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ORIGINAL ARTICLE

Assessment of regional change in nitrate concentrations in groundwater in the Central Valley, California, USA, 1950s–2000s

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Abstract A regional assessment of multi-decadal changes in nitrate concentrations was done using historical data and a spatially stratified non-biased approach. Data were stratified into physiographic subregions on the basis of geomorphology and soils data to represent zones of historical recharge and discharge patterns in the basin. Data were also stratified by depth to represent a shallow zone generally representing domestic drinking-water supplies and a deep zone generally representing public drinking-water supplies. These stratifications were designed to characterize the regional extent of groundwater with common redox and age characteristics, two factors expected to influence changes in nitrate concentrations over time. Overall, increasing trends in nitrate concentrations and the proportion of nitrate concentrations above 5 mg/L were observed in the east fans subregion of the Central Valley. Whereas the west fans subregion has elevated nitrate concentrations, temporal trends were not detected, likely due to the heterogeneous nature of the water quality in this area and geologic sources of nitrate, combined with sparse and uneven data coverage. Generally low nitrate concentrations in the basin subregion are consistent with reduced geochemical conditions resulting from low permeability soils and higher organic content, reflecting the distal portions of alluvial fans and historical groundwater discharge areas. Very small increases in the shallow aquifer in the basin subregion may reflect downgradient movement of high nitrate groundwater from adjacent areas or overlying intensive agricultural inputs. Because of the general lack of regionally extensive long-term monitoring networks, the results from this study highlight the importance of placing studies of trends in water quality into regional context. Earlier work concluded that nitrate concentrations were steadily increasing over time in the eastern San Joaquin Valley, but clearly those trends do not apply to other physiographic subregions within the Central Valley, even where land use and climate are similar.

Keywords Nitrate · Groundwater · Regional land use management · Water quality trends · Central Valley

Introduction

Nitrate is commonly elevated in groundwater beneath developed settings. Many studies have linked nitrate contamination in groundwater to agricultural and urban land-use practices (Nightingale 1970; Strebel et al. 1989; Spalding and Exner 1993; Vitousek et al. 1997; Böhlke 2002; Thorburn et al. 2003; McMahon et al. 2008). A national assessment of nutrients in groundwater of the United States found that 40 % of wells in shallow groundwater beneath agricultural areas and 3 % of wells beneath urban areas had nitrate concentrations above the US Environmental Protection Agency's (USEPA) maximum contaminant level (MCL) (Dubrovsky et al. 2010), with many areas expected to increase under current management (Dubrovsky et al. 2010; Puckett et al. 2011).

California's Central Valley is one of the most productive agricultural regions in the world and has been farmed for

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more than a century. However, aquifers in parts of the valley have also been shown to be among the most vulnerable in the Nation to high nitrate concentrations (California State Water Resources Control Board 2002; Dubrovsky et al. 2010; Anning et al. 2012). In the Central Valley, nitrate concentrations occur at concentrations above the MCL in many wells (Burton and Belitz 2008; Shelton et al. 2008, 2009; Bennett et al. 2010, 2011), especially in shallow groundwater and as a result of agricultural fertilizer inputs on irrigated crops and dairy operations (Bennett et al. 2011; Burow et al. 2008b; Harter et al. 2002; Landon et al. 2011; Schmidt and Sherman 1987; van der Schans et al. 2009). During the last several decades, the population and the size of valley cities have been increasing steadily and the population is expected to double by the year 2050 (Great Valley Center 2009). This increase in population has caused increased competition for water resources in the Central Valley; because of potential issues of groundwater quality, concern is growing over the long-term suitability of the groundwater resource as a reliable source of rural and public drinking-water supply.

Regional assessment of groundwater quality trends is difficult because of the long time frames for movement of groundwater in deep alluvial basins and the lack of established monitoring networks, resulting in sparse or uneven data coverage and the need to aggregate data from a wide variety of well types and data sources. Even with adequate data, interpretation of time series data proves to be challenging (Visser et al. 2009a, b; Stigter et al. 2011), requiring detailed analysis of explanatory variables (Wassenaar et al. 2006; Hansen et al. 2011) that are typically not available over broad spatial scales (such as groundwater age and indicators of source and attenuation processes). These difficulties have spawned a wide variety of methods to best use available data for understanding processes affecting nitrate concentrations at multiple spatial and temporal scales (e.g., Wendland et al. 2002; Broers and van der Grift 2004; Flipo et al. 2007; Browne et al. 2008; McMahon and Chapelle 2008; Merz et al. 2009) and evaluate the efficacy of potential management scenarios aimed at reducing nitrate contamination in the most vulnerable areas.

This study builds on previous work, which showed increasing nitrate concentrations in parts of the Central Valley. Nightingale (1970) and Burow et al. (2007, 2008b) documented increases in nitrate in the eastern San Joaquin Valley (in the southern Central Valley) during the last several decades. Hull (1984) also found significant upward trends in nitrate concentrations in parts of the Sacramento Valley (in the northern Central Valley). None of these studies evaluated trends in nitrate over the entire Central Valley aquifer system. Because of differences in hydrogeology and land use in different parts of the valley, data were aggregated using a consistent approach and assessed valley-wide to determine whether the same increasing trends observed at subregional scale were occurring throughout the valley.

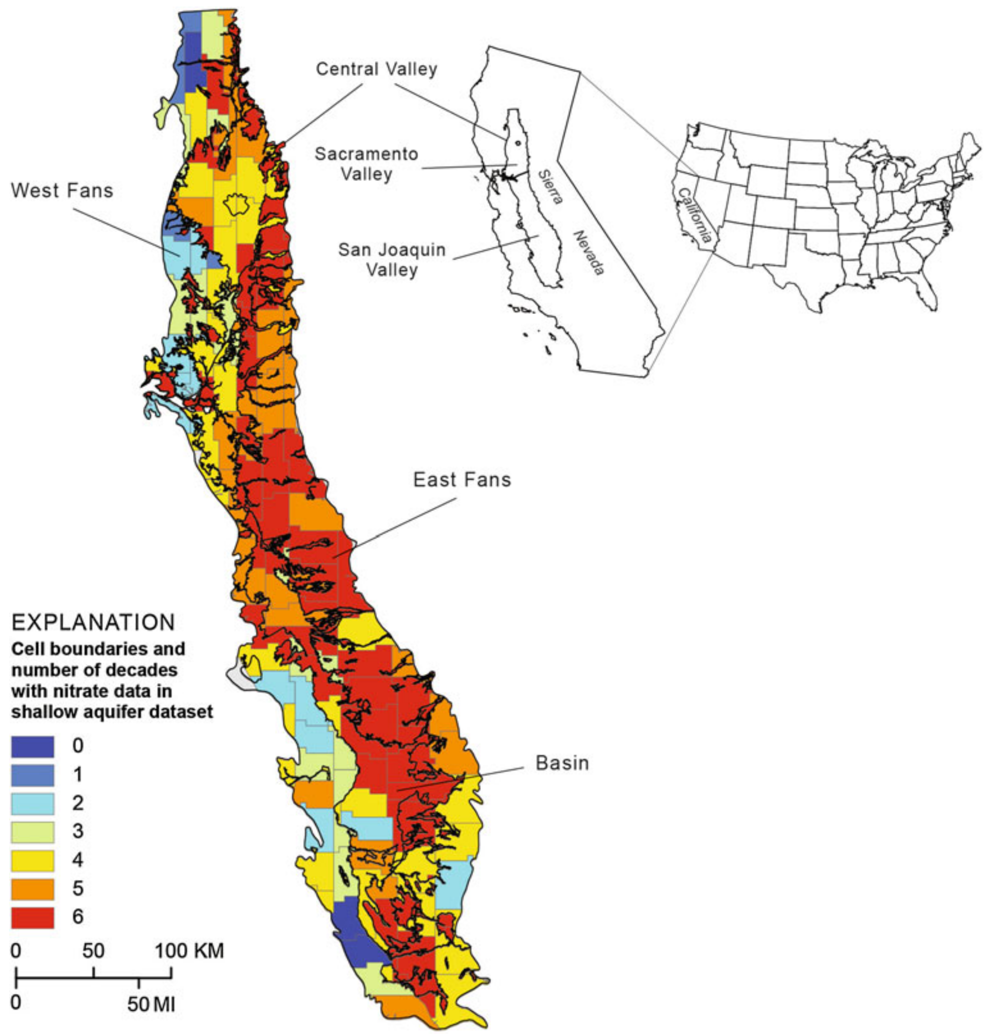
The objective of this study is to use available data sources to provide information on long-term (multi-decadal) changes in nitrate concentration in the Central Valley of California (Fig. 1). Because some areas of the valley have a high density of wells and other areas are very sparsely covered, a spatially unbiased, grid-based approach (e.g., Belitz et al. 2003) was used to decluster densely spaced data and extrapolate sparse data. Because the well networks are spatially distributed in each subregion, each network of grid cells can be taken as statistically representative of the resource in that subregion. In addition to identifying changes in nitrate, manganese (Mn), and iron (Fe) concentrations over time, changes in the proportion of the aquifer over a common threshold of 5 mg/L was also determined for nitrate concentrations (aquifer scale proportion; Belitz et al. 2010). This was calculated as the number of cells with a median concentration of nitrate over 5 mg/L (as N) divided by the total number of cells with data in that subregion. A better understanding of the proportion of the total resource affected by elevated nitrate concentrations, and the spatial distribution of long-term trends in concentration will help water managers evaluate possible management scenarios and focus efforts in areas most vulnerable to increases in nitrate concentration.

Study area

The Central Valley of California covers an area of more than 50,000 km^2 (Fig. 1). This level-floored depression is about 50–100 km wide and nearly 700 km long, bounded by the Sierra Nevada on the east and the Coast Ranges on the west. The Central Valley is composed of parts of four hydrographic drainage basins. The Sacramento Valley occupies the northern one-third of the Central Valley. The San Joaquin Valley occupies the southern two-thirds of the Central Valley and is made up of the San Joaquin Basin in the north and the interior-draining Tulare Basin in the south. The Sacramento-San Joaquin River Delta is a low-lying area where the Sacramento and San Joaquin Rivers drain to the San Francisco Bay, containing wetlands and hundreds of miles of channels and numerous islands (Bertoldi et al. 1991). The climate in the Central Valley is arid to semiarid. Average annual precipitation decreases from north to south: ranging from 33 to 66 cm in the Sacramento Valley to 13 to 46 cm in the San Joaquin Valley.

The Central Valley is an asymmetrical structural trough filled with marine and continental sediments up to 15 km

Fig. 1 Map of Central Valley of California and distribution of grid cells within each physiographic subregion



thick. The aquifer system in the Central Valley is comprised of unconfined, semi-confined, and confined aquifers, which are primarily contained within the upper 300 m of alluvial sediments deposited by streams draining the surrounding Sierra Nevada and Coast Ranges (Page 1986; Faunt 2009). The aquifer sediments are heterogeneous and typically range from 30 to 70 % coarse-grained texture throughout the valley. The Sacramento Valley is distinctly more fine-grained than the San Joaquin Valley, with the exception of the Corcoran Clay, a regional confining unit in the San Joaquin Valley (Faunt et al. 2010).

Materials and methods

Water quality data from 12,846 wells were compiled from three sources: the US Geological Survey (USGS) National Water Information System database (4,616 wells), the USEPA Storage and Retrieval database (3,551 wells), and the California Department of Public Health (CDPH) database (4,679 wells) (See Online Resource 1). The databases were screened for duplicate records and then the concentrations were recensored to a common value for each constituent. Concentrations were generally recensored to the highest detection limit: nitrate was censored at 0.5 mg/L; Fe concentrations were censored at 100 μg/L; Mn concentrations were censored at 30 μg/L. Following censoring, median nitrate, Fe, and Mn concentrations were calculated for each well for each decade. All nitrate concentrations are reported as nitrogen.

Wells were spatially stratified by physiographic subregion, grid cell, and by depth. The physiographic subregions represent different hydrogeologic features: the aquifer sediments in the eastern alluvial fans subregion (east fans; Fig. 1) comprise alluvial fans deposited from glacial-fed streams that drain large watersheds in the predominantly granitic Sierra Nevada to the east; the western alluvial fans subregion (west fans) comprises alluvial fans deposited by intermittent streams that drain small watersheds in the primarily marine sediments of the Coast Ranges to the west;

the basin subregion (basin) comprises flood basin deposits in the axis of the valley and distal portions of the fans from the east and west sides of the valley. The difference in sediment source and depositional processes among the three subregions affects the chemistry of the groundwater; groundwater in the east and west fans subregions is expected to be generally more oxic and younger; groundwater chemistry is further influenced by an increase in geochemically reducing conditions and cation exchange processes (Bertoldi et al. 1991) as the water moves through the sediments toward the basin subregion. These differences serve as the basis for lateral stratification of the basin. The subregions were delineated using geomorphology and data from the Soil Survey Geographic Database [Soil Survey Staff, Natural Resources Conservation Service, US Department of Agriculture. Soil Survey Geographic (SSURGO) Database for Central Valley, California. Available online at http://soildatamart.nrcs.usda.gov. Accessed 08/18/2010]. The basin subregion was defined by selecting geomorphic features indicative of groundwater discharge areas: basin floors, sloughs, mud flats, backswamps, marshes, playas, etc., combined with somewhat poorly to very poorly drained soil drainage class. The east and west fan subregions were defined by alluvial fans and other geomorphic features that were not included in the basin subregion, combined with moderately well to excessively well drained soil drainage class.

Wells were also stratified by well depth into shallow and deep depth zones: the shallow zone representing primarily domestic drinking-water supplies and the deep zone representing primarily public drinking-water supplies. Depth below water table was calculated for each well that had available depth data. To determine an appropriate depth to divide the shallow and deep zones, depths for domestic and public supply wells were compared. The 75th percentile of depth for domestic wells was 57 m below water table and the 25th percentile for depth of public-supply wells was 48 m below water table; therefore, a depth of 46 m below water table was selected to divide the shallow and the deep aquifer. If no depth data were available, wells were classified according to well type: public-supply and irrigation wells were included in the deep zone, domestic and monitoring wells were included in the shallow zone. Other well types were removed from the database if they had no depth information.

A GIS-based program (Scott 1990) was used to compute spatially unbiased grids to facilitate comparison among physiographic subregions. A grid-based approach allows declustering in areas with dense data coverage and extrapolation of data in areas of sparse coverage. Belitz et al. (2010) found that even one well per cell was adequate to represent groundwater quality in areas of sparse coverage, especially for nonpoint source contaminants such as nitrate. In addition to providing a basis for comparison among different data densities, the cell-based analysis allowed for statistical tests of trends in water quality across multiple decades since less than 15 % of the wells were sampled during three decades or more (Fig. 1). This is common with historical water quality datasets as few monitoring programs have been established or maintained for a long enough time to analyze the same wells for long-term trends. Therefore, a grid-based approach to analysis is necessary to aggregate data from different wells and to provide a consistent means to compare between subregions.

Each physiographic subregion was divided into 40 equal-area cells. Cell areas ranged from about 450 km^2 in the west fans and basin subregions to about 650 km^2 in the east fans subregion. A median concentration was computed for each cell for each decade using available well data for that cell to look at trends in concentration over time. Additionally, the percent of wells with nitrate concentrations greater than a threshold of 5 mg/L was computed for each cell for each decade to provide an estimate of the areal proportion of the aquifer impacted by elevated concentrations of nitrate over time. A threshold of 5 mg/L was used because it represents concentrations well above background concentration (estimated as 2–3 mg/L; Hull 1984; Jurgens et al. 2008) and because using a threshold of 10 mg/L (the MCL) could introduce bias because public-supply wells were shut down and removed from the CDPH database if concentrations exceeded the MCL.

Generally, data coverage for cells was good throughout most of the east fans and basin subregions (Fig. 1) with most cells having data for five or six decades. In contrast, data coverage was sparser in the west fans subregion with several cells only having data for one or two (or zero) decades.

The types of wells with available water quality data varied from decade to decade. Both the shallow and deep groundwater system was generally represented across the decades (Table 1), although many fewer shallow wells were available in the 1990s–2000s than deep wells. In the shallow depth zone, the percentage of domestic wells with data remained relatively constant across the decades, whereas data from irrigation wells in the 1950s–1970s were generally replaced by data from observation wells in the 1980s–2000s. Similarly, data from irrigation wells in the deep depth zone in the 1950s–1970s were generally replaced by data from public-supply wells in the 1970s–2000s.

Confidence intervals were computed for each subregion median concentration for each decade and for each percentage of wells with concentrations over 5 mg/L. Confidence intervals for the medians was calculated using the binomial distribution (Conover 1980), and confidence intervals for the aquifer scale proportion was calculated

Table 1 Number of wells and well types used in analysis of nitrate in Central Valley, California

Decade	Domestic		Public		Observation		Irrigation		Other/unknown		Total
	n	Percent of total	*n*	Percent of total	*n*	Percent of total	*n*	Percent of total	*n*	Percent of total	
Shallow aquifer											
1950s	204	28	110	15	44	6.1	240	33	128	18	726
1960s	393	36	167	15	61	5.5	339	31	147	13	1,107
1970s	859	59	216	15	23	1.6	239	16	124	8.5	1,461
1980s	269	24	264	23	431	38	88	7.7	90	7.9	1,142
1990s	114	26	131	30	171	39	8	1.8	14	3.2	438
2000s	140	32	125	29	137	31	11	2.5	24	5.5	437
Deep aquifer											
1950s	190	10	138	7.5	233	13	921	50	355	19	1,837
1960s	187	10	249	14	126	6.9	1,063	58	193	11	1,818
1970s	222	15	499	33	14	0.9	614	40	174	11	1,523
1980s	174	6.8	1,888	74	34	1.3	182	7.1	289	11	2,567
1990s	50	1.9	2,477	93	11	0.4	18	0.7	114	4.3	2,670
2000s	75	1.8	3,790	91	85	2.0	65	1.6	141	3.4	4,156

using the method outlined in Belitz et al. (2010). The Regional Kendall test (Helsel and Frans 2006) was applied to the grid-cell decadal median concentration data to test for trends in concentration over time within each physiographic subregion and depth strata. The Regional Kendall is a non-parametric test adapted from the Seasonal Kendall test to determine whether a consistent regional trend occurs in environmental data (Helsel and Frans 2006). A significance level of $\alpha = 0.05$ was used.

Results

Nitrate occurrence and changes in nitrate concentrations

In the 2000s, nitrate concentrations were highest in the shallow east fans subregion; the lowest nitrate concentrations were in the basin subregion (Fig. 2). Generally oxic conditions prevail on the upper parts of the alluvial fans where sediments are coarse, and groundwater becomes more reduced as it travels toward the center of the basin and sediments become more fine grained and groundwater age increases (Bertoldi et al. 1991; Burow et al. 1998; Landon et al. 2011). Nitrate concentrations are usually lower in reduced groundwater due to the process of denitrification, in which nitrate is converted to nontoxic nitrogen gas (N_2). As would be expected for a contaminant source at the land surface, nitrate concentrations were higher in the shallow depth zone than the deep depth zone in the east fans subregion, but this was not observed in the other subregions. The concentrations in the deep zone in the east fans subregion were similar to concentrations in the west fans subregion, however.

Median nitrate concentrations were low in the 1950s and increased significantly in the shallow and deep zones from the 1950s to the 2000s in the east fans subregion at a rate of 0.6 and 0.2 mg/L per decade, respectively (Table 2; Fig. 3a). Nitrate concentrations in the shallow part of the west fans subregion were higher than the east fans subregion in the 1950s, but then showed no consistent trend from the 1950s–2000s (Table 2; Fig. 3b). Median concentrations increased and decreased from one decade to another, with large error bars indicating high variability in the shallow zone. Median nitrate concentrations increased very slightly but significantly in the shallow zone in the basin subregion from the 1950s to 2000s (Table 2; Fig. 3c); concentrations in the deep zone in the basin subregion did not show a significant trend.

Although the trends in the west fans subregion could be primarily affected by sparse and uneven data coverage, it is possible that concentrations in the west fans subregion are higher and more variable than the east fans subregion due to the source of sediments and mode of sediment deposition in this subregion. Mendenhall et al. (1916) found the natural characteristics of groundwater in the western San Joaquin Valley to be highly varied over short distances, with extremely poor water quality in some areas and good quality water in other areas. This is consistent with the highly heterogeneous debris-flow type deposition of sediments from the Coast Ranges in this subregion. Studies of soil nitrogen content in the western San Joaquin Valley

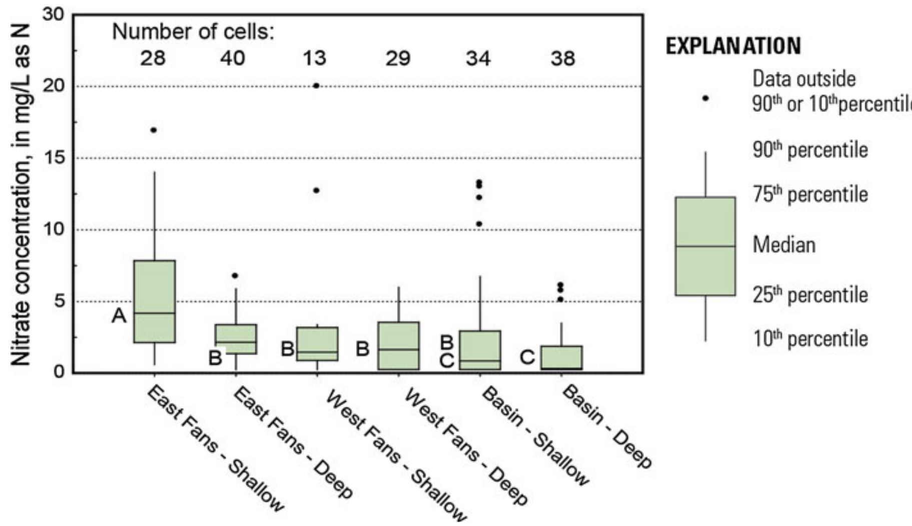


Fig. 2 Nitrate concentrations in the 2000s stratified by physiographic subregion and depth zone. *Boxplots* labeled with *different letters* have medians that were significantly different at the 0.05 level

Table 2 Results of Regional Kendall Test for trends in nitrate concentrations in Central Valley, California

Physiographic region	Depth zone	τ	*p*	Change in nitrate concentration per decade, in mg/L as N
East fans	Shallow	0.54	<0.001	0.6
	Deep	0.37	<0.001	0.2
West fans	Shallow	0.08	0.44	–
	Deep	0.01	1	–
Basin	Shallow	0.24	<0.001	0.05
	Deep	0.08	0.15	–

indicated that high nitrate concentrations in groundwater may be derived, at least in part, from geologic sources with substantial nitrate content in Coast Range sediments, especially in the central and southern San Joaquin Valley. Pore water concentrations in the upper 15 m of sediments under undeveloped (nonirrigated) and irrigated conditions were measured at about 100–300 meq/L as NO3, respectively (1,400–2,800 mg/L as N) during 1962–64 (Dyer 1965), and nitrate concentrations in tile drain effluent in undeveloped (nonirrigated) areas were measured as high as 234 mg/L as N at depths of 1–3 m (Glandon and Beck 1971). Letey et al. (1977) measured concentrations averaging as high as 196 mg/L as N in tile drain effluent in this same area during 1973–74; because the effluent concentrations at sites in the western San Joaquin Valley were anomalously high compared to other sites and concentrations appeared unrelated to anthropogenic nitrogen input history, they concluded that the high concentrations were likely due to a geologic source. Sullivan et al. (1979) noted that the debris-flow type deposits characteristic of the Coast Ranges would likely contribute to the relative storage potential of nitrogen in the sediments. Differences in nitrogen content in sediments derived from different drainage basins in the western San Joaquin Valley were related to specific lithologies and redox potential (Strathouse et al. 1980). Elevated soil nitrogen concentrations have been observed in other study areas with the potential to affect stream (Holloway and Smith 2005) or groundwater concentrations (Walvoord et al. 2003; Scanlon et al. 2008). Mobilization of the soil nitrogen reservoir through irrigation or precipitation recharge was expected to result in nitrate concentrations above the MCL in some places, even with soil N concentrations an order of magnitude lower than what was observed in the western San Joaquin Valley (Scanlon et al. 2008), therefore it is likely that some of the high nitrate concentrations in parts of the west fans are derived from a geologic source.

It is not known to what extent soil nitrogen contributes to current (2000s) concentrations of nitrate in the west fans, relative to inputs from fertilizer and manure. Concentrations in the 2000s were lower than concentrations in previous decades, which could suggest leaching of geologic nitrogen. However, sparse data coverage combined with the highly heterogeneous water quality conditions may cause results from the west fans to be more sensitive to sampling different wells in different decades, thus making it difficult to draw any well-supported conclusions.

In contrast to the west fans, depositional conditions in the east fans subregion are more uniform, and the predominantly granitic source rocks suggest low natural soil nitrogen

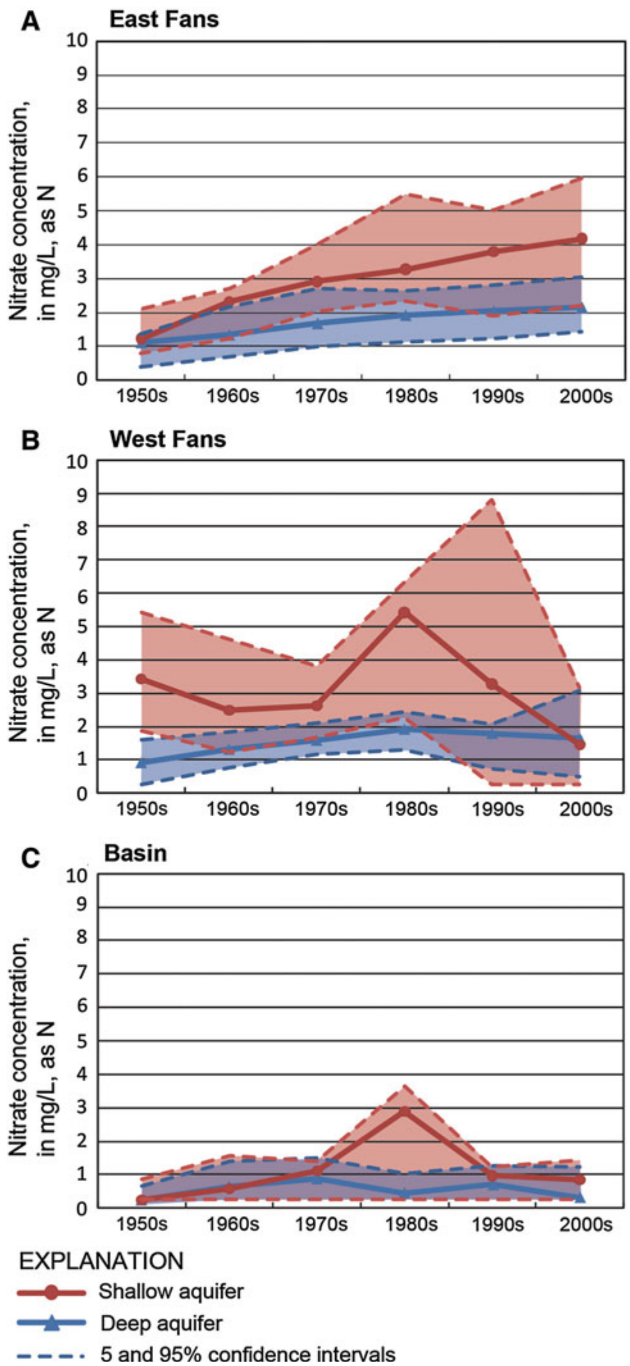


Fig. 3 Median nitrate concentrations for each decade and computed confidence intervals

concentrations. Increases in nitrate concentrations in the east fans subregion are consistent with the introduction and increased use of synthetic fertilizer after the 1940s. The Central Valley also has seen an increase in the use of manure and a steady increase in population during the same time period (Fig. 4). Most of the land area in the valley is agricultural: 63 % agricultural crops that receive fertilizer inputs, compared to less than 4 % urban. Nitrogen inputs from agricultural use are much greater than from rural septic or urban sources, although small amounts can be contributed locally from these sources (Jurgens et al. 2008; Katz et al. 2011). The median concentration of nitrate in the shallow aquifer in the east fans in 1950 is within the range of background concentrations and is similar to concentrations in the deep aquifer. In later decades median nitrate concentrations in the shallow aquifer increased to more than 4 mg/L by the 2000s.

The magnitude of concentration changes was greater in the shallow zone than the deep zone in all subregions (Figs. 3, 5). (See also Online Resource 2–5). This was noted in previous studies (e.g., Burow et al. 2007) and likely results from a combination of dispersion and mixing as water moves deeper in the groundwater system and the fact that the groundwater in the deep zone is older and reflects lower nitrogen fertilizer application rates in the past (Fig. 4). The age of groundwater in the shallow and deep zones is not precisely known, but previous studies suggest that groundwater in the shallow zone may be on the order of 1–2 decades old, whereas groundwater in the deep zone ranges from several decades to thousands of years (Burow et al. 2008a; Jurgens et al. 2008; Bennett et al. 2010, 2011; Landon et al. 2010).

As was noted in the median concentrations over time, the magnitude of the change in nitrate concentration appears to be spatially more consistent in the shallow groundwater in the east fans subregion than the west fans subregion (Fig. 5). The large increase in median nitrate concentrations in shallow groundwater in the west fans and basin subregions in the 1980s is partly due to spatial bias introduced as a result of USGS studies near the Tulare Lake bed in the 1980s (Fig. 5; Fujii and Swain 1995). Most of the wells were not sampled again in subsequent decades. Many of the wells sampled during the 1980s were in areas where the water table was within 6 m of land surface and this shallow groundwater was strongly affected by evaporation, causing nitrate and many other salts to have very high concentrations. However, not all of the high concentrations in the shallow groundwater can be attributed to special studies as other parts of the valley also showed significant increases in concentration in the 1980s (Figs. 3a, 5); climatic or other factors may have influenced concentrations during this time. The decline in concentrations after the 1980s could also reflect the decline in nitrogen fertilizer inputs from about the 1980s–2000s (Fig. 4). If concentrations are influenced by these changes, then it suggests that the time lag between change in nitrogen inputs at the land surface and changes in the shallow aquifer is less than about 5–10 years, and would suggest that concentrations will increase again in the next decade as inputs have increased again since about 2000. It is difficult to establish causal relations between observed

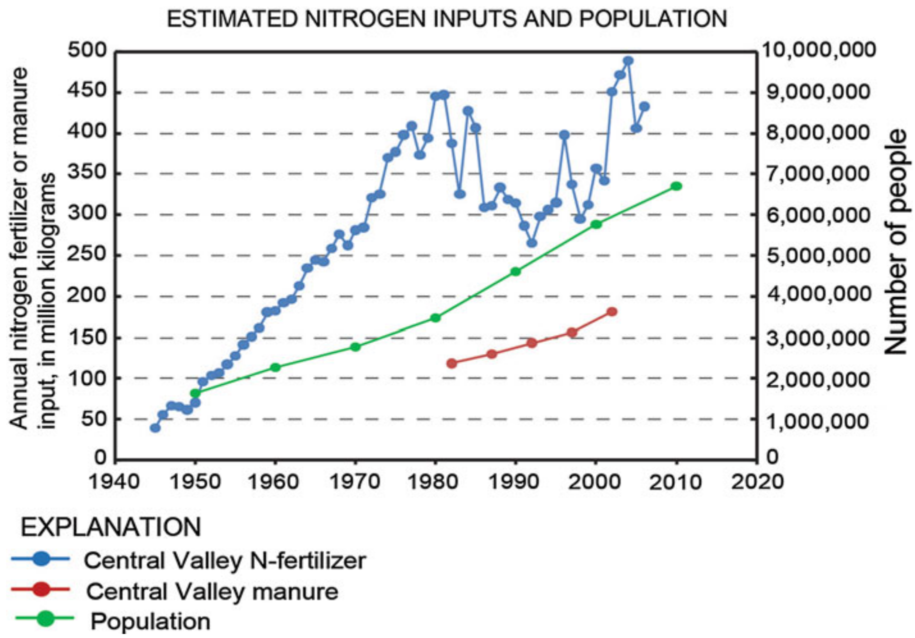


Fig. 4 Fertilizer and manure inputs and population in the Central Valley, California

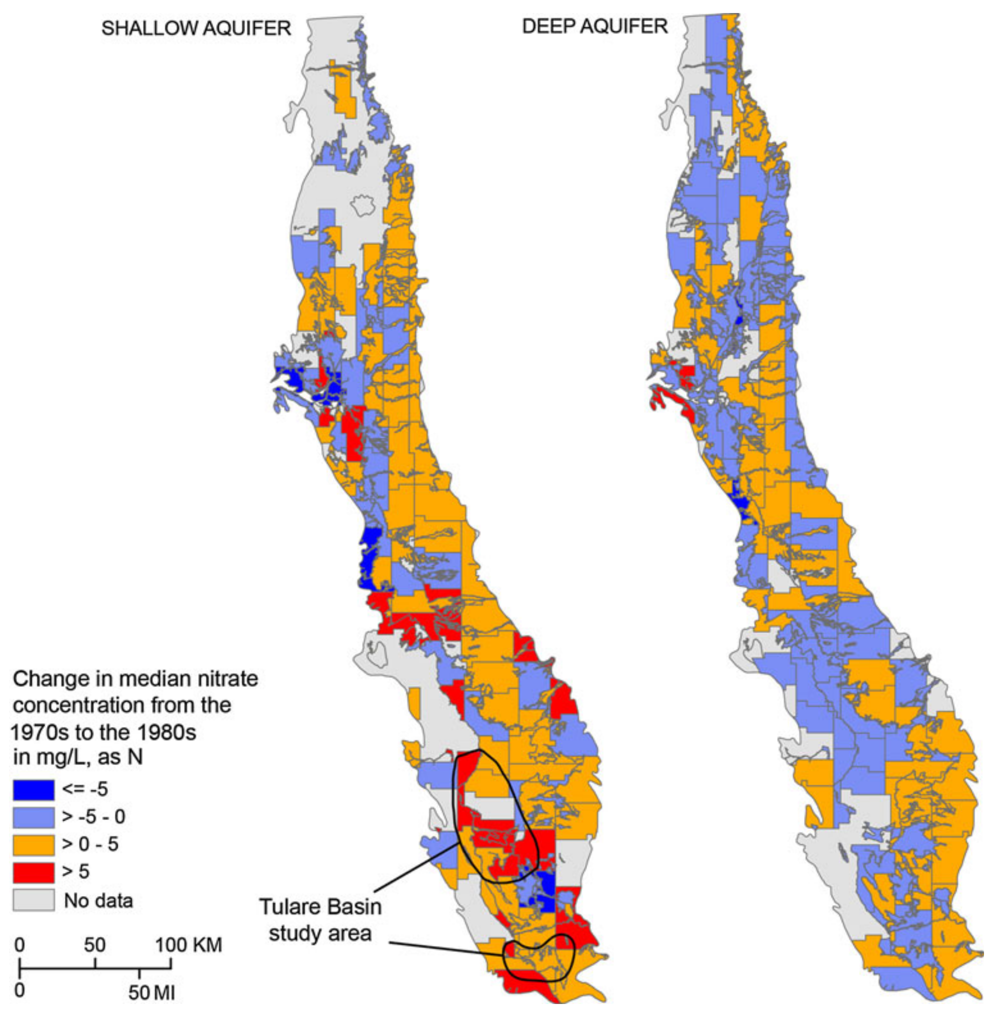


Fig. 5 Map of change in median nitrate concentrations between 1970s and 1980s

concentrations and regional nitrogen fertilizer inputs, however. Additional data such as groundwater age dates to accompany the nitrate concentration data would be needed.

Aquifer scale proportion

Similar to the increase in median concentrations in the east fans subregion, the percent of aquifer with nitrate concentrations over 5 mg/L, termed aquifer scale proportion (Belitz et al. 2010), increased from the 1950s–2000s (Fig. 6a). The change in aquifer scale proportion was extremely variable in the west fans subregion, although the proportion appears to generally increase over time in the deep aquifer in both the west fans and basin subregions. The changes in aquifer scale proportion look similar to the changes in median concentration, although the variability and confidence intervals appear to be greater for the aquifer scale proportion. These results indicate that during the 2000s about 40 % of the shallow aquifer in the east fans subregion had concentrations above 5 mg/L—a significant amount of land area and nitrogen mass considering the size of the subregion. These results are generally consistent with predictions of Anning et al. (2012).

Redox effects on nitrate concentrations

Increasing trends in nitrate concentrations occurred in parts of the valley where groundwater is primarily oxic. In contrast, areas that were geochemically reduced showed variable changes or a trend was not detected in nitrate concentrations. Nitrate concentrations were compared to iron (Fe) and manganese (Mn) concentrations to determine whether geochemical conditions may be affecting the spatial and temporal trends in nitrate concentrations. In areas with organic-rich sediments and low dissolved-oxygen concentrations, bacteria convert nitrate to nitrogen gas in the process of denitrification. There was insufficient dissolved-oxygen data to use in the analysis, however, so elevated Fe and Mn concentrations were used to indicate geochemically reduced conditions. Elevated Fe and Mn occur in anoxic conditions; therefore, elevated Fe and Mn concentrations are expected to be inversely related to nitrate concentrations.

In the east fans subregion, both Fe and Mn were low, with nearly all decades (1970s–2000s) having more than 90 % of the cells with a median concentration at the detection limit in both the shallow and deep aquifers. This is consistent with previous work documenting the primarily oxic conditions in this subregion (Burow et al. 2007, 2008b; Green et al. 2008; Landon et al. 2011).

In the west fans subregion, Fe concentrations were also generally low, with most decades having more than 90 % of

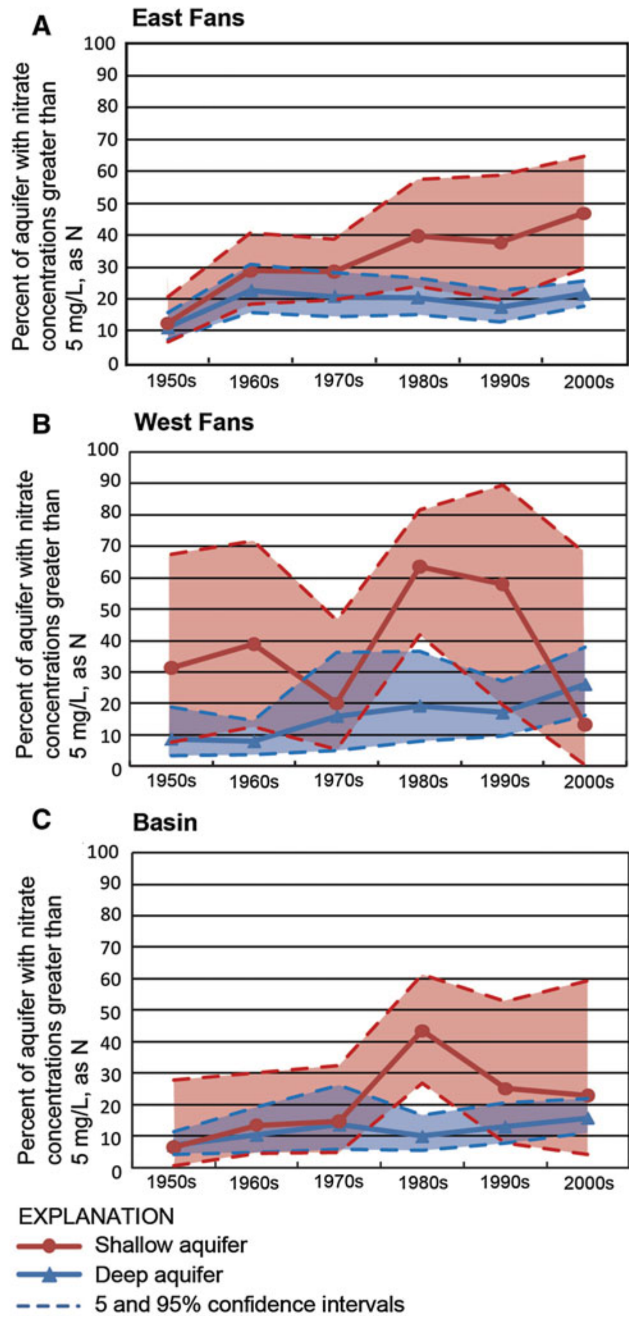


Fig. 6 Percent of cells with median nitrate concentrations greater than 5 mg/L for each decade and computed confidence intervals

the cells with a median concentration at the detection limit in the shallow and deep aquifers. However, a Regional Kendall test on the time series data for Fe indicated a weak but significant increase in Fe concentrations in the shallow aquifer in the basin subregion ($p = 0.008$; $\tau = 0.17$). Combining all the data over time, nitrate concentrations were inversely correlated to Mn concentrations in the shallow aquifer in the basin subregion ($p < 0.001$, $\rho = -0.52$; Spearman's rank correlation) and Fe concentrations ($p = 0.001$, $\rho = -0.30$; Spearman's rank correlation).

Less frequent detections of Fe and Mn in the other subregions precluded further correlation tests.

Mn concentrations in the shallow aquifer in the basin and west fans subregions were higher than the detection limit in up to about 60 % of the cells. In both subregions, median Mn concentrations were at the detection limit in the 1970s, increased above the detection limit in the 1980s and 1990s and then decreased back to the detection limit in the 2000s. These described Mn concentration trends appear to be positively correlated with the nitrate concentration trends rather than inversely correlated, but this apparent correlation is driven by the difference in trends between the Sacramento and San Joaquin Valleys.

Differences in trends between the Sacramento and San Joaquin Valleys

To evaluate the apparent positive correlation between nitrate and Mn concentrations, a separate analysis of nitrate, Mn and Fe concentrations was done for the Sacramento and San Joaquin Valleys (Table 3). Although Mn changes are not statistically significant, median concentrations decrease in the shallow aquifer in the basin in the San Joaquin Valley as nitrate concentrations increase significantly ($p < 0.001$; $\tau = 0.31$). In contrast, Fe concentrations in the Sacramento Valley increase as nitrate concentrations remain unchanged. An analysis of all the non-spatially-weighted data (raw well data without being grouped by cell or depth) suggests a similar pattern (Table 3). Mn and Fe concentrations are consistently higher in the east fans and basin subregions in the Sacramento Valley than the San Joaquin Valley, with as many as 37 % of the wells greater than 50 μg/L for Mn in the basin subregion in the Sacramento Valley.

Although nitrate concentrations increased significantly in the shallow aquifer in the Sacramento Valley east fans subregion ($p = 0.004$; $\tau = 0.37$), concentrations in the San Joaquin Valley east fans subregion increased at nearly 3 times the rate: 0.3 mg/L per decade in the Sacramento Valley and 0.8 mg/L per decade in the San Joaquin Valley. Therefore, it appears that the only area where nitrate concentrations are changing in the Sacramento Valley is the east fans subregion. In addition, concentrations are increasing more slowly in the Sacramento Valley than the San Joaquin Valley.

These results suggest that differences in nitrate trends between the Sacramento and San Joaquin Valley may be related to redox environment. Faunt et al. (2010) noted that the Sacramento Valley had a more fine-grained texture than the San Joaquin Valley, and precipitation in the Sacramento Valley is greater than the San Joaquin Valley. Anoxic conditions are more common in fine-textured sediments and more humid environments (McMahon and Chapelle 2008). Further, differences in nitrate trends cannot be explained by differences in nitrogen inputs alone. Although the northern Sacramento Valley has a large percentage of natural (undeveloped) land, rates of nitrogen fertilizer input on agricultural land are similar between the Sacramento and San Joaquin Valley (average about 80 kg/ha/yr).

Summary and Conclusions

This study attempts to maximize the use of historical data in assessment of multi-decadal trends in nitrate concentrations using a spatially stratified non-biased approach. Data were stratified into physiographic subregions on the basis of soils data to represent zones of historical recharge and discharge patterns in the basin. Data were also stratified by depth to represent a shallow zone generally representing domestic drinking-water supplies and a deep zone generally representing public drinking-water supplies. These stratifications were designed to approximate regional redox and age characteristics. A grid-based approach allowed for statistical tests across multiple decades and for data to be compared across the physiographic subregions by declustering data in some areas and extrapolating data in areas with sparse data coverage.

Overall, increasing trends in nitrate concentrations and the proportion of nitrate concentrations above 5 mg/L were observed in the east fans subregion of the Central Valley. Because groundwater is generally oxic in this subregion, mitigating the impacts of continued nitrogen loading to this aquifer will be extremely difficult if current nitrogen inputs continue to load excess nitrogen to the aquifer in this area.

Whereas the west fans subregion has elevated nitrate concentrations throughout the subregion, temporal trends were not detected, likely due to the heterogeneous nature of the water quality in this area and geologic sources of nitrate, combined with sparse and uneven data coverage. It is not possible to determine to what degree each of these factors has contributed to the results of the analysis, but given the overall changes in median concentration by decade in this subregion it appears that concentrations lack a specific (monotonic) trend as observed in the east fans subregion.

Generally low nitrate concentrations in the basin subregion are consistent with reduced geochemical conditions resulting from low permeability soils and higher organic content, reflecting the distal portions of alluvial fans and historical groundwater discharge areas. Very small increases in the shallow aquifer of the basin subregion in the San Joaquin Valley may reflect downgradient movement of high nitrate groundwater from adjacent areas or overlying intensive agricultural inputs.

Table 3 Trends in Mn and Fe concentrations in the Sacramento and San Joaquin Valley subareas of the Central Valley, California

Physiographic subregion	Median nitrate concentration, in mg/L as N	Manganese (Mn)				Iron (Fe)			
		τ*	*p**	Wells with Mn concentrations above 50 µg/L, in percent (%)	*n*	τ*	*p**	Wells with Fe concentrations above 100 µg/L, in percent (%)	*n*
Sacramento Valley									
East fans	1.4	–	–	16	557	–	–	19	556
West fans	2.4	–	–	7.9	267	–	–	13	268
Basin	0.63	0.11	0.42	37	447	0.25	0.005	28	444
San Joaquin Valley									
East fans	3.1	–	–	5.1	1,693	–	–	13	1,693
West fans	3.6	–	–	15	20	–	–	30	20
Basin	1.5	−0.11	0.39	15	442	0.10	0.33	24	443

Data used in percentage calculations are not grouped by grid cell or depth category

n number of wells; – , not enough detections to compute statistics

* Results of Regional Kendall test on shallow cell data

Because of the general lack of regionally extensive long-term monitoring networks, the results from this study highlight the importance of placing studies of trends in water quality into regional context. Earlier work concluded that nitrate concentrations were steadily increasing over time in the eastern San Joaquin Valley, but clearly those trends do not apply to other physiographic subregions, even where land use and climate are similar. It appears that redox conditions may play a significant role in determining where nitrate concentrations are the highest and where concentrations are most likely to increase.

However, using retrospective data is fraught with issues that could affect the results of the analysis. Using data from multiple sources could introduce bias by differences in sampling protocols or analysis (such as filtered or unfiltered Fe and Mn concentrations). A significant number of wells did not have depth information so the aquifer depth designation is based on well type alone; additionally, the sampled depth horizons could be smeared because some deep wells have long screens that may extend across the boundary imposed between the deep and shallow aquifer. Even in a region that is relatively rich in water quality data, gaps exist in space and time, which limit detailed mapping of nitrate trends and accompanying redox conditions. Spatial variability within cells could result in noisy trend patterns—in some cases, the within-cell variance is larger than the median change in concentration from decade to decade. However, the emphasis of this study is on regional patterns and trends; the results are not intended to be interpreted at the individual cell level.

Further work is needed to develop a better spatially resolved representation of redox conditions throughout the aquifer system. Much of the regional recharge and discharge relations was captured using the geomorphic/soils stratification approach; however, variations due to texture and climate between the Sacramento and San Joaquin Valleys were not differentiated in the algorithm used in this study. Further development of these types of tools will enable water managers to link field-scale process understanding of the effectiveness of best-management practices to the larger regional system.

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