Science of the Total Environment 771 (2021) 145223

Contents lists available at ScienceDirect

Science of the Total Environment

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

Groundwater development leads to decreasing arsenic concentrations in the San Joaquin Valley, California

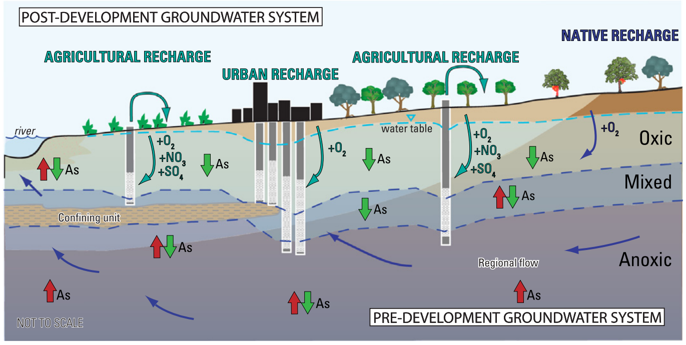
Emily A. Haugen *, Bryant C. Jurgens, Jose A. Arroyo-Lopez, George L. Bennett

U.S. Geological Survey, Sacramento, CA, United States

HIGHLIGHTS

- Arsenic concentrations in most wells (76%) are generally low and are not changing.
- Decreasing arsenic trends are more common (16.6%) than increasing trends (7.2%).
- Decreasing arsenic trends are due in part to downward moving oxidizing groundwater.
- Arsenic trends were inversely related to co-occurring nitrate and sulfate trends.
- Increasing arsenic trends are more common in deep groundwater in the valley trough.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 August 2020
Received in revised form 11 January 2021
Accepted 12 January 2021
Available online 18 January 2021

Editor: José Virgílio Cruz

Keywords:
Arsenic trends
Mann-Kendall
Groundwater development
Subsidence
Nitrate
Time-series
Signed Rank Test

ABSTRACT

In the San Joaquin Valley (SJV), California, about 10% of drinking water wells since 2010 had arsenic concentrations above the US maximum contaminant level of 10 μg/L. High concentrations of arsenic are often associated with high pH (greater than 7.8) or reduced geochemical conditions. Although most wells have low arsenic (<3 μg/L) and do not have changing arsenic concentrations, this study found that most wells with concentrations above 10 μg/L had arsenic trends. Overall, about 24% of wells had time-series trends since 2010 and 59% had paired-sample trends since 2000. Most wells had decreasing arsenic trends, even in wells with higher arsenic concentrations. These wells often had co-detections of increasing nitrate and sulfate trends that reflect oxic groundwater likely derived from agricultural recharge. Wells with increasing arsenic trends were deeper or located in the valley trough where aquifer materials are more fine-grained and where reducing conditions favor arsenic mobility. Wells with arsenic trends also tend to be clustered near areas of higher well density. Groundwater pumping in these areas has likely increased the contribution of younger, more oxic groundwater in wells with declining arsenic or, less frequently, increased the contribution of higher pH or reduced groundwater in wells with rising arsenic. Projections of arsenic trends indicate that 37 wells with high arsenic presently will be below 10 μg/L in ten years. Unfortunately, these improvements will be largely offset by 31 wells that are expected to increase above 10 μg/L in addition to expected rises in nitrate in wells where arsenic decreased. This study shows how human-altered flow systems can impact the natural geochemical character of water in both beneficial and deleterious ways.

1. Introduction

Arsenic is a potential human health concern for people that rely on groundwater for drinking water because it is ubiquitous in most aquifer

---

* Corresponding author at: U.S. Geological Survey, Placer Hall, 6000 J Street, Sacramento, CA 95819, United States.

E-mail address: ehaugen@usgs.gov (E.A. Haugen).

https://doi.org/10.1016/j.scitotenv.2021.145223

types. The U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) for arsenic was lowered from 50 μg/L to 10 μg/L in 2001 (USEPA, 2018a,b). In aquifers, arsenic is commonly adsorbed to clay surfaces and to iron (Fe-III) and manganese (Mn-IV) oxyhydroxide coatings on mineral grains or included in sulfide minerals (such as pyrite) by substitution for sulfur in the mineral structure (Brannon and Patrick, 1987; Raven et al., 1998; Lin and Puls, 2000; Grafe et al., 2002; Goldberg, 2002; Farquhar et al., 2002; Tufano et al., 2008). Arsenic can become mobilized from aquifer materials and released into groundwater by desorption from surfaces as pH increases from <8 to >8.5, or by reductive dissolution of iron and manganese oxyhydroxides under geochemically reduced, or anoxic, conditions, or by oxidation and dissolution of sulfide minerals, or by competitive desorption by increased concentrations of competing anions such as phosphate (Welch et al., 2000; Smedley and Kinniburgh, 2002; Welch and Stollenwerk, 2003; Barringer and Reilly, 2013; Lin and Puls, 2000; Neil et al., 2012).

California is the largest user of groundwater in the United States, and eight counties in California's San Joaquin Valley (SJV) account for 10% of all groundwater pumping for irrigation and drinking water in the United States (Dieter and Maupin, 2017). Over 70% of public and domestic drinking water supplies in the SJV are from groundwater. The growing population, agriculture, and periods of drought have forced more reliance on groundwater that has resulted in water level declines of up to 100 s of feet in the SJV (Faunt et al., 2009).

The California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) completed a statewide assessment of the status of water quality in groundwater resources used for public drinking water in 2015 (Belitz et al., 2003, 2015). This study found that 15% of the area of groundwater resources used for public supply in the SJV had arsenic concentrations greater than the USEPA MCL of 10 μg/L (Belitz et al., 2015). An ongoing assessment of the aquifer used for domestic supply in parts of the SJV found that about 13% of the area assessed as of 2019 had concentrations of arsenic greater than the MCL (Fram, 2017; Fram and Shelton, 2018; Jurgens et al., 2018; U.S. Geological Survey, 2018).

Recently, arsenic in groundwater in the SJV has had increased attention. Ayotte et al. (2016) used boosted regression trees and logistic regression models to map the probability of high arsenic (>10 μg/L) in groundwater in the Central Valley. Deeper wells, such as public-supply wells and wells located in the Valley Trough, were at greater risk to arsenic exceedances because these wells tend to have groundwater with higher pH or reduced geochemical conditions that make arsenic more mobile. Smith et al. (2018), modeled arsenic concentrations from two different periods (1986–1993; 2007–2015) in areas where historical and recent subsidence have occurred. They found that arsenic concentrations were positively correlated with subsidence and concluded that arsenic had increased because pumping induced subsidence caused clays to expel arsenic-laden pore water into the groundwater, much like the results from Erban et al. (2013) in Vietnam. Pumping induced changes in arsenic have been observed in other parts of the world (Harvey et al., 2002; Polizzotto et al., 2005; Winkel et al., 2011; Postma et al., 2017). Most recently, Jurgens et al. (2020) looked at time series records for public-supply wells from 1974 to 2014 in the SJV and found that about 12% of the area used for public-supply had arsenic concentrations above 5 μg/L and had trends that were changing, mostly decreasing. They hypothesized that arsenic was mainly decreasing because of increased oxic conditions caused by long-term groundwater pumping that displaces reducing conditions in the basin and deeper parts of the SJV. Zhang et al. (2020) found that recharge of shallow groundwater with oxic, low arsenic concentration groundwater directly decreased the dissolved arsenic concentrations in deep groundwater in the western Hetao basin, China, by promoting arsenic fixation.

In this paper, we examine arsenic data for drinking water supply wells, and other wells with comparable depths to drinking water supply wells, sampled between 1980 and 2019, to assess arsenic trends in wells in the SJV. We examine arsenic trends for differences among study regions and subsidence areas and use co-detection of trends with other chemical constituents to explain what processes may be responsible for the majority of arsenic trends in groundwater.

1.1. Study area description

The SJV makes up the southern two-thirds of California's Central Valley and is separated into two basins: the San Joaquin Basin in the north and the Tulare Basin in the south. The SJV is bounded by the Sierra Nevada in the east, the Coast Range in the west and the Tehachapi Mountains in the south. The valley has an arid to semi-arid Mediterranean climate with mean annual precipitation, determined from the 1911–1960 period, ranging from 15 in. in the north to <5 in. in the south (Gronberg et al., 1998). Sediments were deposited in the valley from the surrounding mountains from the Jurassic to Quaternary periods and vary in thickness from about 800 m in the north to more than 9 km in the south (Page, 1986; Bartow, 1991).

The freshwater aquifer is mainly composed of the Quaternary to Pliocene age unconsolidated alluvial, fluvial, and lacustrine deposits in the upper 500 m (Page, 1986; Bartow, 1991; Weissmann et al., 2005). The aquifer is generally unconfined but becomes semi-confined with depth, owing to numerous clay lenses. Clay layers lose their impermeability and become susceptible to vertical flow in places where wells have been drilled through, such as the Corcoran Clay member that spans a large portion of the SJV (Fig. S1) (Santi et al., 2006; Page, 1986; Johnson et al., 2011).

Groundwater flows laterally from the valley margins towards the center of the basin. The center of the basin is heretofore referred to as the Valley Trough and is the lowest lying area of the valley fill sediments. Prior to groundwater development, recharge to the groundwater system was mainly from seepage from streams near the valley margins and precipitation. Groundwater discharged in the northern part of the SJV, the San Joaquin Basin, to the San Joaquin River which exits the valley through the Sacramento-San Joaquin Delta. The southern part of the SJV, the Tulare Basin, is a closed basin. Groundwater in this area was discharged to shallow, perennial lakes and evaporated. Since development of the groundwater system for agriculture, irrigation return flow is the primary form of recharge and groundwater withdrawals from wells is the major form of discharge in the SJV (Faunt et al., 2009) (Fig. S1). Extensive agricultural and municipal pumping has altered the original groundwater flow system such that water moves downward six times faster than under predevelopment conditions (Williamson et al., 1989; Faunt et al., 2009).

The SJV was divided into four regions for this study (Fig. 1): North-Eastern SJV (NESJV), South-Eastern SJV (SESJV), Southern SJV (SSJV), and Western SJV (WESJV) (Hansen et al., 2018). NESJV and SESJV are composed of alluvial sediment from the Sierra Nevada, whereas the WESJV is composed of alluvial sediment from the Coast Ranges. The SSJV is composed of a mixture of sediment from the Tehachapi and San Emigdio Mountains, Sierra Nevada, and Coast Ranges. The western portion of the NESJV and SESJV, the eastern portion of the WESJV, and the north-central portion of the SSJV make up the Valley Trough.

Arsenic is mainly adsorbed onto clays and iron and manganese oxyhydroxides in valley sediments. The concentration of arsenic in aquifer sediments varies by parent material and sediment type. Sediments that make up the eastern alluvial fans are dominated by arkosic materials derived from granitic rocks of the Sierra Nevada. Sierra Nevada sediment is commonly stained with iron and manganese oxides and is coarse grained and contains little organic material (Gronberg et al., 1998; Jurgens et al., 2008). In addition to typical arkosic materials (quartz, feldspars, and minor hornblende), Sierra Nevada sediment has a clay content dominated by smectite and lesser amounts of illite and kaolinite (Jurgens et al., 2008). Sediments that make up the western alluvial fan deposits are derived from marine and metamorphic rocks

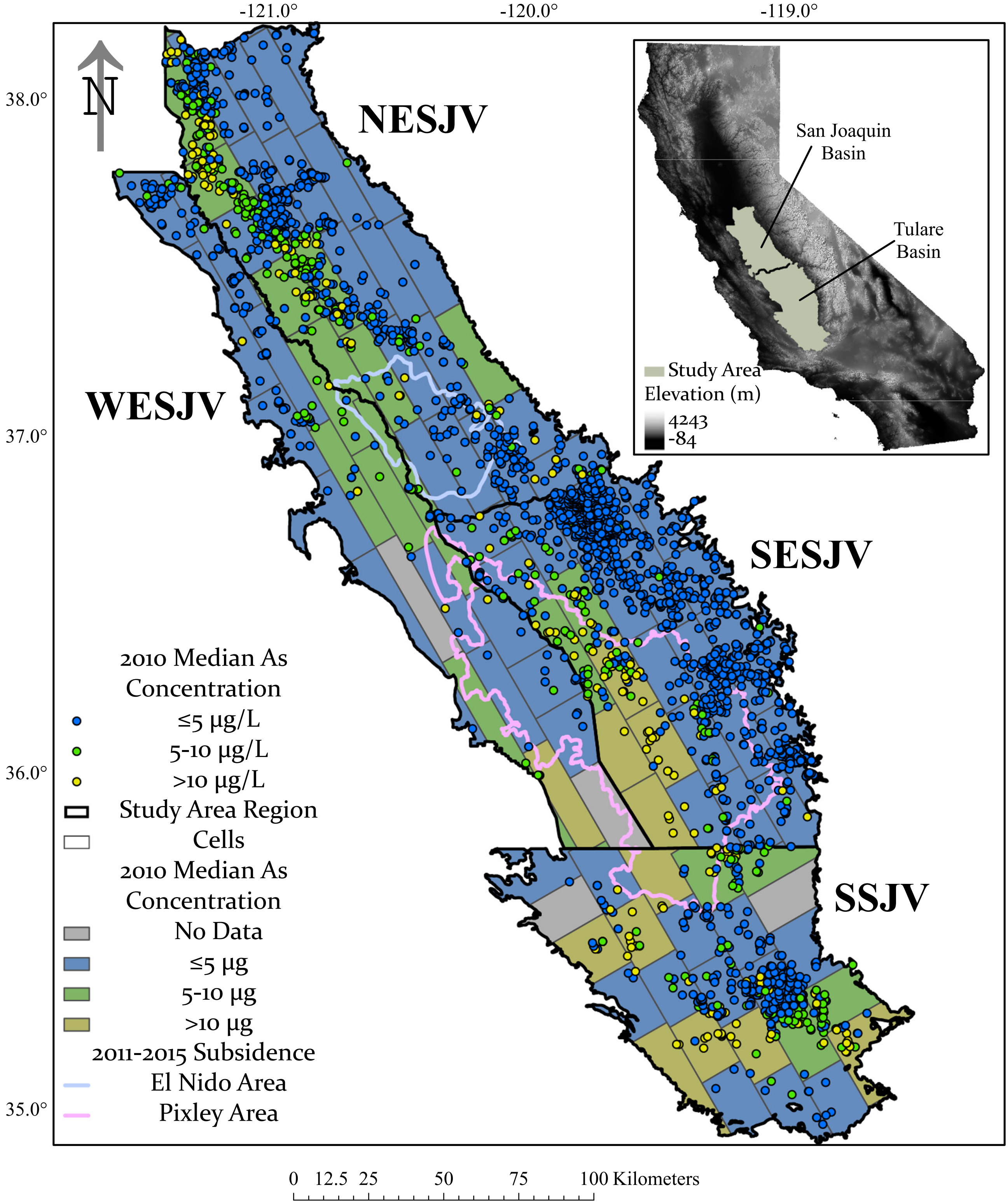


Fig. 1. Median arsenic concentrations for 2010 in groundwater wells and study area grid cells (median of all wells in cell) in the San Joaquin Valley, California, 2010–2019. Study areas include the North-Eastern San Joaquin Valley (NESJV), the South-Eastern San Joaquin Valley (SESJV), the Southern San Joaquin Valley (SSJV), and the Western San Joaquin Valley (WESJV). Grid cells are equal area polygons within each region rotated perpendicular to alluvial fan strike. Subsidence outline from subsidence measured by Faunt and Sneed between 2011 and 2015 (2015).

from the Coast Range. Coast Ranges sediment tends to be clay rich and containing more organic matter than sediment of the Sierra Nevada, in addition, marine sediment hosts a large amount of pyrite and sulfate minerals (Page, 1986; Presser et al., 1990; Fuji and Swain, 1995). In the Valley Trough, sediments from the Sierra Nevada interfinger with sediments from the Coast Range and are typically finer-grained and have larger organic carbon content. Results for the C horizon from the national reconnaissance of soil chemistry show that the Valley Trough had the highest concentration of arsenic in sediment (7.9 mg/kg) and the western alluvial fans have higher concentrations (5.4 mg/kg) than the eastern fans (4.3 mg/kg) (Smith et al., 2014). Results from the national survey were from a compilation of 20 soil samples, but the results are consistent with a more detailed study of soil chemistry in the SJV (Tidball et al., 1986; Belitz et al., 2003). The spatial patterns of arsenic concentrations in sediments at the surface reasonably reflect concentrations of Pleistocene sediments in the subsurface. The Pleistocene sediments were deposited in response to glacial episodes and are the primary water-bearing formations tapped by wells in the SJV.

2. Material and methods

2.1. Data compilation

Well construction and water-quality data for this study were compiled from the State Water Resources Control Board (SWRCB) – Division of Drinking Water (SWRCB-DDW) and the U.S. Geological Survey National Water Information System (USGS-NWIS) (U.S. Geological Survey, 2020). Of the total 7870 wells located within the SJV boundary, many did not meet the requirements for this study, the main one being an arsenic analysis within the 1980–2019 period (Fig. S2). The USGS-NWIS data consist of a mix of domestic, public, monitoring, irrigation, industrial, and other wells. The USGS-NWIS data were screened to exclude wells not within the 5th to 95th percentile of the depths of drinking water wells. This screening removed many wells not representative of the depth zones used for drinking water supply, such as shallow monitoring wells and wells not coded as drinking water or irrigation that lacked well depth data. In addition, wells with a TDS concentration of greater than 10,000 mg/L or specific conductance of greater than 10,000 μS/cm were excluded. Well depth and latitude/longitude data for wells were used in the following order or priority: USGS-NWIS, then SWRCB GAMA Groundwater Information System, then Voss et al. (2019), which used well completion reports to compile well-construction and location data.

A total of 4983 wells are used in this report (Fig. S2). The SWRCB-DDW data used here contain 3305 public-supply wells sampled for compliance monitoring of drinking water standards from 1980 to 2018. The USGS-NWIS data used here contain 1449 wells that were sampled as part of the USGS National Water Quality Assessment project, the GAMA-PBP, and other USGS projects done in cooperation with various federal, state, and local agencies from 1980 to 2019. There were 229 wells that were sampled by both SWRCB-DDW and GAMA-PBP that are combined to prevent duplication.

USGS data are mostly analyzed by Inductively Coupled Plasma Mass Spectrometry on filtered samples (Garbarino, 1999). SWCRB-DDW data can be filtered or unfiltered, depending on the method; however, this information is not readily available. Unfiltered samples in the SWRCB-DDW dataset may contain small amounts of solids which contributes to a higher arsenic concentration (Belitz et al., 2003). The biggest difference between the method of analysis for USGS and SWRCB-DDW data is the detection level. Constituents with detection levels were screened to their most common SWRCB-DDW detection level including arsenic at 2 μg/L, manganese at 30 μg/L, iron at 50 μg/L, nitrate at 0.452 mg/L (as N), and sulfate at 2 mg/L. All detections and non-detections at or below these values were recoded to the appropriate detection level. Any non-detections above these detection levels were removed from the dataset.

The 4983 wells used in this study were sampled at least once for arsenic between 1980 and 2019 (Fig. S2). Additional geochemical constituent data co-detected in these wells, and compiled here, include dissolved oxygen, field-measured pH, iron, manganese, sulfate, nitrate, or water level. Note that field-measured pH, and water level data were only available from the USGS-NWIS database. Additional lab-measured pH data were used from the DDW database which introduces a systemic bias from degassing that is not seen in the field-measured pH.

The number of SJV wells with arsenic data has increased significantly over time, from 1158 wells in the 1980–1989 period to 2913 wells in the 2010–2019 period (Fig. 1). Most of the increase reflects the increasing number of water agencies reporting data electronically to the SWRCB-DDW database of public-supply wells and cooperative projects entering data into NWIS, such as the GAMA-PBP. This also reflects the improvement of analyses at lower analytical levels overtime and the lowering of the detection limit to current levels, which decreases the number of analyses that are below the screening level. The increase in data allows for a higher significance for the results of the statistical methods used in this report.

Decadal datasets were created by dividing the water quality samples into four decades – 1980 through 1989 (1980s), 1990 through 1999 (1990s), 2000 through 2009 (2000s), and 2010 through 2019 (2010s). In cases where wells were sampled multiple times in a decade, the median concentration was computed. Most public-supply wells were sampled multiple times per decade, and many were sampled multiple times per year. Compliance monitoring wells and wells that had higher arsenic concentrations commonly were sampled more frequently. Any public supply well that tests higher than the MCL for any constituent is required to sample quarterly for results up to ten times the exceedance of the MCL. This data processing step prevents wells sampled more frequently from biasing trend results.

2.2. Grid cell networks

Wells in the SJV are unequally distributed so that urban areas have higher densities of wells than rural areas (Fig. S3). These areas tend to bias arsenic concentrations in a regional analysis. To reduce the effects of spatial bias, the SJV was divided into 4 regions based on varying geology and recharge conditions as well as groundwater source (Hansen et al., 2018) that were then divided into equal-area grid cells depending on the number of cells and the size of each region. There are 95 grid cells with 25 cells in the NESJV (~370 km^2 per cell), 25 cells in the SESJV (~340 km^2 per cell), 25 cells in the SSJV (~315 km^2 per cell), and 20 cells in the WESJV (~360 km^2 per cell).

The cells are oriented perpendicular to the strike of the alluvial fan deposits to capture the regional concentration and trend patterns along the regional direction of lateral groundwater flow. Values for each cell are determined by taking the median value of arsenic concentrations, paired-sample changes, or time series changes for wells in the cell. For time-series trends, wells with trends were used for calculating the median change in the cells, even when most wells did not have trend in the cell.

2.3. Statistical methods

Three statistical approaches were used to evaluate trends in arsenic concentrations. The word ‘trends’ is herein used to describe the tendency for changes in concentrations to increase or decrease over time. All methods used non-parametric statistical tests with a significance level (α) of 0.1. These approaches were used to evaluate arsenic concentrations for comparing decadal populations by region and to evaluate arsenic trends (paired-sample trends and time-series trends) based on region, well depth classification, recent subsidence areas, and location in the SJV.

The first approach used the Wilcoxon rank sum test (Wilcoxon, 1945; Mann and Whitney, 1947) to test whether one or more groups of data are different. Here, it was used to detect differences in arsenic concentrations in populations of wells by decade and region. The null hypothesis is that the medians of the two populations are equal. All 4983 wells with arsenic data could be included in these tests.

The second approach used the Wilcoxon signed rank-test for paired samples (Wilcoxon, 1945) to compare differences in arsenic concentrations from a set of wells with measurements from two time-periods. Wells with at least one sample concentration in the 2000s and 2010s were compared. These two time periods had similar numbers of wells sampled, laboratory methods, and reporting levels for arsenic analyses. The null hypothesis is that the paired arsenic concentrations are not systematically different for the population of wells. This is a more rigorous test than the Wilcoxon rank sum test due to the pair requirement, however the number of wells that can be tested is limited to 2256 wells.

The third approach used the Mann-Kendall test (Kendall, 1938; Mann, 1945; Kendall, 1975) paired with the Theil-Sen's slope (Theil, 1950; Sen, 1968) to identify significant monotonic trends in arsenic concentrations in time series data from individual wells. The correlation coefficient (Kendall's tau) is the measurement of correlation of a constituent over time, which gives the direction of trend based on 1 being fully correlated (positive trend) and −1 being fully different (negative trend). The Theil-Sen's slope (called Sen's slope) is the magnitude of the trend, used here to predict the time at which a constituent reaches a specified concentration. Four or more unique arsenic values (no ties) over a time span of five or more years were required to compute the test (Jurgens et al., 2020). A trend in time series concentrations was considered significant if the *p*-value was less than 0.1 and the Sen's slope was not equal to zero. To reduce the effect of serial correlation caused by varying sampling intervals, the median concentration was computed for two time periods in a year when there are two or more samples in a time period – May 1st through October 31st (called Summer) and November 1st through April 30th (called Winter). A total of 2460 wells had two or more samples during Summer and 2204 wells had two or more samples during Winter. This is the same method described by Jurgens et al. (2020). A total of 2071 wells had enough data for testing by this approach.

2.4. Explanatory factors

Arsenic concentrations in groundwater were analyzed by hydrologic and geochemical factors. Hydrologic factors include lateral position, well depth, land subsidence, and water level, and geochemical factors include reduction/oxidation conditions and pH.

2.4.1. Hydrologic

Lateral position is a horizontal position along an east-west cross section of the SJV, normalized to the length of the cross section, with the Coast Range equal to −1, the Valley Trough equal to 0, and the Sierra Nevada equal to 1 (Faunt et al., 2009; Bennett et al., 2010). Lateral position is used to group wells along the regional patterns of groundwater flow. The lateral position categories allow the SJV to be divided so that wells at similar positions from the valley center are grouped together (Fig. S4). This division is perpendicular to the groundwater flow from the valley margins to the Valley Trough. For this study, lateral positions between −0.2 and 0.2 are considered the Valley Trough. This area has more fine-grained and organic material than the alluvial fan deposits west and east of this area, which typically are coarser, particularly near the head of the fans (Weissmann et al., 2005).

Well depth varies by well type and location. Domestic wells are generally shallower with well depths ranging from 3 to 634 m with a median depth of 56 m. Public-supply wells are generally constructed with long screens and have deeper well depths ranging from 7 to 914 m with a median depth of 122 m. Domestic wells overlap in depths of public supply wells in many places in the SJV (Voss et al., 2019).

Wells were classified as shallow or deep relative to the median depth of public supply wells existing in each region. The regional shallow depth cut off is 67, 91, 195, and 116 m for NESJV, SESJV, SSJV, WESJV respectively. Well depth also varies with lateral position, with wells in the Valley Trough typically deeper than wells on the Valley edges, although this difference was smaller than the differences between the four regions and was not considered in the depth classification.

To assess the effect of subsidence on arsenic concentrations, wells located in recent areas of subsidence were classified according to the magnitude of compaction identified by Faunt and Sneed (2015). Areas of recent subsidence are located near the towns of El Nido and Pixley and were identified using Interferometric Synthetic Aperture Radar (InSAR), Global Positioning System (GPS), and extensometer data (Faunt and Sneed, 2015). Subsidence in these areas was caused by groundwater pumping during recent drought periods from 2007 to 2015. The magnitude of subsidence ranges from 0 to 280 mm (~11 in.) near Pixley, to 0–540 mm (~21 in.) near El Nido.

Water level changes over the last decade were used to assess changes in arsenic concentrations. There were 137 wells with enough water level data to test for a time-series trend. Only one well had an arsenic time-series trend codetection based on the prior requirements. Because arsenic concentrations in wells with water level data were all measured in USGS laboratories that had detection limits of 0.1 μg/L or less, the screening level was removed for arsenic time-series trends in order to compare to the water level time-series trends. No censored values were used for the comparison of arsenic and water level trends.

2.4.2. Geochemical

Wells with an arsenic concentration, pH, and redox sensitive constituents were used to assess geochemical factors that affect arsenic concentrations and trends in groundwater. Redox was evaluated for wells having one or more of the following constituents: dissolved oxygen, iron, manganese, sulfate, and nitrate. Wells were categorized as having some indication of reducing conditions if dissolved oxygen was less than 0.5 mg/L, nitrate (as N) was less than 0.5 mg/L, manganese was greater than 50 μg/L, iron was greater than 100 μg/L, or sulfate was less than 4 mg/L. These thresholds and criteria were based on the reduction/oxidation scheme of McMahon and Chapelle (2008).

3. Results and discussion

3.1. Arsenic in recent groundwater

In the SJV, arsenic concentrations in groundwater during the last decade were generally low (less than 5 μg/L). The median arsenic concentration in wells sampled during 2010s was 2.3 μg/L and ranged from the screening level of 2 μg/L to 148.5 μg/L (Table 1). About 10% of wells had median concentrations above the USEPA MCL of 10 μg/L.

Spatially weighted results show that arsenic concentrations remain low throughout much of the valley, but areas near the Valley Trough tend to have higher arsenic concentrations (Figs. 1, S5–S8). Past work in the SJV showed similar spatial patterns for arsenic concentrations in groundwater (Welch et al., 2000; Belitz et al., 2003; Izbicki et al., 2008), which indicates these patterns have persisted over time. The percentage of the gridded area with concentrations above the MCL was 13% over the last decade and the percentage of the gridded area less than half the MCL (<5 μg/L) was 63%. Arsenic concentrations of grid cells were highest in the SSJV and WESJV and lowest in the SESJV (Fig. 1). The median arsenic concentration in the NESJV, SESJV, SSJV, and WESJV was 3.0, 2.3, 3.5, and 3.5 μg/L, respectively.

Arsenic concentrations were related to pH and reduction/oxidation (redox) conditions in groundwater (Fig. 2). Two-thirds of wells with high arsenic (greater than 10 μg/L) had pH values above 7.8. Wells with high arsenic also were twice as likely to have some indication of reducing conditions (low dissolved oxygen, low nitrate, high manganese, high iron or low sulfate). As was found in past research (Belitz et al., 2003; Izbicki et al., 2008; Rosecrans et al., 2017a,b; Ayotte et al., 2016), more alkaline (high pH) and reduced geochemical conditions occur more frequently in wells in the Valley Trough or in wells with deeper well screens like public-supply wells. Overall, the median pH of groundwater was 7.8 and about 33% of all wells had some reducing

Table 1
Count of median arsenic concentration per decade by region and total study area. Results from the Wilcoxon Rank Sum Test by region for differences between decades included.

		1980–1989	1990–1999	2000–2009	2010–2019
NESJV	Total	236	549	1172	963
	Count ≤5	130	325	756	640
	Count 5–10	28	125	254	204
	Count >10	78	99	162	119
	Median (μg/L)	4	4.2	3.8	3.5
Wilcoxon p-value		0.29|0.09|0.04			
SESJV	Total	398	782	1139	1240
	Count ≤5	310	684	995	1086
	Count 5–10	17	44	62	73
	Count >10	71	54	82	81
	Median (μg/L)	2	2	2	2
Wilcoxon p-value		0.02|0.85|<0.001			
SSJV	Total	195	453	484	527
	Count ≤5	113	290	327	351
	Count 5–10	18	90	100	95
	Count >10	64	73	57	81
	Median (μg/L)	3	2.9	2.5	2.7
Wilcoxon p-value		0.02|0.35|0.34			
WESJV	Total	330	72	159	184
	Count ≤5	283	45	120	133
	Count 5–10	19	18	28	36
	Count >10	28	9	11	15
	Median (μg/L)	2	2	2	2.2
Wilcoxon p-value		<0.001|0.40|0.56			
Total	Total	1159	1856	2954	2914
	Count ≤5	836	1344	2198	2210
	Count 5–10	82	277	444	408
	Count >10	241	235	312	296
	Median (μg/L)	2	2.6	2.7	2.3
Wilcoxon p-value		<0.001|0.79|<0.001			

conditions (Table S1). Wells with reduced geochemical conditions could be completely anoxic or be a mixture of oxic and anoxic water. Mixtures of oxic and anoxic groundwater could not be distinguished in public-supply wells because dissolved oxygen was not analyzed.

Eighty-six percent of all wells were public supply wells. Consequently, trend results and geochemical relations tend to reflect conditions of public supply wells more than other well types. Domestic wells are typically shallower and have lower pH and more oxic conditions than public supply wells. Arsenic above 10 μg/L was slightly more common in domestic wells than public supply wells, but this mainly reflects a spatial bias towards the SESJV where most of the domestic wells are located and arsenic exceedances are high in domestic wells. Domestic wells from the SSJV study region are underrepresented in this study. Spatial weighting of the areal populations of domestic and public supply wells indicate that the area used for public supply has higher proportions of high concentrations than areas used for domestic wells, except for SSJV which could not be compared. The areal proportion with high concentrations was 8, 14, and 3% for areas used for domestic supply in the NESJV, SESJV, and WESJV, respectively. For areas used for public supply, the areal proportion with high concentrations was 11, 17, 17, and 12% in the NESJV, SESJV, SSJV, and WESJV, respectively.

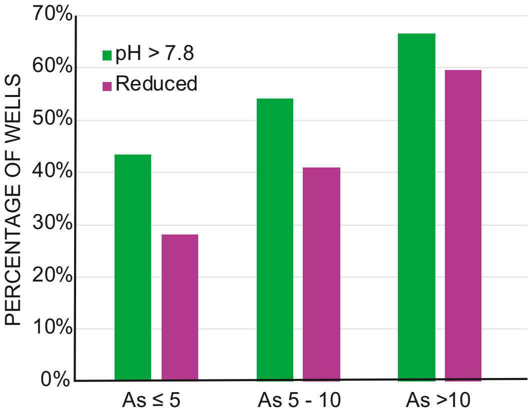


Fig. 2. Percentages of wells with arsenic concentrations having pH greater than 7.8 and reduced geochemical conditions.

Rosecrans et al. (2017a,b) used machine learning methods to predict the likelihood of encountering high pH (pH > 7.4) in wells used for domestic and public supply and redox conditions for different depths in the Central Valley. Results showed that the Valley Trough and western fans have the greatest likelihood of experiencing reducing conditions while the valley margins, mostly the eastern fans, are more likely to experience oxic conditions. Likelihood of pH >7.4 was found mostly in the Tulare Basin and at public-supply well depths. These geochemical patterns frequently reflect the age of groundwater because timescales of hundreds to thousands of years are needed for hydrolysis reactions to raise pH values from circumneutral to above 7.5 and to consume oxygen when organic carbon in sediments is low, such as the eastern alluvial fan deposits (Landon et al., 2011; Green et al., 2016).

3.2. Assessment of trends

Arsenic concentration trends were assessed using a tiered approach that assessed trends by 1) using the entire population of wells in each decade, 2) comparing wells with paired samples in the two most recent decades, and 3) computing trends for wells with enough samples for time-series analysis. Each level of analysis reduces the number of wells that can be tested.

3.2.1. Decadal

Overall, Wilcoxon rank sum test results indicate that arsenic concentrations of wells were increasing between the first successive decades (1980–1990) and were decreasing the last successive decades (2000−2010) in the SJV (Table 1). However, these results were influenced by changing sizes of well populations and statistically significant results of certain study regions (Table 1). In addition, some study regions with statistically significant changes had median arsenic concentrations that were not different. Helsel et al. (2020) reported that the Wilcoxon rank sum test can be unreliable because the sample size requirement for detecting small changes in concentrations among populations may be several thousand. Consequently, changes in arsenic concentrations for study regions and the SJV may not be conclusive.

The percentage of wells with a median arsenic concentration greater than 10 μg/L decreased from 21 to 13% to 11 to 10% for 1980s, 1990s, 2000s, and 2010s, respectively (Table 1). This decrease may be due in part from better detection levels of arsenic and in part from the change in the MCL for arsenic from 50 to 10 μg/L in 2006. Arsenic reported to the state with a non-detection but with higher reporting levels were removed in the screening process, which would tend to inflate the percentage of wells at higher concentrations in early decades. Many wells with arsenic concentrations above the MCL have been preferentially taken out of service. At least 100 wells in the SJV have been destroyed or abandoned that had arsenic concentrations above 10 μg/L before the year 2000. While the majority of wells have low arsenic concentrations, there were areas of the SJV with high arsenic concentrations that will be considered later.

Changes in arsenic concentrations among decades can be difficult to detect using the Wilcoxon rank sum test because the well populations and spatial representation of arsenic concentrations were not consistent for all time periods (Table 1). Public-supply wells are sampled regularly for compliance monitoring, but state compilations show that the population of well records were not consistent until the 2000s. In addition, wells sampled by the USGS are typically collected once rather than periodically, with the exception of long term trends projects that sample the same wells every couple years, like the USGS GAMA and National Water Quality Assessment (NAWQA) programs.

3.2.2. Paired samples

The signed-rank test for paired samples can provide a better assessment of trends over sample population tests, such as the Wilcoxon rank sum test, because it assesses trends in a set of wells where arsenic was measured twice. For paired sample tests, the median concentration in 2000s and 2010s was used because the number of samples and wells were similar (Table 1) and because these samples were more likely to have similar laboratory methods and detection limits.

Overall, 62% of 2256 wells had changes in arsenic concentrations of 0.1 μg/L or more between samples collected in the 2000s and 2010s. These results only reflect the population of public-supply wells in the SJV. In the paired-sample dataset, domestic wells only accounted for 4% of wells and the differences in arsenic concentrations for these wells were not significantly different between decades (Wilcoxon signed-rank test p-value $= 0.77$).

Paired-sample test results indicate that arsenic concentrations have decreased in 41% and increased in 21% of wells in the SJV (Table S2) over the last decade, while the remaining 38% did not change. Changes in arsenic were also significantly different for each study region. Arsenic concentrations decreased in more wells than it increased in each study region (Fig. 3). Most differences in concentrations were small, with the median difference being −0.3, −0.4, −0.3, −0.5 μg/L in the NESJV, SESJV, SSJV, WESJV, respectively.

In wells where arsenic was above 10 μg/L in the 2000s (211 wells), 63% of wells had a concentration that decreased in the 2010s while only 32% had increased (Table S2). Similarly, 61% of wells where arsenic was above 5 μg/L and less than or equal to 10 μg/L (336 wells) had a concentration that decreased during the last decade while 36% had increased. But most changes in arsenic were at lower concentrations because most wells have arsenic concentrations less than 5 μg/L. In these wells (1699 wells), 33% of wells had decreased while 15% had increased over the last decade. The number of wells that did not have a change in concentration for low arsenic values (52%) is largely a result of the screening level.

Arsenic concentration changes were more prevalent in the NESJV than in other areas of the SJV (Fig. 3). The number of wells in which arsenic concentrations decreased (48%) or increased (30%) was higher than the number of wells where arsenic did not change (22%). In all other study regions, arsenic did not change in more wells than where it had decreased or increased.

Cells in Fig. 3 correspond to the median change in arsenic concentrations of wells with paired samples. Cells provide a way of measuring the central tendency of the data when wells are clustered together, as is the case for public-supply wells. About 42% of cells had a median arsenic change of zero and 34% of cells had a median arsenic change that was decreasing and 7% of cells were predominately increasing. There were 16 cells with no paired sample wells. Local variations within cells are also visible in Fig. 3 and reveal places where arsenic concentrations are consistently increasing or decreasing within cells.

3.2.3. Time-series

About three-quarters of the wells tested for time-series trends (2071) did not have an arsenic trend (p-value > 0.1). Since most of these wells had arsenic concentrations near or below the screening level of 2 μg/L, the high occurrence of insignificant trends partially reflects the fact that the analysis of trends in this study does not assess trends at concentrations below the screening level of 2 μg/L.

About 24% of public-supply wells (493) had time-series trends (p-value < 0.1). Seventeen percent of wells were decreasing and 7% were increasing (Table S3). In all four study regions, arsenic was decreasing in more wells than it was increasing (Fig. 4).

The likelihood of having a time-series trend increases with arsenic concentration. Only 14% of wells with low (<5 μg/L) arsenic concentrations had a trend whereas 69% of wells with high arsenic (>10 μg/L) had a trend. About 44% of wells with moderate (5–10 μg/L) arsenic concentrations had a trend. The majority of trends were decreasing for all concentration classes and all study regions (Table S3).

Cells in Fig. 4 correspond to the direction of arsenic time-series trends in the majority of wells with trends in a cell. Most cells were dominated by decreasing trends wells (53%) with only 11% of cells dominated by increasing trends wells. There were 3 cells with an equal number of increasing and decreasing trends wells. The remaining 32 cells had no time-series trends wells. Local variations within cells are also visible in Fig. 4 and reveal places where arsenic concentrations are consistently increasing or decreasing.

The magnitude of trend changes (Sen's slopes) indicates that wells with high arsenic tend to have larger concentration changes and wells with low arsenic tend to have smaller concentration changes (Table 2). Groundwater with high arsenic is an indication that arsenic solubility is not well controlled by sorption processes. So, it is expected that groundwater with higher arsenic would have larger changes in concentrations.

The NESJV had the most arsenic trends (31%) (Fig. 4) but arsenic concentration changes tend to be smaller than other study areas (Table 2). In contrast, the SESJV tended to have the largest changes in arsenic concentrations but the lowest percentage of wells with trends (15%). The differences in magnitude could reflect differences in sediment texture that help limit arsenic solubility. Most wells in the NESJV are closer to the Valley Trough where sediment texture is finer grained than wells in the SESJV, which are closer to the valley margin where sediment is coarser grained.

3.2.4. Relation to drinking water standard

Of the wells with a time-series trend, there are 171 wells with a potential change in exceedance status based on their Sen's slope (Table 2). Twenty-one percent of wells (37) have concentrations above 10 μg/L that are expected to decrease to concentrations below that threshold over the next 10 years. And 18% of wells with concentrations below 10 μg/L are expected to exceed the threshold in 10 years (Table 2). Over the last decade (2000–2010), there were 36 wells that decreased to concentrations below 10 μg/L and 28 wells that had concentrations that rose above that threshold.

These trend patterns are consistent with the long-term decline in the number of wells that exceed 10 μg/L since the 1980s (Table 1). Most of the past and future improvements occur in the NESJV and SESJV, while improvements in other study regions are largely offset by wells expected to exceed the MCL. The WESJV was the only study region that had significantly more wells expected to exceed the MCL than were to decrease. However, the WESVJ study region had the fewest wells (7) with potential changes.

3.3. Anthropogenic factors affecting arsenic trends

3.3.1. Hydrologic factors

Development of the groundwater system to support agriculture has altered the groundwater flow system from one where lateral flow dominated prior to development to a system where vertical flow is much more prominent (Williamson et al., 1989). Irrigation return and groundwater pumping are now the primary forms of recharge to and discharge from the groundwater system (Faunt et al., 2009). Repeated cycles of pumping and application of irrigation water has increased the rate of downward moving groundwater, such that recharge since the 1950s occupies an increasing portion of the groundwater system (Faunt et al., 2009; Jurgens et al., 2016).

Wells with time-series and paired-sample trends tend to be clustered around urban centers with higher well densities (Figs. 3, 4, S3). Most of the wells tested for trends are public-supply wells and therefore

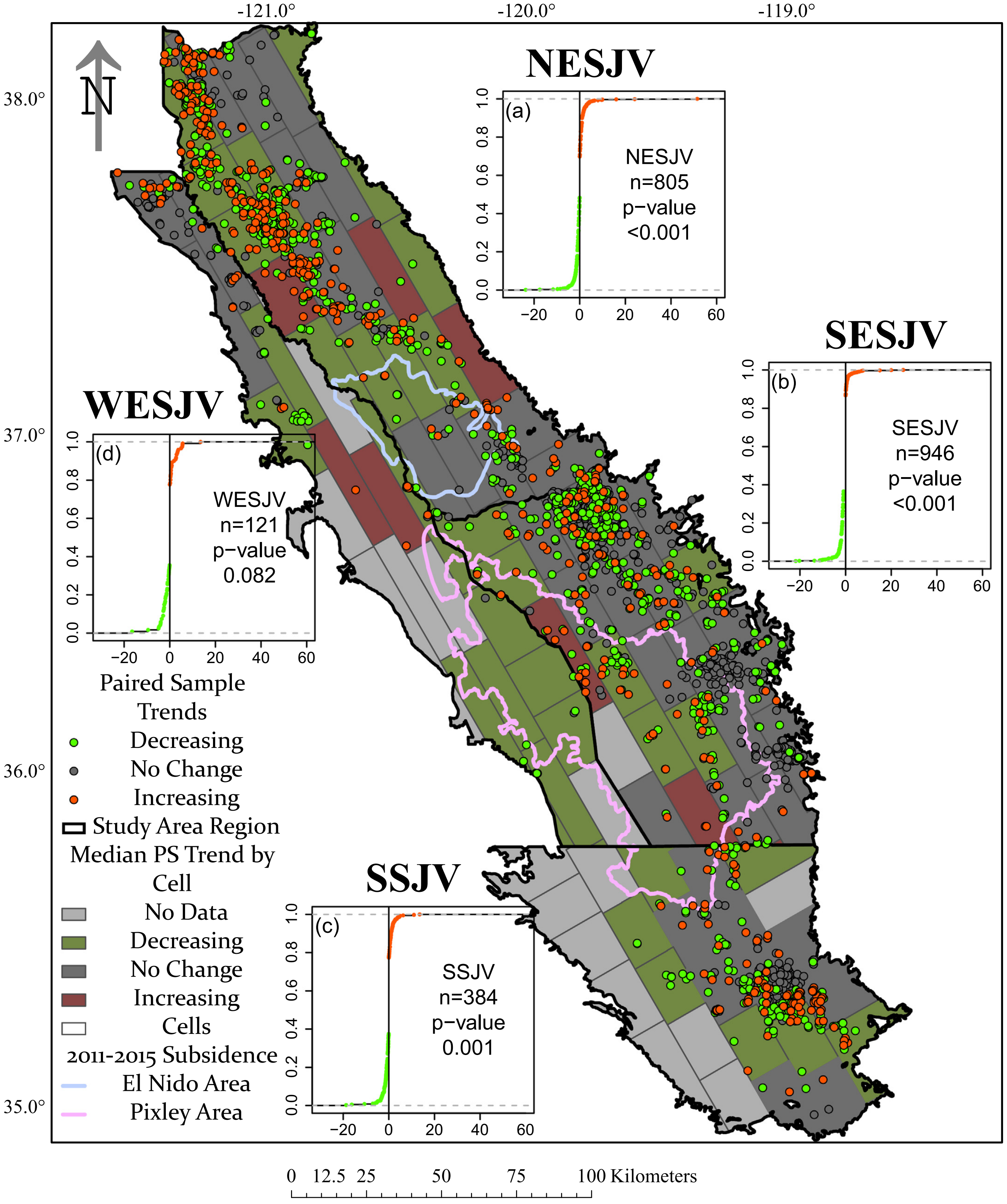


Fig. 3. Arsenic concentration differences in wells from 2000 to 2010 in the San Joaquin Valley (SJV), California. Cell colors correspond to dominant change in paired arsenic samples for each cell. Cumulative distribution function plots depicts the percent of cells with a median paired sample trend in each region with the corresponding *p*-value indicating the significance of the Wilcoxon Signed Rank Test. (a) North-Eastern SJV, (b) South-Eastern SJV, (c) Southern SJV, and (d) Western SJV. Subsidence outline from subsidence measured by Faunt and Sneed between 2011 and 2015 (2015).

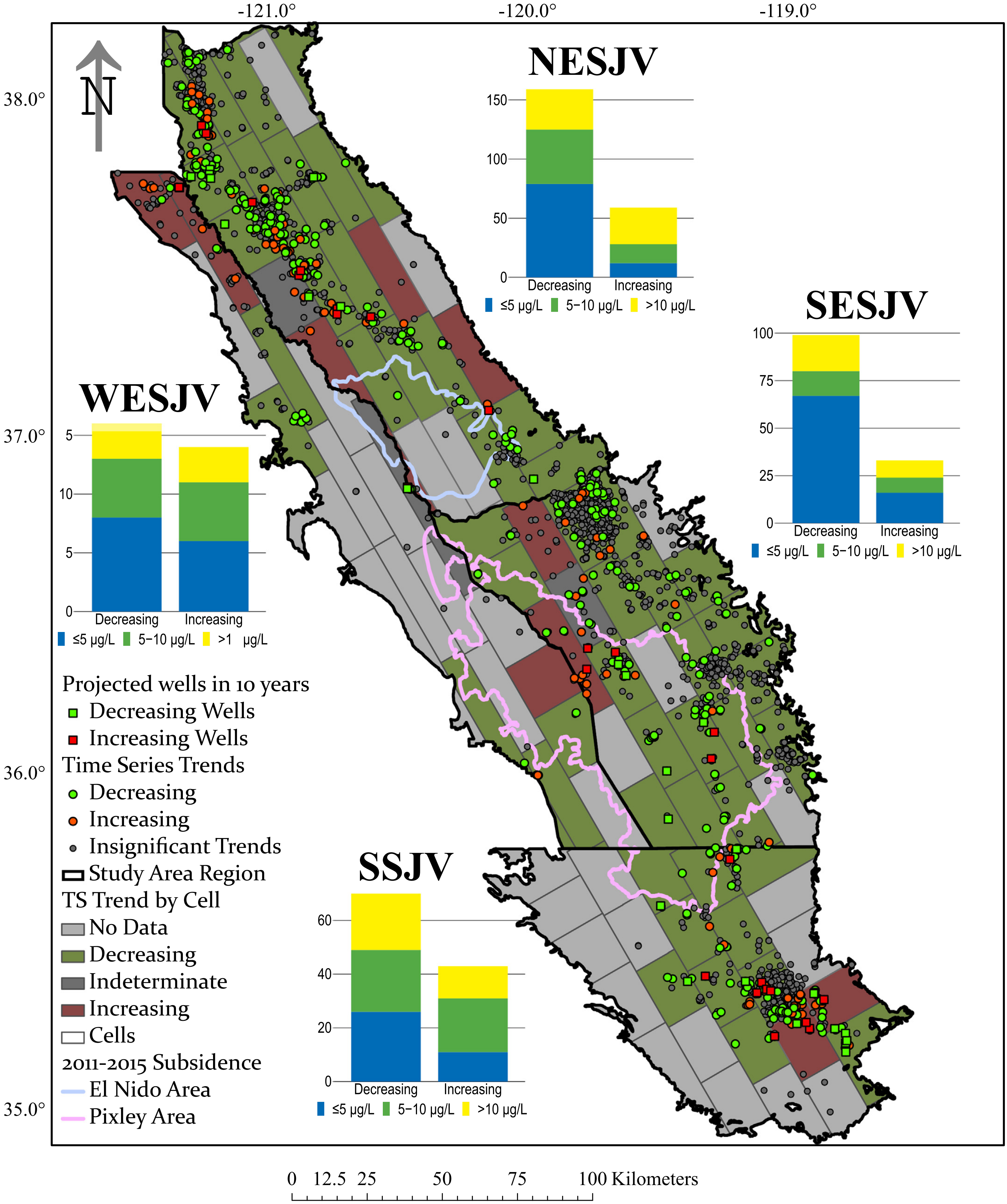


Fig. 4. Time-series trends in arsenic concentration for the San Joaquin Valley (SJV), California. Trends that are insignificant are colored gray. Significant time series trends are colored red or green for increasing and decreasing arsenic trends respectively. Square symbols indicate wells that are projected to increase or decrease beyond the Maximum Contaminant Level (MCL) in 10 years. Bar charts show the number of counts per region for increasing and decreasing trends wells categorized by arsenic concentrations in 2010. Subsidence outline from subsidence measured by Faunt and Sneed between 2011 and 2015 (2015). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Median Sen's slope of wells with arsenic trends by region and direction, and the projected number of wells to obtain an arsenic concentration above or below 10 μg/L in 10 years. Units of Sen's slope are μg/L per year.

	Sen's slope					Number of wells	
	NESJV	SESJV	SSJV	WESJV	All SJV	Last 10 years (2000s–2010s)	Next 10 years (2010s–2020s)
Decreasing arsenic trends							
≤5 μg/L	−0.15	−0.12	−0.19	−0.20	−0.15	–	–
5–10 μg/L	−0.20	−0.41	−0.44	−0.30	−0.28	–	–
>10 μg/L	−0.42	−0.74	−0.60	−0.78	−0.54	36	37
Increasing arsenic trends							
≤5 μg/L	0.12	0.10	0.13	0.08	0.10	0	1
5–10 μg/L	0.27	0.49	0.46	0.53	0.36	28	30
>10 μg/L	0.34	1.19	0.90	0.72	0.60	–	–

may bias arsenic trends towards these areas (Figs. S9, S10). Nonetheless, areas where pumping is more concentrated, particularly from municipal wells with larger pumping rates, are more likely to create strong gradients that move water vertically (downward) more quickly than other areas where pumping is more diffuse or lower (Faunt et al., 2009). Consequently, decreasing arsenic concentrations around municipal pumping centers could reflect the migration of low arsenic recharge that is being drawn downward by pumping.

For most lateral positions, wells with arsenic trends were more likely to have decreasing than increasing concentrations. Wells located in the Valley Trough (−0.2 to 0.2) have an increased likelihood of having increasing arsenic concentrations, particularly in the SESJV and WESJV study areas (Table S4). In the Valley Trough, about 36% of wells with trends had increasing arsenic concentrations (Table S4).

Arsenic trends also were predominately decreasing in both shallow and deep wells in all four study regions (Fig. 5). The SESJV was the

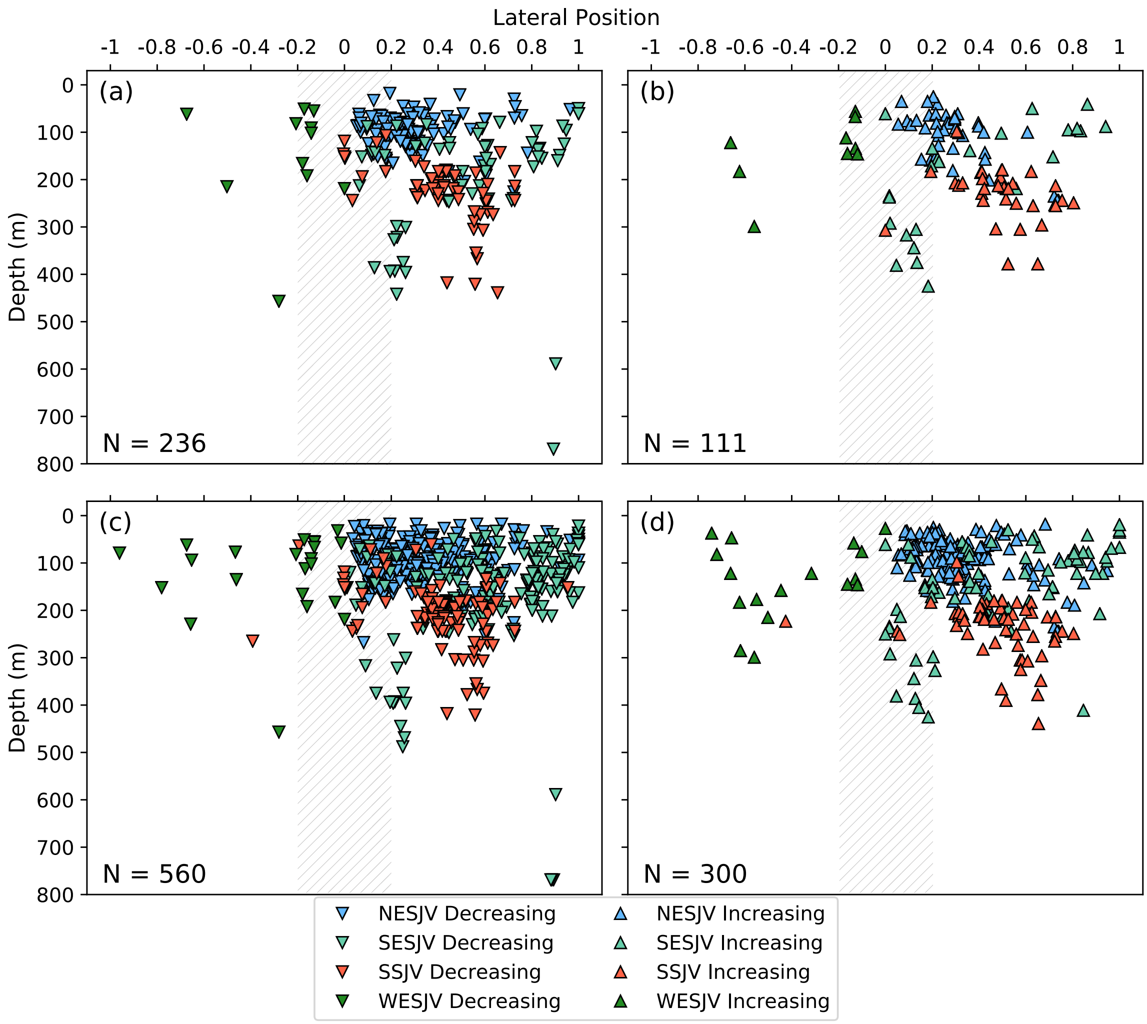


Fig. 5. Arsenic trends by lateral position and depth. Upright triangles indicate increasing trend wells and inverted triangles indicate decreasing trend wells. Chart (a) has decreasing arsenic time-series trends wells plotted. Chart (b) has increasing arsenic time-series trends wells plotted. Chart (c) has decreasing arsenic paired-sample trends wells plotted. Chart (d) has increasing arsenic paired-sample trends wells plotted. Diagonal lines depict the Valley Trough.

only study region where there was a larger percentage of deeper wells (16%) with increasing trends than in shallow wells (5%). In the SESJV, there were more deep wells (200 to 450 m below land surface) with increasing arsenic concentrations in the Valley Trough than wells where arsenic was deceasing (Fig. 5). Wells that were decreasing tend to be shallower (<400 m) and upgradient (lateral position greater than 0.2) than the deeper wells with increasing arsenic in the Valley Trough. These contrasting arsenic trends in wells may indicate that geochemical and physical processes that cause decreasing concentrations in shallower, more upgradient wells has not yet reached deeper wells located in the Valley Trough.

The close and overlapping proximity of wells with increasing and decreasing arsenic concentrations also reflect the heterogeneity of sediments and geochemical processes affecting those trends. Wells with lateral positions within the Valley Trough or wells with deeper screens are more likely to encounter clay lenses, which could explain the larger proportion of wells with increasing arsenic concentrations in this area. If the clay lenses encountered by these wells have high arsenic pore water, then that pore water may be drawn out during pumping (Yan et al., 2000; Stopelli et al., 2020; Mozumder et al., 2020; Mihajlov et al., 2020) or expelled from compaction (Erban et al., 2013; Smith et al., 2018).

Groundwater pumping has led to increases in subsidence in the SJV. Areas of recent subsidence overlap with historical, regional patterns of arsenic concentrations and trends in groundwater and make it difficult to distinguish effects from subsidence from the natural, spatial pattern. In this study, 73 wells with time-series trends are located within areas of recent subsidence: 50 wells had decreasing trends and 23 had increasing trends (Fig. S11). Similarly, about 42% of wells tested had a paired-sample trend that decreased while only 25% of wells had a paired-sample trend that increased (Fig. S12). Wells within 5 mi of the edge of the subsidence areas had a slightly higher percentage of decreasing trends wells (78%) than wells within the subsidence areas (68%) (Figs. S11, S12).

In the Pixley subsidence area, arsenic trends were not different among areas having lesser or greater subsidence. Arsenic trends were primarily decreasing, even in areas of greater subsidence (Fig. S13). If compaction of clays and release of arsenic to groundwater affect trends, it might be expected that areas with greater compaction would have more wells with increasing arsenic trends (Smith et al., 2018). The predominance of decreasing arsenic time-series trends suggests that subsidence has not affected arsenic trends within the subsidence area as a whole but may affect some wells locally. In the El Nido subsidence area, wells with arsenic trends had higher rates of declining arsenic than surrounding areas. Areas with greater or lesser magnitudes of subsidence were not differentiated in the El Nido subsidence area (Fig. S13).

Groundwater pumping has also led to widespread water level declines. Water-level declines have been observed throughout the SJV during the 2012–2015 drought (Faunt and Sneed, 2015) and have generally declined over longer time periods (Faunt et al., 2009). There were 97 wells with water level time-series trends. Eighty-six percent of those wells had water level declines. There were 11 wells with both a water level time-series trend and an arsenic time-series trend (Fig. S14). Eight of the wells have both arsenic and water levels decreasing while three of the wells have increasing arsenic. However, there were not enough data to establish a relationship between arsenic concentrations and falling water levels.

3.3.2. Geochemical

Many wells with arsenic time-series trends had co-detections of nitrate, sulfate, pH, iron, and manganese trends that can help explain why arsenic is changing. Arsenic time-series trends were most often co-detected with nitrate, sulfate, and pH time-series trends. There were 344 wells where arsenic and nitrate trends were co-detected, 161 wells where arsenic and sulfate trends were co-detected, and 111 wells where arsenic and pH trends were co-detected.

Co-detections of trends were grouped by pH and redox conditions of groundwater (Fig. 6). Overall, arsenic trends were more common in groundwater with pH values above 7.8 (61% of trends) and in groundwater where signs of reduced geochemical conditions were absent (65%). In these two groups, trends also were at higher concentrations. Decreasing arsenic concentrations accounted for 70% of trends among pH and redox groups, even in concentrations above 5 μg/L.

Decreasing arsenic concentrations were most closely related to increasing nitrate and sulfate concentrations. In groundwater with reduced conditions (Fig. 6d), these relations suggest the redox state that supports arsenic solubility is changing to a more oxic state where arsenic is less soluble. However, this may only account for 17% of wells with decreasing arsenic because most wells with decreasing arsenic do not have signs of reduced conditions. It is also possible that decreases in arsenic could result from precipitation of sulfide minerals that sequester arsenic but the lack of co-detections of decreasing sulfate trends suggest this does not happen frequently. Wells with decreasing sulfate and arsenic trends only were found in 17 wells, so arsenic sequestration by mineral precipitation may occur in 6% of wells with decreasing arsenic concentrations. Although nitrate reduction is not indicative of sulfidic conditions, wells where nitrate and arsenic concentrations were decreasing may qualitatively indicate a lower redox state that lessens arsenic solubility. Including these wells could indicate that up to 20% of wells with decreasing arsenic could be caused by a lower redox state. Consequently, most decreasing arsenic concentrations are not likely a result of sequestration of arsenic in mineral forms.

For most wells with decreasing arsenic, reduced geochemical conditions were mostly absent (Fig. 6c). In these wells, increasing nitrate and sulfate could be caused by shallow, more oxic and lower arsenic groundwater being pulled downward to deeper depths by regional groundwater pumping. The median nitrate concentration was 3 mg/L in groundwater where reduced geochemical conditions were absent and where pH was less than or equal to 7.8. While some nitrate values were within natural background ranges of 2 to 3 mg/L as N (Burow et al., 2008), many nitrate values are indicative of anthropogenic sources. Nitrogen fertilizers are the most common source of nitrate to the groundwater system (Burow et al., 2008, 2012; Harter et al., 2012). Ayotte et al. (2016) also found that nitrate was predictive of arsenic concentrations, mainly because low nitrate occurs at deeper depths and in the Valley Trough where conditions are more likely to be reduced geochemically. Sulfate has also been linked to soil amendments in parts of the eastern San Joaquin Valley (Mitchell et al., 2000; Lockhart et al., 2013; Hansen et al., 2018), so concomitant increases of sulfate may also be derived from agricultural applications, although oxidation of buried sulfide minerals could also be a source of sulfate.

Increasing arsenic trends were more often associated with groundwater having higher pH rather than reduced conditions (Fig. 6). This result largely reflects that there are more public supply wells with higher pH (51%) than there are public supply wells with reduced geochemical conditions (33%) (Table S1). Increasing arsenic trends were more common in groundwater with elevated (>5 μg/L) and high (>10 μg/L) arsenic concentrations than in groundwater with low arsenic concentrations.

In groundwater with reduced geochemical conditions, increasing arsenic trends were most likely from reductive dissolution of iron and manganese oxyhydroxides (Fig. 6d). Surprisingly, two-thirds of increasing arsenic trends also had increasing nitrate trends. Most of these co-detections were in groundwater that was more oxic. The median pH of this water was 7.9, which could indicate that the increase in arsenic could be from a larger contribution of older and deeper, groundwater or from groundwater with higher dissolved solids in the Valley Trough or WESJV.

Increasing arsenic concentrations in lower pH and oxic groundwater also could result from competitive desorption of arsenic from phosphate loading at the land surface. Orthophosphate is more strongly adsorbed to mineral surfaces than arsenate and may displace arsenate from the

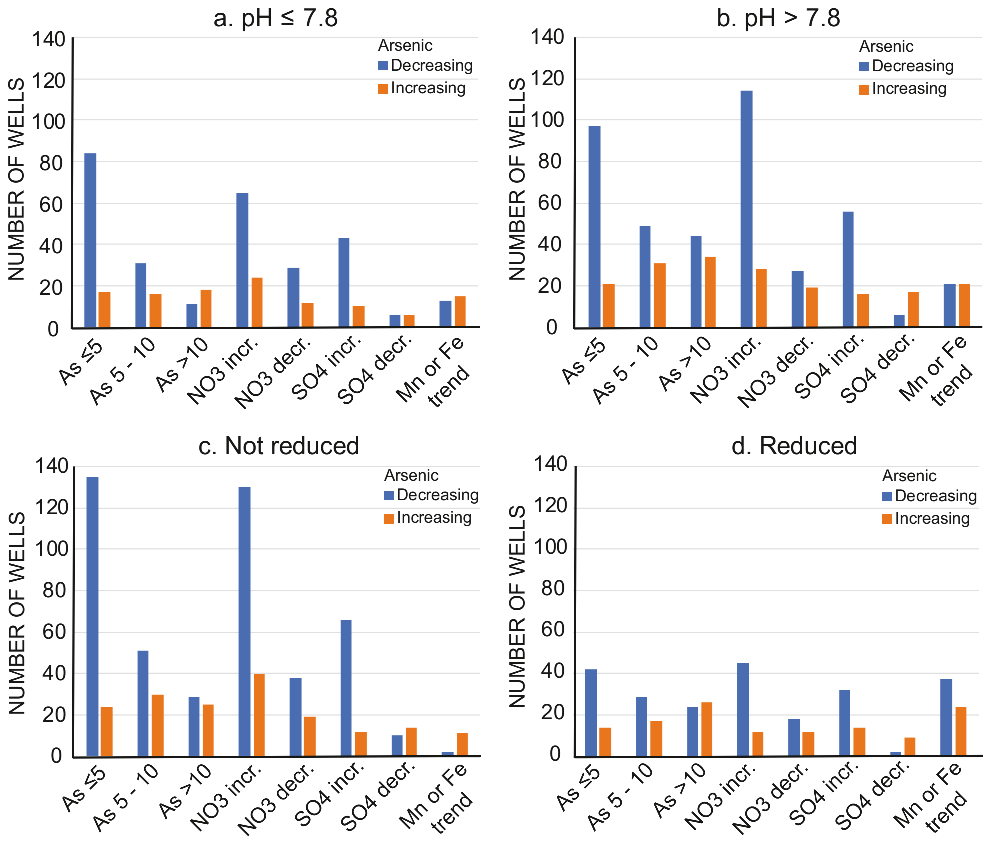


Fig. 6. Number of wells with arsenic time-series trends by concentration class and codetections of time-series trends for nitrate, sulfate, and manganese or iron for groundwater with different pH and redox conditions. A. Wells with a pH of less than or equal to 7.8. B. Wells with a pH of greater than 7.8. C. Wells with a redox condition of not reducing. D. Wells with a redox condition of reducing.

surface when present (Manning and Goldberg, 1996; Smedley and Kinniburgh, 2002). Domagalski and Johnson (2011) found that dissolved orthophosphate concentrations in pore samples from the unsaturated zone and groundwater samples were some of the highest among five agricultural sites in the United States. Kent et al. (2020) found that orthophosphate had increased from 2004 to 2011 in public supply wells in the Central Valley. Although orthophosphate could play an important role in arsenic behavior beneath agricultural land in the SJV, orthophosphate was not analyzed frequently enough in public-supply wells to evaluate its effect in this study.

4. Conclusions

Arsenic concentrations throughout the San Joaquin Valley (SJV) were generally low but concentrations in many wells have changed over the last decade. In wells where concentrations of arsenic were changing, arsenic trends were most often decreasing. Decreasing arsenic trends were associated with rising nitrate and sulfate concentrations, which suggest that wells were pumping more oxic groundwater potentially impacted by agricultural applications of nitrogen fertilizers and soil amendments. Most of the wells with arsenic trends are in areas of high well densities. Concentrated pumping in these areas tends to increase the vertical movement of groundwater. In addition, widespread water level declines over the last several decades along with increasing nitrate and sulfate concentrations suggest that the proportion of younger, more oxidizing water captured by deeper wells is increasing with time.

Wells located in the Valley Trough and deeper wells can have higher arsenic and chemical characteristics that reflect predevelopment conditions. The chemistry of groundwater is changing as agricultural recharge continues to move downward to deeper parts of the aquifer system. Assuming conditions and trends over the last two decades persist into the future, it is projected 37 wells with high arsenic concentrations will decrease below the Maximum Contaminant Level (MCL) of 10 μg/L in the next ten years; however, these improvements will likely be offset by 31 wells that are projected to exceed the MCL.

These findings serve as an example of the complicated ramifications of groundwater development in arid regions where groundwater is used to support drinking water and agricultural supplies. The driving anthropogenic forces behind improving arsenic, namely agricultural recharge and pumping, will likely be offset by water-quality degradation by nitrate, total dissolved solids, and possibly uranium (Hansen et al., 2018). In addition, there will be places in the Valley Trough or deep parts of the system where less permeable material may delay the movement of more oxic groundwater or where geochemical conditions can buffer changes in pH and nitrate. These locations may continue to experience localized arsenic mobilization, despite no regional-scale increase in arsenic concentrations. These combined effects may degrade groundwater quality further over the long term.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145223.

CRediT authorship contribution statement

Emily A. Haugen: Writing – original draft, Conceptualization, Formal analysis, Investigation, Data curation. **Bryant C. Jurgens:** Writing – original draft, Conceptualization, Methodology, Validation, Resources. **Jose A. Arroyo-Lopez:** Methodology, Software, Resources, Data curation. **George L. Bennett:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Funding for this work was provided by the California State Water Resources Control Board's Groundwater Ambient Monitoring and Assessment Program (Agreement 18-005-250) and U.S. Geological Survey Cooperative Water Program Matching Funds.

The authors would like to thank the USGS GAMA Team for collecting and managing the data used in this study and Neil Dubrovsky, Miranda Fram, and two anonymous reviewers for helpful comments on the manuscript.

References

Ayotte, J.D., Nolan, B.T., Gronberg, J.A., 2016. Predicting arsenic in drinking water wells of the Central Valley, California. Environ. Sci. Technol. 50, 7555–7563. https://doi.org/10.1021/acs.est.6b01914.

Barringer, J.L., Reilly, P.A., 2013. Arsenic in groundwater: a summary of sources and the biogeochemical and hydrogeologic factors affecting arsenic occurrence and mobility. In: Bradley, P. (Ed.), Current Perspectives in Contaminant Hydrology and Water Resources Sustainability. InTech, pp. 83–116 https://doi.org/10.5772/55354.

Bartow, J. Alan, 1991. The Cenozoic evolution of the San Joaquin Valley, California (Professional Paper No. 1501). doi:https://doi.org/10.3133/pp1501.

Belitz, K., Dubrovsky, N.M., Burow, K., Jurgens, B.C., John, T., 2003. Framework for a ground-water quality monitoring and assessment program for California (report no. 2003–4166). Water-Resources Investigations Report https://doi.org/10.3133/wri034166.

Belitz, K., Fram, M.S., Johnson, T.D., 2015. Metrics for assessing the quality of groundwater used for public supply, CA, USA: equivalent-population and area. Environ. Sci. Technol. 49, 8330–8338. https://doi.org/10.1021/acs.est.5b00265.

Bennett, G.L., Fram, M.S., Belitz, K., Jurgens, B.C., 2010. Status and understanding of groundwater quality in the Northern San Joaquin Basin, 2005: California GAMA Priority Basin Project. Scientific Investigations Report No. 2010–5175. U.S. Geological Survey.

Brannon, J.M., Patrick, W.H., 1987. Fixation, transformation, and mobilization of arsenic in sediments. Environ. Sci. Technol. 21, 450–459. https://doi.org/10.1021/es00159a005.

Burow, K.R., Shelton, J.L., Dubrovsky, N.M., 2008. Regional nitrate and pesticide trends in ground water in the eastern San Joaquin Valley, California. J. Environ. Qual. 37 (5 Suppl), S249–S263. https://doi.org/10.2134/jeq2007.0061.

Burow, K.R., Jurgens, B.C., Belitz, K., Dubrovsky, N.M., 2012. Assessment of regional change in nitrate concentrations in groundwater in the Central Valley, California, USA, 1950s–2000s. Environ. Earth Sci. 69, 2609–2621. https://doi.org/10.1007/s12665-012-2082-4.

Dieter, C.A., Maupin, M.A., 2017. Public supply and domestic water use in the United States, 2015 (open-file report no. 2017–1131). Open-File Report. U.S. Geological Survey.

Domagalski, J.L., Johnson, H.M., 2011. Subsurface transport of orthophosphate in five agricultural watersheds, USA. J. Hydrol. 409, 157–171. https://doi.org/10.1016/j.jhydrol.2011.08.014.

Erban, L.E., Gorelick, S.M., Zebker, H.A., Fendorf, S., 2013. Release of arsenic to deep groundwater in the Mekong Delta, Vietnam, linked to pumping-induced land subsidence. PNAS 110, 6. https://doi.org/10.1073/pnas.1300503110.

Farquhar, M.L., Charnock, J.M., Livens, F.R., Vaughan, D.J., 2002. Mechanisms of arsenic uptake from aqueous solution by interaction with goethite, lepidocrocite, mackinawite, and pyrite: an x-ray absorption spectroscopy study. Environ. Sci. Technol. 36, 1757–1762. https://doi.org/10.1021/es010216g.

Faunt, C.C., Sneed, M., 2015. Water availability and subsidence in California's Central Valley. SFEWS 13, 8. doi:10.15447/sfews.2015v13iss3art4.

Faunt, C.C., Hanson, R.T., Belitz, K., Schmid, W., Predmore, S.P., Rewis, D.L., McPherson, K., 2009. Groundwater availability of the Central Valley aquifer, California (professional paper no. 1766). Professional Paper. U.S. Geological Survey.

Fram, M.S., 2017. Groundwater quality in the Western San Joaquin Valley study unit, 2010: California GAMA Priority Basin Project (scientific investigations report no. 2017–5032). Scientific Investigations Report. U.S. Geological Survey.

Fram, M.S., Shelton, J.L., 2018. Groundwater quality in the Mokelumne, Consumnes, and American River Watersheds, Sierra Nevada, California (open-file report no. 20181047). Open-File Report. U.S. Geological Survey.

Fuji, R., Swain, W.C., 1995. Areal distribution of selected trace elements, salinity, and major ions in shallow ground water, Tulare Basin, Southern San Joaquin Valley, California. Water-Resources Investigations Report No. 95–4048. U.S. Geological Survey https://doi.org/10.3133/wri954048.

Garbarino, J.R., 1999. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory Determination of Dissolved Arsenic, Boron, Lithium, Selenium, Strontium, Thallium, and Vanadium Using Inductively Coupled Plasma-Mass Spectrometry (Open-File Report No. 99–093). U.S. Geological Survey.

Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. Soil Sci. Soc. Am. J. 66, 413–421. https://doi.org/10.2136/sssaj2002.4130.

Grafe, M., Eick, M.J., Grossl, P.R., Saunders, A.M., 2002. Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. J. Environ. Qual. 31, 1115–1123. https://doi.org/10.2134/jeq2002.1115.

Green, C.T., Jurgens, B.C., Zhang, Y., Starn, J.J., Singleton, M.J., Esser, B.K., 2016. Regional oxygen reduction and denitrification rates in groundwater from multi-model residence time distributions, San Joaquin Valley, USA. J. Hydrol. 543, 155–166. https://doi.org/10.1016/j.jhydrol.2016.05.018.

Gronberg, J.M., Dubrovsky, N.M., Kratzer, C.R., Domagalski, J.L., Brown, L.R., Burow, K.R., 1998. Environmental setting of the San Joaquin-Tulare basins, California. Water-Resources Investigations Report No. 97–4205. U.S. Geological Survey https://doi.org/10.3133/wri974205.

Hansen, J.A., Jurgens, B.C., Fram, M.S., 2018. Quantifying anthropogenic contributions to century-scale groundwater salinity changes, San Joaquin Valley, California, USA. Sci. Total Environ. 642, 125–136. https://doi.org/10.1016/j.scitotenv.2018.05.333.

Hansen, J.A., Jurgens, B.C., Fram, M.S., 2018. Quantifying anthropogenic contributions to century-scale groundwater salinity changes, San Joaquin Valley, California, USA. Sci. Total Environ. 642, 125–136. https://doi.org/10.1016/j.scitotenv.2018.05.333.

Harter, T., Lund, J.R., Darby, J., Fogg, G.E., Howitt, R., Jessoe, K.K., Pettygrove, G.S., Quinn, J.F., Viers, J.H., Boyle, D.B., Canada, H.E., DeLaMora, N., Dzurella, K.N., Fryjoff-Hung, A., Hollander, A.D., Honeycutt, K.L., Jenkins, M.W., Jensen, V.B., King, A.M., Kourakos, G., Liptzin, D., Lopez, E.M., Mayzelle, M.M., McNally, A., Medellin-Azuara, J., Rosenstock, T.S., 2012. Addressing nitrate in California's drinking water: report to the California, 1900–2015. State Water Resources Control Board. Davis Center for Watershed Sciences (January 2012). http://groundwaternitrate.ucdavis.edu/files/138956.pdf.

Harvey, C.F., Christopher H. Swartz, A.B.M. Badruzzaman, Nicole Keon-Blute, Winston Yu, M. Ashraf Ali, Jenny Jay, Roger Beckie, Volker Niedan, Daniel Brabander, Peter M. Oates, Khandaker N. Ashfaque, Shafiqul Islam, Harold F. Hemond, M. Feroze Ahmed, n.d.2002. Arsenic mobility and groundwater extraction in Bangladesh. Science 298, 1602–1606. doi:https://doi.org/10.1126/science.1076978.

Helsel, D.R., Hirsch, R.M., Ryberg, K.R., Archfield, S.A., and Gilroy, E.J., 2020, Statistical methods in water resources: U.S. Geological Survey Techniques and Methods, book 4, chapter A3, 458 p., doi:https://doi.org/10.3133/tm4a3. [Supersedes USGS Techniques of Water-Resources Investigations, book 4, chapter A3, version 1.1.].

Izbicki, J.A., Stamos, C.A., Metzger, L.F., Halford, K.J., Kulp, T.R., V, G.L.B., 2008. Source, distribution, and management of arsenic in water from wells, Eastern San Joaquin Ground-Water Subbasin, California (open-file report no. 2008–1272). Open-File Report. U.S. Geological Survey.

Johnson, R.L., Clark, B.R., Landon, M.K., Kauffman, L.J., Eberts, S.M., 2011. Modeling the potential impact of seasonal and inactive multi-aquifer wells on contaminant movement to public water-supply wells1: modeling the potential impact of seasonal and inactive multi-aquifer wells on contaminant movement to public water-supply wells. J. Am. Water Res. Assoc. 47, 588–596. https://doi.org/10.1111/j.1752-1688.2011.00526.x.

Jurgens, B.C., Burow, K.R., Dalgish, B.A., Shelton, J.L., 2008. 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 (scientific investigations report no. 2008–5156). Scientific Investigations Report.

Jurgens, B.C., Böhlke, J.K., Kauffman, L.J., Belitz, K., Esser, B.K., 2016. A partial exponential lumped parameter model to evaluate groundwater age distributions and nitrate trends in long-screened wells. J. Hydrol. 543, 109–126. https://doi.org/10.1016/j.jhydrol.2016.05.011.

Jurgens, B.C., Jasper, M., Nguyen, D.H., Bennett, G.L., 2018. USGS CA GAMA-PBP Groundwater-Quality Results - Assessment and Trends. U.S. Geological Survey web page https://doi.org/10.5066/P91WJ2G1.

Jurgens, B.C., Fram, M.S., Rutledge, J., Bennett, V., G.L, 2020. Identifying areas of degrading and improving groundwater-quality conditions in the State of California, USA, 1974–2014. Environ. Monit. Assess. 192, 250. https://doi.org/10.1007/s10661-020-8180-y.

Kendall, M.G., 1938. A new measure of rank correlation. Biometrika 301–2, 81–93.

Kendall, M.G., 1975. Rank Correlation Methods. Griffin, London.

Kent, R., Johnson, T.D., Rosen, M.R., 2020. Status and trends of orthophosphate concentrations in groundwater used for public supply in California. Environ. Monit. Assess. 192, 26. https://doi.org/10.1007/s10661-020-08504-x.

Landon, M.K., Green, C.T., Belitz, K., Singleton, M.J., Esser, B.K., 2011. Relations of hydrogeologic factors, groundwater reduction-oxidation conditions, and temporal and spatial distributions of nitrate, Central-Eastside San Joaquin Valley, California, USA. Hydrogeol. J. 19, 1203–1224. https://doi.org/10.1007/s10040-011-0750-1.

Lin, Z., Puls, R.W., 2000. Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. Environ. Geol. 39, 753–759. https://doi.org/10.1007/s002540050490.

Lockhart, K.M., King, A.M., Harter, T., 2013. Identifying sources of groundwater nitrate contamination in a large alluvial groundwater basin with highly diversified intensive agricultural production. J. Contam. Hydrol. 151, 140–154. https://doi.org/10.1016/j.jconhyd.2013.05.008.

Mann, H.B., 1945. Nonparametric tests against trend. Econometrica 13 (3), 245.

Mann, H.B., Whitney, D.R., 1947. On a test of whether one of two random variables is stochastically larger than the other. Ann. Math. Stat. 18 (1), 50–60.

Manning, B.A., Goldberg, S., 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Sci. Soc. Am. J. 60, 121–131. https://doi.org/10.2136/sssaj1996.03615995006000010020x.

McMahon, P.B., Chapelle, F.H., 2008. Redox processes and water quality of selected principal aquifer systems. Ground Water 46, 259–271.

Mihajlov, I., Mozumder, M.R.H., Bostick, B.C., Stute, M., Mailloux, B.J., Knappett, P.S.K., Choudhury, I., Ahmed, K.M., Schlosser, P., van Geen, A., 2020. Arsenic contamination of Bangladesh aquifers exacerbated by clay layers. Nat. Commun. 11, 2244. https://doi.org/10.1038/s41467-020-16104-z.

Mitchell, J.P., Shennan, C., Singer, M.J., Peters, D.W., Miller, R.O., Prichard, T., Grattan, S.R., Rhoades, J.D., May, D.M., Munk, D.S., 2000. Impacts of gypsum and winter cover crops on soil physical properties and crop productivity when irrigated with saline water. Agric. Water Manag. 45, 55–71. https://doi.org/10.1016/S0378-3774(99)00070-0.

Mozumder, M.R.H., Michael, H.A., Mihajlov, I., Khan, M.R., Knappett, P.S.K., Bostick, B.C., Mailloux, B.J., Ahmed, K.M., Choudhury, I., Koffman, T., Ellis, T., Whaley-Martin, K., San Pedro, R., Slater, G., Stute, M., Schlosser, P., Geen, A., 2020. Origin of groundwater arsenic in a rural pleistocene aquifer in Bangladesh depressurized by distal municipal pumping. Water Resour. Res., 56 https://doi.org/10.1029/2020WR027178.

Neil, C.W., Yang, Y.J., Jun, Y.-S., 2012. Arsenic mobilization and attenuation by mineral–water interactions: implications for managed aquifer recharge. J. Environ. Monit. 14, 1772. https://doi.org/10.1039/c2em30323j.

Page, R.W., 1986. Geology of the fresh ground-water basin of the Central Valley, California, with texture maps and sections (professional paper no. 1401–C). Professional Paper. U.S. Geological Survey.

Polizzotto, M.L., Harvey, C.F., Sutton, S.R., Fendorf, S., 2005. Processes conducive to the release and transport of arsenic into aquifers of Bangladesh. Proc. Natl. Acad. Sci. 102, 18819–18823. https://doi.org/10.1073/pnas.0509539103.

Postma, D., Mai, N.T.H., Lan, V.M., Trang, P.T.K., Sø, H.U., Nhan, P.Q., Larsen, F., Viet, P.H., Jakobsen, R., 2017. Fate of arsenic during Red River water infiltration into aquifers beneath Hanoi, Vietnam. Environ. Sci. Technol. 51, 838–845. https://doi.org/10.1021/acs.est.6b05065.

Presser, T.S., Swain, W.C., Tidball, R.R., Severson, R.C., 1990. Geologic sources, mobilization, and transport of selenium from the California Coast Ranges to the western San Joaquin Valley: a reconnaissance study. Water-Resources Investigations Report No. 90–4070. U.S. Geological Survey.

Raven, K.P., Jain, A., Loeppert, R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Technol. 32, 344–349. https://doi.org/10.1021/es970421p.

Rosecrans, C.Z., Nolan, B.T., Gronberg, J.A.M., 2017a. Predicted pH in depth zones used by domestic and public drinking water supply wells, Central Valley, California (scientific investigations map no. 3377). Scientific Investigations Map. U.S. Geological Survey.

Rosecrans, C.Z., Nolan, B.T., Gronberg, J.M., 2017b. Prediction and visualization of redox conditions in the groundwater of Central Valley, California. J. Hydrol. 546, 341–356. https://doi.org/10.1016/j.jhydrol.2017.01.014.

Santi, P.M., McCray, J.E., Martens, J.L., 2006. Investigating cross-contamination of aquifers. Hydrogeol. J. 14, 51–68. https://doi.org/10.1007/s10040-004-0403-8.

Sen, P.K., 1968. Estimates of the regression coefficient based on Kendall's tau. J. Am. Stat. Assoc. 63, 1379–1389.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568. https://doi.org/10.1016/S0883-2927(02)00018-5.

Smith, D.B., Cannon, W.F., Woodruff, L.G., Solano, F., Ellefsen, K.J., 2014. Geochemical and mineralogical maps for soils of the conterminous United States (open-file report no. 2014–1082). Open-File Report. U.S. Geological Survey.

Smith, R., Knight, R., Fendorf, S., 2018. Overpumping leads to California groundwater arsenic threat. Nat. Commun. 9, 2089. https://doi.org/10.1038/s41467-018-04475-3.

Stopelli, E., Duyen, V.T., Mai, T.T., Trang, P.T.K., Viet, P.H., Lightfoot, A., Kipfer, R., Schneider, M., Eiche, E., Kontny, A., Neumann, T., Glodowska, M., Patzner, M., Kappler, A., Kleindienst, S., Rathi, B., Cirpka, O., Bostick, B., Prommer, H., Winkel, L.H.E., Berg, M., 2020. Spatial and temporal evolution of groundwater arsenic contamination in the Red River delta, Vietnam: interplay of mobilisation and retardation processes. Sci. Total Environ. 717, 137143. https://doi.org/10.1016/j.scitotenv.2020.137143.

Theil, H. (1950). A rank-invariant method of linear and polynominal regression analysis (parts 1–3). In Ned. Akad. Wetensch. Proc. Ser. A (Vol. 53, pp. 1397–1412).

Tidball, R.R., Grundy, W.D., Sawatzky, K.L., 1986. Kriging Techniques Applied to Element Distribution in Soils of the San Joaquin Valley, California, in HAZTECH INTERNATIONAL, Hazardous Materials Management Exhibition and Conference, August 13–15, 1986. Pollution Engineering Magazine, Chicago, Illinois, Denver, Colorado, Proceedings, pp. 992–1009.

Tufano, K.J., Reyes, C., Saltikov, C.W., Fendorf, S., 2008. Reductive processes controlling arsenic retention: revealing the relative importance of Iron and arsenic reduction. Environ. Sci. Technol. 42, 8283–8289. https://doi.org/10.1021/es801059s.

U.S. Environmental Protection Agency, 2018a. Drinking Water Requirements for States and Public Water Systems: Drinking Water Arsenic Rule History. Website. accessed November 7, 2018 at:. https://www.epa.gov/dwreginfo/drinking-water-arsenic-rule-history.

U.S. Environmental Protection Agency, 2018b. Drinking Water Standards and Regulations. National Primary Drinking Water Regulations Website, accessed February 21, 2018 at:. https://www.epa.gov/dwstandardsregulations.

U.S. Geological Survey, 2018. National Water Information System: Web Interface Website. accessed February 21, 2018 at:. https://www.waterboards.ca.gov/gama/geotracker_gama.shtml.

U.S. Geological Survey (2020) National Water Information System: U.S. Geological Survey web interface, doi:https://doi.org/10.5066/F7P55KJN. Cited April 7, 2020.

Voss, S.A., Jurgens, B.C., Fram, M.S., V, G.L.B., 2019. Delineation of spatial extent, depth, thickness, and potential volume of aquifers used for domestic and public water-supply in the Central Valley, California (scientific investigations report no. 2019–5076). Scientific Investigations Report. U.S. Geological Survey.

Weissmann, G.S., Bennett, G.L., Lansdale, A.L., 2005. Factors controlling sequence development on Quaternary fluvial fans, San Joaquin Basin, California, USA. Geol. Soc. Lond., Spec. Publ. 251, 169–186. https://doi.org/10.1144/GSL.SP.2005.251.01.12.

Welch, A.H., Stollenwerk, K.G., 2003. Arsenic in Ground Water. Springer, Boston, MA.

Welch, A.H., Westjohn, D.B., Helsel, D.R., Wanty, R.B., 2000. Arsenic in ground water of the United States: occurrence and geochemistry. Ground Water 38, 589–604. https://doi.org/10.1111/j.1745-6584.2000.tb00251.x.

Wilcoxon, F., 1945. Individual comparisons by ranking methods. Biom. Bull. 1 (6), 80–83. https://doi.org/10.2307/3001968.

Williamson, A.K., Prudic, D.E., Swain, L.A., 1989. Ground-water flow in the Central Valley, California (professional paper no. 1401-D).

Winkel, L.H.E., Trang, P.T.K., Lan, V.M., Stengel, C., Amini, M., Ha, N.T., Viet, P.H., Berg, M., 2011. Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century. Proc. Natl. Acad. Sci. 108, 1246–1251. https://doi.org/10.1073/pnas.1011915108.

Yan, X.-P., Kerrich, R., Hendry, M.J., 2000. Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. Geochim. Cosmochim. Acta 64, 2637–2648. https://doi.org/10.1016/S0016-7037(00)00380-X.

Zhang, Z., Guo, H., Liu, S., Weng, H., Han, S., Gao, Z., 2020. Mechanisms of groundwater arsenic variations induced by extraction in the western Hetao Basin, Inner Mongolia, China. J. Hydrol. 583, 124599. https://doi.org/10.1016/j.jhydrol.2020.124599.