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RESEARCH ARTICLE

Assessing potential effects of oil and gas development activities on groundwater quality near and overlying the Elk Hills and North Coles Levee Oil Fields, San Joaquin Valley, California

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Abstract

Groundwater resources are utilized near areas of intensive oil and gas development in California's San Joaquin Valley. In this study, we examined chemical and isotopic data to assess if thermogenic gas or saline water from oil producing formations have mixed with groundwater near the Elk Hills and North Coles Levee Oil Fields in the southwestern San Joaquin Valley. Major ion concentrations and stable isotope compositions were largely consistent with natural processes, including mixing of different recharge sources and water-rock interactions. Trace methane concentrations likely resulted from microbial rather than thermogenic sources. Trace concentrations of benzene and other dissolved hydrocarbons in three wells had uncertain sources that could occur naturally or be derived from oil and gas development activities or other anthropogenic sources. In the mid-1990s, two industrial supply wells had increasing Cl and B concentrations likely explained by mixing with up to 15 percent saline oil-field water injected for disposal in nearby injection disposal wells. Shallow groundwater along the western margin of Buena Vista Lake Bed had elevated Cl, B, and SO_4 concentrations that could be explained by accumulation of salts during natural wetting and drying cycles or, alternatively, legacy surface disposal of saline oil-field water in upgradient ephemeral drainages. This study showed that groundwater had relatively little evidence of thermogenic gas or saline water from oil and gas sources in most parts of the study area. However, the evidence for groundwater mixing with injected disposal water, and possibly legacy surface disposal water, demonstrates produced water management practices as a potential risk factor for groundwater-quality degradation near oil and gas fields. Additional studies in the San Joaquin Valley and elsewhere could improve understanding of such risks

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by assessing the locations, volumes, and types of produced water disposal practices used during the life of oil fields.

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1. Introduction

Management of the large volumes of water coproduced during oil and gas production involves disposal and reuse practices. Previous estimates for the volume of produced water generated annually have ranged between 15 to 21 billion barrels for the United States alone [1, 2]. The chemical composition of produced water varies and is typically saline, containing organic and inorganic compounds from the hydrocarbon reservoir and any fluids injected for disposal or to enhance oil and gas recovery [3–6]. During the early years of oil and gas development, it was common practice to dispose of produced water on the land surface in, for example, natural drainage channels and constructed impoundments [7–9].

Currently, produced water generated in the United States is largely managed by underground injection for either disposal or reuse to enhance recovery [1, 2]. Surface disposal is still practiced in some areas [10, 11]. Other management options being explored include reuse in the industry for hydraulic fracturing [12] and reuse for agricultural purposes when produced water is of sufficient quality to allow economical treatment [6, 13, 14]. In addition to oil and gas well leakage, current and historical produced water disposal practices can potentially contribute to water-quality degradation, motivating recent research investigating the effects of oil and gas activities on water quality [15–20].

California's San Joaquin Valley is one of the top oil and gas producing regions in the United States [21]. Oil and gas production has occurred in the San Joaquin Valley since the late 1800s [22], and the region has been intensively developed with over 100 oil fields and 100,000 oil and gas wells [23]. Concerns about the proximity of oil and gas activities to groundwater resources, which are or could be used for irrigation, domestic, and municipal water supply, have led to recent studies examining aspects of groundwater quality near oil fields in the San Joaquin Valley [4, 10, 11, 24–37]. Some of these studies have focused on characterizing the geochemistry of oil-field water and gases to trace their origin and establish end member compositions for evaluating potential mixing with groundwater [4, 11, 25]. Other studies have used airborne electromagnetic surveys, borehole geophysical log analysis, and total dissolved solids (TDS) measurements to establish locations of fresh and brackish groundwater and understand processes controlling groundwater salinity near oil fields in the San Joaquin Valley [26, 29, 31, 34, 35].

Recent studies also have focused on determining whether groundwater quality has been degraded as a result of disposal practices introducing saline produced water into shallow aquifers [10, 27, 28], including at the Elk Hills and North Coles Levee Oil Fields in the southwestern San Joaquin Valley [36]. Gillespie et al. [36] used borehole geophysical log analysis in combination with historical produced water and groundwater TDS data to describe the distribution of groundwater salinity and identify salinity anomalies associated with saline oil-field water injected for disposal into the Tulare Formation near the southern boundary of Elk Hills Oil Field. In this paper, we expand on previous work by characterizing the geochemistry of groundwater as a means of assessing the potential effects of oil and gas development activities on groundwater quality near and overlying the Elk Hills and North Coles Levee Oil Fields.

The California State Water Resources Control Board (State Water Board) initiated an Oil and Gas Regional Monitoring Program (RMP) as required by Senate Bill 4 (SB4 of 2013) statutes to protect all waters designated for any beneficial use in areas of oil and gas production

[38]. The RMP classified Elk Hills Oil Field as high priority for monitoring based on high densities of production and injection wells and large volumes of water injected for enhanced oil recovery and disposal (Fig 1) [23]. The neighboring North Coles Levee Oil Field was classified as high priority for monitoring based on a high injection well density and large volume of water injected for enhanced oil recovery [23]. This study focuses on RMP objectives to: (1) assess evidence for the presence or absence of oil-field fluids (oil-field water and thermogenic gas) in groundwater; (2) identify pathways or processes responsible for transporting oil-field fluids to groundwater, if present; and (3) assess how oil and gas production activities have potentially affected groundwater quality relative to other processes [38, 39].

To address the above objectives, we sampled 32 water wells near and overlying Elk Hills and North Coles Levee Oil Fields and analyzed the samples for a broad suite of constituents, including chemical and isotopic tracers, hydrocarbon gases, volatile organic compounds (VOCs), groundwater-age tracers, and noble gases. In addition to the new data collected, we included historical water-quality data (see S1 Table for citations) from water wells, surface water recharge sources, and oil-field water to help evaluate potential mixing between groundwater and oil-field fluids and better understand processes controlling baseline regional groundwater quality in the study area. We also assessed potential pathways between oil, gas, and groundwater and the relative risks of groundwater-quality degradation from oil and gas activities based on the hydrologic setting, production and disposal histories of the oil fields, and oil and gas well integrity, among other factors.

2. Study area description

The study area includes the Elk Hills and North Coles Levee Oil Fields and the surrounding approximately 5 km in the southwestern San Joaquin Valley in Kern County, California (Fig 1). The study area is bounded by the Temblor Range (one of the Coast Ranges) to the west and extends eastward into the relatively flat-lying floor of the San Joaquin Valley. The Elk Hills lie in the foothills of the Temblor Range and reach a maximum elevation of about 467 m. Numerous ephemeral streams have deposited eroded sand and soils along the base of the Elk Hills [44, 45] where the topography merges eastward into the San Joaquin Valley at an elevation of about 91 m within North Coles Levee Oil Field, and southward into Buena Vista Valley.

The primary aquifer in the study area is composed of fluvial sands and gravels and lacustrine clays of the Pleistocene Tulare Formation and overlying alluvium (Fig A in S1 Text) [46, 47]. The main source of groundwater recharge was historically infiltration of Kern River water along a gently sloping alluvial fan composed of coarse-grained Kern River deposits extending through the eastern study area to the edge of Elk Hills [47]. The Kern River originates from runoff of high-altitude snowmelt and rainfall in the Sierra Nevada and has been controlled to one main channel along the alluvial fan since 1867–68, with river flows diverted to canals for agricultural uses and excess water discharged to Buena Vista Lake during high river flows [45, 46]. Buena Vista Lake has no surface outlet except during floods [48]. During floods, water from Buena Vista Lake historically overflowed northward into Buena Vista Slough and moved toward Tulare Lake farther north in the San Joaquin Valley [46, 49]. Buena Vista Lake was drained following damming and diversion of the Kern River, and the Buena Vista Lake Bed has been cultivated since 1954 [45], with periodic use for water storage during times of flooding [50], including in spring 2017 just prior to onset of sample collection for this study.

Other sources of recharge include direct rainfall, irrigation return flows, infiltration from unlined canals, managed aquifer recharge, and infiltration from ephemeral streams originating

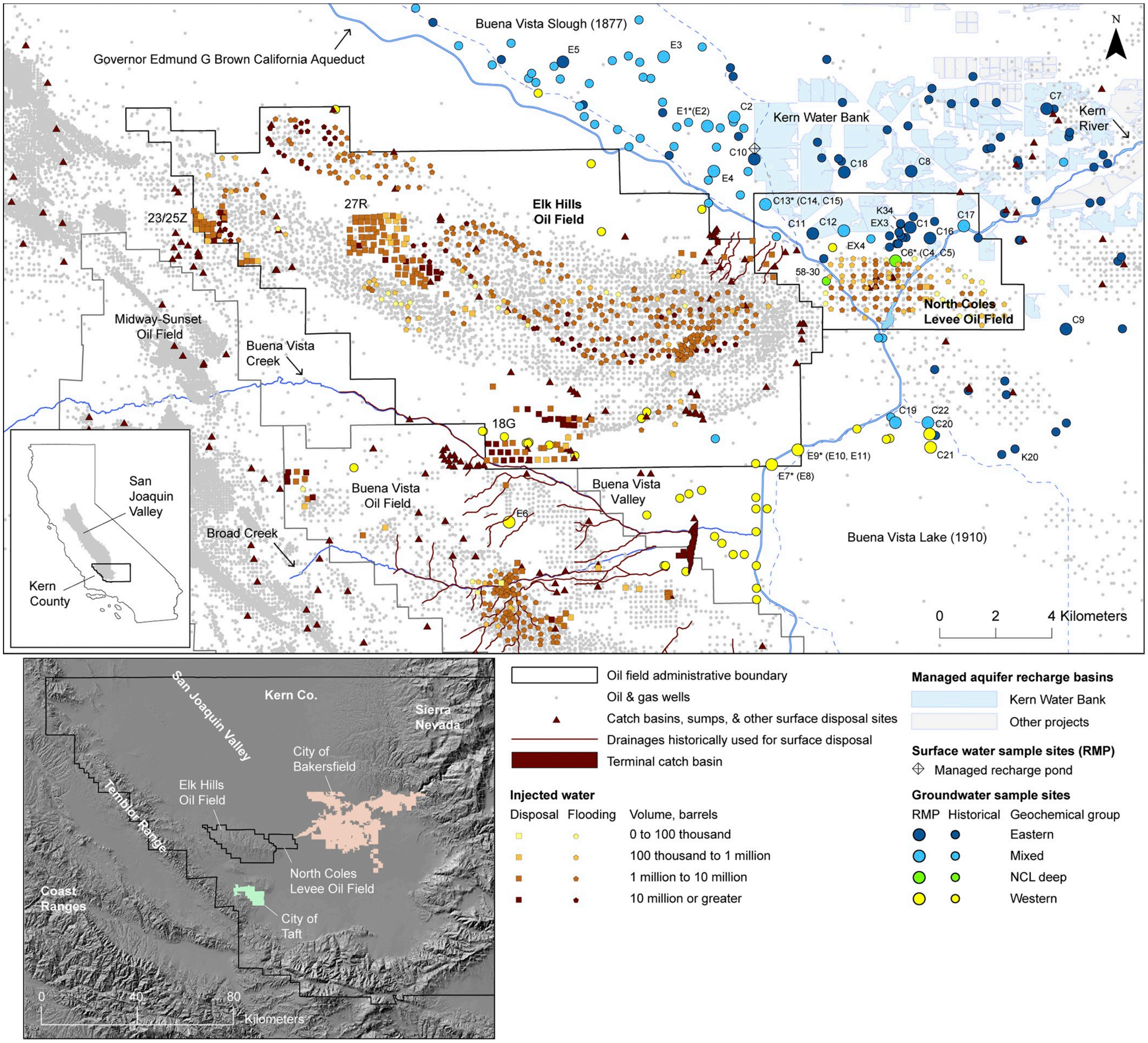

Fig 1. Study area map. Locations of study area including Elk Hills and North Coles Levee Oil Fields, Regional Monitoring Program (RMP) groundwater sites sampled for this study, historical groundwater sites, surface disposal sites [40–43], oil and gas wells, water volumes injected for disposal (1977–2017), water volumes injected for flooding (1977–2017), and selected geographic features. Sample site labels containing asterisks indicate multiple monitoring well sites with sites inside parentheses obscured from map view. Examination of potential risks to groundwater-quality degradation indicates the most important risk factors are surface disposal of produced water and water injected for disposal. Shaded relief base from https://basemap.nationalmap.gov/arcgis/rest/services/USGSShadedReliefOnly/MapServer.

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in the Coast Ranges [47, 51, 52]. The climate is semiarid, with 1991–2020 mean annual temperature of 18.7˚C and mean annual rainfall of 152 mm recorded at the nearby city of Taft, California [53]. Predominant land uses include oil and gas production, open range, irrigated agriculture, and managed aquifer recharge. In 1995, the Kern Water Bank began recharging water sourced from the State Water Project [54], Kern River, and Friant-Kern Canal using managed aquifer recharge basins constructed on coarse-grained deposits of the Kern River alluvial fan in the northeastern part of the study area [55]. The western part of the study area contains smaller alluvial fans deposited by flashy ephemeral streams draining the Coast Ranges as well as lacustrine deposits on Buena Vista Lake Bed [46, 49]. The Coast Ranges bordering the San Joaquin Valley are predominantly composed of Cretaceous to Pliocene marine sedimentary rocks. Sediments deposited on alluvial fans derived from the Coast Ranges typically contain poorly sorted silt, fine sand, and clay with low permeability compared to sediments of the Kern River alluvial fan [49].

Groundwater historically flowed westward following the path of the Kern River until branching to the northwest and southwest near Elk Hills [49], with groundwater flow paths also affected by mounding and pumping depressions since the onset of managed aquifer recharge and recovery operations in 1995 [55]. Water table elevations were higher inside the Elk Hills Oil Field compared to elevations in Buena Vista Valley and the San Joaquin Valley from 1990–2021 (Fig 2 and Fig B in S1 Text; S1 Animation in S1 File and S2 Animation in S2 File). The northern parts of the North Coles Levee Oil Field and adjacent areas to the north and east contain managed aquifer recharge basins (Fig 1). The influences of managed aquifer recharge and recovery on water table elevations are apparent in these areas; for example, aquifer recharge is indicated by higher water table elevations and groundwater mounding in February 2006, and lower water table elevations and pumping depressions in February 2017 indicated recovery operations (Fig 2).

The Elk Hills and North Coles Levee Oil Fields were discovered in 1911 and 1938, respectively, and have long histories of oil and gas production [22]. The two fields are located within a fold-thrust belt that has created numerous anticlinal traps for oil and led to development of multiple oil fields along the west side of the southern San Joaquin Valley [36, 58]. Oil and gas production at Elk Hills Oil Field can be divided into three main zones (Fig A in S1 Text). The Stevens Oil Zone contains three major anticlines producing oil and gas from the Monterey Formation at depths of 1,524–3,048 m. The Shallow Oil Zone contains a single anticline producing oil and gas from the San Joaquin and Etchegoin Formations at depths of 610–1,220 m. The Dry Gas Zone produces gas from sands of the San Joaquin Formation at depths of 305–610 m [45, 59]. The North Coles Levee Oil Field produces oil and gas mostly from the Monterey Formation at depths of 2,438–2,941 m [22].

More than 1.4 billion barrels of oil have been produced from Elk Hills Oil Field since discovery in 1911, with the majority of oil production occurring since the mid-1970s [43, 60]. This time span of major production differs from other west side San Joaquin Valley oil fields (e.g., Belridge, Buena Vista, Lost Hills, and Midway-Sunset Oil Fields), which had large production in the first half of the 1900s [43, 60]. Elk Hills Oil Field consistently ranks within the top 10 largest producing oil fields in California, ranking 8th in oil production and 1st in associated gas production by a substantial margin in 2019; the volume of associated gas produced from Elk Hills Oil Field was more than half the total volume produced from all California Oil Fields in 2019 [61]. Oil production at North Coles Levee Oil Field peaked in the 1940s–1950s, and more than 170 million barrels of oil have been produced since discovery in 1938 [43, 60].

3. Methods

3.1 Risk analysis

The potential risks of oil-field activities on groundwater-quality degradation can be influenced by oil-field factors such as well density, production and disposal practices, and the history of such practices during the life of the field, and by hydrogeologic factors such as groundwater flow directions, locations of used groundwater, and depths of used groundwater relative to oil and gas production depths. To assess oil-field factors, we examined: annual and cumulative

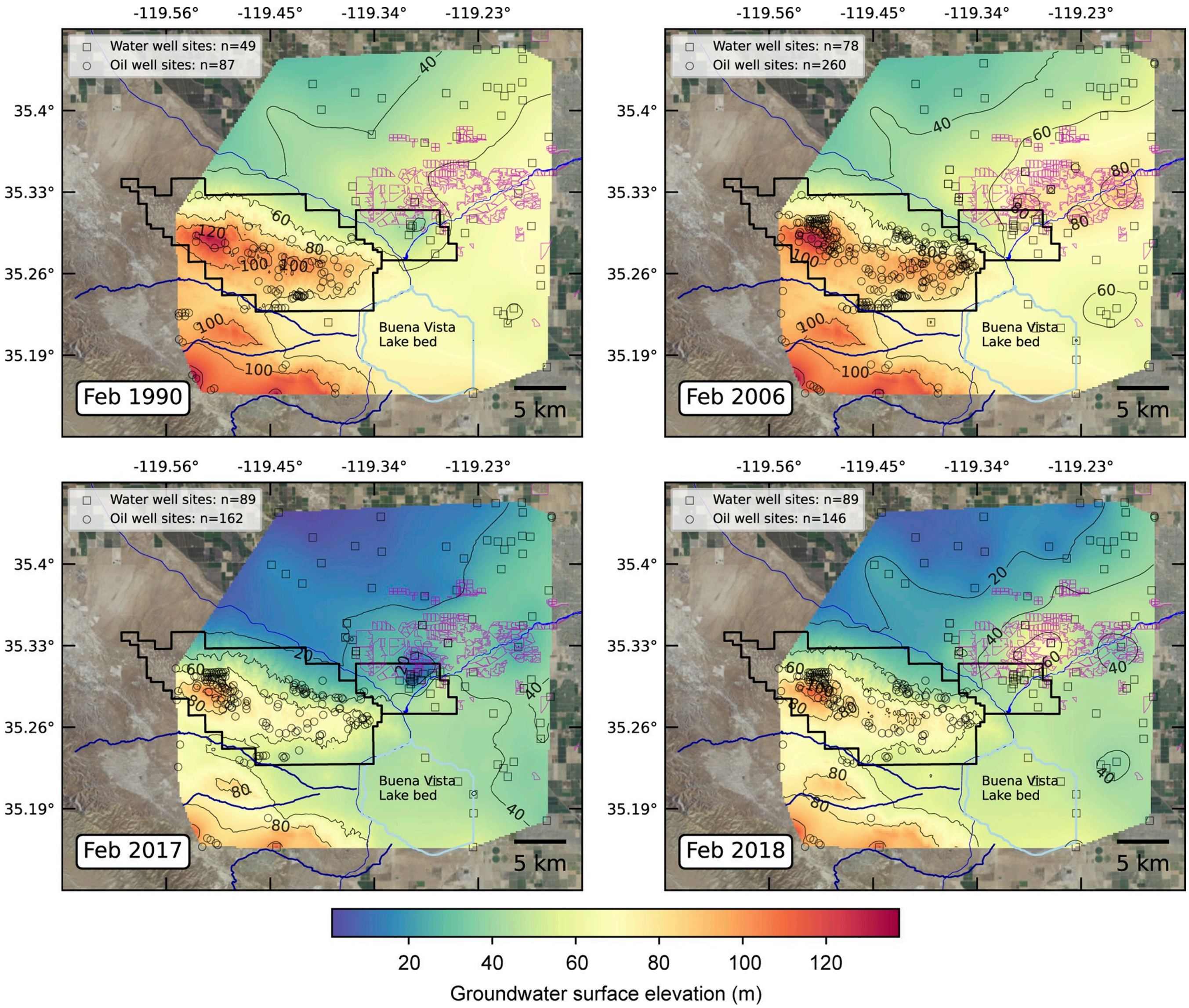

Fig 2. Maps showing water table elevations in February 1990, 2006, 2017, and 2018. These years were chosen to represent water table elevations in 1990 prior to Kern Water Bank managed aquifer recharge activities, in 2006 when water table elevations were high, in 2017 when water table elevations were low, and during the period of RMP sampling in 2017–2018. The maps were created using a combination of (1) water table elevations interpreted from borehole geophysical logs collected at oil and gas well drill sites and (2) groundwater level measurements in water wells. The map shows higher water table elevations on the crest of the Elk Hills anticline and lower elevations in adjacent valleys. Overall, water levels decrease through time with additional variations from managed aquifer recharge activities. Water table maps were generated following previous methods [36, 56], with data available from Stephens et al. [57]. See S1 Animation in S1 File for biannual changes in water table elevations during 1990–2021 and Fig B in S1 Text for uncertainty associated with water table elevations. Imagery base from https://basemap.nationalmap.gov/arcgis/rest/services/USGSImageryOnly/MapServer/.

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volumes of oil-field production and injection from 1920–2017; location, depths, and volumes of production and injection by well from 1977–2017; locations and history of surface disposal; oil and gas well cementing, that is, the depth intervals having cement placed in the annulus around the casing during well construction; and oil and gas well integrity. To assess hydrogeologic factors, we analyzed: groundwater flow directions; location, depths, and zones of used groundwater; annual and cumulative volumes of managed aquifer recharge and recovery; and vertical pressure gradients between groundwater and oil and gas production zones. The occurrence of natural oil and gas shows at depths shallower than the main oil and gas production zones was assessed using mud logs. Additional details on the risk assessment analyses completed for this study are available in S2 Table.

3.2 Sample collection, analysis, and historical data compilation

We collected water samples during July 2017 to March 2018. Groundwater samples were collected from wells within approximately 5 km of Elk Hills and North Coles Levee Oil Fields based on the following criteria: (1) areal and vertical position relative to current and historical oil and gas development activities, (2) location along regional groundwater flow paths, including locations both down-gradient and up-gradient of oil and gas development activities, (3) availability of historical water-quality data, and (4) access to sampling sites. We sampled 26 monitoring, 4 irrigation, and 2 public supply wells that met at least part of the selection criteria (S3 Table). The wells were identified by searching groundwater well databases and contacting local water purveyors, private well owners, and agencies monitoring groundwater. Surface-water samples from the Governor Edmund G Brown California Aqueduct and a managed aquifer recharge pond also were collected to help characterize the composition of managed aquifer recharge sources. The RMP data set also includes data for samples collected from three wells sampled for RMP exploratory sampling in October and November of 2014 [62].

Sample collection procedures are described by Dillon et al. [62] and follow protocols in Koterba et al. [63] and the U.S. Geological Survey (USGS) National Field Manual [64]. Generally, samples were collected after purging at least three casing-volumes of water and after field measurements of dissolved oxygen, temperature, pH, and specific conductance stabilized. Production wells were sampled using existing turbine pumps, and monitoring wells were sampled using either submersible pumps or, when available, dedicated submersible pumps already installed in the well (S3 Table). Samples were analyzed for a broad suite of constituents (S4 Table), including major and minor ions, nutrients, and trace elements; stable isotopes of water (δ^2H and $\delta^{18}O$) and dissolved inorganic carbon ($\delta^{13}C$–DIC); groundwater-age tracers (^3H and ^{14}C–DIC); noble gases (He, Ne, Ar, Kr, Xe); hydrocarbon gases (methane through pentane) and hydrogen and carbon isotopic composition of methane (δ^2H–CH_4 and $\delta^{13}C$–CH_4); and volatile organic compounds (VOCs). Quality control samples, including blanks, replicates, and spikes, were collected to confirm that water-quality data adequately represent environmental conditions. The results of quality control analyses and laboratory analyses, including measured constituents not discussed in this report are available from Warden et al. [65].

Water-quality data were compiled from various publicly available sources to supplement new RMP data and help evaluate processes controlling regional groundwater quality, sources of groundwater recharge, and potential mixing between groundwater and oil-field fluids. Water-quality data were compiled for 251 oil-field sites, mostly for produced water samples collected from oil and gas wells completed in the San Joaquin, Etchegoin, and Monterey Formations but also including four water disposal wells injecting into the Tulare Formation and two surface water disposal sites (Fig C in S1 Text). The available constituents for oil-field waters generally included major ions and some minor ions and trace elements. Surface water data representing potential sources of groundwater recharge were compiled for the Kern River, Buena Vista Lake, Governor Edmund G Brown California Aqueduct (State Water Project water), and sources of State Water Project water; available constituents generally included major ions, and stable isotopes of water for the Kern River and State Water Project source waters. The compiled data set included groundwater data from an additional 187 sites, with sites generally having major and minor ions and some trace element data available and a small number of sites (n) having stable isotopes of water (n = 3), age tracers (n = 2), methane (n = 4), and VOC (n = 4) data available. Depths of water wells, including newly sampled sites and historical sites, ranged from 2.9 to 607 m (median 131 m) below land surface. Additional details about the compiled water-quality data set (hereinafter referred to as historical data), including information on how the quality of historical data was assessed and data sources, are available in the Supporting information (Appendix A in S1 Text; S1 Table).

3.3 Statistical analyses

Hierarchical cluster analysis (HCA) was used to identify groups of groundwater samples that have similar geochemistry based on pH, calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulfate (SO_4), and bicarbonate (HCO_3). The HCA used Ward's clustering method with Euclidean distances on data that were first log-transformed and then standardized using z-scores [66, 67]. Differences in concentrations between geochemical groups were assessed using nonparametric statistics—Kruskal–Wallis rank sum tests were applied to determine if concentrations in a group or groups differ from others and Dunn's multiple pairwise comparison tests with the Benjamini–Hochberg false discovery rate correction were applied to determine which groups differ from others. Concentrations less than reporting levels were set to 0 for Kruskal-Wallis and Dunn tests. Time trends in water-quality data were assessed using the nonparametric Mann-Kendall test with the Theil-Sen estimator to determine the magnitude and direction of trends. Statistical analyses were carried out in R version 4.2.1 [68] using base functions and the 'factoextra,' 'ggstatsplot,' and 'mblm' packages [69–71]. We used an alpha (α) level of 0.05 in statistical tests.

4. Results and discussion

4.1 Assessing potential risks to groundwater quality based on oil-field activities

The potential risks to groundwater-quality degradation vary according to the hydrologic setting, proximity and intensity of oil-field development, and different methods used to manage produced water during the life of the oil fields. More than 3.3 billion barrels of water have been produced with oil and gas at Elk Hills Oil Field, with another 130 million barrels of water produced at North Coles Levee Oil Field (Fig D in S1 Text) [43, 60]. The TDS of the produced water varies by production formation but is typically saline with a median value of about 32,000 mg/L [22, 72, 73] that is similar to the modern seawater value of about 35,000 mg/L.

At the Elk Hills Oil Field, groundwater is not commonly used for supply purposes as shown by the relatively small number of wells inside the field compared to the larger number of wells lateral to the field in adjacent lower elevation valleys (Fig 1). Previous work shows the Tulare Formation is less than (<) 200 m thick and mostly unsaturated in central parts of the Elk Hills Oil Field, with groundwater in deeper formations having greater than (>)10,000 mg/L TDS [36]. However, the thickness of the Tulare Formation increases along the flanks of the Elk Hills structure. The Tulare Formation is about 700 m thick and contains a 500 m saturated thickness of < 10,000 mg/L TDS groundwater along parts of the oil field's administrative boundary [36]. Groundwater flow directions relative to the central parts of Elk Hills Oil Field are generally to the south and southeast toward the Buena Vista Valley and to the east and northeast toward the San Joaquin Valley (Fig 2) [36, 56, 57]. For the Elk Hills Oil Field, the most likely pathways for transporting oil-field fluids to groundwater include: (1) infiltration of produced water disposed of on the land surface and mixing of the infiltrated disposal water with groundwater underlying lower elevation valleys adjacent to the field, and (2) lateral migration of large volumes of water injected for disposal in the Tulare Formation.

Surface disposal of saline produced water was common practice in the San Joaquin Valley during the early years of oil-field development [7, 8]. Beginning in the 1950s, a portion of the produced water was injected for water flooding operations at Elk Hills and North Coles Levee Oil Fields (Fig E in S1 Text) [43, 60]. No other uses of produced water are known prior to the onset of water flooding operations for enhanced oil recovery in the 1950s. We define the legacy surface disposal volume as the estimated volume of produced water discharged to land prior to the onset of water flooding operations in 1956, equal to the volume of water produced at each oil field from 1920 (the year records are first available) through 1955. The legacy surface volumes totaled 155 million and 3 million barrels at Elk Hills and North Coles Levee Oil Fields, respectively [43]. Although surface disposal practices continued after 1955, separating the different uses of produced water requires a more detailed accounting of water sources after 1955 because enhanced oil recovery operations sometimes used external sources of water such as groundwater or produced water from other oil fields in addition to reclaimed produced water. Therefore, the legacy surface disposal volumes are likely less than the volume of produced water discharged to land for the full period of operations.

More than 170 catch basins, ponds, sumps, spills, and seeps representing potential surface sources of oil-field fluids are present within approximately 5 km of Elk Hills and North Coles Levee Oil Fields (Fig 1). These include sites in the neighboring Buena Vista and Midway-Sunset Oil Fields. The relative risk of surface disposal activities on groundwater-quality degradation is higher near Elk Hills Oil Field, which has more sites and a much larger legacy surface disposal volume than North Coles Levee Oil Field (155 million barrels compared to 3 million barrels; Fig E in S1 Text). Dry stream beds in northeastern parts of Elk Hills Oil Field have been reported to contain mixtures of oil and sand—known as brea deposits—where oil-field waters were historically routed down ephemeral drainage channels (Fig 1) [74]. The relative risk of surface disposal activities on water-quality degradation is likely highest in Buena Vista Valley, where produced water discharged into natural drainages as part of legacy disposal practices, primarily in the Buena Vista and Midway-Sunset Oil Fields, flowed downslope toward a terminal catch basin on Buena Vista Creek, about 2,800 meters upgradient of the Buena Vista Lake Bed (Fig 1) [75, 76]. The legacy surface disposal volume for Buena Vista and Midway-Sunset Oil Fields totaled about 935 million barrels [43] with a portion of the produced water disposed of into Broad Creek (and some of its tributaries), which flows into Buena Vista Valley.

The practice of injecting produced water for disposal into non-oil producing zones began at the Elk Hills Oil Field in 1980 and at the Coles Levee Oil Fields in 1963 [36]. The water disposal wells are spatially concentrated, with the 18G area at Elk Hills Oil Field having the largest disposal volume of over 762 million barrels injected during 1977–2017 [36, 60]. The 18G area is on the south flank of the oil field (Fig 1). Disposal water is injected into the upper Tulare Formation with disposal well depths as shallow as 212 m below land surface (median well depth 427 m) [60]. The disposal water migrated at least 1,200 m southward toward the Buena Vista Valley from 1980 to 2002 as recorded by well log resistivity anomalies indicating the presence of saline water (Fig C in S1 Text) [36]. The existing upper Tulare Formation disposal operations are being phased out at the Elk Hills Oil Field [77]. Buena Vista Valley also contains wells used to inject disposal water produced at Buena Vista Oil Field, with three disposal wells near the terminal catch basin on Buena Vista Creek injecting about 39 million barrels of water during 1977–2017 [60]. The other two major disposal injection areas in the Elk Hills Oil Field, the 23/25Z and 27R areas, are likely too far away and geologically isolated to affect groundwater used in the San Joaquin Valley [36].

At North Coles Levee Oil Field, groundwater wells are in closer lateral proximity to areas of oil and gas development and groundwater used for irrigation and public supply overlies hydrocarbon producing formations (Fig 1). In this setting, potential pathways between oil, gas, and groundwater include: (1) natural migration of oil-field fluids from underlying hydrocarbon-bearing formations, (2) migration of oil-field fluids along preferential pathways, including poorly cemented well casings and dry holes (i.e., uncompleted wells), (3) leakage of oil-field fluids through damaged well casings, and (4) spills and surface disposal of produced water. The Supporting information includes assessments (Appendix B in S1 Text) of oil and gas well integrity, oil and gas well cementing, and vertical migration potential completed as part of risk assessment analyses for North Coles Levee Oil Field.

Several managed aquifer recharge and recovery projects occur in the northern parts of North Coles Levee Oil Field and adjacent areas to the north and east (Fig 1). Kern Water Bank —the recharge project closest in proximity to Elk Hills and North Coles Levee Oil Fields—has recharged more than 16 billion barrels of water from freshwater sources since beginning recharge operations in 1995 (Figs D and E in S1 Text). The volume of fresh water recharged is about 3.5 times and 55 times the total volumes of oil and water produced from Elk Hills and North Coles Levee Oil Fields, respectively (Fig D in S1 Text). About 12 billion barrels of groundwater have been recovered from water well pumping at Kern Water Bank (Fig D in S1 Text). The substantial volumes of water recharged and recovered at the Kern Water Bank indicate that oil-field fluids, if present in shallower groundwater containing managed recharge water, could be diluted or pumped from the aquifer, or both. This process might lower the potential risk from any pathways allowing oil-field fluids to enter shallower groundwater in areas affected by managed aquifer recharge and recovery.

4.2 Characterization of major ion chemistry and geochemical groups

Understanding general trends in groundwater quality within the study area helps identify end-member compositions and provides context for samples potentially affected by mixing with oil-field fluids. The hierarchical cluster analysis identified four distinct geochemical groups referred to in this study as the Eastern, Mixed, NCL deep, and Western Groups. The geochemical groups are spatially coherent across the study area and coincide with various geographic and hydrologic features (Fig 1 and S5 Table).

Eastern-Group samples are generally characterized as low TDS (median 193 mg/L) Na–HCO_3 or Ca–HCO_3 fresh waters located within 10 km of the Kern River on the Kern River alluvial fan (Figs 3 and 4). The Eastern Group composition is typical of recharge sourced from the Kern River and subsequent cation exchange and calcium carbonate precipitation resulting in increased Na percentages [47, 49].

Mixed-Group samples are generally characterized as moderate TDS (median 900 mg/L) Na–SO_4 or Ca–SO_4 fresh waters located in or near the historical location of Buena Vista Slough, an area now used mostly for agriculture. Buena Vista Slough was historically a swampy, overland flow region where sediments derived from the Sierra Nevada and Coast Ranges accumulated [47, 74]. The Mixed Group generally has intermediate ion compositions consistent with mixing between Eastern and Western Group waters (Figs 3 and 4). The NCL deep Group consists of Na–Cl type brackish water (median TDS 6,100 mg/L), and only contains samples from two deeper wells (C6 and MW 58–30, screened 195.1–207.3 m and 285.3–326.4 m below land surface) located in North Coles Levee Oil Field.

The Western Group contains highly variable TDS ranging from brackish to saline (median 5,600 mg/L, range 1,450–87,500 mg/L), with typically Na–Cl or Na–SO_4 type water (Figs 3 and 4). Western-Group waters are generally located within Buena Vista Valley and along the margins of Buena Vista Lake Bed and Elk Hills Oil Field. Previous studies have attributed higher salinity, Cl–and SO_4–type groundwater such as that of the Western Group to dissolution of

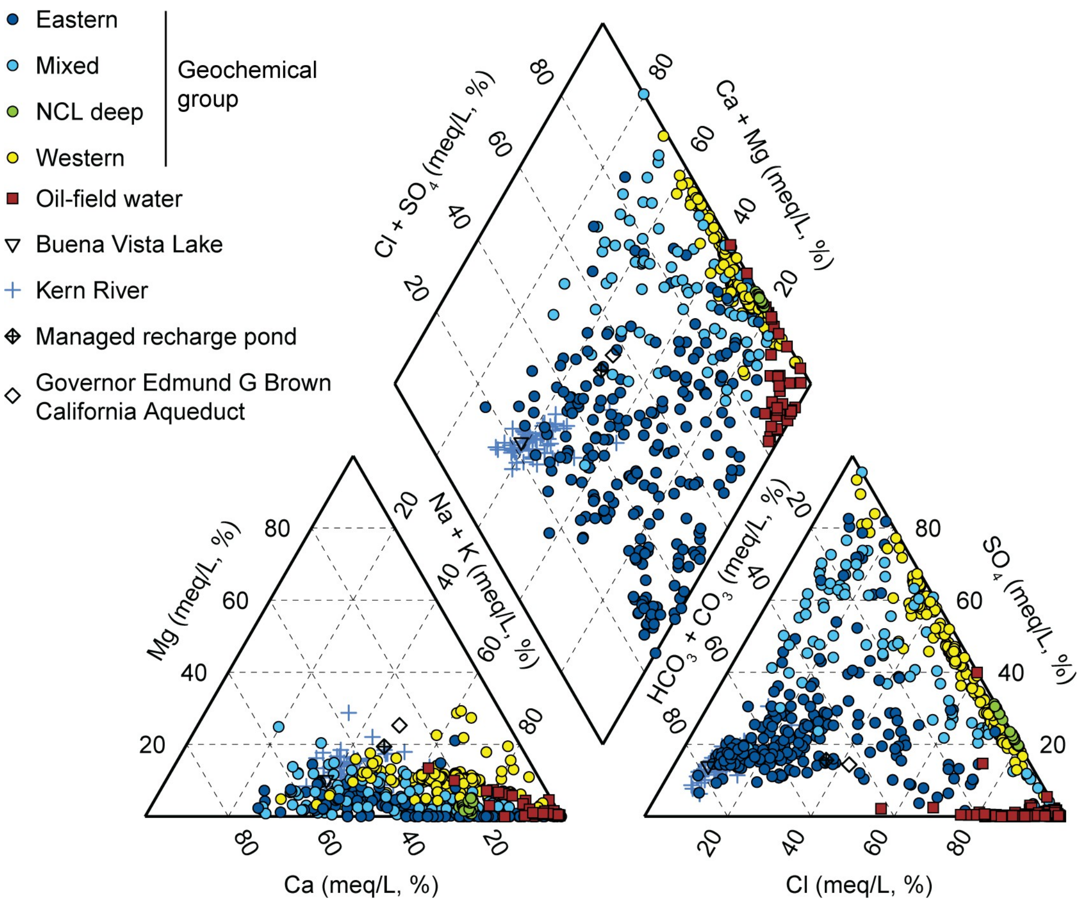

Fig 3. Piper diagram showing groundwater, surface water, and oil-field water samples. Groundwater samples are shown as circles with colors corresponding to geochemical groups identified in hierarchical cluster analysis.

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gypsum and sodium chloride salts in marine sediments derived from the Coast Ranges, and to evaporative concentration of lake water near Buena Vista Lake [46, 51].

The groundwater major ion chemistry largely represents mixing between Kern River and Coast Ranges recharge sources and sediments, with modification by ion exchange and water-rock interactions involving calcium carbonate and gypsum. Potential sources of Cl in the study area include marine sediments derived from the Coast Ranges and accumulation of salts resulting from evaporative concentration of Buena Vista Lake water. Another possible source of Cl is oil-field water, which could potentially mix with groundwater because of surface disposal practices, injection disposal practices, leakage from oil and gas wells, or natural migration. Oil-field waters are all Na–Cl type (Fig 3), with Cl concentrations as high as 31,200 mg/L (median Cl 19,000 mg/L). Oil-field waters typically have higher TDS, Ca, HCO_3, Cl, and B, and lower SO_4 compared to groundwater of the Eastern, Mixed, and Western Groups (Fig 4). Sections 4.6 and 4.7 discuss water-rock interactions and mixing that could account for elevated groundwater Cl concentrations in parts of the study area.

4.3 Characterization of groundwater recharge and age

Age dating tracers (^3H and ^{14}C) and stable isotopes of water (δ^2H and $\delta^{18}O$) can be used to identify groundwater recharge sources, mixing, and potential pathways of mixing between groundwater and oil-field fluids [30, 33, 78, 79]. Concentrations of ^3H and ^{14}C ranged

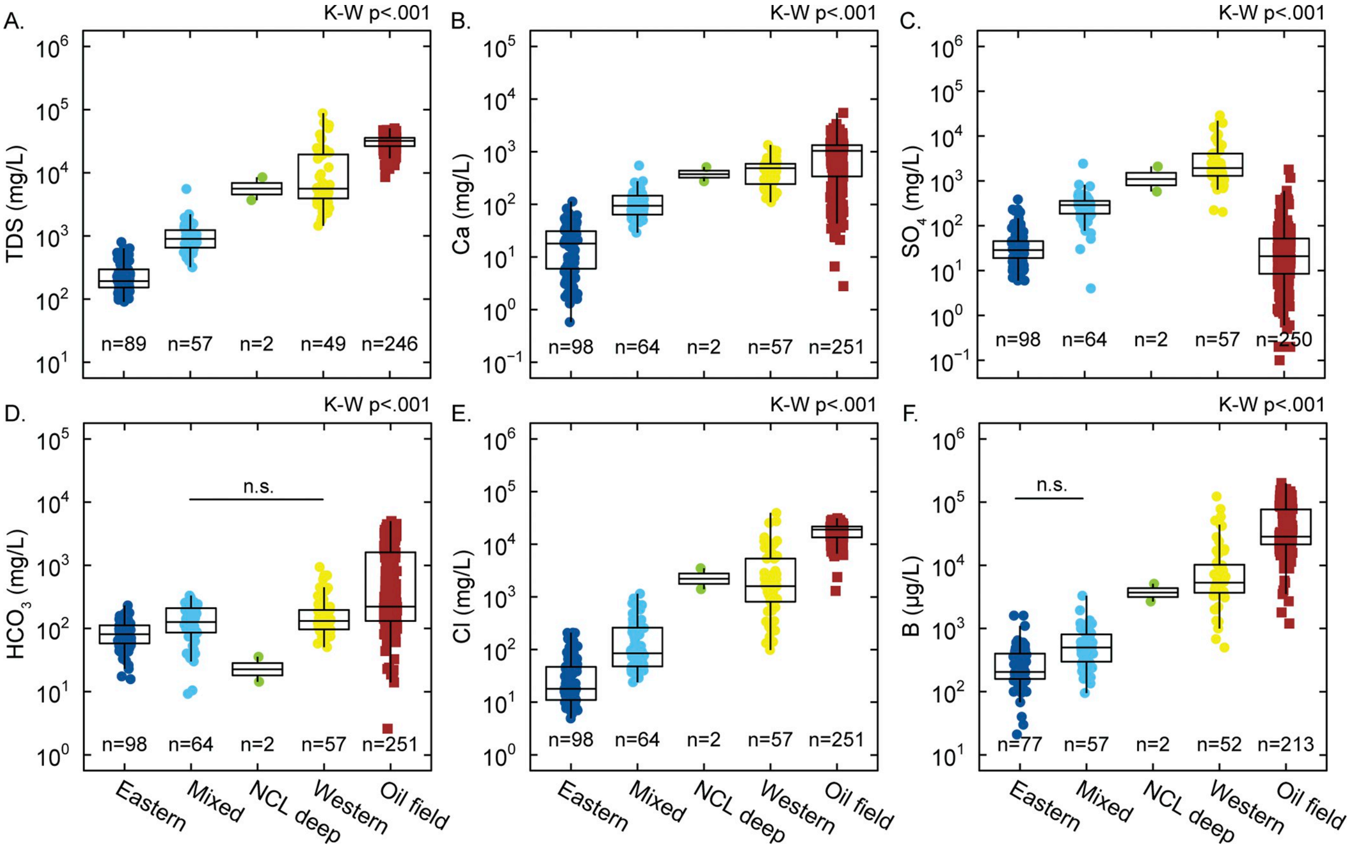

Fig 4. Boxplots showing concentrations of selected constituents for the Eastern, Mixed, NCL deep, and Western geochemical groups and oil-field water samples. The lower and upper quartiles are represented by boxplot hinges and whiskers represent 1.5 times the interquartile range. For each constituent, Kruskal-Wallis (K-W) tests indicating a significant difference between groups were followed with Dunn's multiple pairwise tests. All pairwise comparisons were significantly different ($p<0.05$) with two exceptions shown by the horizontal bars indicating non-significant (n.s.) differences. The NCL deep group was excluded from comparison tests because only two observations were available. The data set was filtered to a single sample per site for statistical comparisons.

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from < 0.1 to 3.2 tritium units (TU) and < 1 to 100.5 percent modern carbon (pmc) in RMP samples collected from 2014 to 2018 and historical samples collected from 2006 to 2015 (Fig 5). Groundwater samples were assigned to modern (recharged in 1953 or later), mixed, or premodern (recharged before 1953) age categories by comparing measured ^3H and ^{14}C concentrations to premodern and modern threshold concentrations estimated following approaches used in previous studies [33, 78–80]. The age-category analysis indicates that 36.8, 26.3, and 36.8% of samples (n = 38) are modern ($^3H > 1.22$ TU and $^{14}C > 74.4$ pmc), mixed ($^3H > 0.13$ TU and $^{14}C < 74.4$ pmc), and premodern ($^3H < 0.13$ TU and $^{14}C < 74.4$ pmc), respectively (Fig 5).

The δ^2H (-96.4 to -69.5 ‰) and $\delta^{18}O$ (-12.9 to -8.2 ‰) values for groundwater are consistent with recharge sourced from Sierra Nevada precipitation, managed aquifer recharge, and local precipitation, including rainfall on the eastern part of the Coast Ranges that drains to the San Joaquin Valley in eastward-flowing streams (Fig 6A). Previous studies of the San Joaquin Valley aquifer system have shown δ^2H and $\delta^{18}O$ values can be useful indicators of recharge sourced from major rivers draining the Sierra Nevada, precipitation falling on the Coast Ranges, and mixtures of both sources [81, 82].

Examination of the stable isotope and chemical data in the context of age categories, location, and available end member data provides additional information on the sources of

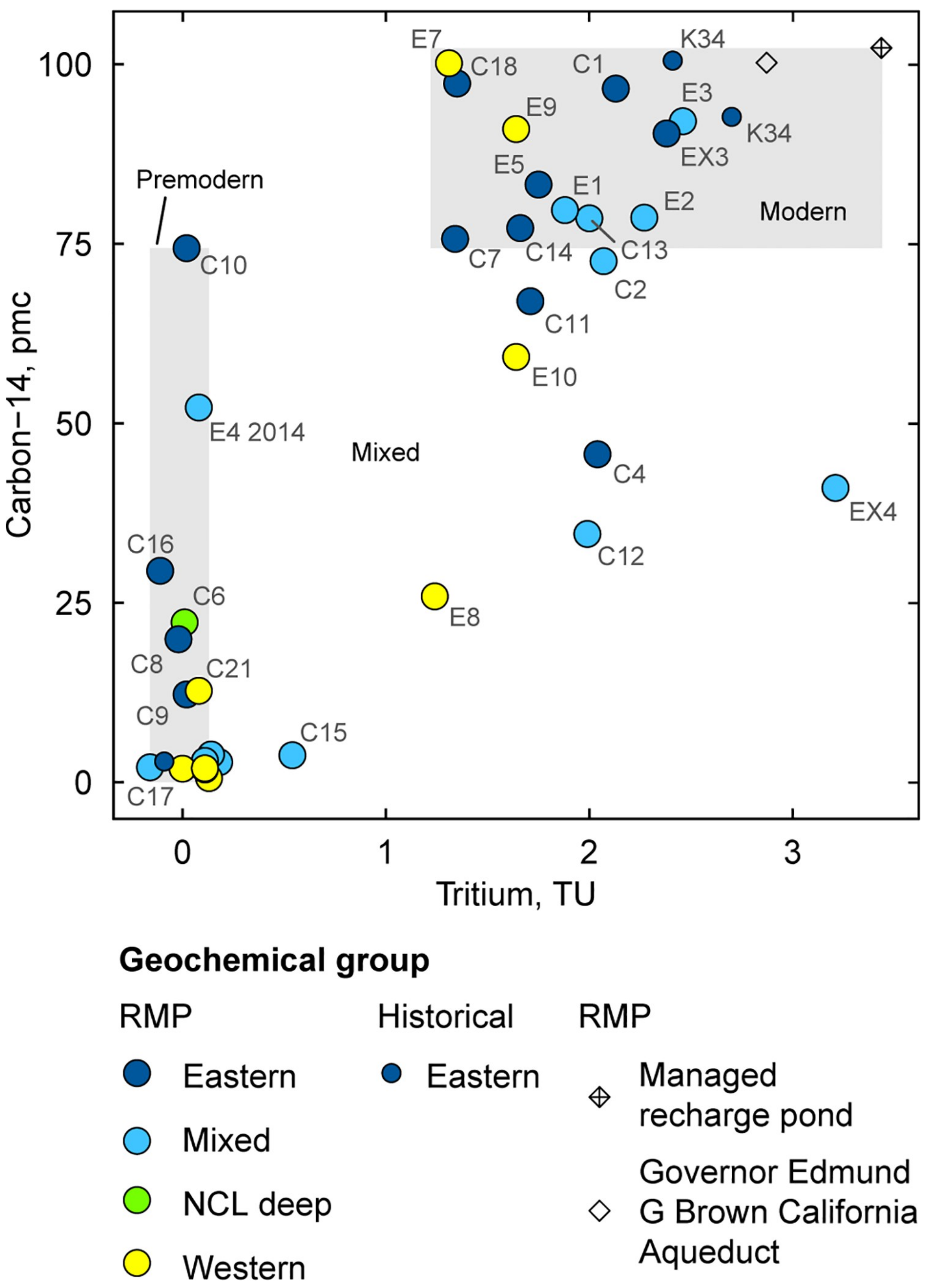

Fig 5. Carbon-14 (^{14}C) in dissolved inorganic carbon in relation to tritium (^{3}H) in groundwater and surface water. Thresholds for modern water, $^{3}H > 1.22$ TU and $^{14}C > 74.4$ pmc; premodern water, $^{3}H < 0.13$ TU and $^{14}C < 74.4$ pmc. RMP, Regional Monitoring Program.

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groundwater recharge for wells sampled in this study. Sample C8 had low Cl (8 mg/L), and $\delta^{2}H$ and $\delta^{18}O$ values were within the range of Kern River samples collected from a site in the southern Sierra Nevada (Fig 6B and S6 Table) [85, 86]. Those data together with the premodern age category for C8 indicate the sample largely represents Kern River water recharged prior to 1953. The highest $\delta^{2}H$ and $\delta^{18}O$ values were measured in a sample from E6, with

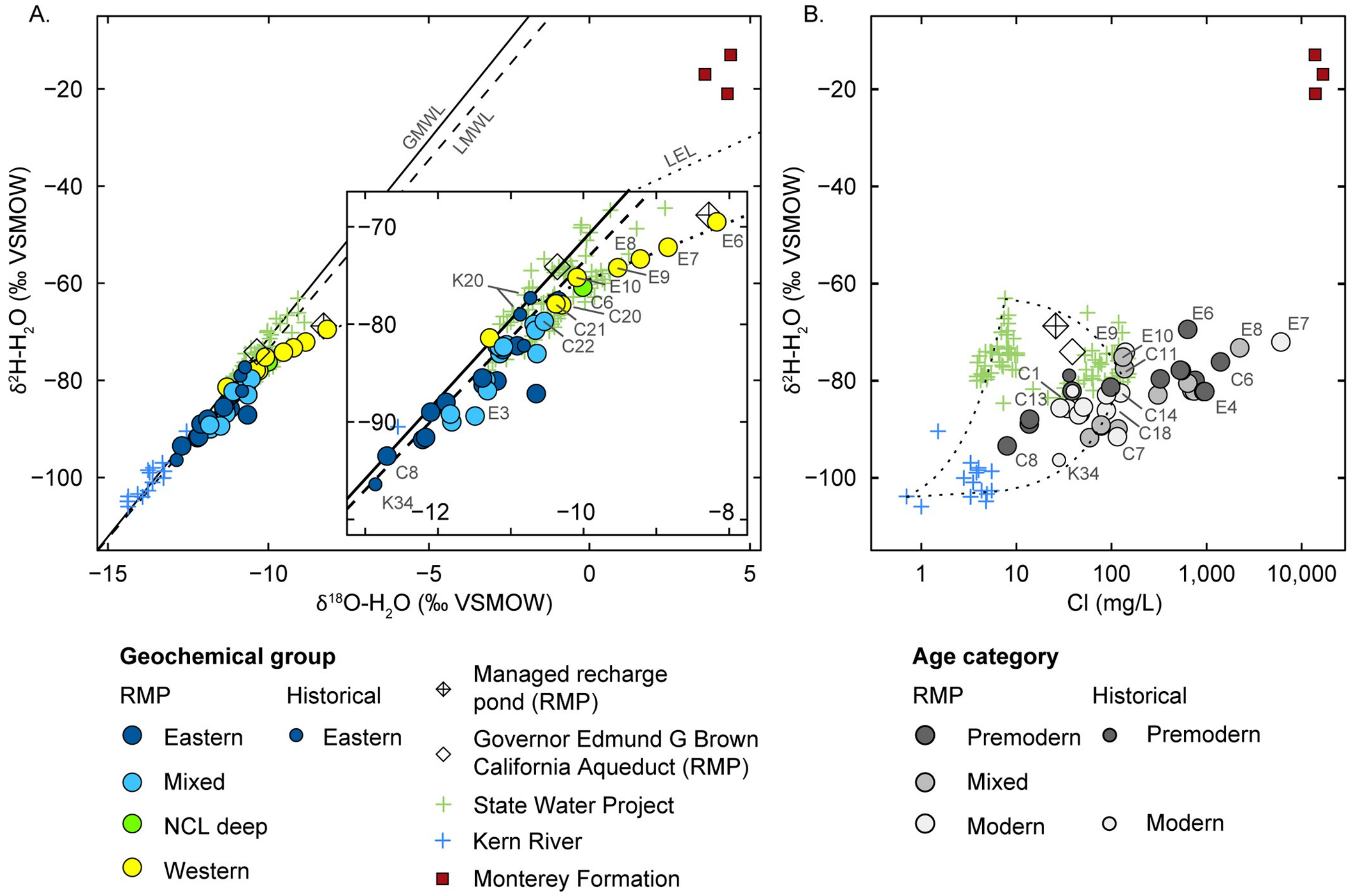

Fig 6. Values of δ^2H in relation to (A) δ^{18}O values and (B) chloride concentrations for groundwater, surface water, and oil-field water. In (B), dotted lines enclose a mixing envelope between Kern River water and State Water Project source waters. RMP, Regional Monitoring Program; VSMOW, Vienna Standard Mean Ocean Water; GMWL, global meteoric water line [83]; LMWL, local meteoric water line [84]; LEL, local evaporation line. Oil-field water is for the Monterey Formation at North Coles Levee Oil Field [73].

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values plotting to the right of the global meteoric water line suggesting water fractionated by evaporation (Fig 6A). E6 is a deeper monitoring well screened 146.3–159.7 m below land surface in western Buena Vista Valley where only precipitation falling on the Coast Ranges is likely to recharge groundwater (Fig 1). The sample from E6 was in the pre-modern age category and was the best available proxy for recharge derived from precipitation falling on the Coast Ranges because stable isotope data were not available for precipitation or streams near western parts of the study area. The remaining premodern groundwater samples have δ^2H and δ^{18}O values consistent with mixing between sources from the Kern River and Coast Ranges, with higher values reflecting a larger Coast Ranges influence in deeper wells near Buena Vista Lake Bed (C20, C21, C22, K20) and deeper wells in North Coles Levee Oil Field (C6, C17).

Water recharged during managed aquifer recharge operations could also be a source of recharge for some modern and mixed samples. State Water Project (SWP) source water, Kern River water, and Friant-Kern Canal source water contributed 59, 24, and 17% of water used for managed aquifer recharge at Kern Water Bank from 1995 through 2016 (Figs D and E in S1 Text). Wells C1, C7, C13, C14, C18, EX3, and K34 are located within or near managed recharge areas, contain modern water, and have Cl and stable isotope compositions falling within the range of compositions expected for mixing between SWP and Kern River water sources (Figs 1 and 6). Those considerations indicate these wells might contain managed recharge water of varying mixtures between Kern River and SWP sources with, for example, K34 containing a larger fraction of Kern River water and C13 containing a larger fraction of SWP source water relative to other samples. However, the similarity in isotopic composition between mixtures of water sourced from the Kern River and Coast Ranges compared to that of SWP source water does not rule out mixtures of all three sources.

Samples with Cl greater than about 150 mg/L and δ^2H values greater than about -84 ‰ were collected from either deeper wells or more westerly wells on margin of San Joaquin Valley in locations likely to have a greater fraction of marine sediments derived from the Coast Ranges. Previous studies have related higher groundwater Cl concentrations to greater fractions of marine sediments in the aquifer, which increase to the west and with depth and can be a Cl source [46, 47, 49, 51, 55]. The highest Cl concentrations were measured in samples from C6 (1,400 mg/L), E7 (6,060 mg/L), and E8 (2,240 mg/L). The elevated Cl concentrations in samples E7 and E8 combined with δ^2H and δ^{18}O values plotting along an evaporation line could indicate these samples are affected by evaporative concentration.

The stable isotope data indicate there is not significant mixing between groundwater and oil-field fluids in the study area because groundwater δ^2H and δ^{18}O values largely fall within the range of values for meteoric recharge sources and are much lower than produced water values. Groundwater δ^2H and δ^{18}O values are about 49 ‰ and 12 ‰ lower than produced water from the Monterey Formation at North Coles Levee Oil Field. However, mixing of small fractions of produced water with groundwater may not be discernable using stable isotope data alone [30], and oil-field fluid data are limited by the small number of produced water samples available with only three produced water samples available from North Coles Levee Oil Field and no samples available from Elk Hills Oil Field. The lack of data creates uncertainty in the stable isotope composition of produced water and corresponding mixing interpretations derived from stable isotope data.

Noble gas concentrations and isotopic ratios can be used to identify interactions between groundwater and deep crustal or mantle fluids, including hydrocarbons (water, gas, oil) [32, 87–94]. Groundwater in proximity of Elk Hills and North Coles Levee Oil Fields generally has noble gas concentrations (He, Ne, Ar, Kr, Xe) consistent with concentrations expected for groundwater primarily derived from air equilibration during recharge with minor amounts of "excess air" (dissolved gas concentrations greater than concentrations expected for atmospheric equilibrium) and trace amounts of terrigenic He produced mainly from radioactive decay of uranium or thorium in aquifer sediments (Fig F in S1 Text). Excess air was generally higher in samples suspected to be affected by managed aquifer recharge (C1, C7, C13, C14, C18, EX3, and K34), suggesting rapid infiltration of recharge water results in greater entrainment of air bubbles [95, 96]. The noble gas data show minimal or no evidence of light gas stripping or heavy gas enrichment that would be expected from oil or hydrocarbon gas phase interactions with groundwater (Fig F in S1 Text). The results indicate most sampled wells have not been affected by migration of gas-rich saline water or extensive gas migration along faults, poorly cemented well annuli, or leakage through well integrity failures.

Noble gas data, in combination with age-tracer data (^{3}H, ^{14}C), indicate groundwater recharge ages in proximity of Elk Hills and North Coles Levee Oil Field range from thousands of years ago to after 1952 (also referred to as "modern"). Helium can be a useful proxy of groundwater age because concentrations generally increase with groundwater residence time due to radioactive decay of uranium or thorium in aquifer sediments and fluxes from mantle sources [97]. Most samples with Cl greater than about 150 mg/L have elevated He concentrations reflecting greater accumulation of He from radiogenic sources and older groundwater in deeper wells and more westerly wells on the margin of the San Joaquin Valley (Fig 7). One

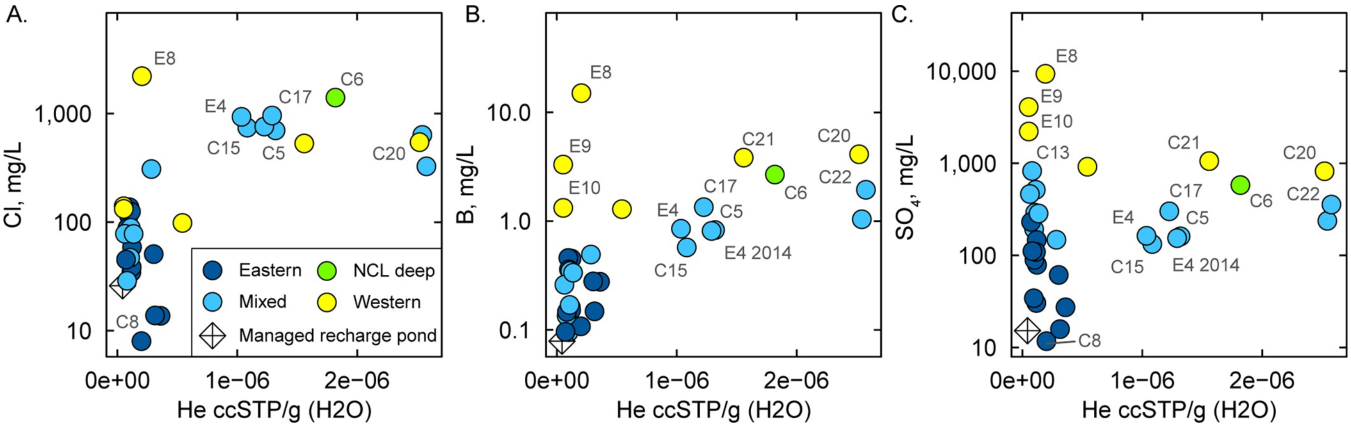

Fig 7. Helium concentrations in relation to (A) chloride, (B) boron, and (C) sulfate.

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exception to this trend is the sample from E8 which was classified as mixed-age, had low He, and had elevated concentrations of Cl (2,240 mg/L), B (15.2 mg/L), and SO_4 (9,380 mg/L). The sample from E7 was not analyzed for He but was classified as modern-age and had even higher concentrations of Cl (6,060 mg/L), B (58.8 mg/L), and SO_4 (29,000 mg/L), indicating groundwater that has been affected by recent sources or processes resulting in high concentrations of these constituents. Wells E7 and E8 are in a shallow monitoring well nest screened 7.5–10.4 and 24.1–30.1 m below land surface, respectively, on the western margin of Buena Vista Lake Bed just east of the Governor Edmund G Brown California Aqueduct (Fig 1). Shallow groundwater in this hydrologic setting has the potential to be influenced by recharge of water that fills Buena Vista Lake Bed during wet years and legacy surface disposal of produced water in Buena Vista Creek (and upstream drainages) that historically drained toward the western margin of Buena Vista Lake Bed [75, 76]. The sample from E8 was the only sample to show evidence for stripping of light noble gases (Fig F in S1 Text) but hydrocarbon gas data are not available to confirm the noble gas stripping is associated with hydrocarbon gas phase interactions with groundwater. Stripping of light noble gases also can occur when the water table intersects the well screen during sample collection, and E8 is a shallow monitoring well completed in an area with clay deposits having low hydraulic conductivity, which could lead to drawdown of water levels during sample collection. Potential sources of elevated Cl, SO_4, and B in E7 and E8 are discussed in greater detail in Section 4.6.

4.4 Light hydrocarbon gas detections

Groundwater can contain microbial CH_4 produced in the aquifer by methanogenic microorganisms [78, 98, 99] and thermogenic CH_4 originating from underlying oil and gas deposits [30, 100–104]. Thermogenic CH_4 is produced at relatively high temperatures during oil and gas formation and typically co-occurs with other hydrocarbon gases such as ethane (C2), propane (C3), isobutane (*i*-C4), and normal butane (*n*-C4) as well as minor amounts of other gases such as nitrogen, carbon dioxide, and hydrogen sulfide [105, 106]. Microbial and thermogenic sources of CH_4 have different carbon and hydrogen isotope signatures which can be used to trace CH_4 sources [107, 108]. The detection of thermogenic CH_4 or C3+ gases, or both, in a sample indicates the gases originate from oil and gas sources.

CH_4 was detected in 30 of 31 RMP samples (range <0.0002 to 0.13 mg/L, median = 0.0057 mg/L) (Fig 8A and S7 Table). Only one sample had CH_4 exceeding 0.1 mg/L. None of the samples had a CH_4 concentration sufficient to measure the carbon and hydrogen isotope

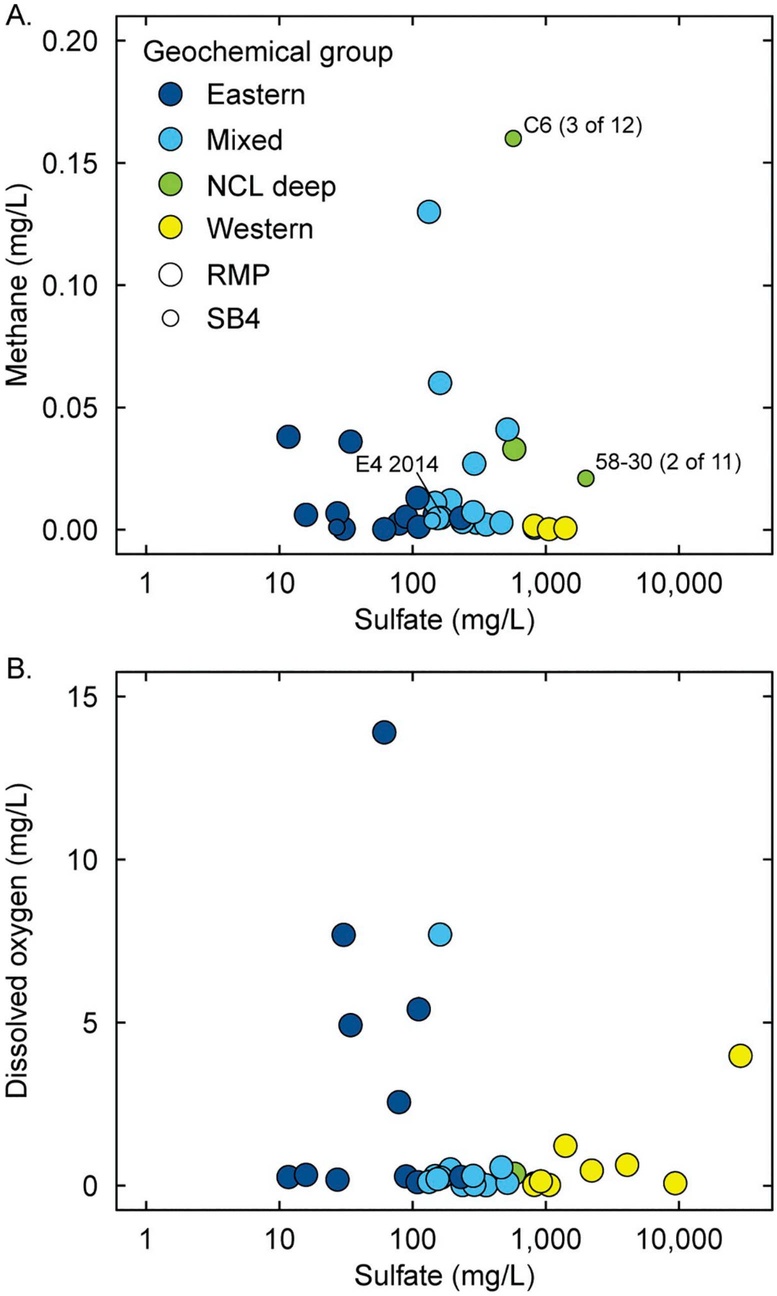

Fig 8. Sulfate concentrations in relation to (A) methane concentrations and (B) dissolved oxygen concentrations. In (A), labels show samples having two or more BTEX detections greater than lab reporting levels; values in parentheses indicate the number of samples having two or more BTEX detections (greater than lab reporting levels) out of the total number of SB4 monitoring samples collected from the well; data for samples having the median methane concentration are shown for SB4 data.

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composition of CH_4; therefore, we could not distinguish thermogenic versus biogenic sources using CH_4 isotopes. Normal butane was detected in one sample (C16) at a low concentration near laboratory reporting levels (S7 Table). Samples collected for SB4 semi-annual monitoring also had low CH_4 (range = <0.001 to 0.569 mg/L, median = 0.0086 mg/L) (Fig 8A and S8 Table).

The low CH_4 concentrations are consistent with redox processes in the upper Tulare aquifer. Classification of redox processes [109] indicated about 71% of RMP samples (25 of 35) are anoxic (S6 Table). Although none of the samples had low concentrations of both dissolved oxygen (<0.5 mg/L) and sulfate (<0.5 mg/L) (Fig 8B), typical of conditions supporting microbial CH_4 production [110, 111], the well screens likely intersect thin clay layers having such conditions and microbial CH_4 production is the most likely explanation for the widespread occurrence of trace levels of methane, particularly in places where thermogenic sources would not be expected because sources are distal. The presence of trace amounts of CH_4 (Fig 8A) without corresponding noble gas modifications such as light gas stripping (Fig F in S1 Text) supports local microbial CH_4 production rather than thermogenesis as the source of CH_4. Furthermore, high SO_4 concentrations in the Tulare Aquifer—particularly in the Mixed, NCL Deep, and Western Groups (Fig 4)—demonstrate capacity for migrating thermogenic CH_4 (if present) to be attenuated. Previous studies have shown that CH_4 oxidation coupled to metal or SO_4 reduction can remove thermogenic CH_4 from groundwater until electron acceptors are depleted [112, 113].

The low CH_4 concentrations in groundwater samples are striking considering that Elk Hills Oil Field is by far the largest natural gas producer in California [61]. Previous studies near oil fields in other parts of the San Joaquin Valley have detected CH_4 concentrations as high as 46.0 mg/L from mixed biogenic/thermogenic sources (Lost Hills Oil Field) and as high as 1.2 mg/L from thermogenic sources (Fruitvale Oil Field) [30, 62, 114]. In this study, the low CH_4 might be explained by the large lateral and vertical distances between hydrocarbon reservoirs and areas of used or monitored groundwater—migrating CH_4 (if any is present) would be required to flow along pathways having long groundwater travel times in geochemical conditions within the upper Tulare aquifer that could attenuate migrating CH_4 via oxidation coupled to SO_4 reduction. Furthermore, the presence of intervening clay layers between production zones and the upper Tulare aquifer might confine migrating CH_4 (if any is present) in deeper formations. Another possible explanation is that natural gas is confined within production zones and produced without leakage from oil and gas wells. The availability of groundwater wells to sample for the RMP could be a factor, especially in the western part of the study area in proximity to Elk Hills Oil Field. Few groundwater wells were available to sample in this area where groundwater is less utilized because of poor water quality (Figs 1 and 4, see Western Group).

4.5 Hydrocarbon VOC detections

Hydrocarbon VOCs, such as benzene, toluene, ethylbenzene, and *o*–, *m*–, and *p*–xylenes (BTEX compounds), are present in crude oil and commonly found in water associated with oil and gas production activities [115–119]. At least one BTEX compound was detected in 9 of 36 RMP samples (S7 Table). Sample concentrations were less than California maximum contaminant levels (MCLs) for drinking water (MCLs: benzene, 1 μg/L; toluene, 150 μg/L; ethylbenzene, 300 μg/L; *o*–, *m*–, and *p*–xylene, 1750 μg/L for sum of isomers) [120]. Toluene was the most frequently detected BTEX compound, with concentrations greater than lab reporting levels in 7 of 36 RMP samples (S7 Table). The sample collected from well E4 in 2014 was the only RMP sample that had two or more BTEX detections greater than lab reporting levels (Fig 8A), containing benzene (0.0408 μg/L), toluene (0.3824 μg/L), ethylbenzene (0.1361 μg/L), *o*–xylene (0.1859 μg/L), and *m*–plus *p*–xylene (0.568 μg/L). Semi-annual SB4 monitoring of wells C6 and MW 58–30 indicates two or more BTEX detections in 3 of 12 (Nov 11, 2014, to Sept 30, 2020) and 2 of 11 (Feb 10, 2015, to Sept 29, 2020) samples, respectively (Fig 8A and S8 Table). Benzene concentrations in MW 58–30 exceeded the California MCL for drinking water in 8 of

11 samples (maximum = 5.9 μg/L; MCL, 1 μg/L), but well MW 58–30 is used for monitoring and not water supply.

Examination of possible pathways and geochemical data indicates the BTEX compounds in well E4 (2014 sample) could be derived from either naturally occurring sources or from oil and gas development activities; however, the data are not definitive. Well E4 is a deep monitoring well screened 183–214 m below land surface, and oil and gas wells are not present within 500 m of E4 (Fig 1 and S9 Table). Well E4 contains premodern water that rules out recent (1953 or later) surface disposal of produced water as a source. Legacy surface disposal (prior to 1956) is considered an unlikely source because the well is greater than 500 m from potential surface sources of oil-field fluids (Fig 1), and low ^{14}C-DIC concentrations (52.2 pmc) indicate that the well contains water recharged before oil-field development (uncorrected ^{14}C age: 5,300 years). E4 had similar Cl concentrations measured in the 2014 (959 mg/L) and 2017 (932 mg/L) samples, but no BTEX compounds detected in the 2017 sample. The lack of BTEX compounds in the 2017 sample, while Cl remained similar, indicates the BTEX compounds in the 2014 sample are probably not associated with saline produced water. However, mixing with small fractions of saline water cannot be ruled out entirely because Cl was 27 mg/L higher in the 2014 sample. The apparent inconsistency between BTEX detections in 2014 and no detections in 2017 might be related to a reversal of the hydrologic gradient, with managed aquifer recovery decreasing water levels in 2014 and managed aquifer recharge increasing water levels in 2017 (S1 Animation in S1 File) [55]. Overall, the data indicate that BTEX compounds detected in E4 (2014) could be associated with naturally occurring sources but do not rule out leakage from a distant oil and gas well as a source. The shallowest evidence of naturally occurring hydrocarbon gases or oil is found at 1,155 m below land surface based on analysis (Appendix B in S1 Text) of a limited number of mud logs in the area (Fig C in S1 Text and S10 Table). Well E4 has a bottom screen depth (214 m) much shallower than 1,155 m, indicating that upward migration of naturally occurring sources from depth would likely be required to explain the detected BTEX compounds, if indeed naturally occurring.

Multiple VOC sources were considered for the remaining six RMP wells having trace amounts of toluene. Toluene is among the most frequently detected VOCs in aquifers of the United States, and occurrences of toluene in groundwater have been associated with surface or shallow subsurface gasoline sources such as leaky underground storage tanks [121, 122]. Four of the six wells contain modern (recharged in 1953 or later) groundwater (C7, C13, E3, and E7), indicating the toluene could be associated with land surface releases of gasoline associated with oil and gas production or other activities. Of those four wells, only C7 is located within 500 m of a known surface source of oil-field fluids (Fig 1 and S9 Table), but unknown surface sources or more distant sources could also be a factor. Although the four wells containing modern water could be affected by surface sources, the lack of co-occurring hydrocarbon gases or other BTEX compounds in these samples make toluene source attribution challenging, and other sources are possible. Leaching of VOCs from materials used to construct wells has the potential to affect water quality [123], and toluene is a component of adhesives [124] sometimes used during well construction. Some studies have attributed toluene occurrences to adhesives used for connecting well piping or installing pumps, particularly in samples where no other BTEX compounds are detected [125–127]. Identification of sources may come from continued monitoring of wells having detections or from a larger data set examining toluene detections in relation to well materials and oil and gas sources.

Multiple VOC sources also were considered for BTEX compounds detected in semi-annual SB4 monitoring of C6 and MW 58–30. Wells C6 and MW 58–30 are deeper monitoring wells screened 195.1–207.3 and 285.3–326.4 m below land surface in North Coles Levee Oil Field. The wells contain Na–Cl type brackish water with samples from both wells clustering into a single group (NCL deep) suggesting the wells have unique major ion composition compared to the Eastern, Mixed, and Western Groups. Elevated Cl concentrations in C6 (range 1,400–1,600 mg/L) and MW 58–30 (range 3,200–3,500 mg/L) compared to nearby wells completed at a similar bottom elevation (Fig G in S1 Text) suggest the BTEX compounds could be associated with a source of Cl. Twelve oil and gas wells are within 500 m of C6, including four wells with documented well barrier failures and one well with a well integrity failure (Appendix B in S1 Text; Fig C in S1 Text; S9 and S11 Tables). However, the well integrity issues occur at depths greater than 1900 m, much deeper than C6, making an oil-field source of Cl or BTEX seem unlikely. Well MW 58–30 is the only well completed in the lower Tulare Formation (i.e., below the Amnicola clay) in the eastern part of the study area, making evaluation of the elevated Cl in the well challenging without any nearby data available for the lower Tulare Formation. Marine sediments in the aquifer also are a potential source of Cl. Previous studies have reported permeability variations in geologic materials underlying western parts of North Coles Levee Oil Field [55, 128, 129], which could suggest a transition to geologic materials containing a larger fraction of deposits derived from marine sources compared to areas farther east. Possible explanations for the permeability variations include both lithologic changes related to faulting and deposition of alluvial fan deposits weathered from the Elk Hills [55, 128, 129]. In summary, the elevated Cl and BTEX compounds in C6 and MW 58–30 have uncertain sources. Continued monitoring of water from the wells may help distinguish sources, and future monitoring of deeper groundwater south of C6 and MW 58–30 may help determine if the elevated Cl is related to changes in lithology. A large gap in deeper groundwater-quality data spans from MW 58–30 and C6 southward through the southern half of North Coles Levee Oil Field all the way to Buena Vista Lake Bed.

4.6 Sources of elevated Cl, B, and SO_4 in shallow wells near margin of Buena Vista Lake Bed

In this section, we consider potential sources or processes that may explain the elevated Cl, B, and SO_4 concentrations in E7 and E8 (see Section 4.3) and other shallow wells near the western margin of Buena Vista Lake Bed. High TDS groundwater up to 87,500 mg/L was encountered about 5.5 m below land surface when the section of the Governor Edmund G Brown California Aqueduct that parallels the western margin of Buena Vista Lake Bed was constructed from 1967 to 1969 [130]. Samples (RMP: n = 5, 2018; historical, n = 26, 1954–1966) collected from shallow monitoring wells (n = 27) near the western margin of Buena Vista Lake Bed contain Western Group water (Fig 1 and Fig H in S1 Text) with high TDS (range 1,870–87,500 mg/L, median 12,200 mg/L), Cl (range 98–39,300 mg/L, median 2,300 mg/L), SO_4 (range 918–29,000 mg/L, median 4,080 mg/L) and B (range 1–123 mg/L, median 6.9 mg/L). The well depths range from 2.9 to 118.9 m below land surface (median 11 m). Geologic assessments conducted during excavation for the Governor Edmund G Brown California Aqueduct identified clay layers, calcium carbonate ($CaCO_3$), and gypsum ($CaSO_4{\bullet}2H_2O$) deposits as well as oil residues where the excavation intersected some natural drainages [130]. Other geologic studies report gypsum-cemented sands and perched groundwater overlying clay layers in the area [74, 131]. The presence of gypsum in the shallow subsurface suggests the high SO_4 reported in shallow groundwater may be related to gypsum dissolution.

The western margin of Buena Vista Lake Bed is about 2,800 meters downgradient of the terminal catch basin on Buena Vista Creek (Fig H in S1 Text). This terminal catch basin was an unlined sump that historically received produced water discharged to Buena Vista Creek and natural drainages leading to Buena Vista Creek, primarily before about 1956 [76, 131]. Buena Vista Lake Bed is a topographic low between converging alluvial fans of the Kern River and streams draining foothills of the Coast Ranges [49]. Groundwater generally flows eastward from the terminal catch basin toward Buena Vista Lake Bed (Fig 2 and S1 Animation in S1 File). Elevated Cl and B in shallow groundwater downgradient of the terminal catch basin could therefore be sourced from legacy surface disposal of produced water, which has significantly higher Cl and B than Western Group groundwater (Fig 4).

Evaporative concentration of lake water also is likely to contribute salts to shallow groundwater on the Buena Vista Lake Bed. The Tulare Lake Bed is located about 90 km north of Buena Vista Lake Bed in a similar hydrologic setting having no surface outlet except during times of flood [48]. Studies of shallow groundwater (less than 7.6 m below land surface) underlying the Tulare Lake Bed reported TDS, Cl, SO_4, and B up to 63,600, 15,000, 34,000, and 27 mg/L, respectively, and attributed the high concentrations to accumulation of salts resulting from evaporative concentration of lake water and shallow groundwater [51].

The potential sources of elevated Cl, B, and SO_4 in shallow groundwater near the western margin of Buena Vista Lake Bed were evaluated by comparing measured data to geochemical pathways calculated in PHREEQC (Appendix A in S1 Text) [132]. We calculated geochemical pathways for evaporative concentration of lake water assuming calcite and gypsum equilibrium with open system conditions for CO_2 and Buena Vista Lake water (sample data from 1954 [76]) as the initial solution composition. The geochemical pathways are conceptually based on a system having cycles of infiltration of recharge sourced from Buena Vista Lake during times the lake is filled with water and subsequent interactions with minerals and evaporation in shallow groundwater once the lake dries. The calculations show increasing SO_4 and HCO_3 concentrations and decreasing Ca concentrations along the geochemical pathway (Fig 9); these concentration trends indicate that Ca and SO_4 are added to solution from gypsum dissolution, leading to calcite oversaturation and precipitation as the solution is evaporatively concentrated. Western Group groundwater having oversaturated calcite saturation indices and gypsum saturation indices near equilibrium are consistent with the geochemical pathways (Fig I in S1 Text).

Comparison of the geochemical pathways to measured data shows that RMP samples collected near the western margin of Buena Vista Lake Bed have Cl, Na, Ca, SO_4, and HCO_3 concentrations that generally plot near the geochemical pathway for a CO_2 pressure of 10^{-2}, indicating evaporative concentration in a system open to CO_2 can explain the concentrations of these constituents in RMP samples (Fig 9). RMP samples from E7 and E8 have δ^2H and $\delta^{18}O$ values plotting along a local evaporation line intersecting the local meteoric water line near E10 (Fig 6A), indicating evaporation of a source water similar in composition to E10. Stable isotope-based evaporation estimates [133] indicate water from E7 and E8 has undergone 5–7% water loss assuming evaporation in non-steady state conditions (i.e., closed basin with no inputs or outputs; Appendix A in S1 Text). However, the sample from E7 has Cl greater than that of the maximum Cl along the geochemical pathway, suggesting the sample has undergone much more than 5–7% water loss. The discrepancy between stable isotope and geochemical pathway results indicates evaporation of lake water under non-steady state conditions does not solely explain the stable isotope and geochemical composition. Rather, the reported concentrations might be explained by accumulation of salts from cycles of wetting and drying. Salts precipitated during drying and evaporative concentration of lake water could be accumulating in Buena Vista Lake Bed sediments and redissolved with each cycle of recharge resulting in high salt concentrations but a stable isotope composition reflecting the composition of recently recharged water which was not highly evaporated when sampled in March 2018. The above interpretation is consistent with the stable isotope composition of a Kern Water Bank managed aquifer recharge pond sample, which plots farther along the local evaporation line than E7 with stable isotope-based evaporation estimates indicating the pond

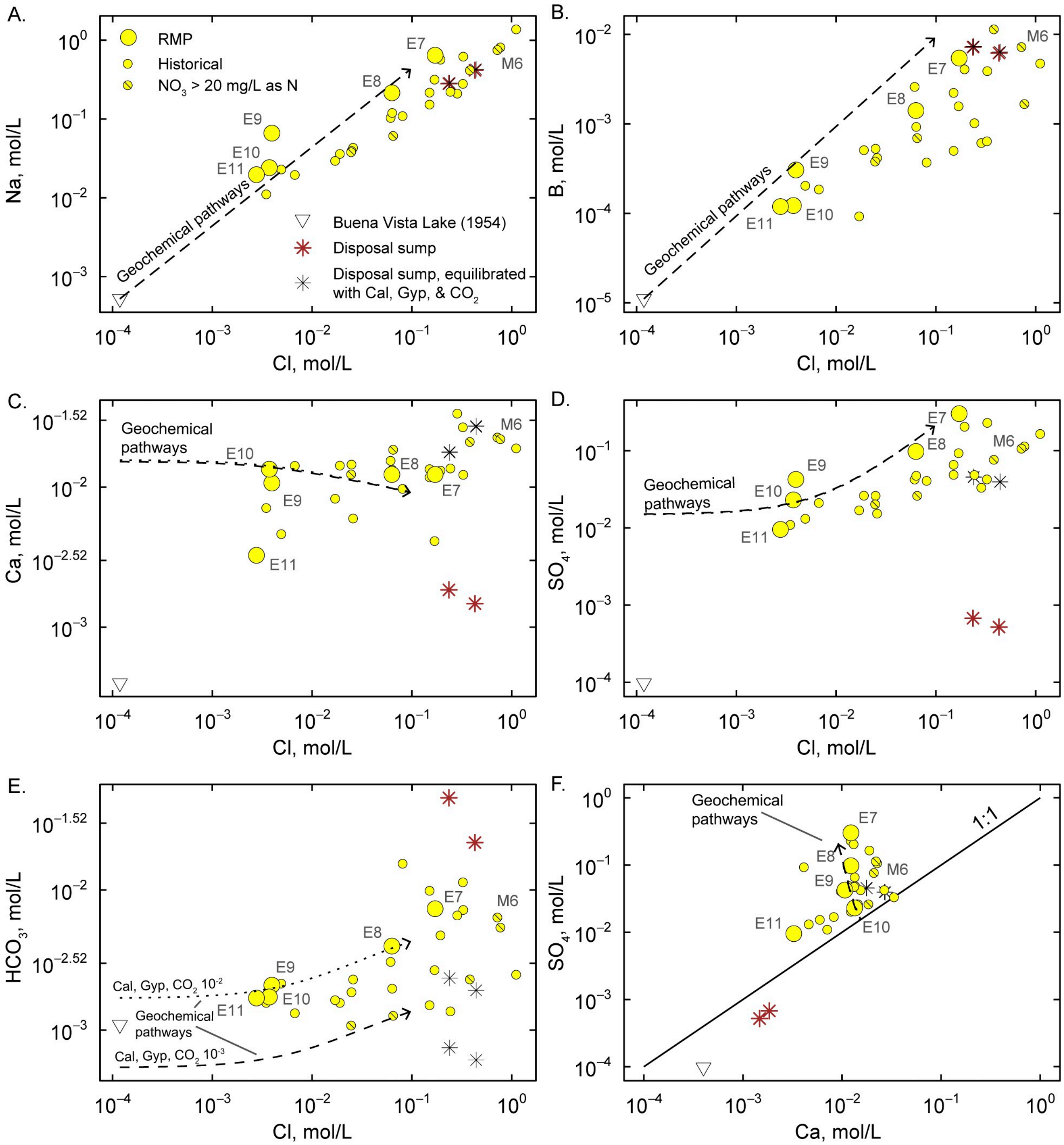

Fig 9. Concentrations of chloride in relation to (A) sodium, (B) boron, (C) calcium, (D) sulfate, (E) bicarbonate, and calcium in relation to sulfate (F) for Regional Monitoring Program (RMP; larger yellow circles) and historical (smaller yellow circles) groundwater samples collected near western margin of Buena Vista Lake Bed. Samples having nitrate concentrations greater than 20 mg/L as N are indicated by a diagonal hash inside circle symbols. Plots also show concentrations for water samples collected from Buena Vista Lake (upside-down triangle) and two terminal catch basins (brown asterisks), and theoretical concentrations for terminal catch basin water equilibrated with calcite (Cal) and gypsum (Gyp) at CO_2 pressures of 10^{-2} and 10^{-3} atmospheres (black asterisks). Lines show concentrations expected for evaporation of Buena Vista Lake water in the presence of calcite and gypsum with open system conditions for CO_2 pressures of 10^{-2} (dotted line) and 10^{-3} (dashed line) atmospheres.

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water had undergone about 10% water loss (Fig 6A and Appendix A in S1 Text). The pond water has low Cl of only 26 mg/L because large salt accumulations are not available for dissolution in the managed recharge basin which has not been subjected to evaporative drying cycles on time scales comparable to the Buena Vista Lake Bed.

We also considered infiltration of sump water as a source for elevated Cl, SO_4, and B. Historical sump data were used in PHREEQC calculations assuming conditions of calcite and gypsum equilibrium in a system open to CO_2 to calculate the likely subsurface chemistry of sump water in the shallow subsurface (Appendix A in S1 Text). The terminal catch basin on Buena Vista Creek does not have the historical sump water data required for the calculations; however, data are available for sump water from a terminal catch basin located farther west in Buena Vista Valley (31S/24E-31K1W) and from the terminal catch basin on Sandy Creek (32S/24E-25D1W) (Fig C in S1 Text), the major drainage to the south that was historically used for disposal of produced water from Midway-Sunset Oil Field [76]. Produced water generally has low SO_4 (Fig 4) likely because of SO_4–reducing conditions in oil and gas reservoirs, and the sump water samples are undersaturated with respect to gypsum (saturation index (SI) = -3.0, 31K1W and -2.7, 25D1W where $SI = \log(IAP/K_{sp})$). The sump water equilibration calculations indicate that Ca and SO_4 are added to solution from gypsum dissolution (Fig 9).

Comparison of the sump water equilibration calculations to measured groundwater data shows that some historical Buena Vista Lake Bed margin samples have Cl, Na, B, Ca, SO_4, and HCO_3 concentrations plotting near equilibrated sump water (Fig 9), indicating the samples may largely contain produced water disposed of at the land surface. Five of these samples have NO_3 concentrations greater than about 20 mg/L as N, possibly indicating a geologic source of N. Although there are no significant geologic sources of NO_3 known in Buena Vista Valley [76], sediments derived from the Coast Ranges are thought to be a source of high NO_3 in other parts of the San Joaquin Valley [134]. One potential source of N is water from hydrocarbon reservoirs, with previous studies noting high NH_4 in oil-field waters sampled from other oil fields on the west side of the San Joaquin Valley, including from fields producing the Monterey Formation [4]. Oxidation of NH_4 or N-containing organic matter in oil-field water would produce NO_2 or NO_3, or both [28]. Sump water samples from 31S/24E-31K1W and 32S/24E-25D1W had NO_2 of 290 and 134 mg/L as N and NH_3 of 109 and 49 mg/L as N, respectively, with both sump waters having NO_3 less than 1 mg/L as N [76]. The highest groundwater NO_3 of 182.53 mg/L as N was reported in a sample (1963) from 31S/24E-26Q001M (M6), a well of unknown depth about 1.3 km downgradient of the terminal sump on Buena Vista Creek (Fig H in S1 Text). Previous studies of shallow groundwater in Buena Vista Valley have attributed high NO_3 to surface disposal of produced water [76, 131].

Chloride concentrations and Cl/Br and Cl/I mass ratios were used to further understand evaporative concentration and potential mixing with produced water. Historical data for samples (1954–1966) collected from shallow wells near the margin of Buena Vista Lake Bed do not have Br and I concentrations available and could not be included in this analysis. RMP (2018) data indicate samples E7 and E8 have been affected by evaporation, with concentrations and ratios plotting along an evaporation line assuming conservative behavior of Cl and Br (Fig 10). Cl/Br mass ratios greater than 360 in E7 and E8 are much higher than sump water ratios of 112 and 203, which is consistent with geochemical pathway interpretations indicating these samples are largely affected by evaporative concentration and dissolution of accumulated salts rather than mixing with sump water. However, the data do not rule out mixing with produced water as a source of small fractions of salts. Hypothetical mixing calculations with E8 and 32S/24E-25D1W sump water end members indicate produced water fractions greater than 8% would be required for Cl/Br ratios to decrease below 300 and be clearly distinguishable from evaporation. Similarly, concentrations of Cl and Cl/I ratios in E7 and E8 plot along an

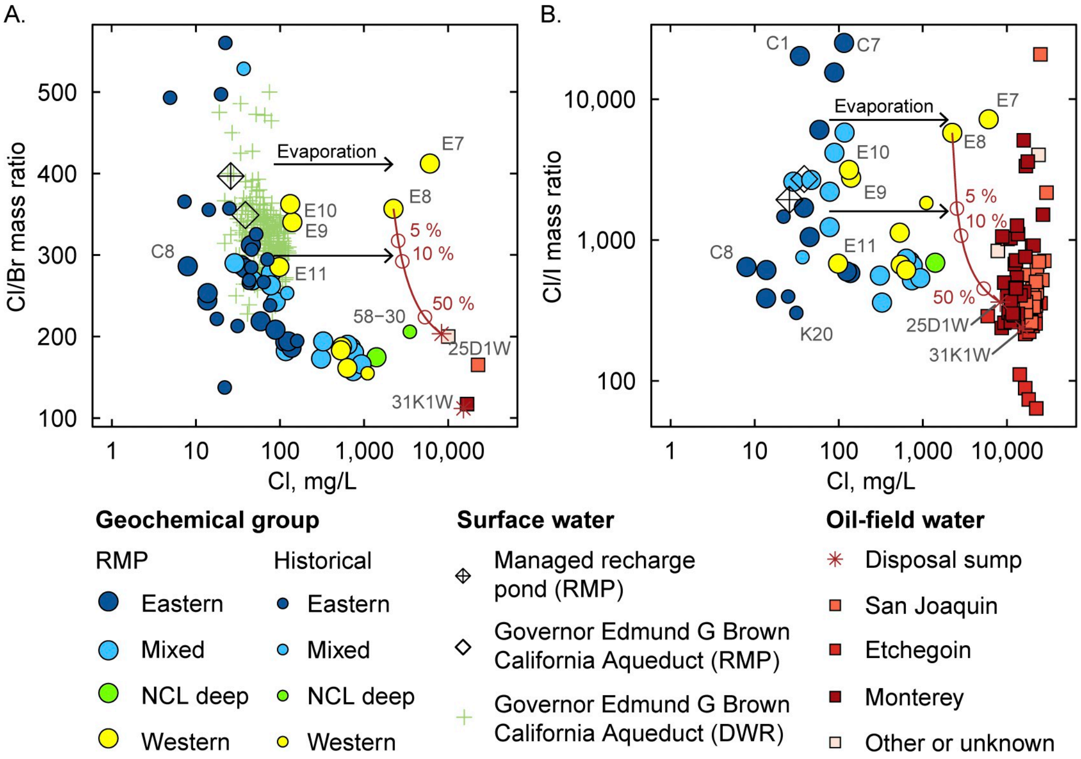

Fig 10. Chloride concentrations in relation to (A) Cl/Br mass ratios and (B) Cl/I mass ratios. The horizontal black arrows show evaporative concentration trends assuming conservative behavior of chloride, bromide, and iodide. Brown lines show hypothetical mixing between E8 and terminal sump 32S/24E-25D1W with open circles representing 5, 10, and 50% sump water.

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evaporation trend with Cl/I mass ratios greater than about 5800, much higher than sump water ratios of 240 and 360 and consistent with Cl/Br interpretations suggesting the composition of these samples can largely be explained by evaporative concentration rather than mixing with produced water.

The discussion in this section highlights that distinguishing evaporative concentration from mixing with sump water is challenging in a hydrologic setting potentially affected by both processes. Samples E7 and E8 appear to be largely affected by evaporative accumulation of salts with high SO_4 concentrations explained by gypsum dissolution and minimal to no mixing with sump water. Some historical groundwater samples have elevated NO_3 with Cl, B, Ca, and SO_4 concentrations similar to expected concentrations for sump water having infiltrated the shallow groundwater zone in the presence of gypsum and calcite (Fig 9 and Fig H in S1 Text). Those considerations, combined with well locations nearer the terminal catch basin on Buena Vista Creek than wells E7 and E8 (Fig H in S1 Text) suggest some historical samples may indeed contain large fractions of sump water. However, the lack of historical Br and I data make it difficult to confirm this interpretation with another line of evidence, and the general trends of the geochemical pathways do not exclude evaporative concentration as affecting these samples to some extent, especially considering uncertainty in starting water composition. Additional insight may be provided from future monitoring of shallow groundwater in this area, especially in locations near the terminal catch basin and west of the Governor Edmund G Brown California Aqueduct, which would avoid complications resulting from recharge of water that fills Buena Vista Lake Bed during wet years.

4.7 Effects of water disposal in 18G area of Elk Hills Oil Field

The upper Tulare Formation has been used for both groundwater withdrawal and produced water disposal at Elk Hills Oil Field's 18G area (Fig J in S1 Text). The withdrawals supply brackish groundwater used in water flooding operations that enhance oil recovery in other parts of Elk Hills Oil Field [135]. The industrial supply wells that withdraw the groundwater are often referred to as water source wells in the oil and gas industry (see "WS" wells, Fig J in S1 Text). Five water source wells in the 18G area had a series of samples collected in the 1990s that can be used to evaluate trends in water quality through time. The water source wells are south of the earliest water disposal wells drilled in the 18G area, which were mostly (18 of 20 wells) drilled prior to 1996 [60]. The location of the water source wells and timing of sample collection are such that the wells could have been withdrawing disposal water, or mixtures of disposal water and groundwater, migrating southward through the upper Tulare Formation, as was described for this area by Gillespie et al. [36] based on salinity anomalies in borehole resistivity logs collected at the time of drilling. All water disposal wells south of the water source wells were drilled after 2000 [60].

Time-series trends were evaluated to test the hypothesis that water source wells contain increasing amounts of disposal water through time. Available constituents included major ions and B. Cl and B concentrations are generally higher in produced water than groundwater (Fig 4); therefore, Cl and B concentrations would both be expected to increase in groundwater mixed with produced water compared to groundwater not mixed with produced water.

Two of the five water source wells had increasing concentrations of both Cl and B in the mid-1990s (Fig 11A and 11B and S12 Table). Theil-Sen slopes estimate yearly increases of 331 and 453 mg/L Cl and 2.8 and 1.8 mg/L B in wells 284WS-13B and 84WS-13B, respectively, for the period of recorded data (S12 Table). Wells 284WS-13B and 84WS-13B are within 100 m of each other about 1,000 m southwest of the nearest upgradient WD well (38WD-7G) (Fig J in S1 Text). Perforation depths below land surface range from 271 to 525 m for 284WS-13B and from 319 to 576 m for 84WS-13B. The nearest wells logged with resistivity anomalies had logs measured in 2002 and 2003, with anomalies recorded at various log intervals ranging between 318 and 529 m below land surface (85WD-13B, 0.3 km south; 25-18G, 0.4 km east; 25A-18G, 0.5 km east; 35A-18G, 0.6 km east) [56]. The water source well screens overlap a length of more than 200 m of logs having intervals with resistivity anomalies of varying thicknesses, after accounting for land surface elevation. The depth intervals with resistivity anomalies have unusually high TDS compared to the expected depth trend [36].

The remaining three water source wells (86WS-18G, 43WS-13B, 282WS-14B) had either no trends or trends that were statistically significant but demonstrated yearly changes less than 5% of median concentrations or were inconsistent in direction between Cl and B (S12 Table), suggesting that water in the three wells was not affected by injected disposal water at the time of sampling. These three wells are located farther from the earliest, largest-volume water disposal areas and on the margins of the areas having resistivity anomalies recorded in well logs by 2003 (Fig J in S1 Text) [36], which is consistent with these wells not being affected by injected disposal water at the time of sample collection in the mid- to late-1990s. The lack of co-occurring Cl and B trends in these three water source wells during the same period that increasing trends are observed in 284WS-13B and 84WS-13B indicates that a regional trend such as decreasing water levels is not responsible for the increasing Cl and B concentrations in 284WS-13B and 84WS-13B.

Taken together, the following lines of evidence are consistent with 284WS-13B and 84WS-13B containing a mixture of groundwater and produced water: (1) the co-occurrence of increasing Cl and B concentrations, (2) the magnitude of yearly Cl and B concentration

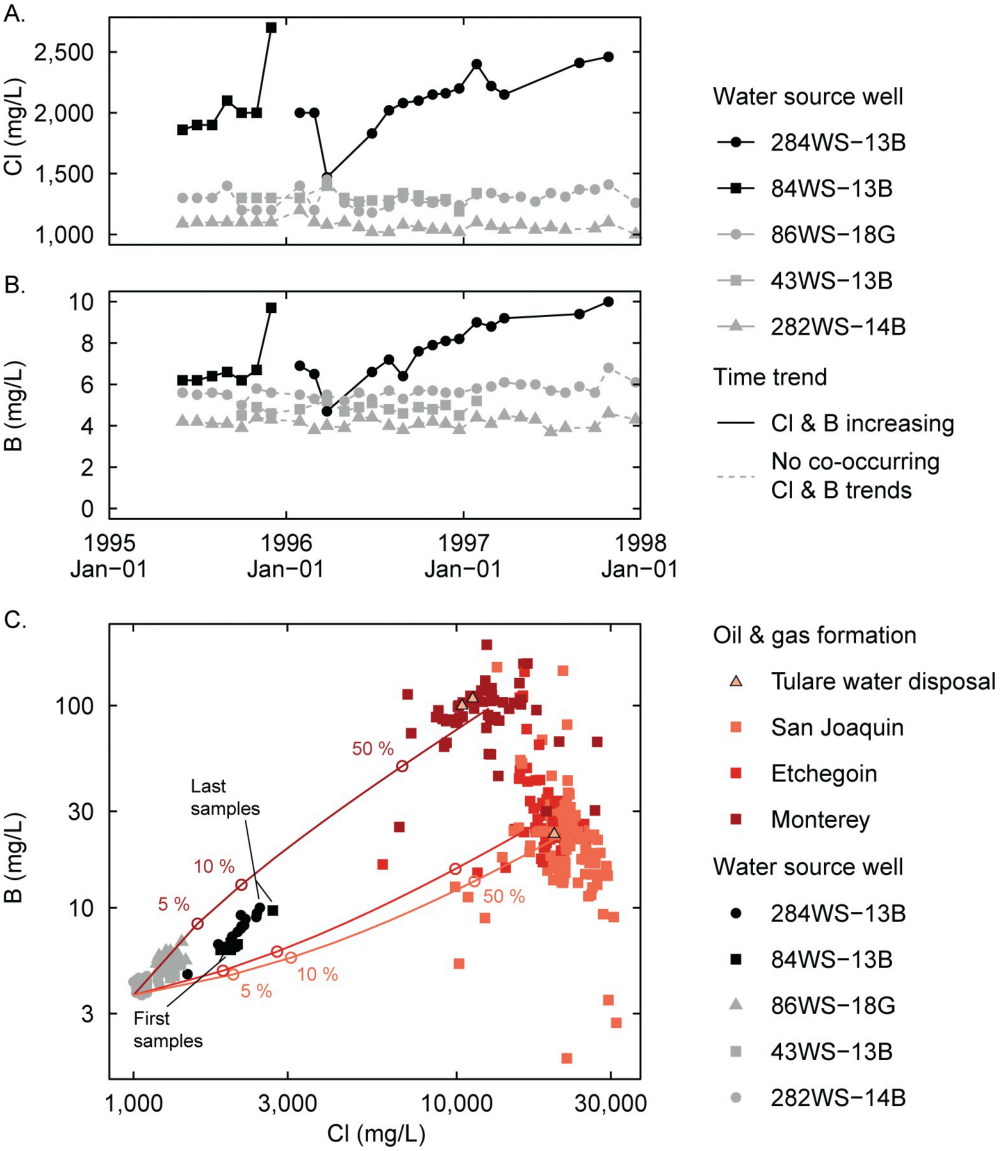

Fig 11. Trends of chloride (A) and boron (B) from 1995 to 1998 for water source wells in the 18G area of Elk Hills Oil Field, and chloride versus boron concentrations (C) for 18G area water source wells and oil-field water from Elk Hills Oil Field. Water source wells having co-occurring increasing trends in both Cl and B are shown in black. In (C), the lines show hypothetical mixing with the open circles representing 5, 10, and 50% oil-field water from the San Joaquin, Etchegoin, and Monterey Formations.

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increases relative to concentration ranges in the three wells not affected by injected disposal water, (3) the location of 284WS-13B and 84WS-13B southwest of injected disposal water migrating south, (4) the timing of water disposal injection beginning in the early 1980s relative to the timing of water source well sampling in the mid- to late-1990s, and (5) screen interval elevations that overlap with the elevations of resistivity anomalies recorded in logs from four wells within 0.6 km of the two water source wells.

Examination of Cl and B concentrations in samples from 284WS-13B and 84WS-13B relative to hypothetical mixing lines between unaffected groundwater and Elk Hills Oil Field water indicates the samples contain up to about 15% oil-field water (Fig 11C). The possible sources of oil-field water injected in the 18G area include water produced from the Monterey, Etchegoin, and San Joaquin Formations (Fig 11C) [136]. These formations have distinct Cl and B concentrations with the Monterey Formation having lower Cl (median 12,600 mg/L) and higher B (median 96.7 mg/L) compared to Cl and B in the Etchegoin and San Joaquin Formations (Cl medians: 18,800, 21,700 mg/L; B medians: 27.4, 23.4 mg/L). Samples from 284WS-13B and 84WS-13B plot inside the mixing envelope defined by hypothetical mixing lines between unaffected groundwater and the Monterey, Etchegoin, and San Joaquin Formations, indicating that the source of the migrating disposal water is a mixture of water injected from all three formations. This interpretation is consistent with sample data from three 18G area disposal wells; samples from two of the disposal wells plot with Monterey Formation water, whereas the third sample plots near Etchegoin and San Joaquin Formation water, indicating all three of these formations could be sources of water injected for disposal at the 18G area (Fig 11C). The earliest samples collected from 284WS-13B and 84WS-13B have Cl and B concentrations that plot closer to the Etchegoin and San Joaquin Formation hypothetical mixing lines whereas the last samples plot closer to the Monterey Formation hypothetical mixing line (Fig 11C). The trend toward mixing with Monterey Formation water indicates injected water in 18G area disposal wells either is sourced mostly from the Monterey Formation or contained a greater proportion of Monterey Formation water through time. The southernmost extent of injected disposal water migration is currently unknown; resistivity anomalies have been recorded in logs for six of the southernmost wells inside Elk Hills Oil Field (Fig J in S1 Text) [36], and neither resistivity log nor water-quality data are available southward of those six wells. The approximately 10-kilometer distance between the 18G area and the valley aquifer system to the east contrasts findings farther north in the San Joaquin Valley where effects of produced water disposal practices on groundwater quality have been identified closer in proximity [10, 20, 27, 28].

5. Conclusions

In this study, we presented water-quality data from newly collected and historical samples to investigate if oil and gas development activities have affected groundwater quality near and overlying the Elk Hills and North Coles Levee Oil Fields. RMP samples collected from 34 wells showed little evidence of thermogenic gases or hydrocarbon VOCs based on noble gas concentrations and trace concentrations of methane and BTEX, indicating little or no migration into sampled wells from natural processes or leakage from oil and gas wells. Trace methane concentrations (RMP maximum 0.13 mg/L) likely resulted from methanogenesis occurring in thin clay layers of the aquifer. The low methane concentrations may in part be explained by capacity to attenuate CH_4 in the upper Tulare Aquifer based on redox processes and high SO_4 concentrations in Mixed and Western Group groundwaters. Stable isotope and major ion compositions were consistent with Eastern Group waters predominantly sourced from Kern River water recharged through the Kern River alluvial fan, and Western Group waters predominantly sourced from infiltration of precipitation through marine sediments of the Coast Ranges. Groundwater salinity in the study area is largely influenced by mixing between Eastern Group fresh water and Western Group brackish water. These results indicated that groundwater in most parts of the study area has not mixed with detectable amounts of thermogenic gas or saline water from oil and gas sources.

Groundwater in one part of the study area had evidence of mixing with produced water injected for disposal. Increasing Cl and B concentrations in two 18G area industrial supply wells indicated groundwater mixing with progressively larger fractions of produced water injected for disposal in the upper Tulare Formation. Samples from the industrial supply wells contained up to 15% oil-field water according to mixing calculation estimates. This finding was consistent with previous work indicating the injected disposal water has migrated southward through the upper Tulare Formation [36]. The extent of southward migration has not been fully evaluated because of a lack of data south of the industrial supply wells. Groundwater in the vicinity of the 18G area generally has poor water quality and one reason for the lack of data is the limited number of wells available to sample because few wells have been installed for water supply or monitoring purposes in this area. In addition, the hydraulic properties and extent of saturated sands possibly connecting the upper Tulare Formation in the 18G area to the valley aquifer system about 10 kilometers eastward are not well characterized. New information filling these data gaps could help determine the extent of migration and evaluate if higher quality groundwater in the valley aquifer system could eventually be affected and, if so, on what time scale. Future studies aimed at addressing the data gaps could include groundwater monitoring south and southeast of the industrial supply wells and variable density groundwater flow modeling to account for the density differences between brackish groundwater and saline injected water.

Shallow groundwater in a different part of the study area had evidence of possible residual effects resulting from legacy surface disposal practices, but additional lines of evidence would be helpful for confirming the interpretation. Alternatively, the data could be explained, or partly explained, by natural wetting and drying cycles associated with closed basin lakes. Elevated concentrations of Cl, B, and SO_4 were measured in samples from shallow monitoring wells (median depth 11 meters) near the western margin of Buena Vista Lake Bed, about 2,800 meters downgradient of a catch basin (i.e., an unlined sump) on Buena Vista Creek that historically received produced water disposed of in ephemeral drainages. RMP samples E7 and E8 had Cl/Br and Cl/I ratios much higher than ratios in disposal sump water suggesting the samples were affected by evaporative concentration rather than infiltration of saline oil-field water. However, some historical samples had elevated NO_3 in combination with Cl, B, Ca, and SO_4 concentrations consistent with concentrations expected from infiltration of disposal sump water and dissolution of gypsum in the shallow subsurface, suggesting the samples could contain large fractions of produced water historically discharged to ephemeral drainages for disposal. Both explanations provide working hypotheses. Additional studies, including airborne electromagnetic surveys to investigate shallow groundwater salinity distributions or groundwater monitoring nearer legacy surface disposal features, could provide additional lines of evidence in support of one or both explanations for the elevated Cl, B, and SO_4 concentrations. This study showed that assessments of produced water management practices—including locations, volumes, and methods of disposal throughout the life of oil fields—can inform interpretations of mixing between groundwater and oil-field fluids by identifying oil field practices posing the greatest potential risk of groundwater-quality degradation.

Supporting information

S1 File. Animation showing water table elevation maps from 1990 to 2021. The maps were created using a combination of (1) water table elevations interpreted from borehole geophysical logs collected at oil and gas well drill sites and (2) groundwater level measurements in water wells. Water table maps were generated following previous methods [36, 56], with data available from Stephens et al. [57]. Groundwater level measurements are referenced to the North American Vertical Datum of 1988 (NAVD88).
(MP4)

S2 File. Animation showing water table elevation uncertainty maps from 1990 to 2021. The method used to generate water table elevation maps estimated the one standard deviation

(sigma, 1σ) uncertainty in water table elevations at each location. The uncertainty maps can be compared with the water table elevation maps to identify areas have lower or higher uncertainty in water table elevations. Areas with higher uncertainty had fewer measurements either spatially or temporally or both. Water table uncertainty maps were generated following previous methods [36, 56], with data available from Stephens et al. [57].
(MP4)

S1 Text.
(PDF)

S1 Table. Summary of regional monitoring program (RMP) and historical water quality data sets.
(XLSX)

S2 Table. Analyses used to assess the potential risks of oil and gas activities on groundwater-quality degradation.
(XLSX)

S3 Table. Site information for regional monitoring program (RMP) sites and selected sites identified in manuscript.
(XLSX)

S4 Table. Analytical methods for regional monitoring program (RMP) samples collected near and overlying Elk Hills and North Coles Levee Oil Fields, July 2017 to March 2018.
(XLSX)

S5 Table. Number of samples, median values of selected constituents, and major water types by geochemical groups.
(XLSX)

S6 Table. Selected chemical data for regional monitoring program (RMP) samples.
(XLSX)

S7 Table. Methane, light hydrocarbon, and BTEX detections in regional monitoring program (RMP) samples.
(XLSX)

S8 Table. Methane and BTEX detections in SB4 semi-annual monitoring samples collected in the study area.
(XLSX)

S9 Table. Oil and gas activity within 500 meters of wells sampled by the regional monitoring program (RMP).
(XLSX)

S10 Table. Mud logs inside north coles levee oil field with shallowest depths of C1, C2, C3+, and oil shows.
(XLSX)

S11 Table. Well integrity data for oil and gas wells having well integrity issues documented in well records.
(XLSX)

S12 Table. Statistical summaries and water quality trend analyses for samples from 18G area wells.
(XLSX)

S13 Table. Kruskal-wallis test results.
(XLSX)

S14 Table. Dunn's multiple pairwise comparison test p values.
(XLSX)

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