



Quantifying anthropogenic contributions to century-scale groundwater salinity changes, San Joaquin Valley, California, USA

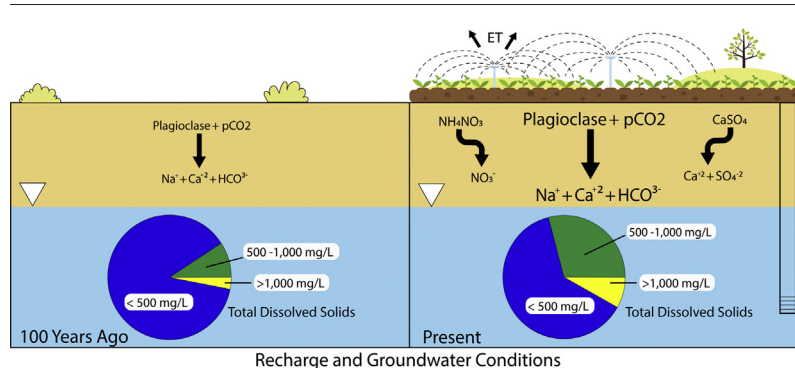
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HIGHLIGHTS

- Changes in TDS and major ions in groundwater were evaluated over the last century in the San Joaquin Valley (SJV).
- TDS has increased in most parts of the SJV and increases are mainly associated with agricultural practices.
- In the eastern SJV, increases in bicarbonate, nitrate, and sulfate in recharge were the main contributors to increased TDS.
- Bicarbonate is primarily the result of dissolution of primary minerals during the agricultural growing season.
- Nitrate and sulfate are mainly derived from applications of fertilizers and soil amendments for agriculture.

GRAPHICAL ABSTRACT



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ABSTRACT

Total dissolved solids (TDS) concentrations in groundwater tapped for beneficial uses (drinking water, irrigation, freshwater industrial) have increased on average by about 100 mg/L over the last 100 years in the San Joaquin Valley, California (SJV). During this period land use in the SJV changed from natural vegetation and dryland agriculture to dominantly irrigated agriculture with growing urban areas. Century-scale salinity trends were evaluated by comparing TDS concentrations and major ion compositions of groundwater from wells sampled in 1910 (Historic) to data from wells sampled in 1993–2015 (Modern). TDS concentrations in subregions of the SJV, the southern (SSJV), western (WSJV), northeastern (NESJV), and southeastern (SESJV) were calculated using a cell-declustering method. TDS concentrations increased in all regions, with the greatest increases found in the SSJV and SESJV. Evaluation of the Modern data from the NESJV and SESJV found higher TDS concentrations in recently recharged (post-1950) groundwater from shallow (<50 m) wells surrounded predominantly by agricultural land uses, while premodern (pre-1950) groundwater from deeper wells, and recently recharged groundwater from wells surrounded by mainly urban, natural, and mixed land uses had lower TDS concentrations, approaching the TDS concentrations in the Historic groundwater. For the NESJV and SESJV, inverse geochemical modeling with PHREEQC indicated that weathering of primary silicate minerals accounted for the majority of the increase in TDS concentrations, contributing more than nitrate from fertilizers and sulfate from soil amendments combined. Bicarbonate showed the greatest increase among major ions, resulting from enhanced silicate weathering due to recharge of irrigation water enriched in CO₂ during the growing season. The results of this study demonstrate

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that large anthropogenic changes to the hydrologic regime, like massive development of irrigated agriculture in semi-arid areas like the SJV, can cause large changes in groundwater quality on a regional scale.

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1. Introduction

Total dissolved solids (TDS) is a quantitative measure of the salt content of water, and elevated TDS concentrations can limit the usability of water resources for drinking water and agriculture. Elevated TDS concentrations in water can influence color, odor and taste, as well as the effectiveness of water for use in agricultural irrigation and stock watering (Hem and Geological Survey (U.S.), 1985; McKee and Wolf, 1963). The U.S. Environmental Protection Agency (USEPA) and California recommended secondary maximum contaminant level (CA-SMCL) for TDS is 500 mg/L and the upper CA-SMCL is 1000 mg/L (California State Water Resources Control Board, 2017a, 2017b). The SMCLs are based on aesthetic qualities for taste and screening for hardness in drinking water. Drinking water is generally preferred to have <500 mg/L TDS. The California Agricultural Water Quality Goal threshold for water used for irrigation of agriculture is 450 mg/L (California State Water Resources Control Board, 2017a), and was developed based on studies of TDS influence on irrigation water effectiveness (Ayers and Westcot, 1985; USEPA, 1986). Water with TDS from 1000 to 10,000 mg/L is generally considered brackish (Stanton et al., 2017), although aquifers containing groundwater with <10,000 mg/L TDS may be protected as an Underground Source of Drinking Water unless exempted from protection (U.S. Code of Federal Regulations, 2016).

Recently, the California Groundwater Ambient Monitoring and Assessment (GAMA) program's Priority Basin Project (PBP), a cooperative program between the California State Water Resources Control Board (SWRCB) and the U.S. Geological Survey, completed an assessment of over 95% of the groundwater resources used for public drinking water supplies statewide (Belitz et al., 2003, 2015). Groundwater resources used for public drinking water supplies in 8 of the 82 study areas investigated had TDS concentrations > 1000 mg/L in >25% of the used resource (Fram, 2017) – and 3 of these study areas were in the San Joaquin Valley (SJV) (Bennett et al., 2010; Fram, 2017).

Increasing groundwater salinity in the Central Valley is projected to result in billions of dollars per year in economic losses by the year 2030 due to its deleterious effects on drinking water supplies and agricultural productivity (Howitt et al., 2009). A diverse group of stakeholders, including federal, state, and local agencies, agricultural and other business groups, resource management, water-quality and environmental coalitions, and others, is developing a nitrate and salinity management plan for the Central Valley (CV-SALTS, 2016). Development of effective management alternatives to control salinity in SJV groundwater will require understanding of the relative importance of the various processes contributing to salinity.

Past groundwater-quality studies in the SJV have focused on anthropogenic contaminants including nitrate loading from fertilizers (Burow et al., 2008, 2007; Dubrovsky et al., 2010; Harter et al., 2012, 2002; Nightingale, 1970) or dairy farms (Harter et al., 2012, 2002; Nightingale, 1970) and pesticides (Domagalski and Dubrovsky, 1992; Burow et al., 1998; Troiano et al., 2001). Naturally-occurring contaminants such as uranium (Jurgens et al., 2010; Burow et al., 2017) and arsenic (Welch et al., 2000; Ayotte et al., 2017) are also potential problems in SJV groundwater, but TDS has not been studied regionally. Both nitrate and uranium concentrations have been shown to be increasing in groundwater in parts of the SJV, but there has not been an assessment of the relative impacts of these constituents on overall TDS of the groundwater system.

This study examines the change in TDS in SJV groundwater from 1910 – before large-scale alteration of the groundwater flow

system – to the present period (1993–2015), and relates those changes to contributions of various geochemical processes and anthropogenic inputs at the land surface. Inverse geochemical modeling between samples from each time period was used to differentiate and quantify the major processes and ions contributing to TDS increases over the past 100 years, and alterations were linked to changes in land-use and hydrology, including anthropogenic influences.

2. Description of study area

California's Central Valley is a large, northwest-trending, asymmetric structural trough filled with marine and continental sediments up to nearly 10 km thick (Page, 1986). The study area is the SJV, which occupies the southern two-thirds of the Central Valley (Fig. 1). The SJV is >400 km long and 30 to 90 km wide and is flanked by two mountain ranges, the Sierra Nevada to the east and the Coast Ranges to the west. Streams in the northern part of the SJV drain northward through the San Joaquin River to the San Francisco Bay, while the southern part of the SJV, the Tulare Basin, is a hydrologically closed basin with no points of natural discharge for surface water or groundwater besides evapotranspiration. The climate is arid-to-semiarid, characterized by cool, wet winters and hot, dry summers. Mean annual precipitation ranges from <13 centimeters (cm) in the south to about 40 cm in the north (Gronberg et al., 1998).

The freshwater aquifer system of the SJV is contained in alluvial, fluvial, and lacustrine deposits and consists of a mixture of unconfined, semi-confined, and confined aquifers (Williamson et al., 1989; Belitz and Heimes, 1990; Bertoldi et al., 1991; Faunt, 2009). Sediments on the eastern side of the SJV are dominated by arkosic materials derived from granitic rocks of the Sierra Nevada. These Sierra Nevada-derived sediments interfinger with sediments derived from the Coast Ranges in the center of the valley. The Coast Ranges adjacent to the western SJV are geologically diverse, ranging from marine shales and sandstones to Franciscan Formation mélange and ultramafic rocks (Page, 1986).

Over the last 100 years, depth-to-water in the SJV has increased dramatically. In 1910, depth-to-water in the majority of the Valley was <10 m below land surface, with <5 m and artesian conditions existing along much of the Valley trough (Mendenhall et al., 1916; Supp. 2). Groundwater in the SJV prior to development was recharged primarily at the Valley margins by streams and runoff during the colder winter and spring months, and discharge was predominantly through evapotranspiration and discharge to streams where groundwater levels were close enough to the land surface. Net recharge and discharge prior to development was estimated to be 2 million acre-feet/year (2.47 km³/year) (Williamson et al., 1989).

As of the year 2000, most of the groundwater in the region is deeper than 10 m below land surface, with much of the southern and eastern regions having depths to water of >25 m (Faunt, 2009; Supp. 2). The increase in depth-to-water in addition to land subsidence of up to 10 m has depleted the supply of groundwater since development of the groundwater system (Faunt, 2009). Deep percolation of irrigation water past crop roots during the warmer summer months is now responsible for nearly 70% of Central Valley groundwater recharge (Faunt, 2009). Water used for irrigation is mainly from diverted surface water and from groundwater pumpage in similar proportions for the Valley as a whole, however this proportion varies spatially and temporally depending upon availability of surface water deliveries (Faunt, 2009). Pumping is the primary form of discharge in the Valley.

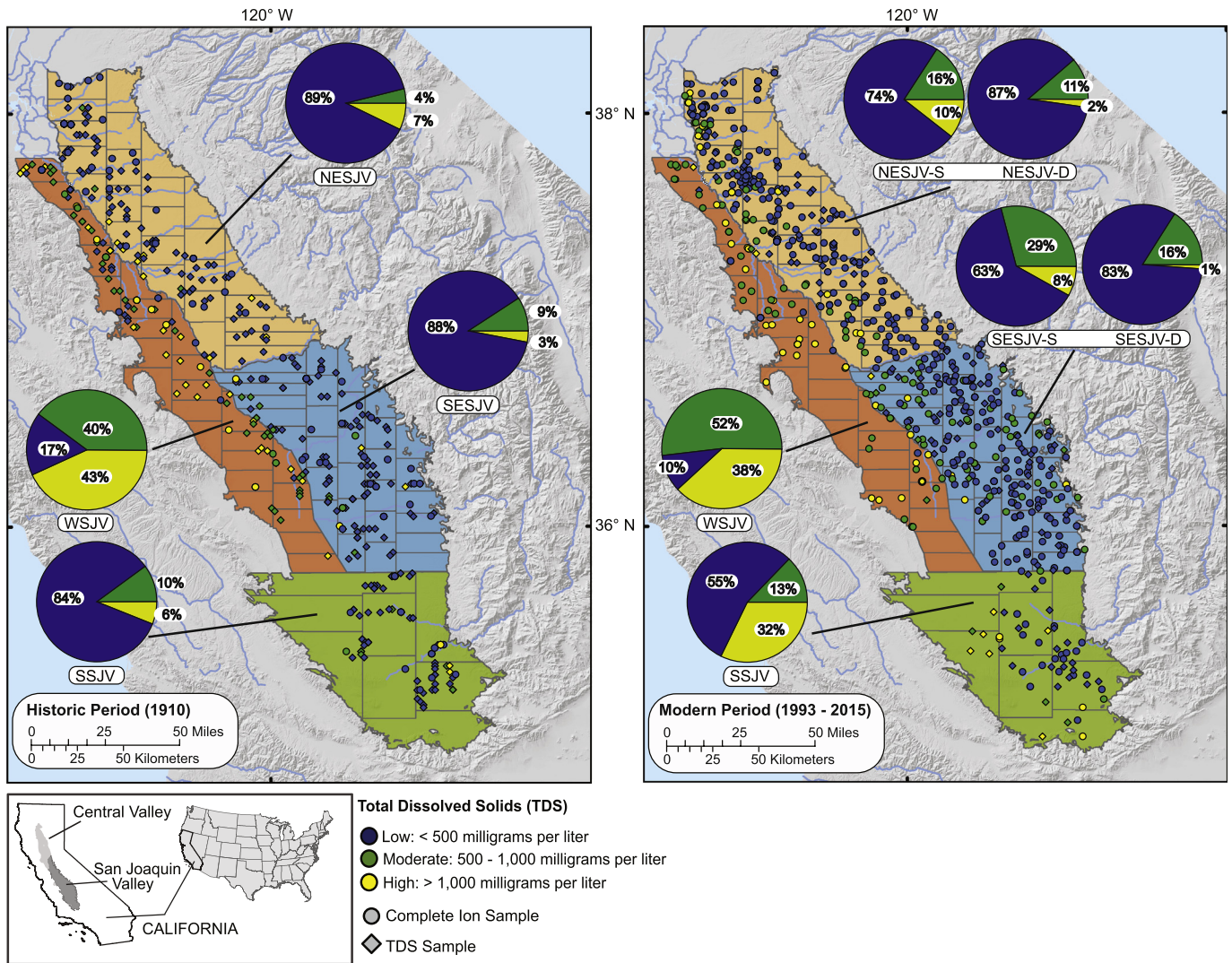


Fig. 1. Maps of the San Joaquin Valley, California, USA (SJV) showing total dissolved solids (TDS) concentrations in groundwater samples collected from drinking water, agricultural, and industrial supply wells during (A) the Historic time period (1910) and (B) the Modern time period (1993–2015). The SJV is divided into four regions: Northeast (NESJV), Southeast (SESJV), Western (WSJV), and Southern (SSJV), and the NESJV and SESJV regions are subdivided into Shallow (S) and Deep (D) regions for the Modern Data. Points denote sampled well locations, where point shape indicates whether the data includes full ion analyses or TDS values only, and point color indicates Low (0–500 mg/L), Moderate (500–1000 mg/L) or High (>1000 mg/L) TDS concentration. Pie charts indicate areal proportions of each aquifer region containing Low, Moderate, and High concentrations of TDS, calculated using a spatially weighted cell declustering method.

Presently, net recharge and discharge in the Valley was estimated to be 12 million acre-feet/year (14.80 km³/year) (Faunt, 2009).

The SJV is one of the most agriculturally productive regions in the world (PPIC, 2017). Agriculture in this region relies heavily on groundwater, particularly during drought years when surface water deliveries are curtailed (California Department of Water Resources, 2003; Faunt, 2009; PPIC, 2017). Approximately 70% of the land of the Central Valley is used for agriculture, and the percentage of urban land has increased steadily since the 1970s (Faunt, 2009). The SJV has nearly 4 million residents, most of whom rely on groundwater for drinking water supplies (PPIC, 2017).

3. Material and methods

This study focuses on groundwater resources used for beneficial purposes including drinking water supply, irrigation, and industrial purposes requiring fresh water (such as boilers). Groundwater-quality data collected by the USGS in 1905–1910 (Historic period)

were compared to data collected by the USGS in 1993–2015 (Modern period).

3.1. Data compilation

Mendenhall et al. (1916) assessed groundwater resources in the SJV in 1905–1910 to estimate the availability of groundwater of suitable quality for agricultural, industrial, and drinking-water supplies. Nearly all existing wells were inventoried, depth-to-water at 4500 wells was compiled, and water-quality data were collected at 485 wells (Fig. 1). Water-quality samples from 114 wells were analyzed for TDS, chloride, sulfate, bicarbonate, carbonate, calcium, magnesium, sodium + potassium, and silica (Mendenhall et al., 1916; Dole, 1909). At the remaining sites (371), field assays were used to measure TDS, chloride, sulfate, bicarbonate, carbonate, and total hardness (Mendenhall et al., 1916; Leighton, 1905). Samples from 32 wells were analyzed using both methods. Comparison between laboratory analysis and field assay results indicated general agreement and cation-anion imbalances for laboratory results were generally <10% (Mendenhall et al., 1916).

Well-construction, water-level, and water-quality data were transcribed from Mendenhall et al. (1916) into an electronic format (Hansen et al., 2018) and wells were assigned latitudes and longitudes corresponding to the centroid of the township-range-section location given by Mendenhall et al. (1916). Nearly all of the water-quality samples collected by Mendenhall et al. (1916) were from wells used for irrigation, stock watering, drinking-water supplies, or boilers. Three samples were excluded from this study: two were samples of produced water from oil wells, and one was from a geothermal well. For wells with water-quality data but no water-level data, interpolated values of the depth-to-water surface were used (Supp. 2) (Hansen et al., 2018). Wells with artesian conditions were assigned a water level of zero.

Groundwater-quality data collected between 1993 and 2015 were compiled from the USGS National Water Information System (NWIS) database for 722 wells in the SJV (Fig. 1). About two-thirds of the wells were sampled for the GAMA Priority Basin Project (GAMA-PBP), a cooperative program between the USGS and the California State Water Resources Control Board that focuses on water-quality assessments for groundwater resources used for drinking-water supplies (<http://ca.water.usgs.gov/gama/>; <http://www.swrcb.ca.gov/>). GAMA-PBP data used in this study include public supply wells across the entire SJV (Landon et al., 2010b; Bennett et al., 2010; Burton et al., 2012; Shelton et al., 2013; Fram, 2017) and domestic wells on the eastern side of the SJV sampled between 2004 and 2016 (Shelton and Fram, 2017; Bennett et al., 2017). About one-quarter of the wells were sampled for the National Water Quality Assessment (NAWQA) Program (<http://water.usgs.gov/nawqa/>). NAWQA sampled primarily domestic wells and monitoring wells on the eastern side of the SJV between 1991 and present (2016) (Dubrovsky et al., 1998; Gronberg et al., 1998, 2004). The remainder of the wells were sampled for a cooperative project between the USGS and the Northeastern San Joaquin Ground Water Banking Authority from 2003 to 2012 (O'Leary et al., 2015; Clark et al., 2012).

For wells that were sampled multiple times between 1993 and 2015, the most recent sample with complete major ion chemistry was used. A total of 613 samples had complete major ion data (calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, bicarbonate, carbonate, silica, and TDS). An additional 109 samples had data only for specific conductance; for these samples, TDS was calculated: $TDS = \text{Specific Conductivity (SC)} \times 0.6617$ as determined from the existing samples with known values of TDS and SC. For sites where depth-to-water was not measured, depth-to-water was estimated from the Spring 2000 water table map generated by the Central Valley Hydrologic Model (Faunt, 2009; Supp. 2).

A total of 634 wells had data for tritium (^3H) activities which can be used to distinguish between groundwater recharged primarily before 1950 and groundwater recharged primarily after 1950. Tritium activities in precipitation increased dramatically as a result of atmospheric testing of nuclear weapons in the 1950's and 1960's. Background natural ^3H activities in precipitation at the latitudes and longitudes of the SJV and its watersheds are approximately 3–5 TU (Michel, 1989; Jurgens et al., 2009), therefore groundwater recharged prior to 1950 would have ^3H activities less than approximately 0.2 TU in 2016. Tritium activities in groundwater samples were corrected for decay of tritium between the date of sample collection (1993–2015) to 2016, and wells with decay-corrected tritium activities < 0.2 TU were defined as *Pre-Modern* (recharged before 1950) groundwater. Wells with decay-corrected tritium activities > 0.2 TU were defined as *ModernOrMixed* and may be comprised of water recharged solely after the 1950's or of a mixture of waters recharged before and after the 1950's.

Samples from 1993 to 2015 were collected following protocols established by the USGS NAWQA program (Koterba et al., 1995) and the USGS National Field Manual (USGS, variously dated; <http://water.usgs.gov/owq/FieldManual/>). Samples were analyzed for TDS, major ions, and nitrate at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado (references in Bennett et al., 2017;

Shelton and Fram, 2017). All well-construction, water-quality, and water-level data used in this study are compiled in an accompanying USGS Data Release (Hansen et al., 2018). Sample data for the modern period are also available through USGS NWIS Web (<https://waterdata.usgs.gov/nwis>).

The nationwide USGS National Land Cover Dataset (Vogelmann et al., 2001; Price et al., 2003) (30 m satellite resolution) was used to assign well locations with land-use characteristics from approximately 1992, a method used in previous national and regional studies relating land use to water quality (Gilliom et al., 2006; Zogorski et al., 2006). The 25 land-cover classifications (Nakagaki and Wolock, 2005) created from this satellite imagery were simplified into three primary land-use categories: urban, agricultural, and natural using a radius of 500 m surrounding each well location. (ArcGIS version 9.2) (Johnson and Belitz, 2009).

3.2. Definition of regions and grids

The SJV was divided into four regions: Northeast SJV (NESJV), Southeast SJV (SESJV), Western SJV (WSJV), and Southern SJV (SSJV) (Fig. 1) consistent with previous SJV groundwater studies, and to account for varying geology and recharge conditions in different regions of the Valley. These regions were primarily defined from the California Department of Water Resources SJV groundwater subbasins (CDWR, 2003). NESJV contains the Cosumnes, Eastern San Joaquin, Modesto, Turlock, Merced, Madera, and Chowchilla subbasins; SESJV the Kings, Kaweah, Tule, and Tulare Lake subbasins; WSJV the Tracy, Delta-Mendota, and Westside subbasins; and SSJV the Kern basin. The boundaries between the WSJV and the NESJV and SESJV were adjusted from the CDWR subbasin boundaries to optimize separation of groundwater derived from the Sierra Nevada to the east and from the Coast Ranges to the west under predevelopment conditions. Runoff from the Coast Ranges generally has higher sulfate concentrations than runoff from the Sierra Nevada and Mendenhall et al. (1916) used sulfate concentrations to estimate the eastward extent of groundwater derived from recharge of Coast Ranges runoff. For this study, the boundaries were adjusted so that wells with sulfate concentration > 20% of TDS concentration in the Historic period were located in the WSJV rather than the SESJV or NESJV.

Wells were not evenly distributed across the four regions and the same wells were not sampled in the Historic and Modern periods. To minimize bias resulting from the uneven distribution of data, the regions were discretized into spatially distributed, equal-area grids (Scott, 1990): NESJV, twenty-five 370 km² cells; SESJV, thirty 280 km² cells; WSJV, twenty-five 280 km² cells; and SSJV, eight 984 km² cells. These cell sizes were the minimum sizes in each region for which 60% of the cells in the region would contain at least 1 well with full major ion data in both time periods (Fig. 1, Table 1) (Hansen et al., 2018).

In the NESJV and SESJV, Modern wells were further subdivided into two depth zones, shallow (NESJV-S, SESJV-S) and deep (NESJV-D, SESJV-D), so that vertical patterns of TDS in Modern groundwater could be compared to TDS in groundwater from the Historic period as a whole. For each well, the depth below the water table to the bottom of the screen (DBWT) was calculated and wells with a DBWT < 50 m were categorized as *shallow* while wells > 50 m were categorized as *deep* (Fig. 2, Supp. 3). For some wells, well depth was used when depth to bottom of screen was not available. A DBWT of 50 m was previously used by Jurgens et al. (2008) in the NESJV to separate shallow and deep zones of the aquifer.

Although the 50 m boundary does not separate wells by water use, most wells used for public supply are deep and most wells used for domestic supply are shallow. Ten wells in the NESJV and 9 wells in the SESJV did not have well construction information. These wells were categorized as shallow where the water use was for domestic supply or deep where water use was for irrigation or public supply.

Table 1

Summary of total dissolved solids (TDS), well depth, and water-level data (in meters below land surface (mbls)) for samples collected during the Historic (1910) and Modern (1993–2015) periods for the San Joaquin Valley (SJV), California by region.

[Regions: NESJV, Northeastern SJV (25 cells); SESJV, Southeastern SJV (30 cells); WSJV, Western SJV (25 cells); SSJV, Southern SJV (8 cells).]

	Number with major ion data		Number with TDS data		Areal weighted TDS concentration (mg/L)		Number with well depth data		Well depth (m bls)		Water level (m bls)	
	cells	wells	cells	wells	Median	Interquartile range	wells		Median	IQR	Median	IQR
Historic												
NESJV	15	33	22	154	205	175–270	139		20	12–40	4	2–7
SESJV	18	36	27	137	215	165–275	132		29	15–162	3	3–5
WSJV	13	26	21	112	810	540–1800	111		40	18–109	8	4–17
SSJV	7	16	7	78	230	155–440	74		40	18–120	5	1–12
Modern												
NESJV-D	25	143	25	167	236	188–336	160		106	85–140	15	10–23
NESJV-S	24	137	24	154	280	199–505	149		38	26–52	10	6–20
SESJV-D	27	104	29	139	271	205–390	129		119	88–165	15	12–20
SESJV-S	27	130	28	135	408	275–621	128		47	34–59	15	11–21
WSJV	18	69	18	72	953	729–1243	70		107	66–182	14	5–26
SSJV	6	30	8	55	471	279–1290	54		214	154–239	29	22–48

The population of wells in the shallow zone is not significantly different from the entire population of wells from the Historic period (Fig. 2; Kruskal-Wallis rank sum test; NESJV p -value = 0.06; SESJV p -value = 0.62). This indicates that groundwater quality data collected from shallow wells over the last 20 years (Modern period) and from the Historic period should provide changes in groundwater quality compositions from nearly the same vertical portion of aquifer but at different points in time. Furthermore, groundwater quality data from deep wells in the Modern dataset are not provided a comparable comparison of Historic

water quality at the same depth in the NESJV and SESJV, however groundwater in the NESJV and SESJV moves from shallower depths to deeper depths over time (Faunt, 2009), so comparison to Historic data may evaluate the degree of similarity between the two sets of groundwater quality data. For WSJV and SSJV, Modern DBWT in wells are deeper than the Historic DBWT, so a comparison between water-quality datasets may not represent change in a part of the aquifer system but rather a difference with depth.

3.3. Calculation of TDS change

Calculations of TDS in each region for each time period were made using a cell declustering method (Belitz et al., 2010; Isaaks and Srivastava, 1989). This method has been used to estimate the areal proportion of groundwater resources with concentrations of a constituent above a threshold concentration (Belitz et al., 2010, 2015):

$$p^t = \frac{\sum W_n^t}{n} \quad (1)$$

where P^t is the proportion of the groundwater resources with concentration greater than the threshold, n is the number of equal-area cells, W_n^t is the number of wells in cell n with concentration greater than the threshold, W_n is the number of wells in cell n with data.

Eq. (1) was used to calculate the proportion of groundwater with TDS concentrations above 500 or 1000 mg/L (the California SMCL values) and to estimate the median TDS in each region. The median was estimated by solving for the threshold value of TDS for which half the groundwater resources had concentration greater than the threshold (Table 1).

3.4. Inverse geochemical modeling

The USGS software PHREEQC version 3 (Parkhurst and Appelo, 2013) was used to compute inverse geochemical models to quantify mole transfers of minerals and phases that account for the change in major ion composition from Historic groundwater to Modern groundwater in the SESJV and NESJV. The inverse modeling implicitly assumes that recharge water is either local surface water, groundwater, or a mixture of the two and that the chemical character of recharge from surface water has been steady for a particular region or grid cell. In the ESJV, surface water and groundwater originally derived from surface water are the primary forms of recharge. In contrast, imported surface water from the Central Valley Project in the WSJV and SSJV has a distinctly different chemical character than local surface water. For this reason and

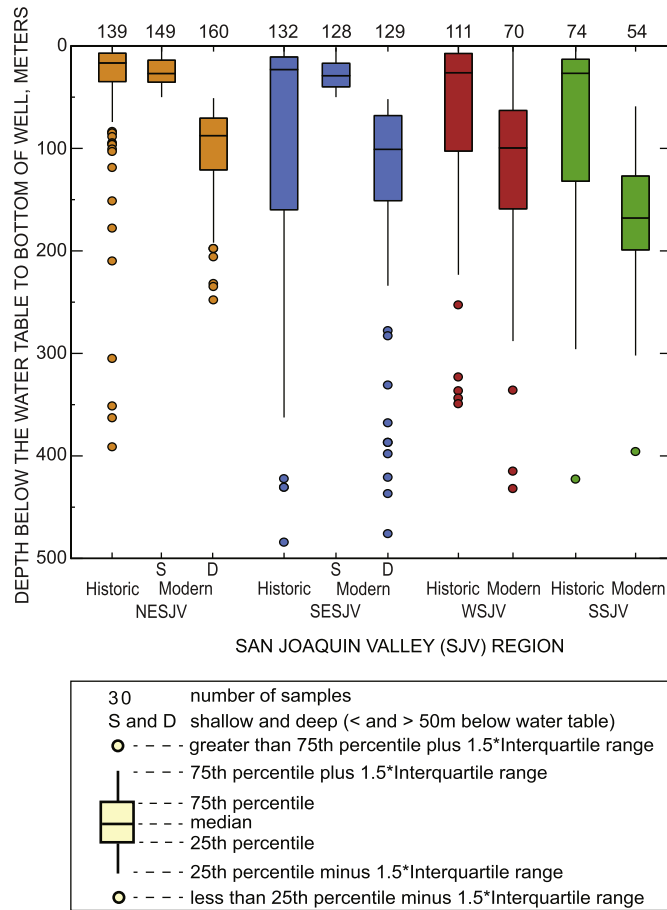


Fig. 2. Box plots showing depth of well below the water table to bottom of well for the Historic (1910) and Modern (1993–2015) periods by region, San Joaquin Valley, California.

because the variability in TDS in the Historic and Modern time periods were too large to estimate TDS change (see Results section), the WSJV and SSJV were not modeled. The modeling reactants and phases included in inverse model simulations were the same as the minerals used in example 16 of PHREEQC (Parkhurst and Appelo, 2013) because sediments in the eastern SJV were derived primarily from rocks of the Sierra Nevada. The model included silicate reactions involving the dissolution of plagioclase and biotite, formation of clay minerals kaolinite and Ca-montmorillonite, and biotite to kaolinite according to the mineral stoichiometries of Garrels and Mackenzie (1967) (Supp. 4). Addition and subtraction of water and halite were included to simulate evaporation and dilution. Halite dissolution was included to account for small differences in chloride content. Calcite was permitted to dissolve and precipitate. Fertilizer and soil amendments, in the form of ammonium nitrate $[(\text{NH}_4)(\text{NO}_3)]$, elemental sulfur and gypsum (calculated as anhydrite, CaSO_4), were included as phases that represent contributions of nitrate, calcium, and sulfate to groundwater from agricultural application of fertilizers and soil amendments. Carbon dioxide gas and oxygen (O_2) were included to account for changes in dissolved inorganic carbon and allow for the oxidation of sulfur and ammonium to sulfate and nitrate, and an exchange species for ammonium (NH_4X) was included to allow for the uptake of excess ammonium. Other forms of nitrogen based fertilizers, such as calcium nitrate, urea, and manure, are used throughout the SJV but a single form of nitrate was used to simplify the model. Additional soil amendments and fertilizers, such as phosphates, are also applied in the Valley and could contribute to changes in major ion chemistry but mole transfers from those phases were expected to be small. Exchange of calcium, magnesium, and sodium between groundwater and clay minerals (cation exchange) was also included in the models to account for small imbalances in model transfers of the primary phases.

The data from the Historic period did not include pH so inverse models were simulated using a pH value of 7.5 to approximate groundwater derived from granitic rocks (Garrels and Mackenzie, 1967). These data also did not include nitrate analysis. For the purposes of modeling, historic natural concentrations of NO_3 were calculated from the imbalance of ions and ranged from 0 to 2 mg/L, with a median < 1 mg/L (Hansen et al., 2018), which are similar in range to estimates of background nitrate concentrations in the area (Burow et al., 2013). Data for dissolved oxygen, iron, and manganese concentrations indicated that most samples from the Modern period were oxic; data for these parameters were not available for samples from the Historic period. Oxic conditions ($p_e = 4$) were assumed for all models. Anoxic conditions resulting in denitrification only are present in a small part of the system (Landon et al., 2011), thus the absence of denitrification in the models likely only results in a small underestimate of the amount of nitrate fertilizer added. Inverse models used the default thermodynamic database, phreeqc.dat, and a water temperature of 25 °C (Supplement 4).

For each period and region, median groundwater was represented by 10 groundwater samples. The sample with the median TDS concentration for each equal-area cell containing samples was determined. The samples from the 10 cells whose median TDS concentrations surrounded the overall median TDS for the period and region were selected as representative samples. Each of the 10 Historic samples was compared to each of the 10 Modern samples in the region, resulting in 100 pairs for each of the four study regions (NESJV Historic/NESJV-D, NESJV Historic/NESJV-S, SESJV Historic/SESJV-D, and SESJV Historic/SESJV-S). Inverse modeling of the 400 sample pairs generated >57,000 models. Only models with sum of residuals < 4 and that produced a calculated TDS change within a factor of 0.5–2 of the observed TDS difference for the sample pair were accepted, yielding conservative estimates of change. This filtering resulted in acceptance of 9833 inverse models and included at least one model for 305 of the 400 modeled pairs.

Model results are presented as the mass (mg/L) contributed to the change in TDS for individual constituents (calcium, magnesium, sodium, potassium, bicarbonate, silica, sulfate, nitrate, and chloride). The

mass contribution of each constituent is computed as the sum of six precipitation (subtraction) and dissolution (addition) reactions included in inverse models: 1) silicate dissolution and precipitation; 2) cation exchange with clays; 3) evaporation, dilution, and halite addition and subtraction; 4) calcite dissolution and precipitation; 5) ammonium nitrate dissolution; and 6) gypsum or sulfur dissolution (Supp. 4). Mass change due to evaporation or dilution is total mass from halite dissolution plus mass from evaporation and dilution. The mass from evaporation and dilution was calculated as the amount of evaporation or dilution of the Historic member of the pair required by a particular model, multiplied by the TDS of the Historic sample.

3.5. Statistical tests

The data analyzed for this study were not normally distributed, so nonparametric, rank-based methods of statistical analysis were employed (Helsel and Hirsch, 2002). A significance level (α) of 5% ($\alpha = 0.05$) was used for hypothesis testing. Spearman's correlation method was used for rank-order correlation coefficient (ρ , rho) calculations between continuous variables. Differences among groups were tested by the Kruskal-Wallis rank-sum test and Tukey's multiple comparison test.

4. Results and discussion

4.1. Century-scale changes in TDS

TDS has increased in most groundwater in the SJV (Figs. 1 & 3) over the past 100 years. The spatial distribution of TDS in both the Modern and Historic periods largely reflect the geologic material of the sediments through which SJV groundwater was recharged, and the geochemical characteristics of recharge waters (Planert and Williams, 1995; Faunt, 2009). TDS is generally much higher in the WSJV because marine sediments of the Coast Ranges are more easily dissolved, and because irrigation driven water-table rises have resulted in the concentration of salts in the soils (Hess, 1910; Belitz and Heimes, 1990; Dubrovsky et al., 1991; Deverel et al., 1994; Fujii and Swain, 1995; Fram, 2017; Supp. 2).

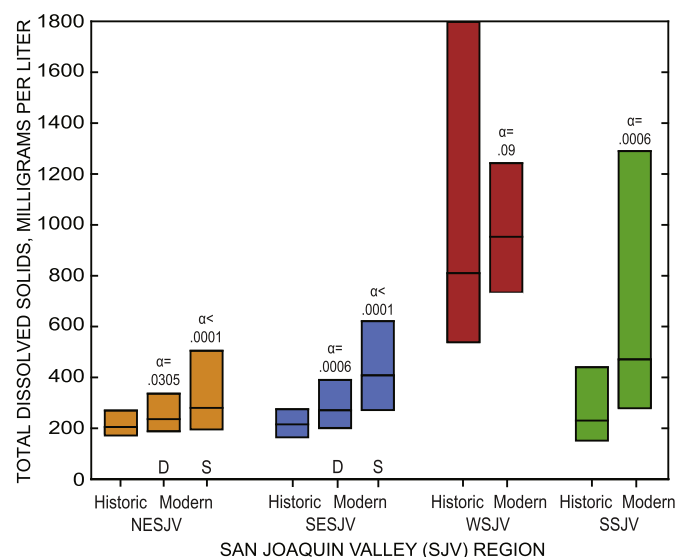


Fig. 3. Boxplots showing Total Dissolved Solids (TDS, mg/L) concentrations in groundwater during the Historic (1910) and Modern (1993–2015) periods in the San Joaquin Valley, California by region. TDS concentrations were calculated using spatially-weighted cell declustering methods. Median TDS represents the TDS concentration for which half of the areally-weighted groundwater resource in the region has lower TDS concentrations and half has higher TDS concentrations. The 75th percentile concentration represents the TDS concentration for which 75% of the groundwater resource in the region has lower TDS concentration and 25% has higher TDS concentrations.

The lowest TDS values tend to be in the NESJV and SESJV where arkosic sediments from Sierra Nevada granitic rocks are much more recalcitrant (Mendenhall et al., 1916; Planert and Williams, 1995; Faunt, 2009). The center of the basin is the major discharge area for regional groundwater flow, and old groundwater discharging in this area can be highly evolved and mineralized. In addition, evapoconcentration of shallow groundwater can be an added source of salinity.

Data from the Historic period largely represent natural conditions in the Valley, and median TDS concentrations in the NESJV and SESJV were just over 200 mg/L around the turn of the century. TDS had the largest increase in the shallow portions of the aquifer in both regions (75 mg/L in NESJV-S, 193 mg/L in SESJV-S). In addition, the areal proportion of the groundwater resource classified as moderate or high (TDS > 500 mg/L) increased in NESJV-S from 11% to 26% and from 12% to 37% in the SESJV-S (Fig. 1).

The largest increase in TDS in the SJV over the past 100 years occurred in the SSJV, which increased from a median of 230 mg/L in the Historic period to 471 mg/L in the Modern period (Fig. 3, Table 1). The large interquartile range in TDS concentrations in the modern samples likely reflect the variety of sediments in the SSJV, which can be derived from the Coast Ranges on the west and the Sierra Nevada on the east, or the Tehachapi mountains in the southern end of the basin. Over the last 100 years, the areal proportion of the groundwater resource classified as moderate or high in the SSJV increased from 16% to 45% and the median TDS concentration of groundwater in the Modern period was 471 mg/L in this region.

The WSJV had the highest TDS concentration in the Historic period (810 mg/L) and the Modern period (953 mg/L) (Fig. 3), which reflects the influence of marine sediments and hydrology of the region. In the Modern period, 90% of the groundwater resource had moderate or high concentrations of TDS, which was about 7% >100 years ago (Fig. 1). TDS in samples from the Modern WSJV were not statistically different from 100 years ago (Kruskal-Wallis rank sum test p -value = 0.099). However, the p -value is low and this result may be due to a lack of spatial continuity in the distribution of samples (Fig. 1).

4.2. TDS relations to depth, age, and land use

In the NESJV and SESJV, TDS concentrations in the Modern period decrease with depth below the water table (DBWT) (NESJV: Spearman's ρ = -0.27; p -value < 0.001; SESJV: Spearman's ρ = -0.33; p -value < 0.001), and shallow groundwater in the NESJV and SESJV has much higher TDS than deeper groundwater (Supp. 3). In contrast, Historic concentrations of TDS were not correlated with DBWT for wells in the NESJV and SESJV (NESJV: Spearman's ρ = 0.10; p -value = 0.264; SESJV: Spearman's ρ = -0.001; p -value = 0.989). These findings suggest that sources of TDS in Modern groundwater in the shallow zone may be derived from land surface activities. TDS in the Modern deep zones of the NESJV and SESJV were not significantly different from Historic groundwater data and could indicate that groundwater from the Historic period has moved to deeper depths in many parts of the aquifer (except in regional discharge areas). Williamson et al. (1989) found that rates of groundwater movement in downward direction has increased on average about 6 times the rate from pre-development conditions and was mainly caused by repeated application of agricultural recharge and withdrawal from public-supply and irrigation wells.

TDS concentrations in the NESJV and SESJV are higher in *ModernOrMixed* (post-1950s recharge present). Samples that were predominantly *PreModern* had median TDS concentration of 215 mg/L, which was significantly lower (Kruskal-Wallis p -value < 0.001) than the median TDS concentration of 335 mg/L for samples that contained predominantly *ModernOrMixed* groundwater (Fig. 4). The lower TDS concentrations found in *PreModern* groundwater likely reflect the TDS content of groundwater in the SJV under more natural conditions, prior to development of the groundwater system.

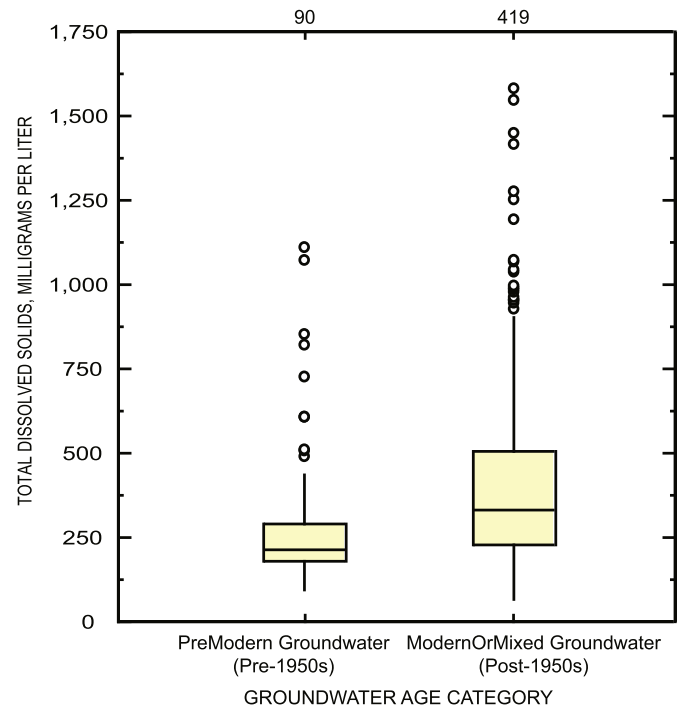


Fig. 4. Box plots showing TDS concentrations in samples collected during the Modern period (1993–2015) of groundwater recharged prior to the 1950's (*PreModern*) and groundwater recharged after the 1950's (*ModernOrMixed*) in the NESJV and SESJV based on tritium (^3H) activities.

Previous studies of the eastern SJV groundwater system have found that the groundwater age structure is discontinuous such that the shallow part of the system has an age structure consistent with high recharge rates governed by agricultural irrigation, and a deep system with an age structure consistent with historic natural low recharge rates (Jurgens et al., 2016). The boundary between the two systems varies at depth in the eastern SJV but wells with long-screens, like many public supply wells, can be screened in both systems and therefore capture varying amounts of pre- and post-1950s groundwater (Jurgens et al., 2016; Landon et al., 2010a). The TDS concentration in *PreModern* groundwater was higher than TDS concentration in samples collected during the Historic period, but both were lower than the TDS concentrations in the *ModernOrMixed* groundwater age category (Figs. 3 & 4).

The relations between DBWT and groundwater age with TDS concentrations indicate that higher TDS in *ModernOrMixed* groundwater have resulted from surface processes occurring since the 1950s that have altered the chemistry of more recently recharged groundwater. Changes in recharge chemistry can reflect changes in sources of water that recharge the groundwater resource or alterations of the chemical composition of recharge sources from land surface activities or from both processes.

TDS concentrations in NESJV and SESJV groundwater were statistically higher in wells surrounded by >70% agricultural land in comparison to wells surrounded primarily by land used for mixed or other purposes (Kruskal-Wallis rank-sum, p -value < 0.001) (Fig. 5). This correlation indicates that agricultural land-use practices have likely affected TDS values to some degree in the eastern SJV. Wells surrounded primarily by natural, urban, and mixed (no single land-use type > 70%) land use likely capture more groundwater unaffected by agricultural recharge and contain lower TDS concentrations than those surrounded predominantly by agricultural land use (Fig. 5). However, even water sampled from wells surrounded by land with <70% agricultural land use have higher TDS than all groundwater in the Historic period (p -value < 0.001), which likely indicates that many of these wells

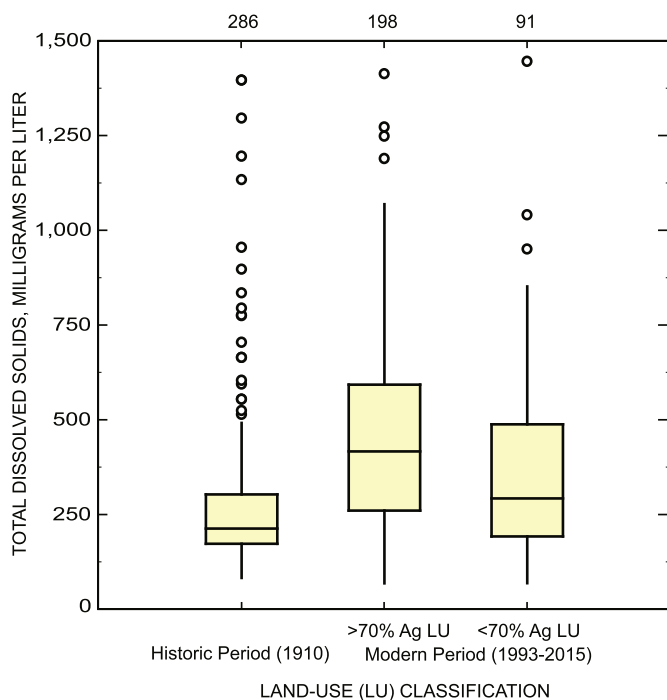


Fig. 5. Box plot of total dissolved solids concentrations in samples collected during the Historic period (1910) and samples collected during the Modern period (1993–2015) from shallow (<50 m below the water table) wells in the eastern San Joaquin Valley (NESJV-S and SESJV-S). Samples from the Modern period are separated into two groups by percentage of agricultural land use in a 500-m radius area around the well in 1992.

also capture some agricultural recharge. This finding is not surprising since agricultural irrigation return is the primary form of recharge to the modern groundwater system in the eastern SJV (Faunt, 2009) so it might be expected that wells in largely urban areas capture water that originally recharged beneath irrigated, agricultural land.

4.3. Changes in geochemical composition of groundwater

Inverse geochemical modeling results indicated that weathering of primary silicate minerals, was the largest cause of increases in TDS concentrations from Historic to Modern periods in the SESJV and NESJV (Fig. 6). Inverse geochemical modeling was not completed for samples in the WSJV or SSJV due to the limited quantity and spatial variability of samples in these regions. Silicate weathering contributed the majority of the total TDS increase in model results in the SESJV (median: 34% in SESJV-S, 55% in SESJV-D) and >100% of the TDS change in the NESJV (median: 121% in NESJV-S, 188% in NESJV-D) – some results were offset by processes that decreased TDS such as dilution from surface water sources. In the NESJV, the contribution of silicate weathering to TDS increases was larger than the combined contribution of surface applications of soil amendments and nitrogen based fertilizers. In the SESJV, increases to TDS due to silicate weathering were approximately double the increases from sulfur or nitrogen-based applications to the soil.

These findings suggest that the dissolution of silicate minerals has increased during development of the land for agricultural purposes. Irrigated recharge, which occurs primarily during the summer months, increases plant growth and microbial decomposition of plant matter in SJV soils leading to greater CO₂ partial pressures (P_{CO2}) and carbonic acidity in the soil. These conditions promote the dissolution of primary minerals and the formation of secondary minerals, primarily clays, while bicarbonate and dissolved ions – the by-products of geochemical weathering (Garrels and Mackenzie, 1967; Feth et al., 1964) – are leached from the soil.

Bicarbonate (HCO₃), formed from silicate weathering, increased by >60 and 85 mg/L in inverse models in the NESJV-S & D and SESJV-S, respectively (Fig. 7). Soil carbonates could be an added source of bicarbonate to the groundwater system although inverse modeling indicates that calcite precipitation may occur more frequently than dissolution.

Evaporation and dilution factors calculated from PHREEQC model results indicate that groundwater in the NESJV required contributions from a more dilute source of water in order to balance chloride concentrations (Fig. 6). Median chloride concentrations in the NESJV have decreased by >12 mg/L over the last 100 years (Fig. 7). This change is likely explained by the abundant use of dilute, low-TDS surface water for irrigation in the NESJV. This finding does not preclude evaporation of irrigation water, either surface water or groundwater, from occurring in the NESJV, but its effect is small in comparison to the other mass balance processes. Substantial use of surface water for irrigation, combined with export of solutes through discharged surface water to the delta has likely helped to mitigate some of the TDS increase in the NESJV.

In contrast to the NESJV, groundwater in the SESJV required evaporation to explain changes in TDS over the last 100 years (Fig. 6). Median chloride concentrations in the SESJV increased by >15 mg/L over the last 100 years in the SESJV-S, and >20 mg/L in the SESJV-D (Fig. 7). The southern SJV (referred to as the Tulare Basin in Faunt, 2009) utilizes >5 times more groundwater than the northern SJV (referred to as the San Joaquin Basin in Faunt, 2009) so evaporation or transpiration of groundwater used for irrigation is an important process affecting TDS of groundwater recharge in this region. Because the southern part of the SJV is a hydrologically closed basin, repeated pumpage and evaporation of groundwater for irrigation likely will continue to increase TDS concentrations in groundwater.

Dissolution of gypsum and/or sulfur contributed from 14% to 32% of the total increase to modeled TDS changes in the NESJV and SESJV (Fig. 6). In the eastern SJV gypsum is often added as a soil amendment to improve infiltration of irrigation water by exchanging sodium for calcium in clay minerals. Applications of elemental sulfur are also used as fungicide on vineyards to prevent mildew (CDPR, 2000; Fuller et al., 2014). Both processes lead to increased sulfate in recharge water that will contribute to TDS increases and may change the water-type where bicarbonate concentrations are low. PHREEQC models indicate that sulfate concentrations were required to increase about 30 mg/L on average in the NESJV-S, and by about 35 mg/L and 25 mg/L on average in the SESJV-S & D (Fig. 7). These increases likely indicate dissolution of soil amendments from agriculture applications and in part from evaporation/transpiration discussed above.

Nitrogen-based fertilizers – defined as ammonium nitrate [NH₄NO₃] – was another major source of TDS increases in PHREEQC models of SJV groundwater chemistry changes (Fig. 6). Nitrate fertilizer comprised from 17% to 24% of the total increase in modeled TDS changes, which is similar to the percentage of gypsum contributions (14% to 32%) but the combined contribution of agricultural sources of TDS – nitrogen fertilizers and gypsum – was less than silicate weathering (34% to 189%) in all areas of the eastern SJV.

Nitrate increases in groundwater have largely been associated with agricultural land-use practices in the SJV and other parts of the world (Nightingale, 1970; Strebel et al., 1989; Spalding and Exner, 1993; Vitousek et al., 1997; Bohlke, 2002; Thorburn et al., 2003; McMahon and Chapelle, 2008; Burrow et al., 2013; Dubrovsky et al., 2010). Groundwater samples in the SJV often contain nitrate concentrations in excess of the US EPA MCL (USEPA, 2006) of 10 mg/L, particularly in shallow groundwater as a result of the application of nitrogen-based agricultural fertilizers (ammonium nitrate, urea, manure, etc.) and in runoff from dairy operations (Harter et al., 2002; Burton and Belitz, 2008; Bennett et al., 2010). The coarse sediments of the eastern SJV can promote the rapid infiltration of nitrogen inputs to the groundwater system and nitrate tends to persist because the groundwater system is predominately oxic (McMahon and Chapelle, 2008; Jurgens et al., 2009). Nitrate concentrations in most of the SJV have steadily risen between 0.2 and

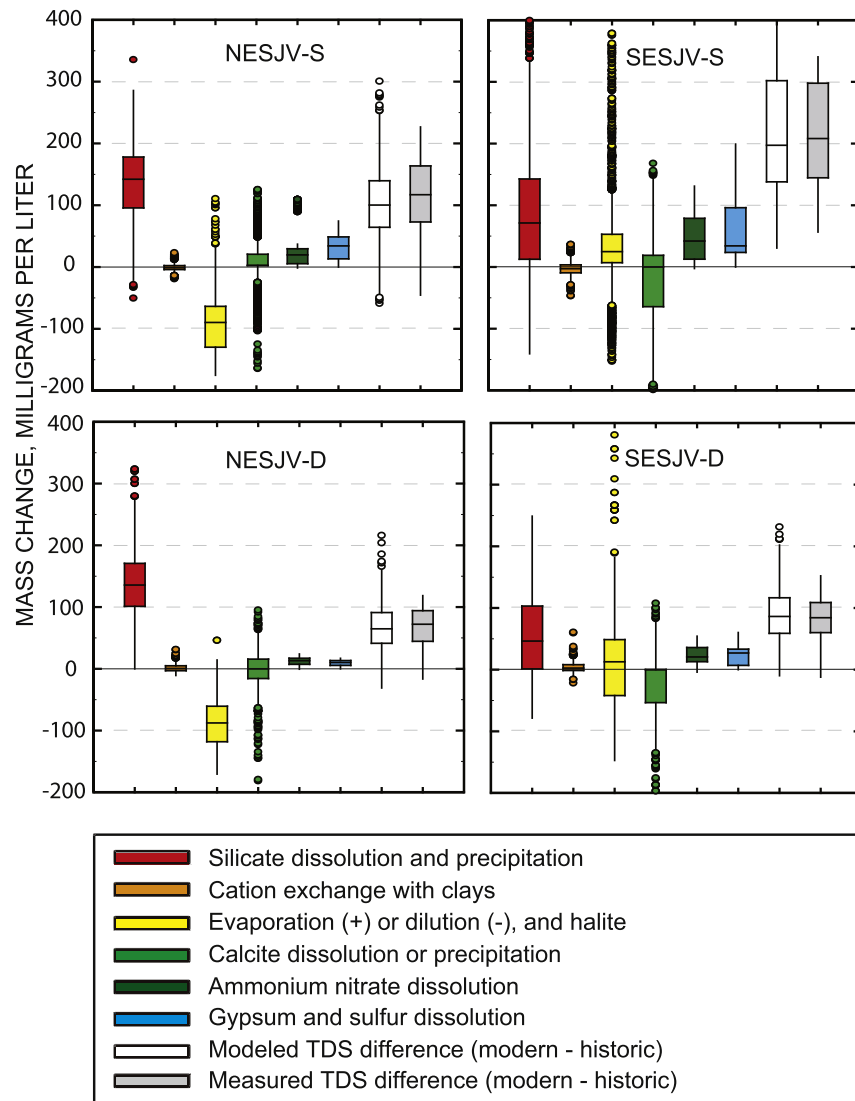


Fig. 6. Box plots describing modeled effects of geochemical phases and processes in groundwater as TDS Mass (mg/L) from the Historic period (1910, pH = 7.5) to the Modern period (1993–2015) in the eastern San Joaquin Valley, California. The eastern Valley was divided into Northeast Shallow and Deep (NESJV-S,D) and Southeast Shallow and Deep (SESJV-S,D) regions. Modeled and measured TDS changes for each region are also shown in white and grey box plots.

0.6 mg/L each decade since the 1950's, increasing from a median of <2 mg/L to >5 mg/L by the 1980's (Burow et al., 2013; Ransom et al., 2017).

Other sources of TDS that were not considered in the inverse geochemical models include applications of other agricultural amendments, such as phosphate fertilizers and organic fertilizers. Domagalski and Johnson (2011) found that applications of phosphate fertilizers in the NESJV exceeded the sorptive capacity of sediments and excess phosphate has been leached to the groundwater system. Phosphate was not measured 100 years ago and concentrations are typically <1 mg/L. Since the bulk of phosphate loading is likely bound to sediments, it is likely that phosphate fertilizers have not significantly contributed to the change in TDS.

5. Conclusions

Total Dissolved Solids (TDS) in groundwater has increased in many parts of the San Joaquin Valley (SJV) over the last 100 years (Figs. 1 & 3). Historic groundwater chemistry data collected during the early 1900s (Mendenhall et al., 1916) was compared to groundwater chemistry data collected from 1993 to 2015 by the USGS GAMA Program and various other USGS projects. Chemistry data from each dataset-time

period were aggregated using equal-area grids so that century scale chemistry changes would be spatially unbiased. The grid was composed of four regions of the SJV: Northeast SJV (NESJV), Southeast SJV (SESJV), Western SJV (WSJV), and Southern SJV (SSJV).

TDS in the Northeast and Southeast San Joaquin Valley (NESJV and SESJV) increased, particularly in the shallow part of the system, and TDS in those areas were primarily associated with agricultural land (Fig. 5). Correlations between TDS and depth below the water table and tracers of groundwater age indicate that pumping for municipal and irrigation supply has caused shallow, higher TDS groundwater to be driven downward, and has stratified the chemistry of the groundwater system. Continued irrigation and pumping will likely cause TDS to increase in deeper parts of the groundwater system. The SSJV had the largest median increase in TDS, though data from the modern period had a large interquartile range due to varied geology and could not be modeled due to lack of spatial variability and quantity of complete ion samples. In the WSJV, TDS was not shown to be statistically different from 100 years ago, but this finding may be due to a lack of spatially comparable data.

Inverse geochemical modeling indicated that dissolution of silicate minerals was the largest contributor to the observed increases in TDS over the last 100 years in the NESJV and SESJV (Figs. 6 & 7). Bicarbonate

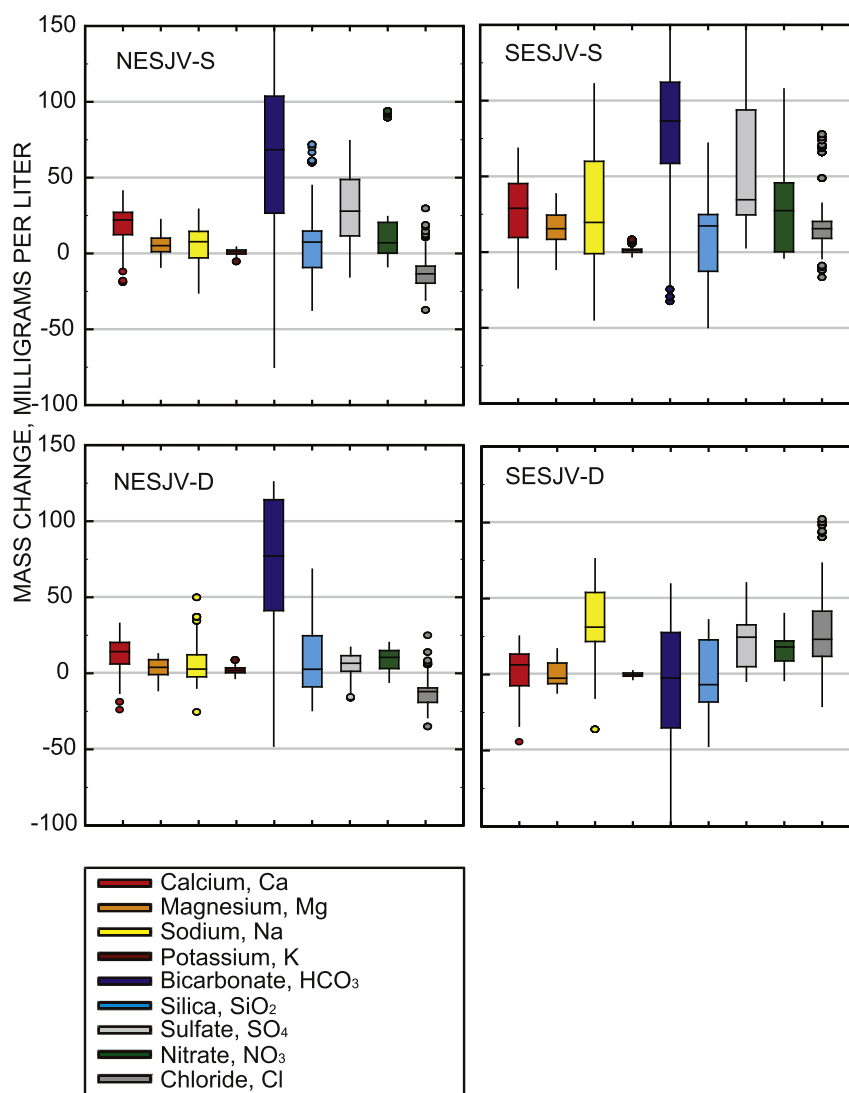


Fig. 7. Box plots of the modeled mass increase or decrease of major ions in groundwater (mg/L) from the Historic period (1910, pH = 7.5) to the Modern period (1993–2015) in the eastern San Joaquin Valley, California. The eastern Valley was divided into Northeast Shallow and Deep (NESJV-S,D) and Southeast Shallow and Deep (SESJV-S,D) regions.

had the largest change in concentrations and results primarily from silicate weathering. Jurgens et al. (2010) suggested bicarbonate increases in groundwater in the ESJV result from higher biological productivity during the summer growing season as irrigated water passes through soils. Increased acidity in water due to plant root respiration and decomposition of organic matter causes minerals to dissolve, allowing bicarbonate and other major ions to form in the residual water which is transported to the aquifer system as recharge.

Fertilizers and soil amendments have also contributed to TDS increases in the SJV and are often applied at the land surface to promote crop growth and infiltration of irrigation water. Individually, the contribution of these amendments was less than mineral dissolution but taken collectively, the contribution of agricultural chemicals had a large effect on TDS.

This study showed that TDS in groundwater in the SJV has been substantially increased as a result of wide-spread development of the groundwater resource, primarily for agricultural purposes. Agricultural irrigation now supplies the majority of recharge to the groundwater system of the SJV, and this recharge can contain a variety of major ions derived from fertilizers and soil amendments, salts stored in the unsaturated zone, or from evapotranspirative enrichment, or mineral weathering, all of which increase the salinity

content of water recharging the aquifer system. Although much of the focus of past work in the area has been on nitrate, results from this work illuminate other important processes and constituents that contribute to the salt content and TDS of groundwater recharge. Increases in bicarbonate concentrations were the largest contributor to TDS in the SJV over the past 100 years, and past research showed that these increases release uranium from aquifer solids (Jurgens et al., 2009; Burow et al., 2017). Consequently, these results have important implications for the long-term sustainability of groundwater as a resource for drinking and irrigation water in the SJV and other arid and semi-arid areas around the world with intensive agricultural development.

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