Science of the Total Environment 452–453 (2013) 125–136

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trends in concentrations of nitrate and total dissolved solids in public supply wells of the Bunker Hill, Lytle, Rialto, and Colton groundwater subbasins, San Bernardino County, California: Influence of legacy land use

Robert Kent *, Matthew K. Landon

U.S. Geological Survey California Water Science Center, 4165 Spruance Road, Suite 200, San Diego, CA 95101-0812, USA

HIGHLIGHTS

- ► Groundwater nitrate and total dissolved solids (TDS) concentrations were evaluated.
- ► NO3 and TDS concentrations generally correlate with the same explanatory variables.
- ► Nitrate and TDS were increasing in about one-third of wells.
- ► Wells with increasing nitrate tended to also be increasing in TDS.
- ► Increasing nitrate concentrations are associated with legacy agricultural land use.

ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form 31 January 2013
Accepted 13 February 2013
Available online 15 March 2013

Keywords:
Groundwater
Trends
Nitrate
Total dissolved solids
Public supply

ABSTRACT

Concentrations and temporal changes in concentrations of nitrate and total dissolved solids (TDS) in groundwater of the Bunker Hill, Lytle, Rialto, and Colton groundwater subbasins of the Upper Santa Ana Valley Groundwater Basin were evaluated to identify trends and factors that may be affecting trends. One hundred, thirty-one public-supply wells were selected for analysis based on the availability of data spanning at least 11 years between the late 1980s and the 2000s.

Forty-one of the 131 wells (31%) had a significant ($p<0.10$) increase in nitrate and 14 wells (11%) had a significant decrease in nitrate. For TDS, 46 wells (35%) had a significant increase and 8 wells (6%) had a significant decrease. Slopes for the observed significant trends ranged from −0.44 to 0.91 mg/L/yr for nitrate (as N) and −8 to 13 mg/L/yr for TDS.

Increasing nitrate trends were associated with greater well depth, higher percentage of agricultural land use, and being closer to the distal end of the flow system. Decreasing nitrate trends were associated with the occurrence of volatile organic compounds (VOCs); VOC occurrence decreases with increasing depth.

The relations of nitrate trends to depth, lateral position, and VOCs imply that increasing nitrate concentrations are associated with nitrate loading from historical agricultural land use and that more recent urban land use is generally associated with lower nitrate concentrations and greater VOC occurrence. Increasing TDS trends were associated with relatively greater current nitrate concentrations and relatively greater amounts of urban land. Decreasing TDS trends were associated with relatively greater amounts of natural land use. Trends in TDS concentrations were not related to depth, lateral position, or VOC occurrence, reflecting more complex factors affecting TDS than nitrate in the study area.

Published by Elsevier B.V.

1. Introduction

1.1. Environmental setting

Groundwater is the main source of water supply in the Bunker Hill, Lytle, Rialto, and Colton groundwater subbasins of the Upper Santa Ana Valley Groundwater Basin (Duell and Schroeder, 1989; Woolfenden and Kadhim, 1997), and it is actively managed to control the concentrations of nitrate and total dissolved solids (TDS) (Danskin et al., 2006). Management strategies there include desalting operations, targeted pumping to hydraulically control the movement of high-salinity groundwater, creation of treatment wetlands, and limits on concentrations of nitrogen and TDS in wastewater discharged to the watershed (Wildermuth Environmental Inc., 2000). High concentrations of nitrate in groundwater used for water supply are of concern because of the association between nitrate concentrations greater than the USEPA maximum contaminant level (MCL) of 10 mg/L and infant methemoglobinemia (Johnson and Kross, 1990; Greer and Shannon, 2005) and the association between certain types of cancer and nitrate concentrations even less than the USEPA

* Corresponding author. Tel.: +1 619 225 6151; fax: +1 619 225 6101.
E-mail address: rhkent@usgs.gov (R. Kent).

0048-9697/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.scitotenv.2013.02.042

MCL (Neill, 1989; Weyer et al., 2001). Nationwide, fertilizers and septic leachate are the primary sources of nitrate concentrations higher than drinking water thresholds in groundwater used for public supply (Dubrovsky et al., 2010). All groundwater contains some dissolved solids, and groundwater may be naturally-high in TDS in some settings, such as geothermal and arid areas of groundwater discharge (Hem, 1992). In addition to natural sources, TDS can enter groundwater by engineered recharge of water that has been degraded by human use. In the Upper Santa Ana Watershed, most municipal wastewater and agricultural drainage are returned to the groundwater basins (Santa Ana Regional Water Quality Control Board, 1994). High concentrations of TDS in groundwater used for water supply make the water less acceptable to consumers because TDS can cause an objectionable taste or odor (U.S. Environmental Protection Agency, 2006). Therefore, an understanding of the distribution of concentrations of nitrate and TDS and whether these are generally increasing, decreasing, or remaining constant over time is of value to water resource managers.

The Bunker Hill (A and B), Lytle, Rialto, and Colton groundwater subbasins cover approximately 440 square kilometers (km^2), and are located in the northeast corner of the Upper Santa Ana Valley Groundwater Basin in San Bernardino County, California (Fig. 1). Annual precipitation ranges from 300 to more than 750 mm within the study area drainages, with higher precipitation in the adjacent San Bernardino and San Gabriel Mountains (California Department of Water Resources, 2004; Danskin et al., 2006). Historical land use in the study area, starting in the early 1800s, was primarily agriculture, but agricultural land use has been declining since the mid-1940s, and has been replaced by urban land use (Scott, 1977).

Regionally, groundwater flows from the San Bernardino Mountain front, where recharge from mountain runoff (both natural and engineered) is focused, and from the Lytle subbasin into the Bunker Hill subbasins and, subsequently discharges across the San Jacinto fault into the Rialto and Colton subbasins (Duell and Schroeder, 1989). Precipitation on the valley floor and urban and agricultural return flows also contribute areally-distributed recharge across the study area. Aquifer materials are mostly coarse-grained near the mountain front and grade to finer grained sand, silts and clays where groundwater exits the study area at focused discharge areas near the San Jacinto and Rialto-Colton faults (Izbicki et al., 1998; Wildermuth Environmental Inc., 2000; Dawson et al., 2003). The major ion composition of groundwater in the study area is dominated by calcium and bicarbonate, but this composition shifts slightly to higher percentages of sodium and sulfate as groundwater flows downgradient (Izbicki et al., 1998).

Groundwater quality in the Upper Santa Ana Watershed is being assessed as part of the California State Water Boards' Groundwater Ambient Monitoring and Assessment (GAMA, http://www.waterboards.ca.gov/gama/) Priority Basin Project, conducted in cooperation with the U.S. Geological Survey (USGS) (http://ca.water.usgs.gov/gama/; Kent and Belitz, 2009, 2012). The present study, conducted as part of the GAMA Priority Basin Project, examines current concentrations and temporal trends for concentrations of nitrate and total dissolved solids (TDS) in 131 public supply wells located in the Bunker Hill, Lytle, Rialto, and Colton groundwater subbasins.

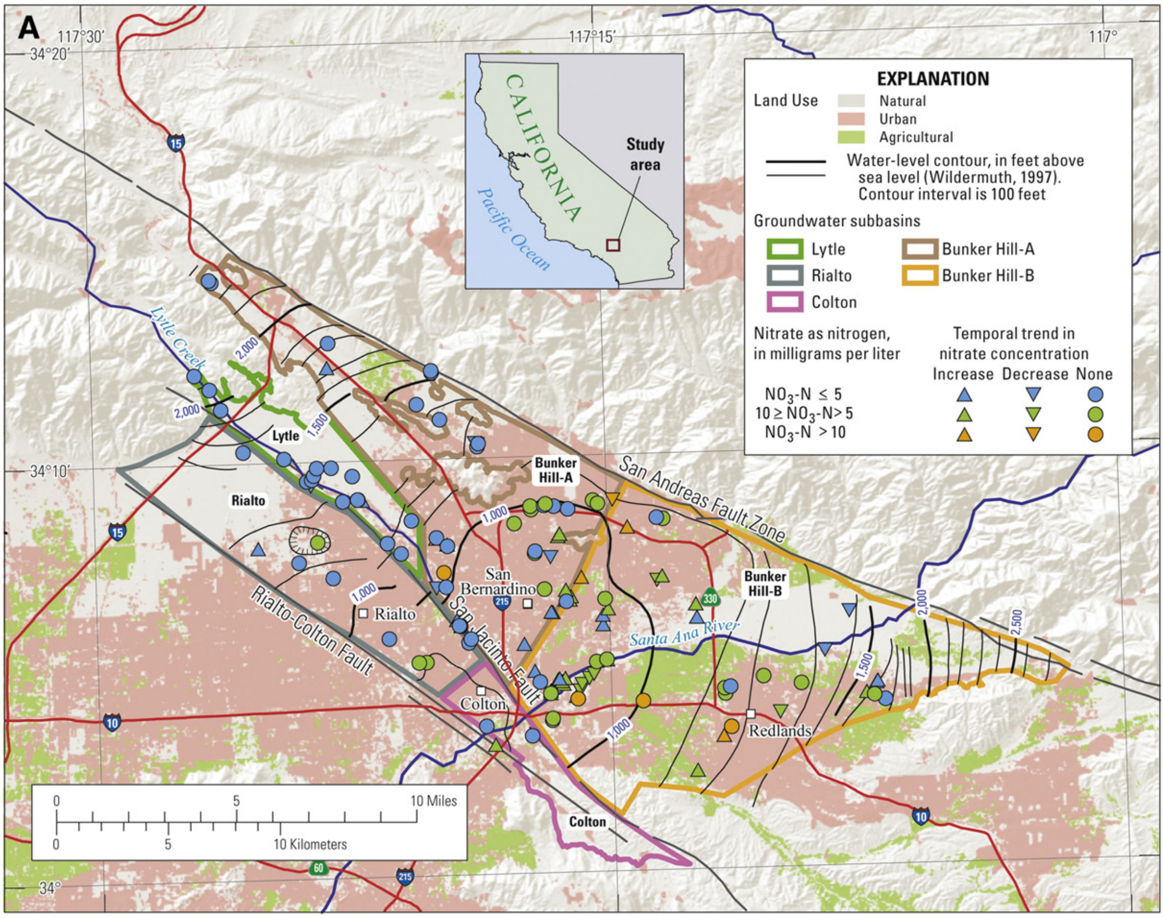
1.2. Previous work

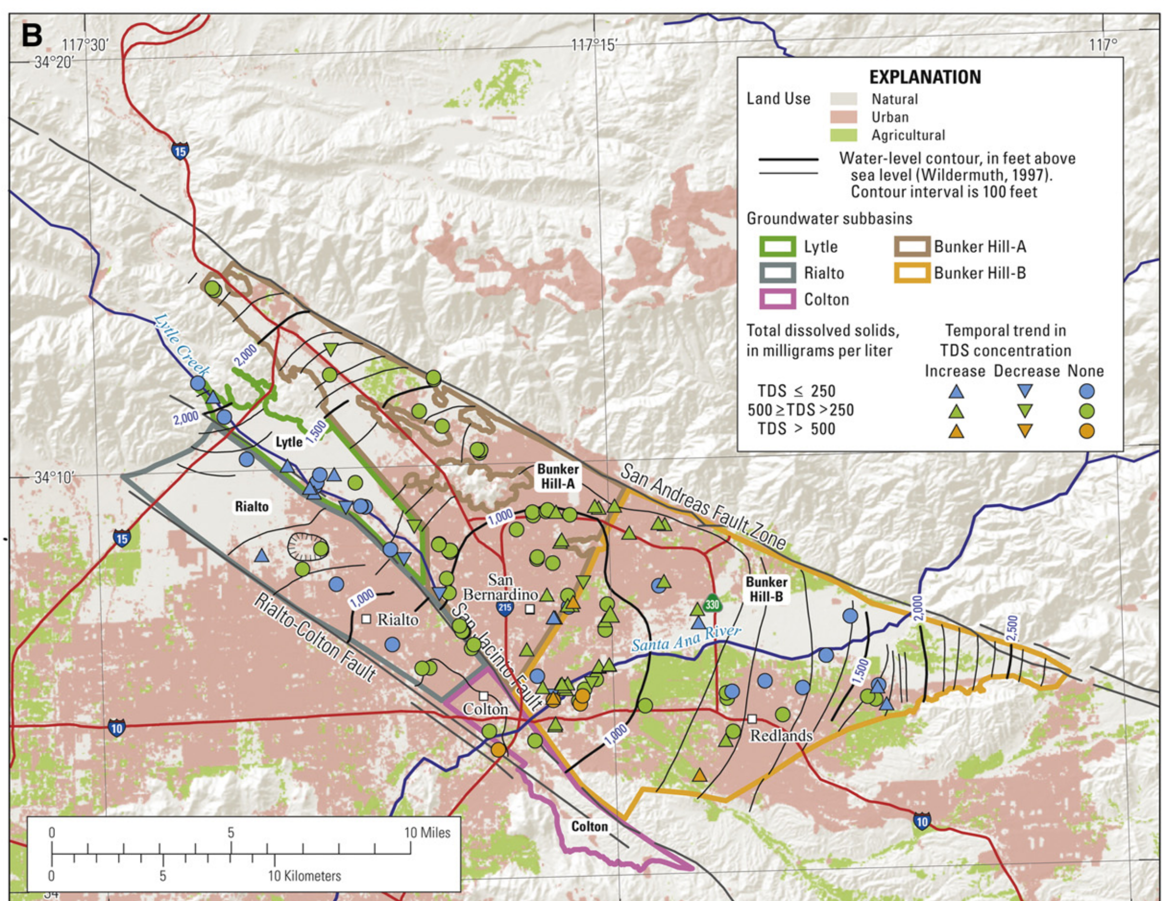
For several decades, the Santa Ana Regional Water Quality Control Board (SARWQCB) and the Santa Ana Watershed Project Authority (SAWPA) have recognized that TDS and total inorganic nitrogen (TIN) are the most important water-quality issues in the Santa Ana Basin, and much work has been done to monitor concentrations of these constituents in its water sources (Eccles, 1979; Duell and Schroeder, 1989; Santa Ana Regional Water Quality Control Board, 1994; Wildermuth Environmental Inc., 1998, 2000; Hamlin et al., 2002; Kent and Belitz, 2004; Santa Ana River Watermaster, 2010). Monitoring has resulted in a variety of water-quality management strategies along with regular public reporting of nitrate and TDS concentrations (Wildermuth Environmental Inc., 2000; Santa Ana Regional Water Quality control Board, 2004; Santa Ana Watershed Project Authority, 2009—Chapter 5.2). However, a statistical analysis of changes in concentrations of TDS and nitrate in individual wells over decadal or longer periods has not been performed to date.

Reviews on methods to perform water-quality trend analysis (Hirsch et al., 1991; Loftis, 1996) reveal that it is necessary to have a working definition of the word “trend.” The term “trend”, as used here, refers to a statistically significant change in concentration (decrease or increase) over time. There are two primary types of trend estimation: step trend hypothesis (measuring differences before and after a specific time), and monotonic change (without direction reversal) over time (Hirsch et al., 1991).

Temporal trends of groundwater quality are difficult to assess due to the long time scales involved with groundwater movement and the resulting changes in quality, although relatively short-term studies may be used to monitor the progress of remediation efforts (Eberts et al., 2005). Lindsey and Rupert (2012) performed step-trend analyses using the results from decadal-scale sampling of 56 well networks in the United States, supplemented with time-series (monotonic change) analyses using the results from biennial-scale sampling for a subset of the same networks, and found significant changes (mostly increases) in the concentrations of chloride, dissolved solids, and nitrate in many of the networks at both time scales. Several studies have compared methods aimed at detecting trends, and have evaluated the ability of these methods to predict future changes in groundwater quality (Stuart et al., 2007; Visser et al., 2009). In the eastern San Joaquin Valley of California, Burow et al. (2007, 2008) used several methods to evaluate temporal trends in groundwater nitrate concentrations, and concluded that concentrations in the deep part of the aquifer system are lower than in the shallower parts, but that the deep parts are likely to see increases with time. In a part of the eastern San Joaquin Valley, Landon et al. (2011) determined that trends in groundwater nitrate concentrations in public-supply wells were primarily related to land use, stratigraphy, and depth and only slightly influenced by oxidation–reduction conditions. Wildermuth Environmental Inc. (2005, 2008) have assessed nitrate and TDS concentrations for groundwater in the Upper Santa Ana Watershed, and have identified where these constituents may be currently increasing or decreasing. For the five groundwater subbasins investigated here, Wildermuth Environmental Inc. found TDS to currently be at higher concentrations compared to historical ambient conditions in two subbasins (Bunker Hill A and Colton), at lower concentrations in two subbasins (Bunker Hill B and Lytle), and at approximately equal concentrations in one subbasin (Rialto). They found nitrate to currently be at higher concentrations in all of these subbasins except for Bunker Hill B, where current nitrate concentrations were found to be lower than historical ambient conditions. While changes in water quality over time may be generally assessed by comparing the findings of these, and other reports on groundwater quality in the Upper Santa Watershed (Eccles, 1979; Duell and Schroeder, 1989; Hamlin et al., 2002; Kent and Belitz, 2009), to our knowledge, no previous study has performed a statistical evaluation of temporal trends in TDS or nitrate concentrations in wells of the Upper Santa Ana Valley groundwater basin, and attempted to relate these trends to potential explanatory factors.

Fig. 1. A. Map showing nitrate concentrations and trends, land-use categories, water level contours (1997), location and cultural and hydrogeological features of the Bunker Hill, Lytle, Rialto, and Colton subbasins. B. Map showing TDS concentrations and trends, land-use categories, water level contours (1997), location and cultural and hydrogeological features of the Bunker Hill, Lytle, Rialto, and Colton subbasins.


A
117°30′
34°20′
117°15′
117°
CALIFORNIA
Pacific Ocean
Study area
EXPLANATION
Land Use
Natural
Urban
Agricultural
Water-level contour, in feet above sea level (Wildermuth, 1997). Contour interval is 100 feet
Groundwater subbasins
Lytle
Rialto
Colton
Bunker Hill-A
Bunker Hill-B
Nitrate as nitrogen, in milligrams per liter
Temporal trend in nitrate concentration
Increase Decrease None
NO_3-N ≤ 5
10 ≥ NO_3-N > 5
NO_3-N > 10
34°10′
Lytle Creek
Lytle
Rialto
Bunker Hill-A
Bunker Hill-B
San Andreas Fault Zone
San Bernardino
Rialto
Rialto-Colton Fault
San Jacinto Fault
Santa Ana River
Colton
Redlands
2,000
1,500
1,000
2,500
0 5 10 Miles
0 5 10 Kilometers
34°


B
117°30′
34°20′
117°15′
117°
EXPLANATION
Land Use
Natural
Urban
Agricultural
Water-level contour, in feet above sea level (Wildermuth, 1997). Contour interval is 100 feet
Groundwater subbasins
Lytle
Rialto
Colton
Bunker Hill-A
Bunker Hill-B
Total dissolved solids, in milligrams per liter
Temporal trend in TDS concentration
Increase Decrease None
TDS ≤ 250
500 ≥ TDS > 250
TDS > 500
34°10′
Lytle Creek
Lytle
Rialto
Bunker Hill-A
Bunker Hill-B
San Andreas Fault Zone
San Bernardino
Rialto
Rialto-Colton Fault
San Jacinto Fault
Santa Ana River
Colton
Redlands
2,000
1,500
1,000
2,500
0 5 10 Miles
0 5 10 Kilometers

The Bunker Hill, Lytle, Rialto, and Colton groundwater subbasins are part of a critical aquifer system of great importance for a growing urban population, and they have been studied extensively (Woolfenden and Kadhim, 1997; Woolfenden and Koczot, 2001; Danskin et al., 2006). This area has nearly 300 public-supply wells that have been sampled for groundwater quality by the USGS and the California Department of Public Health (CDPH) over approximately two decades. This study identifies an approach for assessing trends in groundwater quality making use of historical data and accounting for driving forces, including the sampling position (well location) in the flow system.

2. Methods

2.1. Selection of wells and data

Wells in the study area were selected based on the availability of >10 years of data in which at least one sample was collected between 1986 and 1990, and at least one sample was collected between 2001 and 2008. In addition, at least four analyses for each well are necessary to attain a p-value less than 0.1 for the Mann–Kendall test (see below); thus, a minimum of 4 data points was necessary for a well to be selected for the study. The study uses groundwater quality data for public supply wells from sampling for regulatory compliance made available to the GAMA program by the CDPH along with data from the USGS National Water Information System database including GAMA data. It should be noted that using data on groundwater from public supply wells may introduce a bias toward water suitable for drinking since wells that produce non-potable water are removed from a public supply system. The predominant source of data for most wells was from the CDPH, supplemented with USGS data. For a few wells the predominant source of data was the USGS. Comparability of data from the CDPH and the USGS was verified by statistically testing the differences and relative standard deviations (standard deviation of the two measured concentrations divided by their means) between nitrate and TDS results reported by the CDPH and the USGS for the same wells. Wilcoxon signed-rank tests were performed on 66 matched pairs of samples collected by each agency for both nitrate and TDS. Samples in each pair were collected at the same well within 2 months of each other and the 66 pairs ranged in date from 1989 to 2007 (nearly the entire study period). No statistical difference between CDPH and USGS data was found ($\alpha = 0.1$) for either nitrate or TDS by the Wilcoxon signed-rank tests, suggesting that nitrate and TDS data from the two agencies are comparable. The mean relative standard deviations (Mueller and Titus, 2005) were <7% for nitrate, and <4% for TDS, suggesting that the variability in results between the two data sources was low.

To test whether seasonal fluctuations in concentrations occur and could affect the analysis of long-term trends, the months during which samples were collected, were categorized as “wet” (November thru April) and “dry” (May thru October). The categories were based on normal precipitation data for San Bernardino County and compiled by the National Climatic Data Center, the National Oceanic and Atmospheric Administration, and the National Weather Service (http://www.idcide.com/weather/ca/san-bernardino.htm, accessed November 2, 2012). A Wilcoxon rank-sum test was used to determine if there were significant differences between the samples collected during “wet” months from those collected during “dry” months. The Wilcoxon rank sum test is a nonparametric alternative to a two-sample t-test that is not dependent upon data distribution (Helsel and Hirsch, 2002). Results from the Wilcoxon rank-sum test indicated that samples collected during “wet” months had significantly lower TDS concentrations than those collected during “dry” months suggesting that the annual seasonal cycles of precipitation or groundwater pumping affect the measured TDS concentrations. A significant difference between wet and dry months was not found for nitrate concentrations. However, data were often not available for both wet and dry seasons of a given year. More data were available for the dry season than for the wet season. Therefore, samples collected during “wet” months were excluded from the analyses. If more than one set of results for nitrate and TDS concentrations was available for a dry season, the median result for each parameter was used to represent that season. It should be noted that, by excluding results from the wet season, the TDS concentrations reported here are biased slightly high. One-hundred and thirty-one wells met the data requirements described above, and were included in the trend analyses. Including wells with as few as 4 measurements fails to satisfy the EU Groundwater Directive recommending at least 8 points for trend analysis (Grath et al., 2001). Of the 131 wells evaluated for trends, 27 wells had fewer than 8 measurements, and the power of the test to detect trends for those wells was likely less than for the other 104 wells. The study period and number of observations were variable for the wells included in the study (Table 1).

Table 1
Summary statistics for wells analyzed for trends in concentrations of nitrate and TDS.

Number of wells analyzed	131	
	Range	Median
Duration of record (years)	13–22	19
Number of values for each parameter	4–21	13
Start year	1986–1990	1987
End year	2001–2008	2005

2.2. Determination of categories for trends and concentrations

The nonparametric Mann–Kendall trend test (Mann, 1945; Helsel and Hirsch, 2002) was used to test for the significance of a Kendall's τ correlation of nitrate or TDS concentration and time in the 131 wells. The Sen slope estimator (mg/L/yr) was calculated to estimate trend magnitude (Sen, 1968; Hirsch et al., 1991). For the purpose of this study an attained significance level (p) less than or equal to a threshold value (α) of 0.1 was considered statistically significant. Based on the results of the trend test, the wells were categorized as decreasing, increasing, or no detected trend with regard to nitrate and TDS. Similarly, current nitrate and TDS concentrations in samples from the wells were categorized as low, moderate, or high, similar to the characterization scheme used in assessment reports produced by the GAMA program (Landon et al., 2010; Kent and Belitz, 2012). High concentrations are those greater than the drinking water benchmark concentration for the constituent: 10 mg/L as N for nitrate, and 500 mg/L for TDS. The benchmark used for nitrate is the USEPA MCL. The benchmark of 500 mg/L for TDS is the USEPA secondary maximum contaminant level (SMCL) and the lower of two recommended SMCLs used by the California Department of Public Health (CDPH). The GAMA program uses the upper recommended level used by the CDPH of 1000 mg/L. Moderate concentrations are those greater than half the benchmark and less than or equal to the benchmark. Low concentrations are at or less than half the benchmark. The current concentrations used in this study are the median of all values measured during the 2000s for each constituent.

2.3. Evaluation of well attributes and potential explanatory factors

Current concentrations and the trend categorical groups (decreasing, increasing, or no detected trend) for each constituent were tested for relations with other water-quality parameters and well characteristics. Other water-quality parameters evaluated as potential explanatory factors included occurrence of volatile organic compounds (VOCs) and perchlorate concentrations. VOCs were evaluated in three ways as potential explanatory factors: number of VOCs detected in the most recent available sample, the summed concentrations of detected VOCs in the most recent available sample, and the mean concentration of the sum of detected VOCs in all available samples. VOC occurrence and concentration data investigated for relations with nitrate and TDS had some limitations. USGS data on volatile organic compounds (VOCs) were available for only 35 of the 131 wells evaluated in this study. In contrast to the limited availability of USGS data, VOC results were available from the California Department of Health for all of the wells spanning the study period, but the analytical reporting levels for these data were generally an order of magnitude greater than those for USGS data. Therefore, the data were not comparable, making it necessary to perform the three evaluations described above separately for each of the two data sources.

Well characteristics that were evaluated included well depth, depth to the top of the uppermost perforation, land use surrounding the well, and position of the well in the regional groundwater flow system. Depth was hypothesized to be related to water-quality trends because it has commonly been observed to be related to aquifer geochemistry and can be a surrogate for groundwater residence time (Appelo and Postma, 1999; McMahon et al., 2008). Well-construction data were determined from driller's logs, ancillary records of well owners, or NWIS (Kent and Belitz, 2009).

Groundwater quality has been linked to land use characteristics (U.S. Geological Survey, 1999). Land-use statistics for circles with a radius of 500-m around each well (Johnson and Belitz, 2009) were used to assess the relation of 3 broad categories of land use—urban, agricultural, and natural—to concentrations and trends of nitrate and TDS. Johnson and Belitz (2009) demonstrated statistically that land use in a 500-m circle around a well is likely to be predictive of land use in the contributing area of a well, which is inaccurately known due to uncertainties in flow paths. Land use was classified into the three major categories for 1992, near the beginning of the study period (Nakagaki et al., 2007), and 2001, near the end of the study period (Homer et al., 2004). The "natural" land use classification included forest and shrub land, as well as bare land without vegetation.

Nitrate and TDS trends were hypothesized to be related to horizontal position in the flow system because groundwater residence time and flow-path length should generally increase from the proximal to the distal end of the flow system. Recharge also occurs along the flow path so that younger water mixes with older water in unconfined and semi-confined zones of the flow system. Normalized lateral position is a proxy for the horizontal position of a well in the regional groundwater-flow system (Landon et al., 2011). Groundwater flow in the study area primarily flows from the northeastern, northwestern, and southeastern margins of the valley-fill deposits along the mountain fronts, converging towards the valley center, near where the Santa Ana River crosses the southwestern boundary of Bunker Hill subbasin and exits the study area (Izbicki et al., 1998; Dawson et al., 2003) (Fig. 1). Groundwater flow at this outlet may be constrained by the San Jacinto and Rialto-Colton faults at the southwestern margins of the Bunker Hill and Colton subbasins, respectively. For this study, the normalized lateral position of each well in the flow system was quantified in 2 ways: land-surface elevation, and normalized distance to the down-gradient end of the flow system. Groundwater in alluvium moves under a natural hydraulic gradient that generally conforms to surface topography (Toth, 1963). Therefore, the land-surface elevation of a well typically corresponds to its water level and, consequently, to its horizontal position in the flow system. The second measure of lateral position, normalized distance to the down-gradient end of flow system, was calculated by determining the relative distance remaining for water in the well to exit the study area flow system. This normalized distance varies from 0 at the downgradient or distal end to 1 at the upgradient or proximal end of the flow system based on flow paths suggested by Izbicki et al. (1998) and Dawson et al. (2003).

TDS consists of major cations and anions (including nitrate). An examination of the changes in the proportions of individual ions in the groundwater over the study period might suggest processes contributing to trends in the concentrations of nitrate and TDS, and may signal changes in water sources. For each well, changes over the study period were calculated for the cationic charge percentages contributed by calcium, magnesium, sodium, and potassium. This was done for each well by subtracting the median charge percentage contributed by each cation to the total cationic charge in samples collected in the 1980s from the median value in samples collected in the 2000s. Changes in the anionic charge percentage values for bicarbonate, carbonate, sulfate, chloride, fluoride, and nitrate were calculated the same way. Changes in concentrations of the major ions over the study period were also examined.

2.4. Statistical tests used to evaluate potential explanatory factors

Kendall's τ tests were performed to determine whether current nitrate and TDS concentrations were significantly correlated with the potential explanatory factors. The potential explanatory factors were then evaluated for relationships with the wells in the three trend categories for nitrate and TDS. Kruskal–Wallis rank-sum tests were performed to determine whether or not there were statistically significant differences in potential explanatory factors between categories of wells having increasing trends, decreasing trends, or no detectable trends. The Kruskal–Wallis rank-sum test is a nonparametric alternative to a one-way analysis of variance (Helsel and Hirsch, 2002). Finally, one-sided Wilcoxon rank-sum tests were performed for just the wells exhibiting increasing or decreasing temporal trends. For this test, the no-trend group was excluded to more specifically define the differences between increasing and decreasing wells. The justification for this one-sided approach is that it cannot be assumed that the influence of explanatory factors on the direction and magnitude of temporal trends will act like a gradient that passes through a neutral or "no-trend" outcome. Rather, it seems more likely that the wells not exhibiting temporal trends are wells that possess some, as yet unidentified, characteristic that makes the water quality in those wells less vulnerable to change in either direction.

3. Results

3.1. Current concentrations of nitrate and TDS

High concentrations of nitrate and TDS occur infrequently in the study area but moderate concentrations are relatively widespread. Six percent (6%) of the wells analyzed for trends had current nitrate concentrations that were high (>10 mg/L as N), 37% had moderate nitrate concentrations (>5≤10), and 57% had low nitrate concentrations (≤5) (Table 2). Current TDS concentrations were high (>500 mg/L) in 5% of the wells, moderate (>250≤500) in 67%, and low (≤250) in 28%

Table 2
Concentration and trend categories for nitrate and TDS in study area wells.

	Number of wells			
	Increasing	Decreasing	No significant change	Sum
Nitrate				
All wells	41	14	76	131
High >10 mg/L as N	3	1	4	8
Moderate >5≤10 mg/L	19	6	23	48
Low≤5 mg/L	19	7	49	75
TDS				
All wells	46	8	77	131
High>500 mg/L	2	0	4	6
Moderate >250≤500 mg/L	32	4	52	88
Low≤250 mg/L	12	4	21	37

Table 3
Results of tests for significance of relations between potential explanatory factors and concentrations and trends in concentrations for nitrate and TDS.

Potential explanatory factor	Kendall's tau correlation with current constituent concentrations[a]		Kruskal–Wallis test p-value for differences between three trend categories[b]		Wilcoxon rank-sum test p-value for difference between wells with increasing vs. decreasing trend[c]	
	Nitrate	TDS	Nitrate	TDS	Nitrate	TDS
Current constituent concentrations						
Nitrate	–	0.39	0.076	0.018	ns	0.034(+)
TDS	0.39	–	0.082	ns	ns	ns
Perchlorate	0.33	0.12	0.032	0.054	ns	ns
Total VOC (USGS samples)	0.22	0.21	0.011	ns	0.003(−)	ns
Total VOC (CDPH samples)	0.24	0.18	ns	ns	0.080(−)	ns
Hydrologic and land-use factors						
Depth to top of well perforation	ns	−0.22	0.082	ns	0.041(+)	ns
Well depth	ns	ns	0.016	0.025	0.007(+)	ns
Percent urban land use	0.16	0.21	ns	ns	ns	0.088(+)
Percent natural land use	−0.27	−0.25	ns	ns	0.049(−)	0.043(−)
Percent agricultural land use	0.17	ns	0.020	ns	0.096(+)	ns
Elevation	−0.19	−0.27	<0.001	0.026	0.035(−)	ns
Normalized distance to down-gradient end of flow system	−0.10	−0.12	0.001	ns	0.028(−)	ns
Changes in constituent concentrations						
Nitrate	0.28	0.13	<0.001	<0.001	0.005(+)	0.005(+)
TDS	0.24	0.22	<0.001	<0.001	<0.001	<0.001
Changes in constituent ionic proportions						
Bicarbonate	−0.10	−0.17	<0.001	<0.001	<0.001(−)	0.003(−)
Sulfate	ns	0.22	0.040	<0.001	ns	0.001(+)
Chloride	ns	−0.12	ns	ns	ns	ns
Sodium + potassium	ns	ns	0.007	ns	0.002(−)	0.035(−)
Magnesium	ns	ns	ns	ns	ns	0.075(+)

[a] Positive Kendall's tau value indicates direct correlation between current constituent concentration and value of potential explanatory factor; negative tau value indicates inverse correlation. Tau values only given for tests with p-values < 0.1. ns denotes not significant, p-value ≥ 0.1.

[b] Kruskal–Wallis p-value < 0.1 indicates that there is a significant difference in the median value of the potential explanatory factor between at least two of the three trend categories: wells showing trend of increasing constituent concentration, wells showing trend of decreasing concentration, and well showing no significant trend in constituent concentration.

[c] Wilcoxon p-value < 0.1 indicates that there is a significant difference in the median value of the potential explanatory factor between wells showing trend of increasing constituent concentration and wells showing trend of decreasing constituent concentration. Positive (+) indicates that wells showing trend of increasing constituent concentration have higher median value of the potential explanatory factor. Negative (−) indicates that wells showing trend of decreasing constituent concentration have higher median value of potential explanatory factor.

(Table 2). The frequency of wells having high, moderate, and low concentrations in this study, is similar to the results of Kent and Belitz (2012) for the present study area within an assessment of the entire Inland Santa Ana Basin when the lower benchmark for TDS used in the present study is taken into account.

3.2. Relations of current concentrations of nitrate and TDS to explanatory factors

Most of the potential explanatory factors evaluated in this study were determined to be directly or inversely correlated with current concentrations of nitrate and TDS (Table 3). Nitrate concentrations were directly correlated with TDS concentrations, and nitrate and TDS concentrations were generally correlated with the same potential explanatory variables. Both were directly correlated with the occurrence of VOCs and perchlorate, as well as with urban land use. Both were inversely correlated with natural land use and flow-length remaining to the end of the flow system as well as with land-surface elevation. Nitrate concentrations were directly correlated with urban and agricultural land use, and inversely correlated with natural land use (Table 3). TDS concentrations were also directly correlated with urban land use and inversely correlated with natural land use and depth to the top of well perforations (Table 3).

Temporal changes in groundwater cationic proportions were not related to current concentrations of nitrate or TDS. Similarly, changes in anionic proportions were not related to current nitrate concentrations, with the exceptions of a weak inverse correlation with changes in bicarbonate percentages and, as would be expected, a strong direct correlation with changes in nitrate ionic percentages. In contrast, current TDS concentrations were significantly correlated with changes in the proportions of the 3 most abundant anions—bicarbonate, chloride, and sulfate. Changes in bicarbonate and chloride percentages were inversely correlated with TDS concentrations, and changes in sulfate percentages were directly correlated with TDS concentrations. The strongest such relationship indicates that TDS concentrations tend to be high in wells of this study area where the anionic proportion of sulfate has been increasing over time (Table 3).

3.3. Trends in concentrations of nitrate and TDS

Analysis of changes in concentrations over time showed that both nitrate and TDS had no detected change in a small majority of wells (58% for nitrate and 59% for TDS), increasing trends in about one-third of the wells (31% and 35%), and decreasing trends in a relatively small proportion of wells (11% and 6%) (Table 2). Rates of change in concentrations were similar in wells with increasing and decreasing trends, in terms of magnitude. In the 41 wells (of 131) with significantly positive trend slopes for nitrate, rates of increase ranged from 0.01 to 0.90 mg/L/yr, with a mean of 0.19 mg/L/yr. In the 14 wells with significantly negative trend slopes for nitrate, rates of decrease ranged from −0.04 to −0.44 mg/L/yr, with a mean of −0.20 mg/L/yr. In the 46 wells with significantly positive trend slopes for TDS, rates of increase ranged from 0.50 to 13.5 mg/L/yr with a mean of 5.2 mg/L/yr. In the 8 wells with significantly negative trend slopes for TDS, rates of decrease ranged from −0.65 to −7.5, with a mean of −3.2 mg/L/yr.

3.4. Relations among trends in nitrate and TDS concentrations

A fundamental question for this study is whether wells that exhibit a temporal trend in either direction for TDS or nitrate tend to

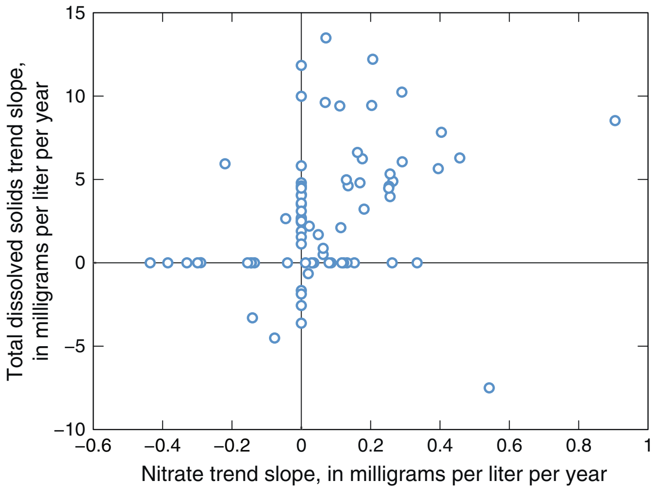


Fig. 2. Graph showing trend slope values for concentrations of nitrate and TDS (mg/L/yr) in the study area. Only wells with a significant trend for nitrate, TDS, or both are represented.

exhibit the same trend for the other parameter. This generally appears to be the case (Figs. 1A and B, 2). Temporal TDS trends were found to directly correlate with temporal nitrate trends. Paired TDS and nitrate trend slope values were directly correlated regardless of whether slopes that had failed the significance test ($p > 0.1$) were included in the correlation (Kendall's $\tau = 0.35$), excluded from it (Kendall's $\tau = 0.34$), or assigned a slope value of zero (Kendall's $\tau = 0.26$).

Of the 60 wells with significant increasing trends for either TDS or nitrate, 27 wells had increasing trends for both parameters, and 33 wells had increases in either TDS or nitrate, but not both (Fig. 2).In contrast, only 2 wells decreasing in nitrate were also decreasing in TDS. Moreover, 4 wells with a significant decreasing trend for one parameter had a significant increasing trend for the other parameter (Fig. 2).

3.5. Spatial patterns for observed trends in nitrate and TDS

Most wells with significant increasing trends for both parameters were located near the boundary between the Bunker Hill A and Bunker Hill B subbasins, north of the Santa Ana River (Fig. 1a and b). In other parts of the study area, trends, in either direction, were generally observed for only one of the two parameters. Only one well (of 11) in the Rialto subbasin had a significant trend, and that well had increasing trends for both parameters. In contrast, half of the wells (9 out of 18) in the Lytle subbasin had significant trends, but almost exclusively for TDS; increasing in the northern half, decreasing in the southern half. Wells located north of the Santa Ana River tended to be increasing for nitrate, while those located south of the river tended to be decreasing or exhibiting no trend for nitrate.

3.6. Relations of trends in nitrate and TDS to their current concentrations

Trends in nitrate and TDS were not related to current concentrations of nitrate and TDS in most cases, except for an association of higher nitrate concentrations with increasing TDS trends. There were no significant differences in current TDS concentrations among wells categorized as having increasing, decreasing, or no detected trends for either nitrate or TDS (Table 3). While current nitrate concentrations were significantly different among wells categorized as having increasing, decreasing, or no detected trends for nitrate (Table 3), they were not significantly different between wells with increasing nitrate trends and wells with decreasing nitrate trends. Current nitrate concentrations were significantly different among wells categorized as having increasing, decreasing, or not detected trends for TDS. Specifically, wells with increasing TDS trends had higher current nitrate concentrations than wells with decreasing TDS trends (Table 3).

3.7. Relations of trends in concentrations of nitrate and TDS to explanatory factors

Wells with an increasing trend in nitrate concentrations had significantly greater total depth and depth to the top of perforations than did wells with decreasing nitrate trends. Well depth and depth to top of perforations were significantly different among wells categorized as having increasing, decreasing, or no detected trends for nitrate (Table 3). There was not a significant relationship between TDS trend groups (increasing or decreasing) and well depths (Table 3).

Wells with an increasing trend in nitrate concentrations had significantly lower VOC concentrations (Table 3) and numbers of VOCs detected than wells with decreasing nitrate concentrations. In contrast with nitrate, VOC occurrence did not correlate with trends in TDS concentrations (Table 3).

The results of this study do not indicate clear relations between perchlorate concentrations and trends in nitrate and TDS concentrations (Table 3). Perchlorate contamination constitutes a groundwater-quality concern that may rival those of nitrate and TDS in the study area, particularly in the western part of the study area; the Rialto-Colton subbasin (Woolfenden, 2007).

Natural and agricultural land uses were related to trends in nitrate concentration in the study area (Table 3). Land use in the study area as a whole in 1992 (near the beginning of the study period) was 45% natural, 8% agricultural, and 47% urban (Nakagaki et al., 2007). The study area has undergone increasing urban land use before, during, and since the study period, and by 2001 land use was 28% natural, 3% agricultural, and 69% urban (Homer et al., 2004). Wells with an increasing trend in nitrate concentrations had significantly higher proportions of agricultural land use in 1992. Seventy-one percent of the wells located in areas with at least 20% agricultural land use had increasing trends for nitrate (Fig. 3A). Wells with increasing trends in nitrate or TDS concentrations had significantly lower natural land use than did wells with decreasing nitrate or TDS trends (Table 3, Fig. 3a and b). Similarly, wells located in areas with higher percentages of natural land use were more likely to have decreasing trends in both nitrate and TDS concentrations than areas with less natural land use. In contrast, wells located in areas with relatively higher percentages of urban land use were slightly more likely to have increasing trends for TDS concentrations (Table 3). There was not a significant correlation between urban land use and trends in nitrate concentrations (Table 3).

Statistically significant relations were identified between position in the regional groundwater flow system and temporal trends in nitrate concentrations. Wells with increasing trends for nitrate concentrations tended to be located at significantly lower elevations and at significantly more distal positions in the regional groundwater flow system (normalized distance to down-gradient end of flow system) than were wells with decreasing trends for nitrate. No statistically significant relations were identified between either of these measures of hydrologic position and TDS trends.

There were a number of significant relations between changes in the proportions of the various major ions and trends in concentrations for both nitrate and TDS. Changes in the cationic proportion of calcium were directly correlated with trends in nitrate concentrations. Changes in proportion for the cations of sodium and potassium and the anions of bicarbonate, carbonate and fluoride were inversely related to trends in nitrate concentrations (Table 3). Changes in ionic proportions for wells that had significant increasing trends for nitrate concentrations are shown in a trilinear “Piper” (Piper, 1944) plot (Fig. 4A).

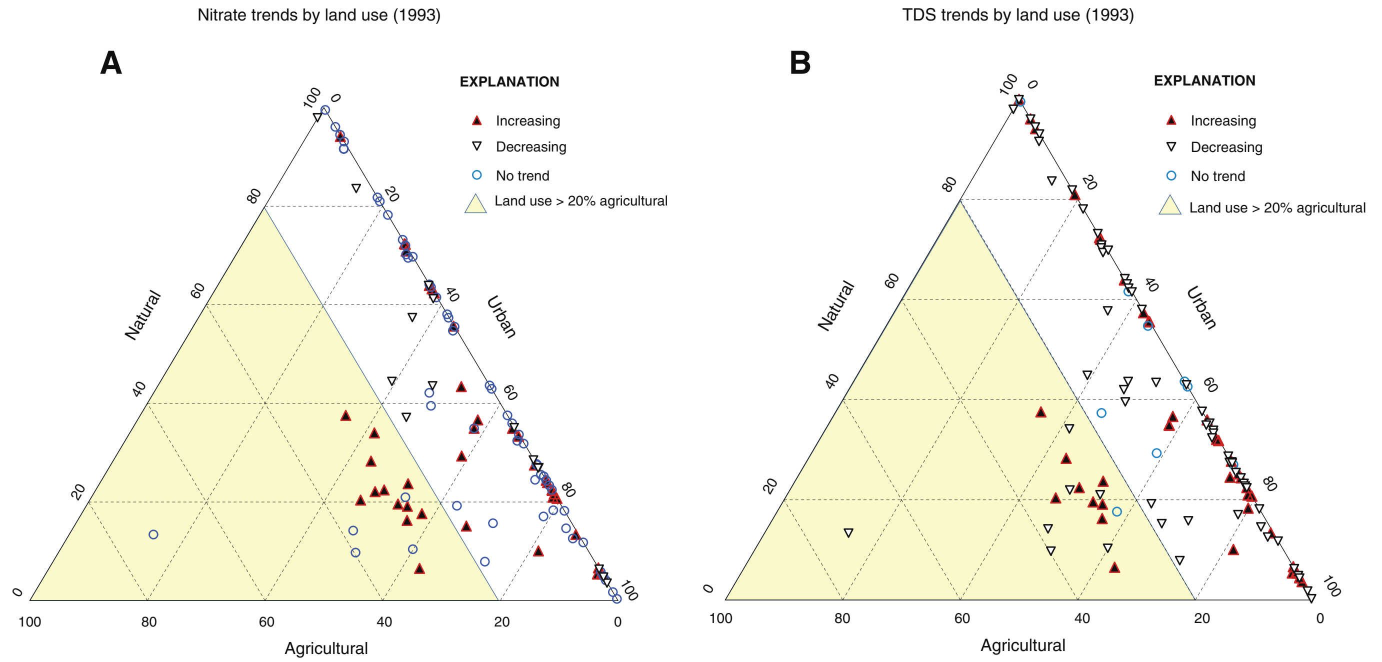


Fig. 3. A. Trilinear diagram showing nitrate trend direction for groundwater in study area wells by major land-use category, and highlighting wells in areas with greater than 20% agricultural land use. B. Trilinear diagram showing TDS trend direction for groundwater in study area wells by major land-use category, and highlighting wells in areas with greater than 20% agricultural land use.

Changes in cationic or anionic proportions were significantly related to trends in TDS concentrations for all major ions except for potassium and chloride. The relations were direct for changes in the proportions of calcium, magnesium, and sulfate. The relations were inverse for changes in the proportions of sodium and bicarbonate (Table 3). The anionic proportion of sulfate has increased, while the proportion of bicarbonate has decreased in wells that had significant increasing trends in TDS concentrations from the 1980s to the

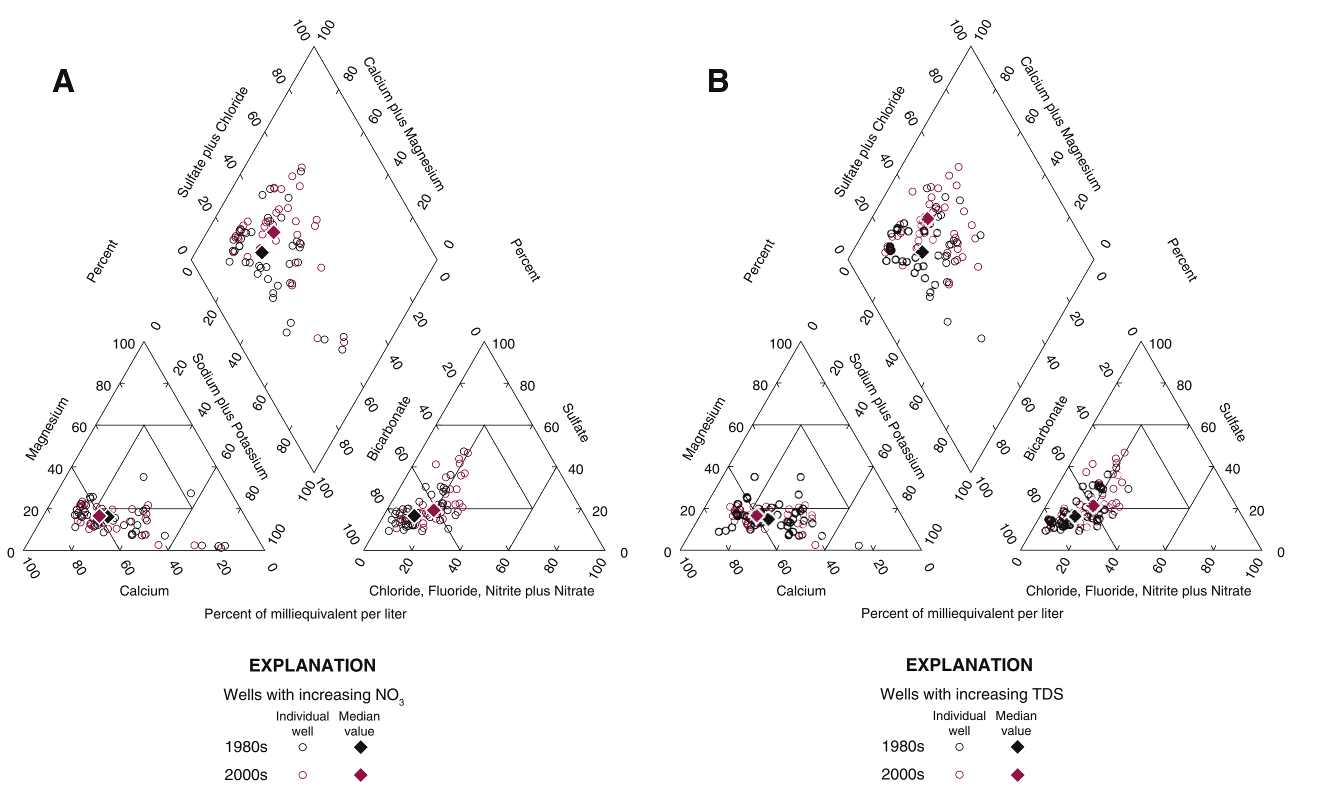


Fig. 4. A. Trilinear "Piper" plot of ionic proportions in the 1980s compared to the 2000s for groundwater in wells with increasing trends in nitrate concentrations. B. Trilinear "Piper" plot of ionic proportions in the 1980s compared to the 2000s for groundwater in wells with increasing trends in TDS concentrations.

2000s (Fig. 4B). Changes in cationic proportions during this period were less notable than anionic changes in the trend wells with increasing TDS. The proportions of calcium and magnesium increased slightly, while the proportion of sodium + potassium decreased slightly (Fig. 4B).

4. Discussion and conclusions

The pattern of increasing nitrate concentrations through time in relatively deep and downgradient wells likely reflects the legacy of historical agricultural land use. Wells with increasing trends in nitrate concentrations had significantly greater total depths and depths to the top of perforations than wells with decreasing trends in nitrate concentrations. This finding may seem surprising, since shallow groundwater is often considered more susceptible to contamination than is deep groundwater (Duell and Schroeder, 1989; Nolan et al., 2002; Dubrovsky et al., 2010). Indeed, VOCs occur more at shallow well depths in the Inland Santa Ana Basin (Belitz et al., 2004) and, nationwide, increasing urban land use and shallow well depths were among the most important factors associated with VOCs in aquifers (Zogorski et al., 2006). VOCs enter the study area groundwater primarily from the most important current sources of recharge: urban runoff (Belitz et al., 2004) and engineered recharge (Carter et al., 2008). These more recent sources of recharge to the now-urbanized Bunker Hill, Lytle, Rialto, and Colton groundwater subbasins have lower nitrate concentrations than did historical recharge when the land use was primarily agricultural. Agricultural land use, which can typically have nitrate nitrogen concentrations greater than 5 mg/L (U.S. Geological Survey, 1999), has been declining in the Santa Ana Basin since the mid-1940s (Scott, 1977), and has been replaced by urban land use. Urban runoff in the Upper Santa Ana Watershed has nitrate6 nitrogen concentrations of about 1 mg/L (Kent and Belitz, 2004). Mountain runoff, which recharges these subbasins both naturally and through engineered recharge operations (Danskin et al., 2006), typically has nitrate nitrogen concentrations less than 1 mg/L (Kent and Belitz, 2004). Imported water delivered by the Metropolitan Water District is also used for engineered recharge in the subbasins (Woolfenden and Koczot, 2001; Danskin et al., 2006), and has nitrate nitrogen concentrations of about 1 or 2 mg/L (California State Polytechnic University, Pomona, 2010). By the 1990s, relatively few wells in the study area were located near agricultural activity, but of those few wells, most showed increasing trends for nitrate concentrations (Fig. 3a).

Increasing nitrate trends were also associated with lateral position in the study area (measured by each well's elevation and normalized distance to down-gradient end of flow system). Wells located a relatively short distance along the groundwater flow path were more likely to have decreasing trends for nitrate, and wells located further along the flow path were more likely to have increasing trends. Based on tritium and carbon-14 age tracers and distributions of modern anthropogenic constituents, results of Izbicki et al. (1998, figure 8) and Kent and Belitz (2012, figure D3) indicate that groundwater in the downgradient portions of the flow system predominantly entered the flow system as recharge before the decline of agriculture in the study area starting in the mid-1940s (Scott, 1977). Available age-tracer data for the specific wells analyzed in this study were insufficient to investigate this directly. Such data only exists for 12 of the 131 wells, and it is expected that there would be mixing of groundwater of different ages in the relatively long screens.

It should be noted that, similar to VOC occurrence, well lateral position covaries inversely with well depth, meaning that wells high in the watershed tend to be shallower than wells on the valley floor. This observation complicates interpreting the apparent relations between nitrate trends and depth (direct) and nitrate trends and lateral position (inverse). To evaluate whether the relation of nitrate trends and depth occurred independently of lateral position, wells in the upgradient or proximal portion of the flow system (with a land surface elevation > 1400 feet) were excluded. As a group, the 22 excluded wells had relatively shallow depths. The depths of the remaining 86 wells with depth data located at elevations below 1400 feet were evenly distributed over the depth range represented in the study area. Almost half (42) of the wells with depth data and located at elevations below 1400 feet showed temporal trends, either increasing or decreasing, for nitrate concentrations. A Wilcoxon test performed on only those trend-exhibiting wells located at elevations below 1400 feet indicated a significant direct relation between well depth and nitrate trend ($p = 0.007$). Therefore, it is concluded that, independent of lateral position, groundwater in relatively deeper wells is more likely to have an increasing trend for nitrate concentration than groundwater in relatively shallow wells, and groundwater in relatively shallow wells is more likely to have a decreasing trend for nitrate concentration than groundwater in relatively deep wells.

Similar to the observed covariation between lateral position and well depth, elevation (a proxy for lateral position) also covaries with all 3 land use categories evaluated here. In the study area there is a direct correlation between elevation and natural land use (natural land use is predominant at high elevations), and inverse correlations between elevation and both urban and agricultural land uses. To evaluate whether the observed significant relations between nitrate trends and agricultural and natural land uses occurred independently of elevation, the same procedure as described above for well depths and lateral position was performed for land use and elevation. Results from the Wilcoxon tests performed only on wells located at elevations below 1400 feet indicated that there is still a significant direct relation between agricultural land use and nitrate trend ($p = 0.084$). However, the inverse relation between natural land use and nitrate trend observed when the test was performed on all wells was not found to be significant for the lower-elevation subset of wells. Therefore, results from this study cannot definitively separate the effects of elevation from those of natural land use on the inverse relation that both potential explanatory factors were determined to have with nitrate trends.

Regardless of the processes involved, the observed relation between natural land use and decreasing trends in concentration for both TDS and nitrate suggests that human activities play a role in explaining nitrate and TDS trends. Natural land use serves as a reverse proxy indicator of human (urban and agricultural) land uses, and human land use has been linked to increases in groundwater TDS (Thiros, 2010). Most of the present study area with natural land use is steep, hindering both urban and agricultural development (Belitz et al., 2004). Most of this steep terrain has never been under intensive human land use. In contrast, land that is relatively flat in the study area has been subject to intensive human land use; first mostly for agriculture, then, largely converted to residential and urban use (Scott, 1977; Danskin et al., 2006).

Significant correlations observed between changes in proportions of the various major ions and trends in TDS concentrations also suggest an anthropogenic explanation for increasing TDS. The strongest ionic relation was a direct one between sulfate concentrations and proportions (replacing bicarbonate) and increases in TDS. In a Los Angeles groundwater basin study, increases in groundwater sulfate concentrations were assumed to indicate increased presence of recharge water imported from the Colorado River (Sloss et al., 1999). Agricultural activities can cause increases in sulfate in groundwater by application of fertilizers containing sulfur (Jurgens et al., 2008) and/or through mobilization of natural sulfate in soil moisture or minerals in the unsaturated zone by agricultural irrigation return flows or artificial recharge (Thornton, 1997; Schoups et al., 2006). Engineered recharge facilities are prevalent in the present study area. While these mostly use local surface water diversions from the Santa Ana River, Mill Creek, and Lytle Creek for their recharge (San Bernardino Valley Water Conservation District, 2011), imported water delivered by the Metropolitan Water District is also used for engineered recharge in the subbasins (Danskin et al., 2006; Woolfenden and Koczot, 2001). However, wells with increasing proportions of sulfate in the present study did not tend to be close to recharge facilities. Whereas recharge facilities tend to be close to the mountain fronts in the study area, wells with increasing proportions of sulfate tend to be at lower elevations and at significantly more distal positions in the regional groundwater flow system. There was also a significant direct correlation between increasing proportions of sulfate and urban land use (p-value for Kendall's τ test = 0.02). This finding is consistent with a study on water sources of streams in the Santa Ana Basin that found that a stream for which base flow consisted primarily of urban runoff, had the highest sulfate anionic proportion, with the exception of a site receiving geothermal discharges (Kent and Belitz, 2004).

The lack of correlation between concentrations and increasing or decreasing trends in nitrate in this study probably reflects that the source of high nitrate is past rather than current land use. Such lack of correlation is in contrast with the results of Landon et al. (2011) in a portion of the eastern San Joaquin Valley of California that found that nitrate concentrations and increasing trends were correlated. In the eastern San Joaquin Valley the source of relatively high nitrate concentrations and increasing nitrate concentrations is ongoing modern agricultural land use (Burow et al., 2008). In contrast, in the Bunker Hill, Lytle, Rialto, and Colton subbasins, urban land use with low nitrate loading has replaced much of the agricultural land use that was the predominant land use in the first half of the 20th century. Wells with increasing nitrate trends in relatively deeper wells predominantly in the downgradient portion of the groundwater system may be capturing a larger fraction of agriculturally-recharged groundwater, which is mixing with groundwater of different ages and lower initial nitrate concentrations. As a consequence of this mixing in relatively deep public-supply wells at the downgradient end of the flow system, nitrate concentrations could be increasing over time but would not necessarily have nitrate concentrations that are higher than nitrate concentrations in other parts of the system. Thus, the lack of correlation of nitrate concentrations and nitrate trends is consistent with other evidence described earlier that the effects of legacy agricultural land use primarily explain nitrate trends in this study area.

The statistically significant direct correlation between nitrate and TDS trend slopes suggests some common explanatory factors for increasing trends in both parameters when they were observed (Table 3). In contrast, wells with decreases in nitrate and wells with decreases in TDS rarely corresponded (Fig. 2), suggesting that different processes may explain decreases in the two constituents. The general lack of correlation between TDS trends and most of the potential explanatory factors evaluated here suggests that the causes for TDS trends are more complex than for nitrate trends. TDS is derived from a variety of both natural and human sources (Hem, 1992). Natural sources of TDS in groundwater are the result of the dissolution of minerals contained in the aquifer rocks and soils. Human-derived sources of TDS in the Bunker Hill and Rialto-Colton groundwater basins include imported water, urban runoff, and agricultural return water (Anning et al., 2007).

It is unlikely that denitrification is significantly affecting nitrate concentrations in the study area. Previous studies have indicated that decreases in nitrate concentrations can occur as a result of denitrification in some aquifers with geochemically reduced groundwater (Korom, 1992; Tesoriero et al., 2007; McMahon and Chapelle, 2008). However, most groundwater in public supply wells of the Upper Santa Ana Watershed is oxic (dissolved oxygen > 0.5 mg/L) (Hamlin et al., 2002; Kent and Belitz, 2012). In laboratory studies, the O_2 concentration threshold required for the onset of denitrification has generally been observed to be <0.3 mg/L (Tiedje, 1988; Seitzinger et al., 2006; Coyne, 2008) but evidence for denitrification has been noted in well samples with O_2 of up to 2 mg/L (Böhlke et al., 2002, 2007; Beller et al., 2004; McMahon et al., 2004, 2008; Green et al., 2008) as a consequence of mixing of waters with different age and chemical characteristics (Green et al., 2010). Nevertheless, this study area is more oxic than that of a recent study in the eastern San Joaquin Valley of California where, about 80% of the groundwater system is oxic and about 20% is reducing groundwater. Landon et al. (2011) found that trends in nitrate concentrations in the eastern San Joaquin Valley study were primarily controlled by agricultural land use effects and were only slightly affected by groundwater oxidation–reduction conditions.

This study, along with that conducted by Landon, et al. (2011) provides a pilot demonstration of trend analysis in a large number of wells using historical data. It represents a systematic effort to find relations between observed trends and a wide array of explanatory factors, complementing previous status assessments (Eccles, 1979; Duell and Schroeder, 1989; Santa Ana Regional Water Quality Control Board, 1994; Hamlin et al., 2002) and long-term monitoring efforts (Wildermuth Environmental Inc., 1998; 2000; Santa Ana River Watermaster, 2010). Results from the present study indicate that it is possible to identify trends after just over a decade of study if there are enough observations (a minimum of four with methods used here). Trend analyses are better able to discern existing trends with a greater number of samples. Most of the wells evaluated for this study continue to be monitored for nitrate and TDS concentrations, providing an opportunity for periodic trends analysis in the future.

Conflict of interest

All the authors have no conflicts of interest.

Acknowledgments

The authors appreciate the financial support of the California State Water Resources Control Board, the cooperation of well owners in California, the efforts of USGS colleagues who participated in the sampling program, and the reviewers at the USGS and STOTEN who helped improve the paper.

References

Anning DW, Bauch NJ, Gerner SJ, Flynn ME, Hamlin SN, Moore SJ, Schaefer DH, Anderholm SK, Spangler LE. Dissolved solids in basin-fill aquifers and streams in the southwestern United States. U.S. Geological Survey Scientific Investigations Report 2006-5315; 2007 [revised 2010 v. 1.1. 168 pp.].

Appelo CAJ, Postma D. Geochemistry, groundwater, and pollution. Rotterdam, the Netherlands: A.G. Balkema; 1999 [649 pp.].

Belitz K, Hamlin SN, Burton CA, Kent R, Fay RG, Johnson T. Water quality in the Santa Ana Basin, California, 1999–2001. U.S. Geological Survey Circular 1238; 2004 [37 pp.].

Beller HR, Madrid V, Hudson GB, McNab WW, Carlsen T. Biogeochemistry and natural attenuation of nitrate in groundwater at an explosives test facility. Appl Geochem 2004;19:1483–94.

Böhlke JK, Wanty R, Tuttle M, Delin G, Landon M. Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota. Water Resour Res 2002;38(7):1105.

Böhlke JK, O'Connell ME, Prestegaard KL. Ground water stratification and delivery of nitrate to an incised stream under varying flow conditions. J Environ Qual 2007;36(3):664–80.

Burow KR, Dubrovsky NM, Shelton JL. Temporal trends in concentrations of DBCP and nitrate in groundwater in the eastern San Joaquin Valley, California, USA. Hydrogeol J 2007;15:991-1007.

Burow KR, Shelton JL, Dubrovsky NM. Regional nitrate and pesticide trends in groundwater in the Eastern San Joaquin Valley, California. J Environ Qual 2008;37(5_Supplement):S-249–63.

California Department of Water Resources. Upper Santa Ana Valley groundwater basin. Bunker Hill subbasin: California's Groundwater Bulletin, 118; 2004 [Accessed October 25, 2012 at http://www.water.ca.gov/pubs/groundwater/bulletin_118/basindescriptions/8-2.06.pdf].

California State Polytechnic University, Pomona. 2009 Water Quality Report. Accessed October 25, 2012 at http://www.csupomona.edu/~fpm/management/mechanical/waterqualityreport2009.pdf2010.

Carter JM, Lapham WW, Zogorski JS. Occurrence of volatile organic compounds in aquifers of the United States. J Am Water Resour Assoc 2008;44(2):399–416.

Coyne MS. Biological denitrification. In: Schepers JS, Raun W, editors. Nitrogen in agricultural systems. Madison, WI: Aeron Mongr 49, Am Soc of Agron/Crop Sci Soc of Am/Soil Sci Soc of Am; 2008. p. 201–53.

Danskin WR, McPherson KR, Woolfenden LR. Hydrology, description of computer models, and evaluation of selected water-management alternatives in the San Bernardino Area, California. U.S. Geological Survey Open-File Report 2005-1278; 2006. [178 pp. and 2 pl].

Dawson BJM, Belitz K, Land M, Danskin WR. Stable isotopes and volatile organic compounds along seven ground-water flow paths in divergent and convergent flow systems, Southern California, 2000. U.S. Geological Survey Water-Resources Investigations Report 03-4059; 2003. [79 pp.].
Dubrovsky NM, Burow KR, Clark GM, Gronberg JM, Hamilton PA, Hitt KJ, et al. The quality of our Nation's waters—nutrients in the Nations streams and groundwater, 1992–2004. U.S. Geological Survey Circular 1350; 2010. [174 pp.].
Duell LFW, Schroeder RA. Appraisal of ground-water quality in the Bunker Hill Basin of San Bernardino Valley, California. U.S. Geological Survey Water-Resources Investigations Report 88-4203; 1989. [69 pp.].
Eberts SM, Jones SA, Braun CL, Harvey GJ. Long-term changes in ground water chemistry at a phytoremediation demonstration site. Ground Water 2005;43(2):178–86.
Eccles LA. Ground-water quality in the Upper Santa Ana River Basin, Southern California. U.S. Geological Survey Water Resources Investigations Report 79-113; 1979. [51 pp.].
Grath J, Scheidleder A, Uhlig S, Weber K, Kralik M, Keimel T, et al. The EU Water Framework Directive: statistical aspects of the identification of groundwater pollution trends, and aggregation of monitoring results. Final Report. Austrian Federal Ministry of Agriculture and Forestry, Environment and Water Management (Ref.: 41.046/01-IV1/00 and GZ 16 2500/2-1/6/00), European Commission (Grant Agreement Ref.: Subv 99/130794), in kind contributions by project partners. Vienna: European Commission; 2001.
Green CT, Puckett LJ, Böhlke JK, Bekins BA, Phillips SP, Kauffman LJ, et al. Limited occurrence of denitrification in four shallow aquifers in agricultural areas of the United States. J Environ Qual 2008;37:994-1009.
Green CT, Böhlke JK, Bekins BA, Phillips SP. Mixing effects on apparent reaction rates and isotope fractionation during denitrification in a heterogeneous aquifer. Water Resour Res 2010;46:W08525. http://dx.doi.org/10.1029/2009WR008903.
Greer FR, Shannon M. Infant methemoglobinemia: the role of dietary nitrate in food and water. Pediatrics 2005;116(3):784–6.
Hamlin SN, Belitz K, Kraja S, Dawson BJ. Ground-water quality in the Santa Ana watershed, California: overview and data summary. U.S. Geological Survey Water-Resources Investigations Report 02-4243; 2002. [137 pp.].
Helsel DR, Hirsch RM. Statistical methods in water resources. U.S. Geological Survey Techniques of Water-Resources Investigations, bk.4:chap.A3; 2002. [510 pp. Available at: http://water.usgs.gov/pubs/twri/twri4a3/].
Hem D. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water-Supply Paper, 2254; 1992 [263 pp.].
Hirsch RM, Alexander RB, Smith RA. Selection of methods for the detection and estimation of trends in water quality. Water Resour Res 1991;27(5):803–13.
Homer C, Huang C, Yang L, Wylie B, Coan M. Development of a 2001 national land cover database for the United States. Photogramm Eng Remote Sens 2004;70(7):829–40.
Izbicki JA, Danskin WR, Mendez GO. Chemistry and isotopic composition of ground water along a section near the Newmark Area, San Bernardino County, California. U.S. Geological Survey Water-Resources Investigations Report 97-4179; 1998. [27 pp.].
Johnson TD, Belitz K. Assigning land use to supply wells for the statistical characterization of regional groundwater quality: correlating urban land use and VOC occurrence. J Hydrol 2009;370:100–8.
Johnson CJ, Kross BC. Continuing importance of nitrate contamination of groundwater and wells in rural areas. Am J Ind Med 1990;18:449–56.
Jurgens BC, Burow KR, Dalgish BA, Shelton JL. Hydrogeology, water chemistry, and factors affecting the transport of contaminants in the zone of contribution of a public-supply well in Modesto, eastern San Joaquin Valley, California. U.S. Geological Survey Scientific Investigations Report 2008-5156; 2008. [78 pp.].
Kent R, Belitz K. Concentrations of dissolved solids and nutrients in water sources and selected streams of the Santa Ana Basin, California, October 1998–September 2001. U.S. Geological Survey Water-Resources Investigations Report 03-4326; 2004. [61 pp. Available at: http://pubs.usgs.gov/wri/wrir034326/].
Kent R, Belitz K. Ground-water quality data in the Upper Santa Ana Watershed Study Unit, November 2006 to March 2007: results from the California GAMA Program. U.S. Geological Survey Data Series, 404; 2009 [116 pp. Available at: http://pubs.usgs.gov/ds/404].
Kent R, Belitz K. Status of groundwater quality in the Upper Santa Ana Watershed, November 2006—March 2007: California GAMA Priority Basin project. U.S. Geological Survey Scientific Investigations Report 2012-5052; 2012. [88 pp.].
Korom SF. Natural denitrification in the saturated zone: a review. Water Resour Res 1992;28(6):1657–68.
Landon MK, Belitz K, Jurgens BC, Kulongoski JT, Johnson TD. Status and understanding of groundwater quality in the Central Eastside San Joaquin Basin, 2006: California GAMA Priority Basin Project. U.S. Geological Survey Scientific Investigations Report 2009-5266; 2010. [97 pp.].
Landon MK, Green CT, Belitz K, Singleton MJ, Esser BK. Distribution of reduction oxidation conditions and changes in nitrate concentrations over time in groundwater, Central-Eastside San Joaquin Valley, California. Hydrogeol J 2011;19:1203–24.
Lindsey BD, Rupert MG. Methods for evaluating temporal groundwater quality data and results of decadal-scale changes in chloride, dissolved solids, and nitrate concentrations in groundwater in the United States, 1988–2010. U.S. Geological Survey Scientific Investigations Report 2012-5049; 2012. [46 pp.].
Loftis JC. Trends in groundwater quality. Hydrol Process 1996;10:335–55.
Mann HB. Nonparametric test against trend. Econometrica 1945;13:245–59.
McMahon PB, Chapelle FH. Redox processes and water quality of selected principal aquifer systems. Ground Water 2008;46(2):259–71.
McMahon PB, Böhlke JK, Christenson SC. Geochemistry radiocarbon ages, and paleorecharge conditions along a transect in the central High Plains aquifer, southwestern Kansas, USA. Appl Geochem 2004;19(11):1655–86.
McMahon PB, Böhlke JK, Kauffman LJ, Kipp KL, Landon MK, Crandall CA, et al. Source and transport control on the movement of nitrate to public supply wells in selected principal aquifers of the United States. Water Resour Res 2008;44(W04401). [16 pp.].
Mueller DK, Titus CJ. Quality of nutrient data from streams and ground water sampled during water years 1992–2001. U.S. Geological Survey Scientific Investigations Report 2005-5106; 2005. [27 pp.].
Nakagaki N, Price CV, Falcone JA, Hitt KJ, Ruddy BC. Enhanced National Land Cover Data 1992 (NLCDe 92). U.S. Geological Survey Raster digital data; 2007 [Available at http://water.usgs.gov/lookup/getspatial?nlcde92].
Neill M. Nitrate concentrations in river waters in the south-east of Ireland and their relationship with agricultural practice. Water Res 1989;23(11):1339–55.
Nolan BT, Hitt KJ, Ruddy BC. Probability of nitrate contamination of recently recharged groundwater in the conterminous United States. Environ Sci Technol 2002;36(10): 2138–45.
Piper AM. A graphic procedure in the geochemical interpretation of water analyses. Am Geophys Union Trans 1944;25:914–23.
San Bernardino Valley Water Conservation District. Engineering Investigation of the Bunker Hill Basin 2010–2011: Groundwater Conditions in the San Bernardino Valley Water Conservation District. Accessed October 25, 2012 at http://www.sbvwcd.dst.ca.us/reports-data/bunkerhill/2011EngineeringInvestigation.pdf2011.
Santa Ana Regional Water Quality Control Board. Water Quality Control Plan: Santa Ana River basin. Santa Ana Region VIII, Riverside, California; 1994 [variously paged].
Santa Ana Regional Water Quality Control Board. Resolution No. R8-2004-0001, Resolution amending the water quality control plan for the Santa Ana River Basin to incorporate an updated total dissolved solids (TDS) and nitrogen management plan. Accessed October 25, 2012, at http://www.waterboards.ca.gov/rwqcb8/board_decisions/adopted_orders/orders/2004/04_001.pdf2004.
Santa Ana River Watermaster. Thirty-ninth annual report of the Santa Ana River Watermaster for water year October 1, 2008–September 30, 2009. 159 pp. Accessed November 22, 2010 at http://webserver.sbvmwd.com/imgs/reports/SARWM_2008-09.pdf2010.
Santa Ana Watershed Project Authority. 2009 Santa Ana Integrated Watershed Plan—An Integrated Regional Water Management Plan. Available at http://www.sawpa.org/owow-generalinfo.html2009.
Schoups G, Hopmans JW, Tanji KK. Evaluation of model complexity and space-time resolution on the prediction of long-term soil salinity dynamics, western San Joaquin Valley, California. Hydrol Process 2006;20:2647–68.
Scott MB. Development of water facilities in the Santa Ana River Basin, California, 1810–1968. U.S. Geological Survey Open-File Report 77–398; 1977. [247 pp.].
Seitzinger S, Harrison JA, Böhkje JK, Bouwman AF, Lowrance R, Peterson B, et al. Denitrification across landscapes and waterscapes: a synthesis. Ecol Appl 2006;16(6): 2064–90.
Sen PK. Estimates of the regression coefficient based on Kendall's Tau. J Am Stat Assoc 1968;63:1379–89.
Sloss EM, McCaffrey DF, Fricker RD, Geschwind SA, Ritz BR. Groundwater Recharge with Reclaimed Water: Birth Outcomes in Los Angeles County, 1982–19930-8330-2770-0; 1999 [149 pp.].
Stuart ME, Chilton PJ, Kinniburgh DG, Cooper DM. Screening for long-term trends in groundwater nitrate monitoring data. Q J Eng Geol Hydrogeol 2007;40: 361–76.
Tesoriero AJ, Saad DA, Burow KR, Frick EA, Puckett LJ, Barbash J. Linking ground water age and chemistry data along flow paths: implications for trends and transformations of nutrients and pesticides. J Contam Hydrol 2007;94:139–55.
Thiros SA. Section 12. Conceptual understanding and groundwater quality of the basin-fill aquifers in the Santa Ana Basin, California. In: Thiros SA, Bexfield LM, Anning DW, Huntington JM, editors. U.S. Geological Survey Professional Paper, 1781. ; 2010. p. 219–65.
Thornton EC. Origin of Increased sulfate in groundwater at the ETF disposal site, Prepared for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830, Pacific Northwest National Laboratory Richland, Washington 99352; 1997 [Accessed October 25, 2012, at http://www.osti.gov/bridge/servlets/purl/548888-AscOkj/webviewable/548888.pdf].
Tiedje JM. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. In: Zhender AJB, editor. Biology of anaerobic microorganisms. New York: Wiley; 1988. p. 179–244.
Toth J. A theoretical analysis of groundwater flow in a small drainage basin. J Geophys Res 1963;68(16):4795–812.
U.S. Environmental Protection Agency. 2006 edition of the drinking water standards and health advisories, updated August 2006: U.S. Environmental Protection Agency, Office of Water EPA/822/R-06-013; 2006 [Available at http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf].
U.S. Geological Survey. The quality of our Nation's waters—nutrients and pesticides. U.S. Geological Survey Circular, 1225; 1999 [82 pp.].
Visser A, Dubus I, Broers HP, Brouyère Korcz M, Orban P, Goderniaux P, et al. Comparison of methods for the detection and extrapolation of trends in groundwater quality. J Environ Monit 2009;11:2030–43.
Weyer PJ, Cerhan JR, Kross BC, Hallberg GR, Kantamneni J, Breuer G, et al. Municipal drinking water nitrate level and cancer risk in older women: The Iowa Women's Health Study. Epidemiology 2001;12(3):327–38.
Wildermuth Environmental Inc. Nitrogen losses from recycled water systems, TIN/TDS Study Phase 2A-Task 1.4. 415 North El Camino Real, Suite A, San Clemente, California 92672: Wildermuth Environmental, Inc.; 1998.
Wildermuth Environmental Inc. TIN/TDS study—phase 2A of the Santa Ana watershed, development of groundwater management zones, estimation of historic and current TDS and nitrogen concentrations in groundwater, final technical memorandum, July; 2000.

Wildermuth Environmental Inc. Recomputation of ambient water quality in the Santa Ana River Watershed for the period 1984 to 2003, Final Technical Memorandum, Prepared for Basin Monitoring Program Task Force, November; 2005 [Accessed October 25, 2012 at http://www.sawpa.org/documents/roundtable/basinmonitoring/AWQ_2003.pdf].
Wildermuth Environmental Inc. Recomputation of ambient water quality in the Santa Ana River Watershed for the period 1987 to 2006, Final Technical Memorandum, Prepared for Basin Monitoring Program Task Force, August; 2008 [Accessed October 25, 2012 at http://www.sawpa.org/documents/roundtable/basinmonitoring/AWQ_2006.pdf].
Woolfenden LR. Aquifer susceptibility to perchlorate contamination in a highly urbanized environment, GQ07: securing groundwater quality in urban and industrial environments. Proc. 6th International Groundwater Quality Conference held in Fremantle, Western Australia, 2–7 December; 2007.
Woolfenden LR, Kadhim D. Geohydrology and water chemistry in the Rialto-Colton Basin, San Bernardino County, California. U.S. Geological Survey Water Resources Investigations Report 97-4012; 1997. [101 pp.].
Woolfenden LR, Koczot KM. Numerical simulation of ground-water flow and assessment of the effects of artificial recharge in the Rialto-Colton Basin, San Bernardino County, California. U.S. Geological Survey Water Resources Investigations Report 00-4243; 2001. [148 pp.].
Zogorski JS, Carter JM, Ivahnenko T, Lapham WW, Moran MJ, Rovew BL, et al. The quality of our Nation's water—volatile organic compounds in the Nation's groundwater and drinking-water supply wells. U.S. Geological Survey Circular, 1292; 2006 [101 pp.].