29% in 2001-02 (Table 3). Nitrate concentrations did not change significantly between 1993-95 and 2001-02 in a regional network of 15 monitoring wells screened near the water table beneath agricultural land-use settings ($p = 0.4$; Wilcoxon signed-rank test).

Results of the analysis of the historical dataset indicate that concentrations of nitrate increased in wells screened in the shallow part of the aquifer system, characterized by well depths less than 36 m below the water table. Concentrations were significantly different among the decades ($p < 0.001$; Kruskal-Wallis test), and median concentrations increased from 1.8 mg L^{-1}

in the 1950s to 6.4 mg L⁻¹ in the 2000s (Fig. 9a). Concentrations were significantly higher between successive decades from the 1950s to the 1960s and the 1980s to the 1990s ($p < 0.001$; Multiple-stage Kruskal–Wallis test). As expected, concentrations of nitrate were lower in wells screened in the deep part of the aquifer system than in the shallow system for each decade (Fig. 9a). However, concentrations in the deep part of the aquifer also were significantly different among the decades ($p < 0.001$; Kruskal–Wallis test), and median concentrations increased from 1.1 mg L⁻¹ in the 1950s to 3.6 mg L⁻¹ in the 2000s. Similar to the shallow dataset, concentrations of nitrate were significantly higher between successive decades from the 1950s to 1960s and the 1990s to 2000s ($p < 0.001$; Multiple-stage Kruskal–Wallis test).

Similar to the local and regional network analysis, increasing nitrogen fertilizer applications over time generally correspond to an increase in concentrations of nitrate over time in the shallow and deep part of the aquifer system (Fig. 9b). Median concentrations for samples from each decade were plotted at the inferred date when ground water in each depth zone was recharged. Water from monitoring wells screened near the water table was inferred to be about 10 yr old, water from wells in the shallow dataset was inferred to be about 20 yr old, and water from wells in the deep dataset was inferred to be about 40 yr old, based on mean ground-water ages determined from the local-scale networks (Fig. 7).

Although increasing concentrations of nitrate over time correspond to increasing fertilizer applications over time, concentrations in the historical dataset for ground water estimated to have been recharged in the 1960s to 1980s are lower than expected from nitrogen fertilizer applications (Fig. 9b). In contrast, median concentrations in the regional network of monitoring wells screened near the water table were higher than expected from nitrogen fertilizer applications. Manure inputs could increase the concentration of nitrate expected in recharge by 38 to 66% if manure sources were included in the estimates. Although nitrogen fertilizer is the dominant source of nitrogen applications in the study area, approximately one third of the wells in the monitoring well and domestic well networks are located within 0.8 km of a confined animal feedlot, which can result in high concentrations of nitrate in ground water (Harter et al., 2002). Most of the wells with a nearby confined animal feedlot are in the corn, alfalfa, and vegetable land-use network. It could be expected that the domestic and monitoring wells would be similarly affected by manure inputs. However, median concentrations in the monitoring well network were also higher than the historical data network median concentrations in the shallow part of the aquifer for the same decade (Fig. 9b). The historical data network includes wells in urban and agricultural settings, which could result in lower median concentrations than if recharge to the wells were derived exclusively from agricultural areas. Additionally, median concentrations were not corrected for geochemically reduced wells because redox indicators were not available for most of the historical data. To evaluate the potential effects of nonagricultural land-use settings and redox conditions, median concentrations were recalculated for the wells with estimated recharge dates in the 1980s; redox indicator data were available for wells in the agricultural setting in the monitoring well network and the historical dataset. The revised median concentration in

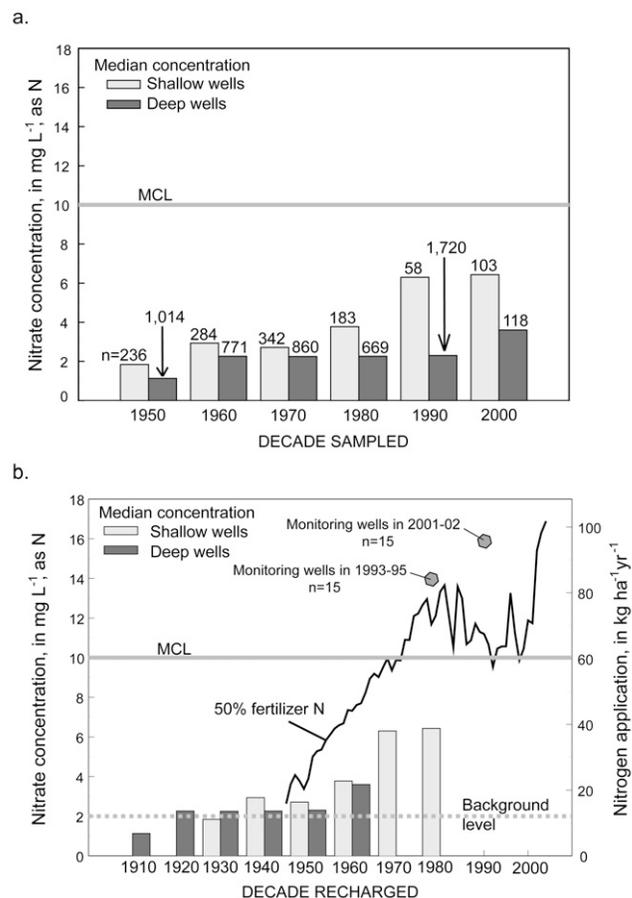


Fig. 9. Median nitrate concentration for each decade in historical data networks. (a) median concentrations for each decade. (b) Median nitrate concentrations for each decade plotted at estimated date of recharge and estimated nitrate concentrations in recharge from nitrogen fertilizer applications. Estimated concentrations of nitrate from nitrogen fertilizer applications represent 50% of the nitrogen fertilizer applications divided by the area of fertilized land, dissolved in 0.6 m yr⁻¹ of recharge. MCL, maximum contaminant level; n, number of wells.

the monitoring wells screened near the water table was 8.2 mg L⁻¹ after removing four geochemically reduced wells from the dataset. Similarly, the revised median concentration in the shallow historical dataset was 8.3 mg L⁻¹ after removing 20 wells in urban areas and six wells that were geochemically reduced. Median concentrations of nitrate, however, are still below expected concentrations from nitrogen fertilizer applications. Uncertainties in the estimates of ground-water age, fertilizer losses, recharge rate, and the use of county-wide average fertilizer use could affect the comparison between nitrogen input and observed concentrations.

The similarity in concentrations of nitrate between the monitoring wells screened near the water table and domestic wells in the shallow historical dataset suggests that concentrations were not significantly attenuated as ground water moved from the water table to shallow depths in the system. Minor attenuation is also suggested by the similarity in median concentrations between the shallow and deep datasets for earlier decades (Fig. 9b). To further corroborate the similarity in concentrations of nitrate between wells screened near the water table and wells in the shallow dataset,

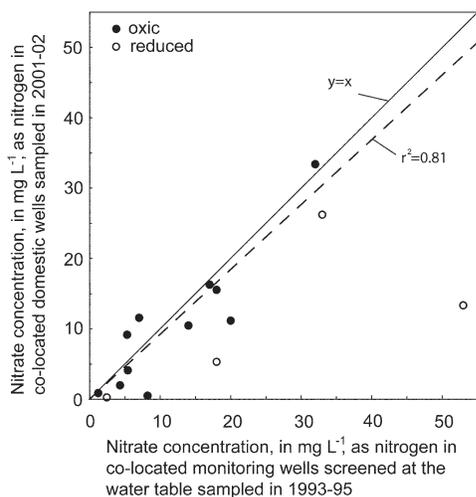


Fig. 10. Concentrations of nitrate in domestic wells sampled in 2001–02 and in monitoring wells sampled in 1993–95 at the same site. The estimated dates of recharge of sampled water are in the 1980s.

concentrations from monitoring wells screened near the water table in 1993–95 were paired with concentrations from domestic wells at the same site sampled in 2001–02 (Fig. 10), which should capture water that recharged during the same time period. The paired samples were generally well correlated, showing a slight bias toward higher concentrations of nitrate in the monitoring wells near the water table. Some of the outliers were sites in which water in both the monitoring well and the domestic well was geochemically reduced; yet concentrations of nitrate were high in 1993–95.

The results of the analysis of the regional datasets suggest that whereas the concentrations of nitrate in the shallow part of the aquifer may level off due to the leveling off of the fertilizer applications in about 1980, concentrations in the deep part of the aquifer will likely continue to increase over the next few decades. Because of the time lag between input at the water table and arrival in the deep part of the aquifer and increased mixing and dispersion with depth in the system, it will likely take several decades until the nitrate in the deep part of the system reaches concentrations of concern for drinking water.

Conclusions

Results from the analysis of nitrate and pesticides in ground water in the eastern San Joaquin Valley at the local and regional scale demonstrate that anthropogenic chemicals from nonpoint source inputs are being recharged to the ground-water system and are moving downward with time as a response to pumping and irrigation recharge. The regional spatial and temporal trends in nitrate and pesticides have been shown to be related to well depth in the flow system, which is a proxy for ground-water age.

Concentrations of nitrate and pesticides in the shallow part of the aquifer system at depths of domestic wells in the study area have increased over time. Concentrations were greater than the MCLs for nitrate or DBCP in 44% of domestic wells sampled during 2001–03, indicating that domestic drinking water supplies have been significantly affected by inputs of nonpoint source agricultural chemicals over time.

Concentrations of nitrate and pesticides at depths of public-supply wells, which are typically screened in the deep part of the aquifer system, are lower than concentrations in the shallow part of the system, although concentrations of nitrate have gradually increased during the last 50 yr. Because of the time of travel between the water table and the deep part of the aquifer system, current concentrations in public-supply wells likely reflect the effects of 40- to 50-yr-old management practices. Therefore, concentrations of nitrate and detection of pesticides will likely increase as the proportion of highly affected water contributed to these wells increases with time. Attenuation processes do not seem to significantly affect concentrations of nitrate and pesticides as they are transported through the ground-water system, although processes such as dispersion and mixing influence concentrations as solutes move further away from sources. Without additional analysis of the distribution of age of water in the deep part of the aquifer, it is difficult to predict the length of time for public-supply wells to reach concentrations of concern.

Acknowledgments

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