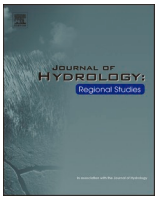
Journal of Hydrology: Regional Studies 41 (2022) 101065

Contents lists available at ScienceDirect

Journal of Hydrology: Regional Studies

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



Occurrence of water and thermogenic gas from oil-bearing formations in groundwater near the Orcutt Oil Field, California, USA

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ARTICLE INFO

Keywords:
Groundwater quality near oil fields
Salinity tracers
Thermogenic hydrocarbon gas
Multiple lines of evidence

ABSTRACT

Study region: Santa Barbara County, California, USA.
Study focus: To analyze a wide array of newly collected chemical, isotopic, dissolved gas, and age dating tracers in conjunction with historical data from groundwater and oil wells to determine if water and/or thermogenic gas from oil-bearing formations have mixed with groundwater in the Orcutt Oil Field and surrounding area.
New hydrological insights for the region: Three of 15 groundwater samples had compositions indicating potential mixing with water and/or thermogenic gas from oil-bearing formations. Relevant indicators included salinity tracers (TDS, Cl, Br), NH_3, DOC, enriched δ^{13}C-DIC, δ^{2}H-CH_4, δ^{13}C-CH_4, and δ^{13}C-C_2H_6 values, and trace amounts of C3-C5 gas. The potential sources/pathways for oil-bearing formation water and/or thermogenic gas in groundwater overlying and adjacent to the Orcutt Oil Field include: (1) upward movement from formations developed for oil production due to: (a) natural migration; or (b) anthropogenic activity such as injection and/or movement along wellbores; and (2) oil and gas shows in overlying non-producing oil-bearing formations. Groundwater age tracers, elevated ^{4}He concentrations, and isotopic compositions of noble gases indicated legacy produced water ponds were not a source. This phase of the study relied on samples and data from existing infrastructure. Additional data on potential end-member compositions from new and existing wells and assessments of potential vertical head gradients and pathways between oil and groundwater zones may yield additional insight.

1. Introduction

Efforts to assess the potential effects on groundwater quality from gas and water associated with hydrocarbon production activities have increased with recent oil and gas drilling activities throughout the United States (Brantley et al., 2014; Vengosh et al., 2014; DiGiulio and Jackson, 2016). The degradation of shallow groundwater quality from saline water derived from oil and gas production activities has been the focus of some studies (Warner et al., 2012, 2013; McMahon et al., 2015). Groundwater quality may also be affected by natural sources of saline water and hydrocarbon gas from oil and gas shows in aquifer sediments overlying the hydrocarbon

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https://doi.org/10.1016/j.ejrh.2022.101065
Received 5 April 2021; Received in revised form 22 December 2021; Accepted 21 March 2022
Available online 11 April 2022

production zone (Warner et al., 2012; Flewelling and Sharma, 2014; Siegel et al., 2015a, 2015b; Engle et al., 2016; Harkness et al., 2017).

Many studies have focused on determining the sources of methane, and other hydrocarbon gases, observed in shallow groundwater in areas of oil and gas production (Osborn and McIntosh, 2010; Hunt et al., 2012; Jackson et al., 2013a; Molofsky et al., 2013; Sherwood et al., 2016a and 2016b; Woda et al., 2018). Microbial or biogenic gas, which is almost entirely composed of methane (> 99 mol%) although minor amounts of microbial ethane (< 0.1 mol%) have been detected in some settings (Taylor et al., 2000), is produced by methanogenic microorganisms in anoxic environments at relatively low temperatures in aquifers using three main substrates: acetate, CO_2, and substances containing a methyl group (Coleman et al., 1988; Aravena et al., 1995; Darling and Gooddy, 2006; Schloemer et al., 2016; McMahon et al., 2017a; Lackner et al., 2018). Alternatively, some groundwater in aquifer systems near active oil and gas development activities can also contain methane and heavier hydrocarbon gases from the underlying oil-bearing formations or associated geologic natural gas shows accumulating in overlying aquifers (Jackson et al., 2013a; Darrah et al., 2014; McMahon et al., 2018b; Wen et al., 2018; Kreuzer et al., 2018). Hydrocarbon gases in many of those oil-bearing formations are produced by abiotic processes at relatively high temperatures (thermogenic gas) and are enriched in heavier hydrocarbon gases (ethane, propane, butane, and pentane) compared to microbial gas (Schoell, 1980; Whiticar, 1999). Although produced at depth, thermogenic methane can migrate into shallow aquifers through advection by deeply circulating groundwater and as the result of diffusion (from high to low concentration) (Baldassare et al., 2014; Moritz et al., 2015). Oxidation-reduction condition indicators, abundances of methane and higher chain hydrocarbons, hydrogen (H) and carbon (C) stable isotopes in methane (δ^2H-CH_4, δ^{13}C-CH_4), C stable isotopes in dissolved inorganic carbon (δ^{13}C-DIC), and other geochemical tracers have been used to differentiate between microbial and thermogenic gas in shallow groundwater (Coleman et al., 1988; Aravena et al., 1995; Jackson et al., 2013b; Darrah et al., 2014; Wright et al., 2019; McMahon et al., 2019).

Other recent studies have examined aspects of the quality of groundwater near some oil field areas in California (Kang and Jackson, 2016; McMahon et al., 2017b, 2019; Kulongoski et al., 2018; Wright et al., 2019; Gillespie et al., 2019; Rosecrans et al., 2021), while others have characterized the chemistry of produced water or casing gas from oil fields (McMahon et al., 2018a; Tyne et al., 2021). For example, the study of the Fruitvale Oil Field near Bakersfield determined that groundwater quality was primarily influenced by high rates of recharge from the Kern River, with only trace detections of water and thermogenic gas from oil-bearing formations (potentially including that from producing and non-producing oil-bearing formations) in a few wells (Wright et al., 2019). In the study of the Oxnard Oil Field in Ventura County, an oil and gas production area not dominated by high regional, freshwater recharge, the highest concentrations of thermogenic gas in groundwater were observed in proximity to relatively high density of oil wells, large injection volumes of water disposal and cyclic steam, shallow oil development, and hydrocarbon shows in sediments overlying the producing oil reservoirs (Rosecrans et al., 2021).

The California State Water Resources Control Board (State Water Board) has implemented a regional groundwater-monitoring program in cooperation with the U.S. Geological Survey (USGS) to address concerns about groundwater quality in regions of oil and gas development activities. The Oil and Gas Regional Monitoring Program (RMP) was authorized by California Senate Bill 4 (SB 4 statutes of 2013) and includes assessment of potential impacts to groundwater quality associated with well stimulation (hydraulic fracturing), enhanced recovery injection (water and steam flooding) and production in oil-producing formations, and produced-water disposal in injection wells and surface ponds (California State Water Resources Control Board, 2019). The RMP is designed to: (1) assess the location of groundwater resources with < 10,000 mg/L total dissolved solids in proximity to oil and gas fields; (2) assess evidence for the presence/absence of water and/or thermogenic gas from oil-bearing formations mixed with groundwater, and if present, identify potential pathways or processes that may be responsible; and (3) determine how oil and gas sources have affected groundwater quality relative to other processes (U.S. Geological Survey, 2019b; California State Water Resources Control Board, 2019). The Orcutt Oil Field, located in Santa Barbara County, California, and one of several oil fields in the onshore Santa Maria Basin, is the first oil field in this basin to be studied as part of the RMP. The Orcutt Oil Field has a longer history of oil field development then most other oil fields in California (California Department of Conservation, 1992), beginning in 1901 after the discovery of surface occurrences of hydrocarbons from petroleum saturated fissures and exposed oil-bearing sands and shales in upland areas of the field. Early conventional development was followed by more than a half-century of use of enhanced recovery practices including injection of water and steam (California Department of Conservation, 1992). Furthermore, groundwater resources used intensively for drinking water and irrigation are located in the adjacent San Antonio Creek and Santa Maria River Valleys and not directly overlying the oil field as has been the case in other recently studied oil field settings (Wright et al., 2019; Rosecrans et al., 2021). The combination of naturally occurring shallow oil and gas resources and century long oil field development in lateral proximity to used groundwater resources makes this a relevant setting for evaluating relations of groundwater quality to oil and gas sources not previously studied as part of the RMP (Davis et al., 2018).

This study uses multiple lines of evidence including the local hydrogeologic setting, the geologic structure of the Santa Maria Basin, oil-field development and production/injection information, and geochemical end-member analyses to: (1) determine if water and thermogenic gas from oil-bearing formations occur in groundwater overlying and adjacent to the Orcutt Oil Field; and (2) explore possible pathways for these occurrences. To achieve these goals a wide array of newly collected chemical, isotopic, dissolved gas and age dating tracers, and historical water chemistry data, from groundwater and oil wells were analyzed in conjunction with potential explanatory factors. A conceptual schematic of the oil and gas terminology (fig. S1) and glossary used in this work is provided in the Supplementary Information.

2. Materials and Methods

2.1. Study area description

The study area boundary is a 5-kilometer (km) buffer around the administrative boundary of the Orcutt Oil Field, which is located in the Solomon Hills south of the unincorporated town of Orcutt in Santa Barbara County (Fig. 1). The Orcutt Oil Field is approximately bounded by the foothills of California's south Coast Ranges to the east and west, the trough of the Santa Maria Valley to the north and the San Antonio Creek Valley to the south. The region has a Mediterranean climate, with cool and rainy winters, and dry summers during which the heat is greatly diminished by fog and northwesterly winds from the cold water of the Pacific Ocean, which is about 24 km west of the field. Average annual precipitation ranges from 33 to 48 centimeters (cm), with a typical rainy season lasting from around November to April (California Department of Water Resources, 2003).

Regional groundwater flow in the study area is generally westward toward the Pacific Ocean (California DWR, 2003). Contours of the elevation of the water table indicate groundwater flows to the southwest into the San Antonio Creek Valley groundwater basin (Hutchinson, 1980) and northwest into the Santa Maria River Valley groundwater basin (Hughes, 1977) from the oil field, which straddles the two groundwater basins (fig. S2). Previous water-quality studies have noted irrigation return flow, upward migration of deep groundwater, natural-occurring water-rock interaction, lateral seepage from the surrounding outcrops of marine rocks, and point sources of discharge of wastewater from oil refineries and domestic wastewater-treatment facilities in the City of Santa Maria can affect groundwater salinity in the region, although not all of these sources occur within 5 km of the Orcutt Oil Field (Worts, 1951; Muir, 1964; Hughes, 1977; Hutchinson, 1980). A more detailed description of the hydrogeologic setting is provided in the Supplementary Information.

2.2. Orcutt Oil Field

The Orcutt Oil Field, with an area of almost 44.5 km^2, is one of several oil fields in the onshore Santa Maria Basin. Discovered in 1901, the proven productive area of the Orcutt Oil Field is approximately 17.1 km^2, or 38.4% of the total area (California Department of Conservation, 1992). Although the area of the Orcutt Oil Field is relatively small, it represents a setting with intensive oil and gas development in upland areas adjacent to downslope groundwater aquifers used for drinking and irrigation supply that is common in

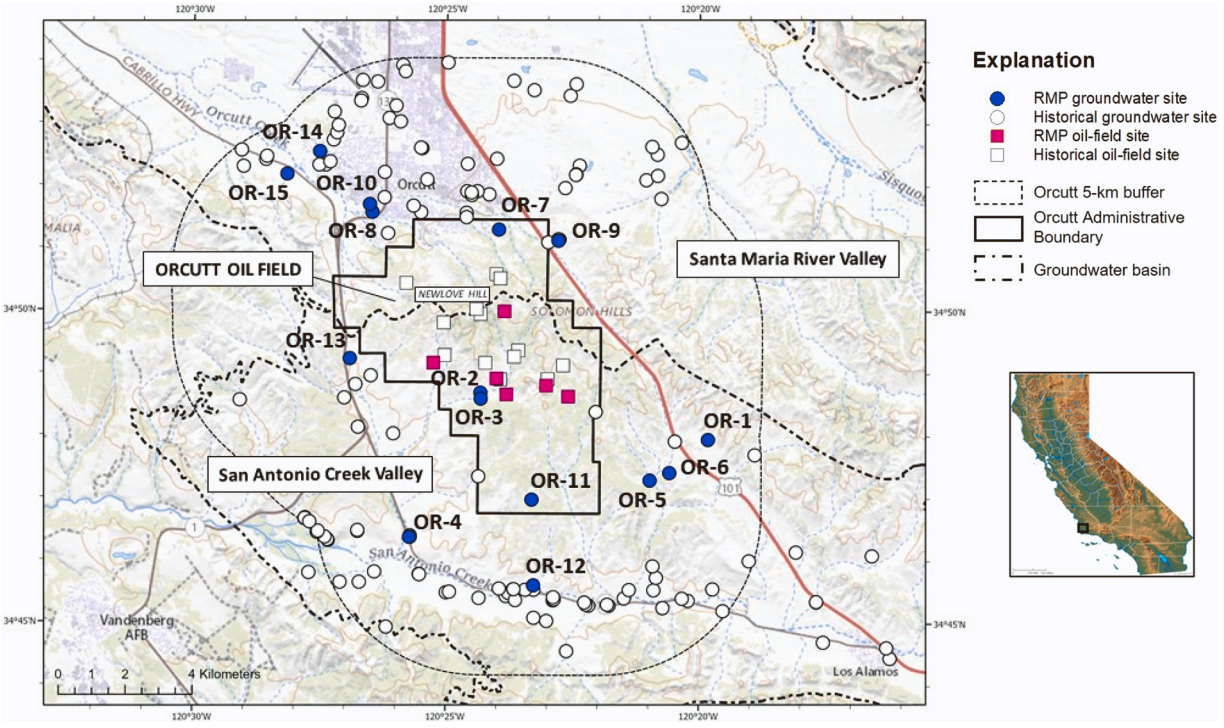

Fig. 1. (a) Study area map showing Oil and Gas Regional Monitoring Program (RMP) groundwater sites (blue circles); historical groundwater sites (open circles); RMP oil-field sites (purple squares); historical oil-field sites (open squares) in the San Antonio Creek and Santa Maria River Valley groundwater basins (California Department of Water Resources, 2003) where water chemistry data have been collected. (b) Also shown are the Orcutt Oil Field administrative boundary and the 5-km buffer around the administrative boundary (California Department of Conservation, 2017; U.S. Geological Survey 2018b; U.S. Geological Survey 2020). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

many other coastal and inland groundwater basins of California (Davis et al., 2018; Planert and Williams, 1995), and other tectonically active areas of the world (Schenk et al., 2012), where oil fields often occur in uplands adjacent to basin aquifers. The stratigraphy of the Santa Maria Basin in the area of the Orcutt Oil Field is composed of lower Miocene and younger Tertiary formations through Quaternary sedimentary rocks that lie above the regional unconformity associated with the late Eocene to early Oligocene Ynezian orogeny (Namson and Davis, 1990; Sweetkind et al., 2010) (fig. S3). A more detailed description of the stratigraphy of the Santa Maria Basin is provided in the Supplementary Information.

The Monterey Formation, rich in organic matter, is the principal source of oil in the Santa Maria Basin with most production from depths between 600 and 1200 m (Isaacs and Rullkötter, 2001). Petroleum traps within the Santa Maria Basin are of two major types:

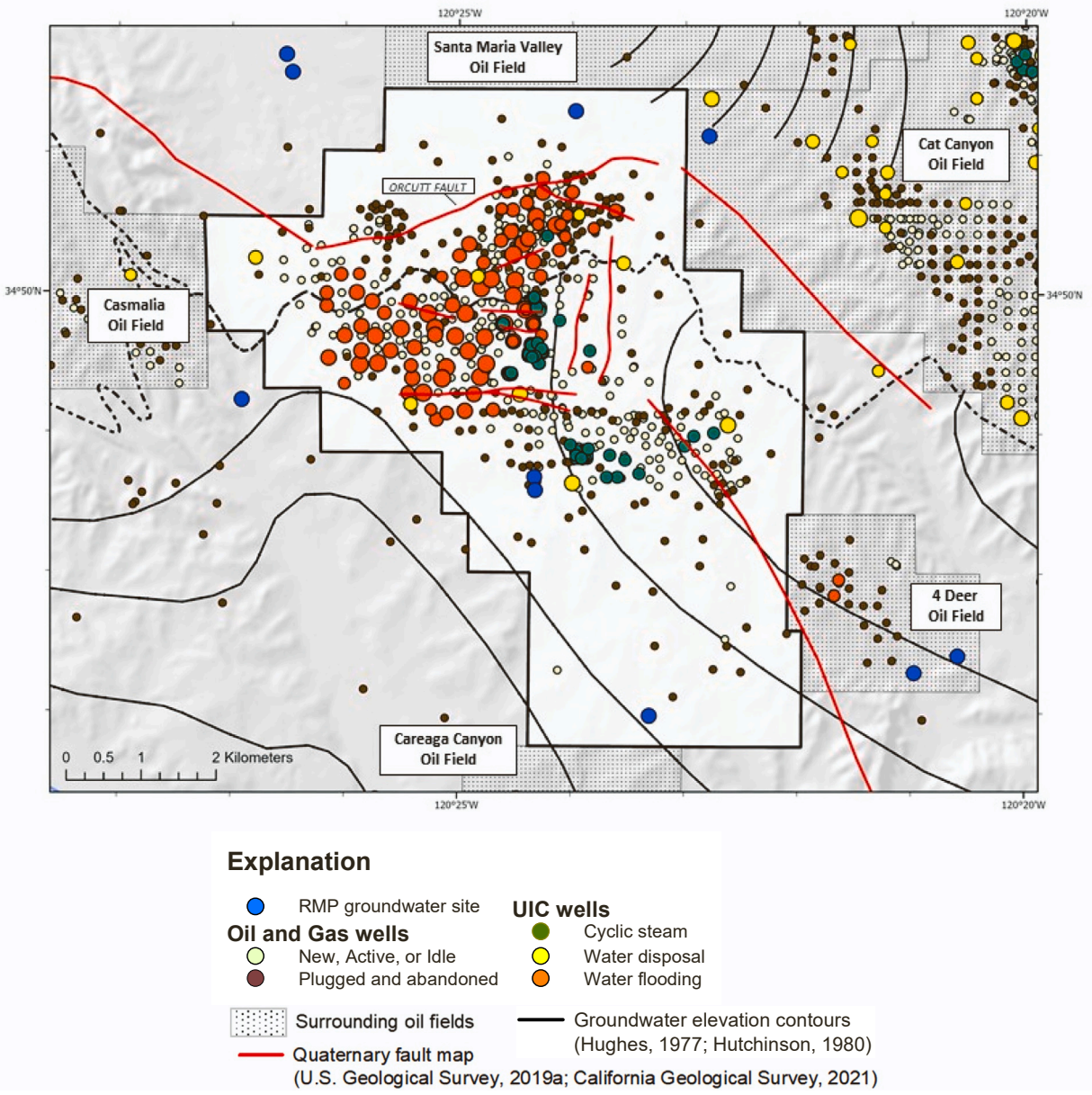

Fig. 2. Map showing the location of new, active, or idle (NAI) oil wells (light green circles), plugged and abandoned (PA) wells (brown circles), and underground injection control (UIC) wells in the Orcutt Oil Field and surrounding oil fields. UIC wells used for enhanced oil recovery (EOR) include cyclic steam (dark green circles), water flooding (orange circle) and water disposal (yellow circles) wells. Also shown are the locations of Oil and Gas Regional Monitoring Program (RMP) groundwater sites (blue circles), groundwater elevation contours for the San Antonio Creek Valley (Hutchinson, 1980) and Santa Maria River Valley (Hughes, 1977) groundwater basins, and mapped Quaternary faults (U.S. Geological Survey, 2019a; California Geological Survey, 2021). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

structural (anticlinal) and stratigraphic (overlap truncation or sandstone pitchout) (Isaacs, 1992). Oil in the Orcutt Oil Field is trapped in a faulted, asymmetrical anticline with a broad flat crest, gently dipping south limb, and steeply dipping or overturned north limb (Namson and Davis, 1990) (fig. S3). The north limb of the anticline is cut by the steeply dipping Orcutt fault, a reverse fault that offsets Miocene and lower Pliocene strata 600–1525 m from the crest of the anticline to the downthrown northern footwall (Fig. 2, S3).

In the Orcutt Oil Field, the Monterey Formation produces oil with low to moderate gravity whereas shallower pools have generally heavier oil (Isaacs and Rullkötter, 2001). Peak oil production occurred in 1908; production began to slow as early as the 1920s and waterflooding to enhance oil recovery began in 1951. Diatomite and SX zones of the Sisquoc Formation have been developed for oil production over approximately the last 15 years when the Diatomite cyclic steam pilot program provided the necessary information to determine the commercial viability of these oil deposits using thermal cyclic steam technology developed for similar formations in the San Joaquin Valley (California Department of Conservation, 1992; Pacific Coast Energy Company, 2017).

During 1977–2017, the cumulative production volumes for the Orcutt Oil Field were about 1060 MMbbl (10^6 barrels) of produced water and 38.1 MMbbl of oil (California Department of Conservation, 2020a). In this work, produced water is defined as water withdrawn from an oil well and brought to the surface and may include oil, water, and gas from the geologic formation and water and/or gas injected for enhanced recovery (see the glossary of terms provided in the Supplementary Information). Cumulative water injection volumes for enhanced oil recovery (EOR) between 1977 and 2017 were about 1004 MMbbl into the Monterey Formation, with smaller injection volumes (15.6 MMbbl) into the shallower Diatomite and SX units of the Sisquoc Formation (table S1). During the same 40-yr period, injection volumes for produced water disposal were about 68.3 MMbbl into the Monterey Formation and 1.3 MMbbl into the deeper Point Sal and Lospe Formations (table S1). Enhanced oil recovery in the Orcutt Oil Field has typically been accomplished by water flooding, although due to the increased use of cyclic steam injection, the shallower Diatomite and SX units have become more targeted zones for oil recovery where present (Fig. 2).

In 2016, the Orcutt Oil Field contained 455 new, active, or idle oil wells and 257 plugged and abandoned wells, mostly in the northern part of the field; SPUD or construction dates are available for 635 oil wells (Fig. 2, S4; California Department of Conservation, 2020a, b, c). The majority of wells in the oil field were installed before 1976 (62%), although recent activity targeting the shallower Diatomite and SX units in the Newlove Hill area has resulted in the recent construction of many more oil wells. In contrast, well plugging and abandonment saw little activity from about 1930 to the present-day suggesting oil wells constructed many years ago still exist in the oil field (fig. S4). State requirements for cementing wellbores during installation and abandoning oil wells have become more rigorous over time, including statewide regulations to protect useable groundwater in 1976 (California Department of Conservation, 2019). Although the timing of implementation of oil well construction practices to protect groundwater in the Orcutt Oil Field could differ from those statewide, the history of changes in well construction practices in this specific field was not apparent from available records. Therefore, 1976 was used as an approximate date for classifying oil wells into older and newer periods of construction (California Dept. of Conservation, 2019). Older wells may generally be more likely to have unsealed boreholes and/or leaky casings that have the potential to facilitate the movement of water and gas between oil-bearing formations and overlying groundwater. Additional discussion on oil well construction activity in the Orcutt Oil Field is provided in the Supplementary Information.

2.2.1. Oil and gas shows

Surface outcrops or shallow oil sands and seeps, many of which are up dip or lie above some of the largest oil and gas fields in California, have been known for thousands of years (Heizer, 1940; Mulqueen, 2007). There are numerous occurrences of tar sands, asphalt dikes, oil-impregnated sandstone, surficial oil-sand deposits, and oil and thermogenic gas detected during drilling in shallow sediments (oil and gas shows) in the Sisquoc and Careaga Formations in the area of the Orcutt Oil Field (Hein, 2013). Arnold and Anderson (1907) noted the presence of asphalt deposits across Graciosa Ridge as a surface indication for the presence of oil in appreciable quantities in the region. Although there is no recorded history of natural seepage in other areas of the Orcutt Oil Field, Newlove Hill (Fig. 1) has historically had many naturally occurring oil seeps (Leck, 1921); field operators observe 2–4 new seeps per year in this area (Marine Research Specialists, 2016). The presence of oil and gas shows in aquifer sediments overlying oil-producing zones at some locations in the study area may indicate that upward movement of oil, gas, and perhaps water from deep formations occurred in response to natural hydrocarbon migration over geologic time (Hornafius et al., 1999; Quigley et al., 1999; Leifer, 2010). Oil seeps, releases of crude oil formed by low energy, non-eruptive leakages of oil and gas to the ground surface from accumulations in the Sisquoc and Careaga Formations, can result from either natural occurring forces (plate tectonics) or the heating, cooling and imbalance of injection fluids into the shallow Diatomite unit of the Sisquoc Formation (Pacific Coast Energy Company, 2017). Additional description of oil and gas shows is provided in the Supplementary Information.

Mud logs allow for the identification of oil shows, or detections, and concentration measurements (ppm) of light hydrocarbon gas (methane through pentane) during the drilling process and are reported as vertical profiles of observations with depth for selected oil wells and depth intervals. Analysis of 33 available mud logs from oil wells indicate oil and gas shows occur in sediments in some areas overlying producing zones where commercial oil extraction occurs in the Orcutt Oil Field (see Section 2.3.2).

2.3. Compilation of existing data

During 2017–2019, the USGS compiled and analyzed information for the Orcutt Oil Field and surrounding area. The information included available groundwater and produced water chemistry data, water and oil well construction and geophysical records, oil field development history and injection data, and hydrogeologic information such as regional groundwater flow directions. Oil companies were invited to share relevant information for inclusion in the study; USGS scientists also consulted with California Geologic Energy Management Division (CalGEM) staff familiar with the oil field. The goal of these compilation efforts and consultations was to obtain

the most complete record of information possible.

2.3.1. Historical water chemistry data

Water chemistry data were compiled for a limited available set of analytes from 27 groundwater sites sampled in 2017 for a study investigating water availability in the San Antonio Creek Valley groundwater basin (U.S. Geological Survey, 2020) and 121 sites with groundwater data collected between 1927 and 2016, and are referred to as historical groundwater chemistry data, hereinafter (Fig. 1). The historical groundwater chemistry data came from the USGS National Water Information System (U.S. Geological Survey, 2018a), the California State Water Resources Control Board Division of Drinking Water Database (California State Water Resources Control Board, 2018), and the California Department of Water Resources (California Department of Water Resources, 2018). Historical produced water chemistry data for inorganic constituents from a compilation of available oil-field water sample data from 1971 to 2016 (median date 1993) were used in the analysis (Blondes et al., 2018; Metzger and Herrera, 2020).

2.3.2. Attribution of wells with potential explanatory factors

Data were compiled for three major categories of potential explanatory factors: (1) oil field development density and proximity, (2) hydrogeologic variables, and (3) presumed natural geologic distribution of oil and gas shows (observations) in the subsurface from available oil well mud logs. The 15 groundwater wells sampled for the RMP (see Section 2.4) were attributed with potential oil development explanatory factors assembled from available information. Potential explanatory factors representing oil field development density and proximity describe the distance and characteristics of the nearest oil well and the number, status, type, year drilled, and the 1977–2017 vol of oil and water produced and water injected for enhanced recovery and produced water disposal for oil wells within a 500-m radius (table S2). Also attributed were oil well cement seals and plugs, potential well integrity issues (casing damage or collapse, leaks, and surface expressions), and reported depth to base of freshwater within 500 m of sampled water wells (table S3). The data were extracted from well reports and databases available from the California Department of Conservation (2020a, b). The 500-m radius was selected to provide a consistent basis for comparing the relative abundance of various factors in proximity to sampled wells and has been previously used in studies of regional groundwater quality (Johnson and Belitz, 2009), although the actual radius around a sampled well in which potential sources could influence groundwater quality is unknown and could vary by site. The data available for direct comparison of water chemistry and potential oil development variables were limited because only 2 of the 15 wells sampled (OR-2, −3) were located within the oil field boundary and in proximity to active oil development; 5 sampled water wells had 15 oil wells located within the 500-m radius (fig. S5; table S3). Away from the limited locations with groundwater sample data within the Orcutt Oil Field, the spatial distribution of factors that have the potential to affect risk to groundwater are discussed generally based on the distribution of oil wells, well ages, and injection volumes.

Hydrogeologic variables evaluated included the conceptual position of sampled wells along regional groundwater flow directions based on the regional groundwater elevation contours in the San Antonio Creek Valley and Santa Maria River Valley groundwater basins (fig. S2), well perforation depths, and well type (see Section 2.4).

The distribution of oil shows and light hydrocarbon gas with depth in the aquifers overlying the oil production zones was compiled from 33 available mud logs located within the Orcutt Oil Field boundary (California Department of Conservation, 2020b). Mud logging, also known as hydrocarbon well logging, entails gathering qualitative and semi-quantitative data from hydrocarbon gas detectors that record the level of natural gas brought up in the drilling mud combined with oil-field gas chromatograph instruments that determine the individual gas components—most commonly methane, ethane, propane, butane, and pentane (Crain, 2010). The recorded concentration of gas in mud logs do not represent the actual quantity of oil or gas in the sediments (Crain, 2010) but rather the gas detected in the drilling mud with respect to depth. Oil shows as a percent of mud log cuttings are determined by hydrocarbon fluorescence, a method in which hydrocarbons in cuttings are examined under ultraviolet light with a reagent that can indicate the presence of oil (Swanson, 1981). In this work, a list of mud logs in the Orcutt Oil Field (table S6) and recorded occurrence of the shallowest C3-C5 hydrocarbon gas and oil show were used to evaluate the presence or absence of light hydrocarbons and depths for which the hydrocarbon gas were observed relative to first appearance of trace amounts of oil (oil shows). Relations of water chemistry to these factors and potential shallow geologic sources of hydrocarbons indicated by mud logs are discussed later in this manuscript.

2.4. Well selection procedure and type of wells sampled

Wells were selected for sampling for this study by using a geochemical end-member mixing approach based on the following criteria: (1) areal and vertical position overlying and adjacent to the oil field, including locations with shallow and deep well pairs; (2) proximity to current and historical oil production activities within a 500-m radius; and (3) filling gaps in historical water-quality data.

The compilation of existing data, in combination with contacting local water purveyors and field canvassing, identified 15 wells available for sampling that satisfied at least part of the selection criteria for the RMP (table S5; Fig. 1). These 15 groundwater wells were sampled in the fall of 2017 through the spring of 2018 (McCarlson et al., 2021). The wells sampled included nine domestic, four irrigation, and two monitoring wells which covered a broad range of depths (total well depths 56–299 m) and settings (wells located in areas of dense oil development to agricultural areas surrounding the oil field) (table S5). One other well (OR-16) sampled as part of the RMP was later determined to be a cathodic protection well; the sample obtained from this well was not considered representative of actual groundwater conditions in the area and the data were rejected for use in the study.

In addition to data from water wells, five oil wells and one injectate tank containing recycled produced water used for injection into the Orcutt Oil Field were sampled in the spring of 2018 (Fig. 1; Seitz et al., 2021).

2.5. Sample collection and analysis

Detailed protocols for groundwater samples collected by the USGS for the RMP are described by Dillon et al. (2016) following protocols established by the USGS National Water Quality Assessment (NAWQA) program (Koterba et al., 1995) and the USGS National Field Manual (U.S. Geological Survey, variously dated); only a brief description is given here. These sampling protocols were followed so that representative samples of groundwater are collected at each site, and the samples are collected and handled in ways to minimize the potential for introduction of target analytes during the sampling process. Samples of produced water were collected at the well head of oil wells and injectate sites by using methods described by McMahon et al. (2018a).

Groundwater and produced water samples collected for the RMP were analyzed for a wide array of dissolved organic, inorganic, and gas constituents, water and solute isotopes, and age tracers based on the results from the RMP exploratory study conducted in 2014 and 2015 (Dillon et al., 2016; McMahon et al., 2017b). The complete list of analytical methods and references used in evaluation of RMP groundwater wells sampled in the area of the Orcutt Oil Field from September 2017 to March 2018 are provided in table S6. For the produced-water data presented in this report, methods for field processing of samples and laboratory analyses were similar to those used for groundwater samples, except that major ions and trace elements in produced water were analyzed by the USGS Biogeochemical Processes in Groundwater Laboratory in Reston, Virginia, rather than the USGS National Water Quality Laboratory in Lakewood, Colorado. A discussion of quality control (QC) data collected for this study are reported in McCarlson et al. (2021) and Seitz et al. (2021). Additional description of sample collection and analysis is provided in the Supplementary Information.

3. Results and Discussion

3.1. Spatial distribution of groundwater chemistry

3.1.1. Salinity tracers (TDS, Cl, Br), NH_3 and DOC

Measured concentrations of total dissolved solids (TDS), bromide (Br) and their ratios relative to chloride (Cl) concentrations, along

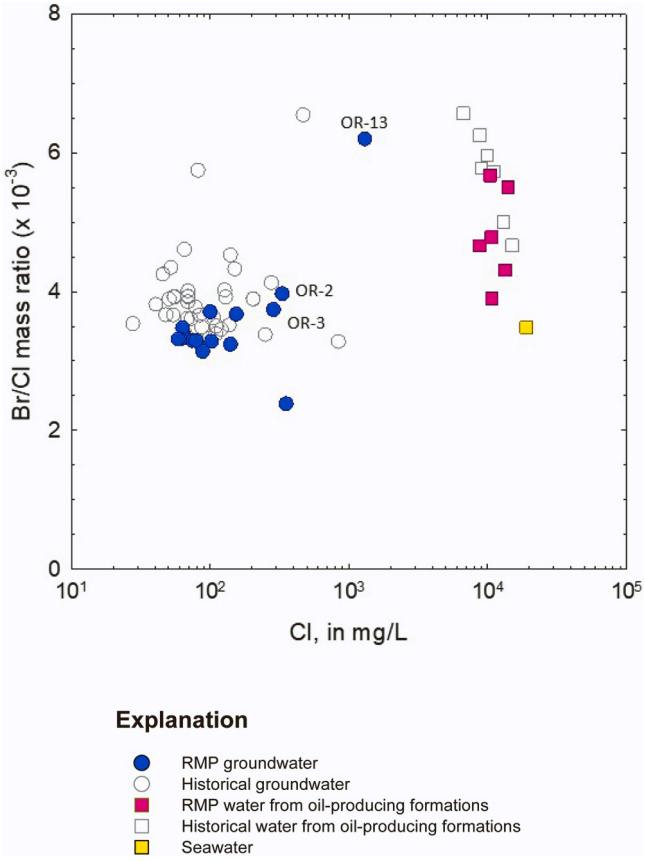

Fig. 3. Br/Cl mass ratio versus Cl plot for Oil and Gas Regional Monitoring Program (RMP) groundwater samples (blue circles); historical groundwater samples (open circles); RMP samples of water from oil-producing formations (purple squares); historical samples of water from oil-producing formations (open squares); seawater (yellow square). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with total ammonia (NH_3) and dissolved organic carbon (DOC), for some groundwater samples collected as part of the RMP (OR-2, −3, −13) are consistent with being mixtures of native groundwater and a smaller fraction of water similar in composition to that from oil-producing formations. However, variability in results between the different salinity tracers for some samples suggests the possibility of more complex mixtures of different sources of oil-field water (Collins, 1975) or a naturally brackish source.

Groundwater samples with TDS concentrations of between 1000 and 3000 mg/L occur within the boundary of the Orcutt Oil Field in relative proximity to historical dense oil development, within the San Antonio Creek Valley groundwater basin to the southwest and to the south along San Antonio Creek and in some agricultural areas surrounding the oil field compared with most groundwater in the study area having TDS < 1000 mg/L (fig. S6). Historical produced water chemistry data indicate water from oil-producing formations had TDS concentrations of 4000 to 82,400 mg/L (median = 19,900 mg/L) (fig. S7). Values of TDS in groundwater overlying (OR-2, −3) and adjacent (OR-13) to the oil field may be consistent with some amount of mixing with water from oil-producing formations, although there are other water sources that could produce similar compositions.

Ratios of Br/Cl for RMP groundwater samples range from 2.4×10^{-3} to 6.2×10^{-3} (median = 3.3×10^{-3}) (Fig. 3). Ratios of Br/Cl in groundwater close to the seawater value of 3.48×10^{-3} (Davis et al., 1998), or only slightly elevated, reflect Cl and Br derived from local precipitation originating from the nearby ocean and not from the redissolution of evaporative salts preferentially enriched in Cl relative to the slightly more soluble Br (Jones et al., 1999). For RMP water samples from oil-producing formations, Br/Cl ratios range from 3.9×10^{-3} to 5.7×10^{-3} (median = 4.7×10^{-3}). Br/Cl ratio for OR-13 (6.2×10^{-3}), located adjacent to the oil field, appears to be enriched in Br and Cl and suggest these values could be derived from mixing of oil-bearing formation water with native groundwater (Fig. 3), although Br/Cl ratios greater than seawater also have been associated with other sources such as landfills in some settings (Mullaney et al., 2009). Intermediate Br/Cl ratios for OR-2 (4.0×10^{-3}) and OR-3 (3.7×10^{-3}) suggest water from oil-bearing formations could be a source of Br to groundwater overlying the oil field, although the variability of Br/Cl ratios of oil-bearing formations means that Br/Cl ratios are not conclusive (Fig. 3).

The highest NH_3 concentration of 28 mg/L as N was in RMP groundwater sample OR-13, located adjacent to the oil field; concentrations of NH_3 in the remaining RMP groundwater samples ranged from < 0.01–1.06 mg/L as N (Fig. 4). DOC concentrations in groundwater collected as part of the RMP ranged from 0.14 to 4.4 mg/L. The highest DOC concentrations were measured in groundwater samples adjacent to (OR-13) and overlying (OR-2, −3) the oil field whereas groundwater samples away from the oil field

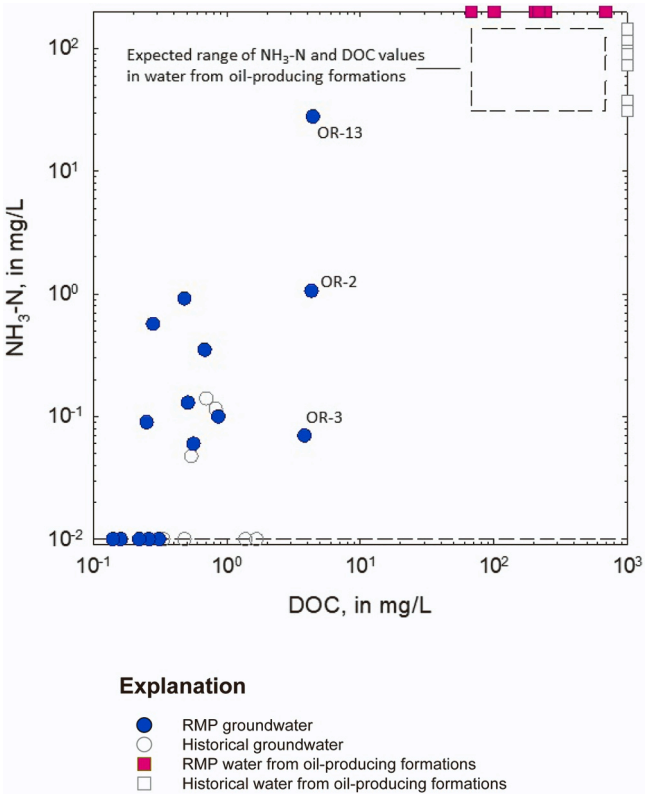

Fig. 4. NH_3-N versus DOC plot for Oil and Gas Regional Monitoring Program (RMP) groundwater (blue circles) and historical groundwater (open circles) samples; DOC concentrations for RMP samples of water from oil-producing formations (purple squares); NH_3-N concentrations were measured for the RMP samples of water from oil-producing formations; NH_3-N concentrations for historical samples of water from oil-producing formations are shown (open squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

had DOC concentrations < 1.0 mg/L (Fig. 4). Possible explanations for the high NH_3 and DOC concentration in these groundwater samples (OR-2, −3, −13) could be N-bearing matter in the reducing environment provided by aquifer sediments with appreciable organic matter (Harkness et al., 2014) and/or mixing between groundwater and small amounts of oil-bearing formation waters with much higher NH_3 and DOC concentrations. It is implausible that the high NH_3 and DOC concentration at OR-13 could be from reduction of NO_3 in irrigation water (recharge) by interaction with organic matter because the groundwater is too old to contain modern recharge (see next section).

Additional constituents including major-ion chemistry, additional salinity tracers including iodide (I), stable isotopes of water (δ^2H and $\delta^{18}O$), and volatile organic compounds (VOCs) were evaluated but did not show consistent evidence of mixing of substantial quantities of water from oil-producing formations in groundwater; these results are discussed in the Supplementary Information.

3.1.2. *Apparent groundwater ages*

The range of tritium (^3H) and carbon-14 (^{14}C) age tracer values indicates that 12 of the 15 RMP groundwater samples were pre-modern (recharged prior to 1953), similar to results in historical data collected from the study area (see Supplementary Information, fig. S11). Tritium was detected at 0.2 tritium units (TU) in three samples (OR-4, −5, −6) indicating traces of groundwater recharged after 1953 mixed with water containing premodern ^{14}C values (^{14}C < 75% modern carbon (pmC)). Sites OR-2, − 3, and − 13 all had premodern-aged groundwater; OR-13 appears to have some of the oldest groundwater in the study area with an uncorrected ^{14}C activity of 2.8 pmC.

The older apparent groundwater ages are also the groundwater samples with enriched $\delta^{13}C$-DIC (Fig. 5). For OR-12, the slightly enriched $\delta^{13}C$-DIC value may reflect the addition of DIC by the dissolution of calcite or dolomite along the groundwater flow path. In contrast, much greater enrichment of $\delta^{13}C$-DIC in OR-13 is more likely from input of older sedimentary organic carbon to the DIC via methanogenesis, mixing between groundwater and oil-bearing formation water with much heavier $\delta^{13}C$-DIC values, and/or degradation of organic carbon derived from oil-bearing formations (Fig. 5). A lack of $\delta^{13}C$ values for many of the carbon sources (e.g. organic matter, DIC in soil water and surface water, and calcite from the soils or aquifers) and the absence of a consistent relation between $\delta^{13}C$-DIC values and ^{14}C activities complicates any correction for ^{14}C radioactive decay to obtain a "true" groundwater age (in elapsed time since recharge (years)) and suggests quantitative interpretation of groundwater age based solely on ^{14}C would be problematic. However, a recent analysis of ^3H, ^4He, and ^{14}C data indicate the water from OR-3 and OR-13 could be > 1000 years old (McMahon et al., 2021). Additional discussion on the use of age tracer data (^3H, ^{14}C) to classify groundwater ages is presented in the

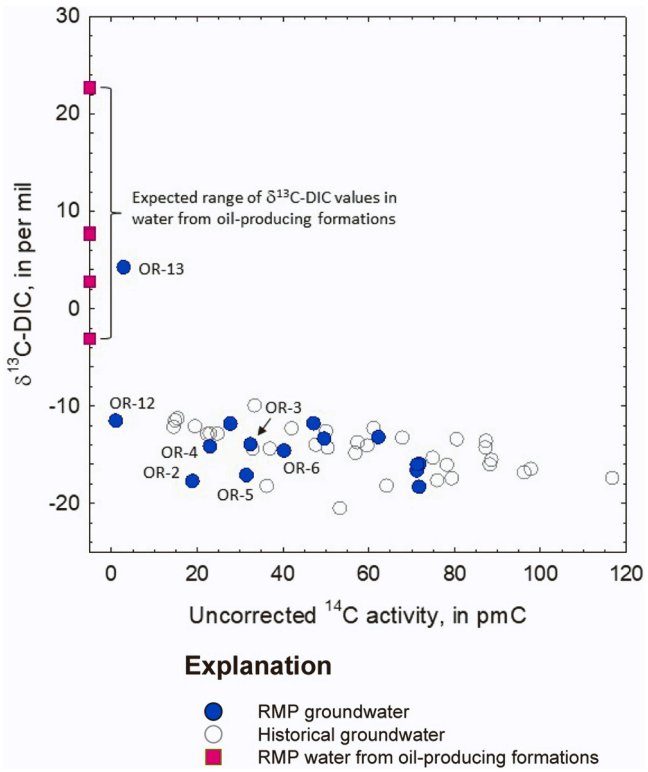

Fig. 5. Groundwater age plot for $\delta^{13}C$-DIC versus uncorrected ^{14}C activity for Oil and Gas Regional Monitoring Program (RMP) groundwater (blue circles) and historical groundwater (open circles) samples; $\delta^{13}C$-DIC values for RMP samples of water from oil-producing formations (purple squares). C-14 activities in RMP samples of water from oil-producing formations is unknown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Supplementary Information.

3.1.3. Light hydrocarbon gas

Groundwater samples within the boundary of the Orcutt Oil Field had methane (CH_4; C1) concentrations of 41 mg/L (OR-2) and 22 mg/L (OR-3) reflecting supersaturated and slightly undersaturated conditions, respectively, relative to equilibrium methane solubility in water at observed temperatures and pressures (methane solubility in water equals 22.7 mg/L at 25 °C and 1 atm (Haynes, 2016)) (Fig. 6). These samples also contained ethane (C_2H_6; C2) and propane (C_3H_8; C3) in concentrations of 0.12 and 1.6 × 10^{-3} mg/L (OR-2) and 2.8 × 10^{-2} and 1.2 × 10^{-3} mg/L (OR-3), respectively; in addition, traces of isobutane (C_4H_{10}; C4) were also detected in these two samples (5.0 ×10^{-4} and 3.0 ×10^{-4} mol%, respectively) (McCarlson et al., 2021). The presence of propane and trace amounts of isobutane indicate a thermogenic source is contributing hydrocarbon gas to these samples. The groundwater sample located adjacent to the oil field had methane and ethane concentrations of 47 and 6.1 × 10^{-2} mg/L (OR-13) (Fig. 6). Methane and ethane were detected at 4 other groundwater samples located near the oil field in concentrations of 0.4 and 3.4 × 10^{-3} mg/L (OR-5), 0.19 and 2.0 × 10^{-3} mg/L (OR-4), 2.4 × 10^{-3} and 6.1 × 10^{-4} mg/L (OR-14), and 2.0 × 10^{-3} and 4.7 × 10^{-4} mg/L (OR-8) respectively (Fig. 6). Microbial methane generally occurs in aquifers with low oxygen and low sulfate concentrations (both < ~0.5 mg/L) (Chapelle et al., 1995; McMahon and Chapelle, 2008)). While all these samples with elevated methane concentrations have dissolved-oxygen concentrations < 0.5 mg/L, the sulfate concentrations (up to 619 mg/L) are high relative to aquifer conditions typically conducive to microbial methane production. Despite the high sulfate conditions, methanogenesis is still a potential source of

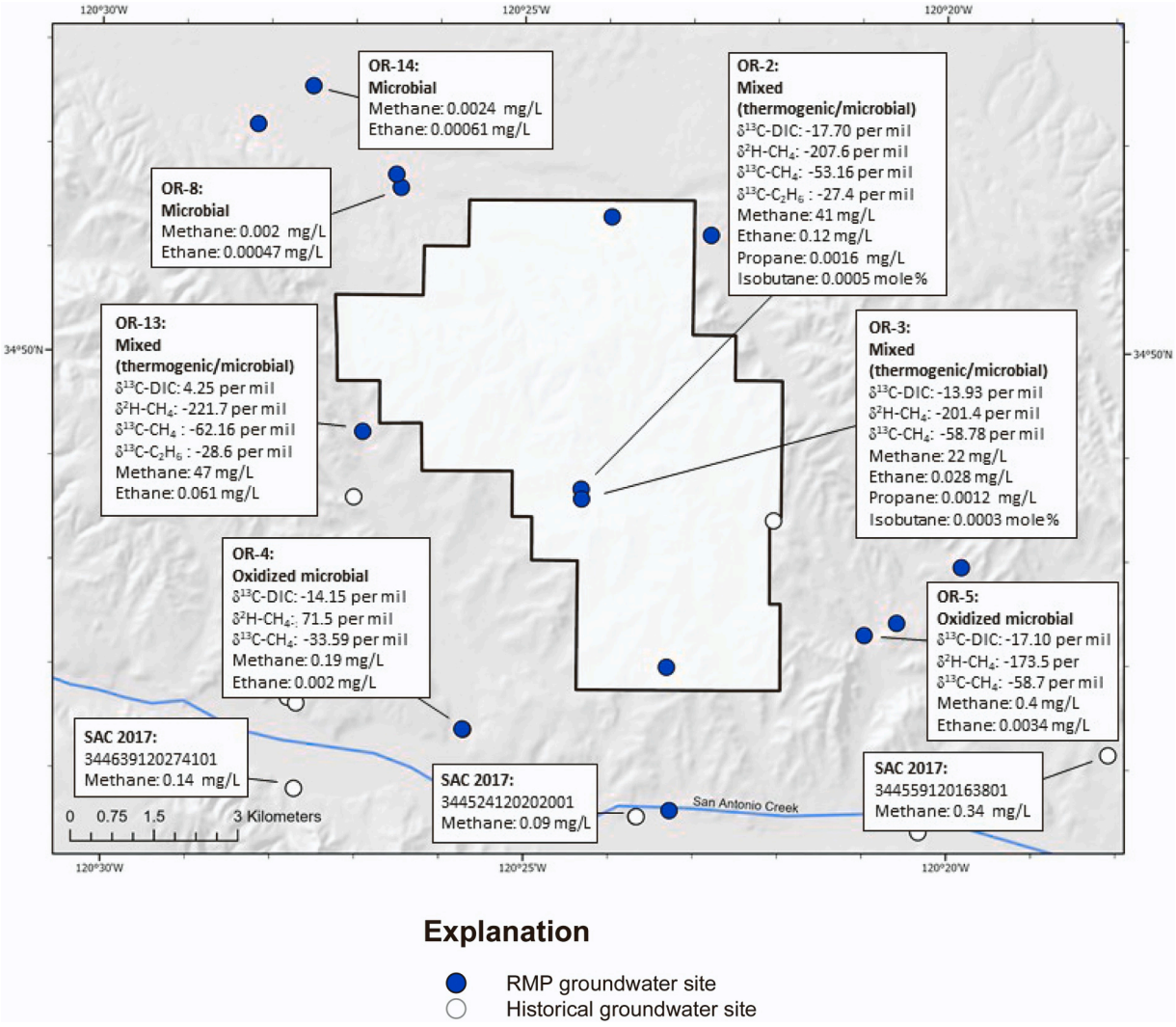

Fig. 6. Map showing light hydrocarbon gas concentrations and isotopic values for Oil and Gas Regional Monitoring Program (RMP) groundwater sites (blue circles) and methane concentrations for historical groundwater sites (open circles) in the San Antonio Creek Valley. No description indicates no detection of ethane (RMP groundwater sites) or no detection of methane (historical groundwater sites). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

methane because the wells in question likely allow for a mixture of water from more than one oxidation-reduction zone in the wellbore during sampling (McMahon and Chapelle, 2008). Methane was detected in the remaining Orcutt groundwater samples collected for the RMP at concentrations ranging from 2.0×10^{-4} to 6.3×10^{-3} mg/L, while produced water samples had methane concentrations that ranged from 0.9 to 100 mg/L (McCarlson et al., 2021; Seitz et al., 2021).

The δ^2H-CH_4 and δ^{13}C-CH_4 values for 5 groundwater samples that had methane concentrations high enough for isotopic analysis (> 0.05 mg/L) ranged from − 62.16 to − 33.59 per mil and − 221.7 to 71.5 per mil, respectively (Fig. 7a). Using the classification provided by Whiticar (1986) and considering microbial methane tends to exhibit depleted δ^{13}C-CH_4 values in the range of − 60 to − 90 per mil (Taylor et al., 2000), the methane isotopic values for the two groundwater samples overlying the oil field and in relative

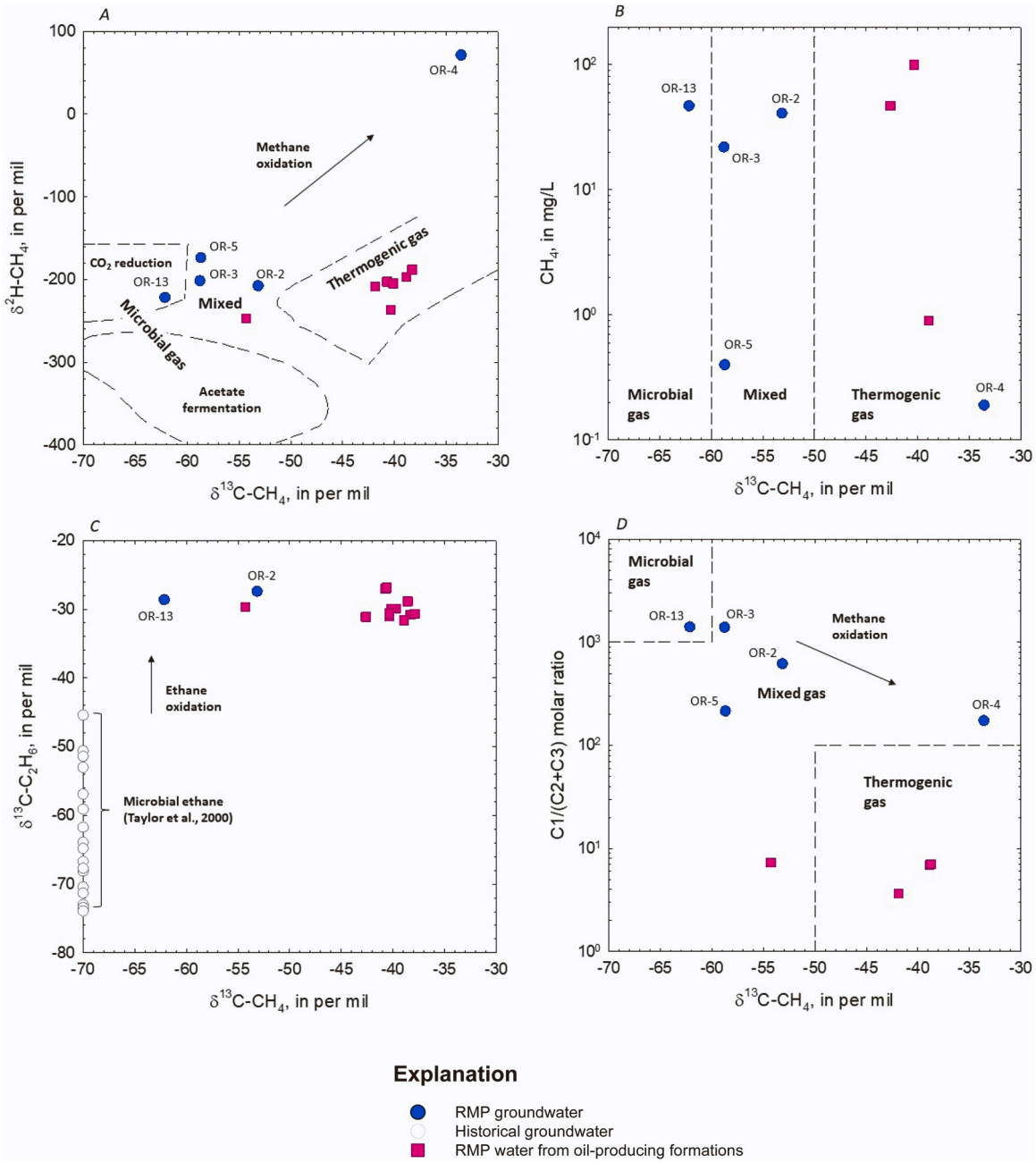

Fig. 7. Light hydrocarbon gas concentrations and isotopic values for Oil and Gas Regional Monitoring Program (RMP) groundwater samples (blue circles) and historical groundwater samples (open circles) from Taylor (2000); RMP water from oil-producing formations (purple squares): A. δ^2H-CH_4 versus δ^{13}C-CH_4; B. δ^{13}C-CH_4 versus CH_4 concentration; C. δ^{13}C-C_2H_6 versus δ^{13}C-CH_4; and D. δ^{13}C-CH_4 versus C1/(C2 +C3) molar ratios. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

proximity to historical dense oil development (OR-2, −3) suggest the source of the methane in these wells is mixed microbial/thermogenic in origin (Fig. 7a, b). Furthermore, the lack of δ^{13}C-DIC enrichment in OR-2 and OR-3 (Fig. 5), despite the high methane concentrations, is not consistent with in situ methanogenesis and instead suggests the methane is sourced from outside the shallow aquifer overlying the oil field.

For the groundwater sample collected adjacent to the oil field (OR-13), the methane isotopic values suggest the source of the methane is microbial (Fig. 7a, b). The higher concentration of methane at this site in comparison with other sites with microbial methane (Fig. 7b), in combination with the isotopically lightest methane (Figs. 6, 7a), may reflect CO_2 reduction in water from oil-bearing formations. Recall, the groundwater sample adjacent to the oil field (OR-13) exhibits an anomalously enriched δ^{13}C-DIC value (Fig. 5) which suggests the methanogenic activity supported by a high DOC concentration in this sample could be why the microbial methane is so much higher in this sample compared to other sites with microbial methane.

Two of the 5 groundwater samples (OR-2 and OR-13) contained enough ethane for isotopic analysis and the δ^{13}C-C_2H_6 values appear to be characteristic of thermogenic ethane (Figs. 6, 7c). The measured δ^{13}C-C_2H_6 values of − 28.6 per mil (OR-2) and − 27.4 per mil (OR-13) are similar to those measured in the produced water samples and are much heavier than values for microbial ethane described by Taylor et al. (2000) (Fig. 7c).

For the other groundwater samples that had methane concentrations high enough for isotopic analysis (OR-4, −5), the combination of δ^{13}C-CH_4, δ^{2}H-CH_4, and C1/(C2 +C3) molar ratios suggest the methane is microbial in origin and has undergone various amounts of methane oxidation rather than being derived from thermogenic sources (Fig. 7a, d). Microbially mediated methane oxidation favors isotopically light methane; thus, methane oxidation causes ^{13}C enrichment in the residual methane, which could shift light δ^{13}C-CH_4 values in microbial gas toward heavier δ^{13}C-CH_4 values more characteristic of thermogenic gas (Schoell, 1980; Whiticar, 1999).

Historical groundwater samples collected in the San Antonio Creek groundwater basin during 2017 indicate methane was widely detected in wells (12 out of 27 sites sampled) with concentrations of 0.09 to 0.34 mg/L at three sites to the south of the Orcutt Oil Field (Fig. 6). Although no other hydrocarbon gas concentration or isotopic data were measured in the San Antonio Creek Valley groundwater basin prior to this study, similarity to RMP samples outside the boundary of the oil field indicates microbial methane is sometimes present at concentrations up to about 0.4 mg/L and is widespread in groundwater at concentrations ranging from about 8.0×10^{-4} to 7.0×10^{-3} mg/L.

3.1.4. *Noble gas compositions*

The isotopes of the atmospherically derived noble gases (^{20}Ne, ^{36}Ar, ^{84}Kr, and ^{132}Xe) were analyzed to identify groundwater that has interacted with oil and gas sources, deep crustal or mantle sources, has excess atmospheric gases indicating recent atmospheric exposure, or has been affected by gas/water partitioning processes during groundwater flow through aquifers (Hunt et al., 2012; Darrah et al., 2014; Karolytė et al., 2021). The majority of samples reflect air-equilibration with entrainment of excess air, however, two groundwater samples located overlying the oil field (OR-2, −3), and to a lesser extent one groundwater sample adjacent to the oil

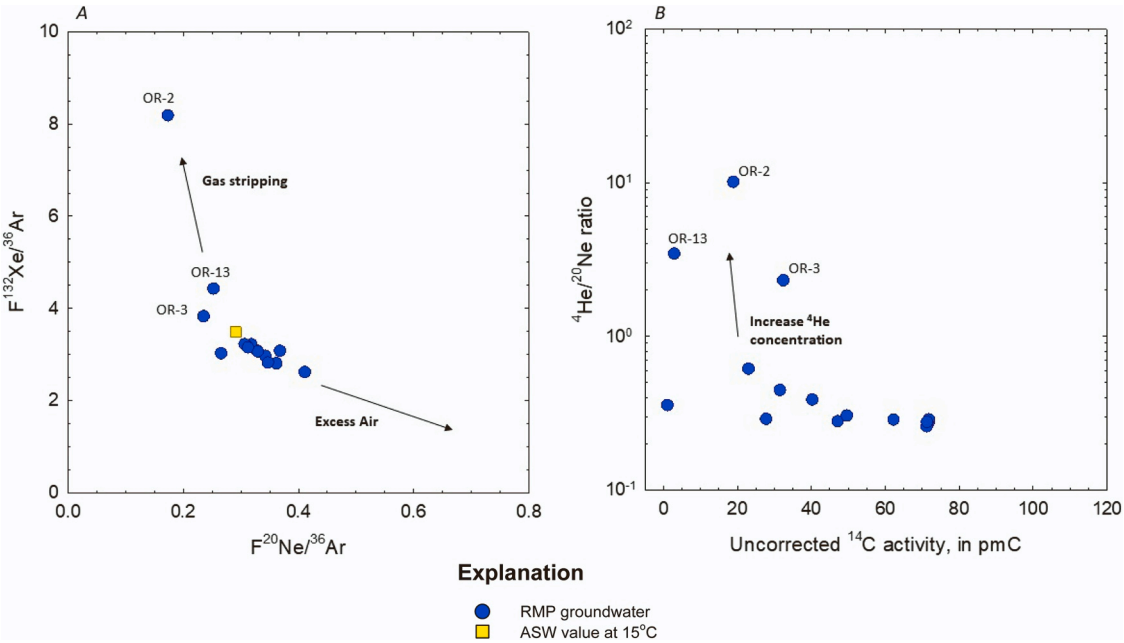

Fig. 8. Noble gas concentrations and isotopic compositions for Oil and Gas Regional Monitoring Program (RMP) groundwater samples (blue circles); air-saturated water (ASW) value at 15 °C (yellow square): A. ^{132}Xe/^{36}Ar versus ^{20}Ne/^{36}Ar ratios, normalized (F) to the ASW values; B. ^{4}He/^{20}Ne ratio versus uncorrected ^{14}C activity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

field (OR-13), exhibited deviations from ASW (air-saturated water) values. Values of $^{20}Ne/^{36}Ar$ versus $^{132}Xe/^{36}Ar$, normalized to the ASW values, exhibit depletion of the lighter noble gases along with enrichment of the heavier noble gases in OR-2, OR-3, and OR-13 (Fig. 8a) and indicate these groundwaters may have been affected by degassing, preferentially stripping the lighter noble gases out of the groundwater. These samples also contained mixed thermogenic-microbial methane or ethane and elevated ^4He and chloride concentrations, suggesting a mixture of thermogenic gas and water from oil-bearing formations with native groundwater. The stripping of the lighter noble gases, along with enrichment in crustal fluids and gases (^4He, Cl, and mixed microbial/thermogenic CH_4 or C_2H_6), provide evidence for two-phase migration during transport of thermogenic gas and water from oil-bearing formations into the shallow aquifer system overlying and possibly adjacent to the Orcutt Oil Field. Furthermore, the age tracer data (^{14}C) in these samples and elevated ^4He concentrations suggest the groundwater has been isolated from the atmosphere for some time (thousands to tens of thousands of years before present) (Fig. 8b), and as such, the high chloride concentrations are unlikely the result of a surface spill.

The remaining groundwater samples exhibited concentrations and isotopic compositions of noble gases, in combination with age tracer data, consistent with ancient (likely thousands of years old) groundwater in equilibrium with atmospheric gases from recharge with minor amounts of excess-air bubble entrainment, and trace amounts of in situ produced ^4He (Fig. 8a, b). These results indicate no evidence for groundwater interaction with water, oil, or thermogenic gas from oil-bearing formations in the majority of samples collected as part of the RMP. Additional discussion on the evidence for light noble gas degassing in the Orcutt groundwater samples is presented in the Supplementary Information.

3.2. Relevant indicators of oil-bearing formation water and thermogenic gas in groundwater

Comparison of salinity tracers (TDS, Cl, and Br), NH_3, DOC, and $\delta^{13}C$-DIC values in groundwater and oil-field water in the area of the Orcutt Oil Field indicated up to three groundwater samples adjacent to (OR-13) and overlying the oil field (OR-2, −3), in decreasing order of likelihood, may be mixed with oil-bearing formation water, other water sources similar in composition, or more complex mixtures of different sources of relatively brackish water. The well adjacent to the oil field (OR-13) appeared to contain groundwater mixed with oil-bearing formation water based on having the highest measured groundwater values of salinity tracers (TDS, Cl, Br), NH_3, and DOC, intermediate between most groundwater values and oil-producing formation water. The enriched $\delta^{13}C$-DIC isotopes and high methane concentrations for this groundwater sample adjacent to the oil field (OR-13) cannot be explained solely by inorganic carbonate reactions (Aravena et al., 1995) and suggests that the $\delta^{13}C$-DIC values are influenced by methanogenesis supported by organic carbon derived from oil-bearing formation water and/or mixing between groundwater and oil-bearing formation waters with much heavier $\delta^{13}C$-DIC values. Finally, the presence of thermogenic ethane, as indicated by a $\delta^{13}C$-C_2H_6 value of − 27.4 per mil, is consistent with a mixture of native groundwater with some deeper water similar in composition to oil-bearing formation water. The absence of other indicators of thermogenic hydrocarbon gas in this sample (e.g. propane) could indicate the thermogenic component is very small and/or the heavier hydrocarbon gases have been oxidized.

Concentrations of TDS, Cl, Br, and DOC, in the two wells overlying the oil field, OR-2 and OR-3, were intermediate between most groundwater and oil-bearing formation water, potentially indicating mixing, but concentrations were lower than those in OR-13, adjacent to the oil field, and not all tracers (e.g. I, $\delta^{18}O$-H_2O) unambiguously indicate mixing with an oil-bearing formation water. A possible explanation is that these samples are complex mixtures that include oil-bearing formation water of variable composition and/or other sources of naturally brackish groundwater near the oil field.

The presence of thermogenic gas in OR-2 and OR-3, overlying the oil field, is indicated by elevated ^4He concentrations, enriched methane isotopes, detection of C3-C5 gas, and hydrocarbon gas ratios. The presence of thermogenic gas in OR-2 is further indicated by enriched ethane isotopes. For OR-13, the presence of thermogenic gas adjacent to the oil field is indicated by slightly elevated ^4He concentrations and enriched ethane isotopes relative to microbial ethane (Fig. 7c). It is important to note that detections of thermogenic gas in groundwater are not by themselves an indication of groundwater-quality degradation associated with oil and gas sources. Instead, these gas detections are an indicator that there are potential pathways connecting groundwater to hydrocarbon sources, whether in oil production zones or non-producing geologic sources near groundwater wells. Methane and other light hydrocarbon gases are not regulated drinking water constituents posing any known health risk and the presence of these gases does not indicate degraded water quality, although the presence of these gases in high concentrations may represent an explosion hazard in confined spaces in some cases (Eltschlager et al., 2001). The three groundwater samples that appear to be influenced by water from oil-bearing formations had concentrations of chloride higher than the recommended 250 mg/L secondary maximum contaminant level (California State Water Resources Control Board, 2019) created to ensure that water does not cause undesirable aesthetic effects in drinking water, although groundwater from these wells is not used for drinking water.

3.3. Potential sources/pathways for water and thermogenic gas from oil-bearing formations

The presence of elevated concentrations of ^4He and mixed microbial/thermogenic methane in two water wells directly overlying the Orcutt Oil Field and completed at shallower depths than the oil-producing formations, OR-2 and OR-3, along with thermogenic ethane present in OR-2, may indicate thermogenic gas migration along natural flow paths through formations or faults, if present, or could follow anthropogenic pathways such as compromised wells/wellbores potentially influenced by oil-field development activities that may affect lateral and vertical pressure gradients. Migration of stray gas from oil-field formations has been implicated as a source of methane, and to a lesser extent ethane, observed in groundwater in other oil producing regions (Jackson et al., 2013b; Sherwood et al., 2016a and 2016b; Whyte et al., 2021) but have been attributed to both anthropogenic and natural pathways and processes.

Likewise, the enrichment in ^{4}He and mixed microbial/thermogenic methane, without the corresponding increase in salinity tracers, could potentially result from natural oil and gas shows within the aquifer sediments in oil-bearing formations overlying the zones where commercial oil extraction occurs. Other chemical and isotopic data previously discussed (TDS, Cl, Br, NH_3, DOC, and $\delta^{13}C$-DIC) do not indicate definitive evidence that oil-bearing formation water has mixed with groundwater being tapped by these wells, although small amounts of mixing could be indicated by the data.

Although there is not enough information to determine specific sources of thermogenic gas to nearby RMP sampled groundwater wells, there are potential anthropogenic pathways located in proximity to some groundwater wells with detections of thermogenic gas. Review of available records and data described below indicate that potential pathways exist in places between oil production and groundwater zones; these conditions could allow upward movement of water and/or thermogenic gas from oil zones into overlying

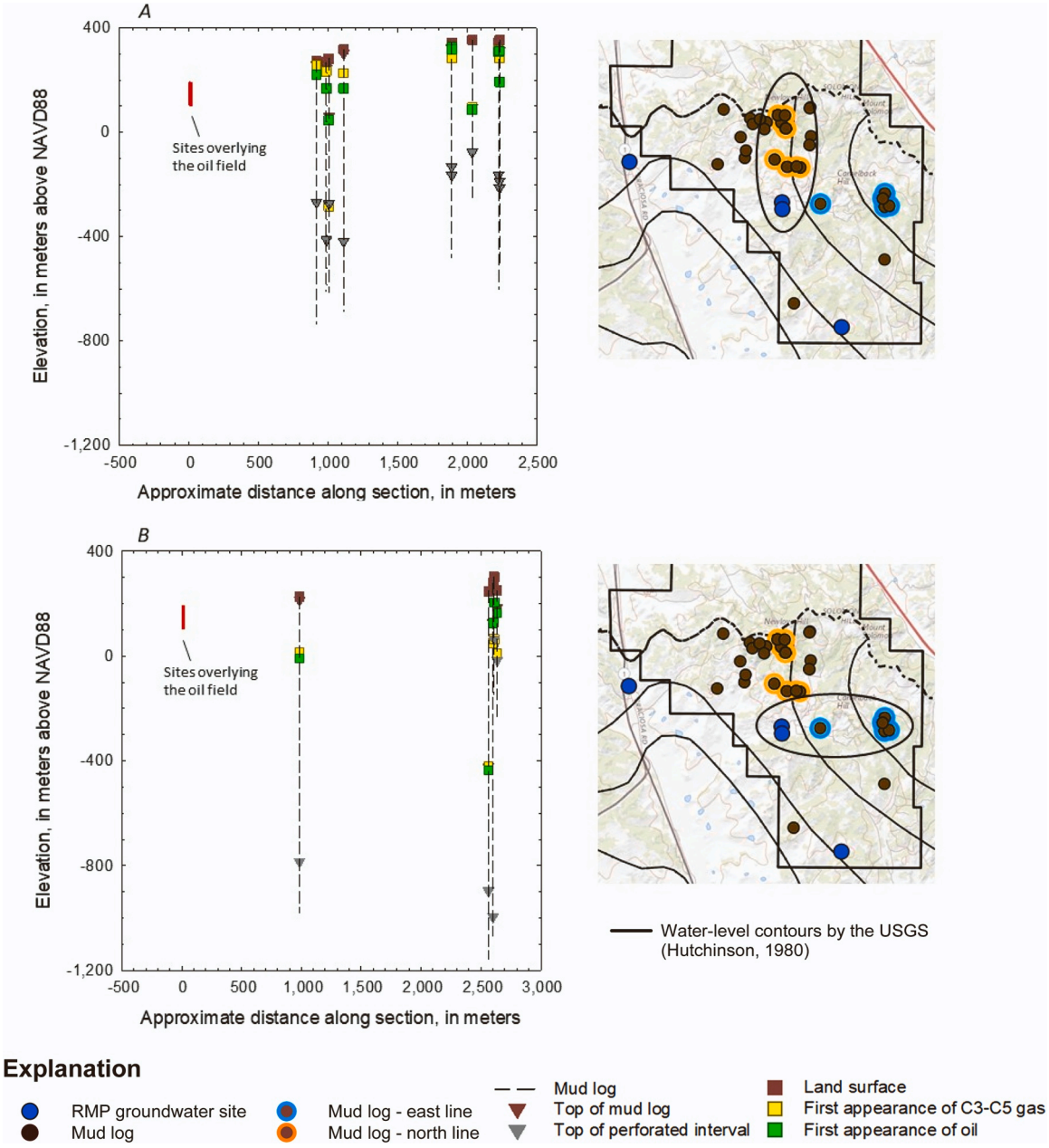

Fig. 9. Plot shows elevation of land surface, top of mud log, first appearance of oil and gas shows, and top of perforated interval of mud logs located: A. north of Oil and Gas Regional Monitoring Program (RMP) groundwater sites OR-2 and OR-3 (north line); B. east of RMP groundwater sites OR-2 and OR-3 (east line). Map shows locations of 33 mud logs (brown circles) within the Orcutt Oil Field boundary. Also shown are the 10 mud logs (orange circles) in the north line and 5 mud logs (cyan circles) in the east line. The information for selected mud logs obtained from the CalGEM website. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

groundwater. We examined several factors including the distance and characteristics of the nearest oil well, the well status, the depth of wells used for oil-production and injection, depth to base of freshwater, well integrity issues, the presence of oil and gas shows in sediments overlying the Orcutt Oil Field, and the 1977–2017 vol of injection for enhanced recovery and produced water disposal in proximity to RMP sampled groundwater wells.

Of the 15 oil wells within 500 m of RMP sampled groundwater wells (specifically OR-2, −3, −5, −9, −11); approximately 87% of the wells were classified as plugged and abandoned (7 wells abandoned before 1976), whereas new, active, or idle wells made up the remaining 13% (fig. S5; table S2). Groundwater wells OR-2 and OR-3 have 10 and 8 oil wells located within 500 m, respectively; 6 of the 12 oil wells within 500 m of either water well were constructed and plugged and abandoned before 1976 (tables S2, S3). As an example, the closest oil well (API 08302063) to OR-2 is 76 m away, and has potential pathways, and historical observations of leakage (tables S2, S3). That oil well was drilled in 1906 to a total depth of 1133.9 m with no record of cement in the borehole annulus above 716 m, and was plugged and abandoned in 1946, with damaged casing below 99 m and cement plugs installed above that depth (table S3); site inspections related to new planned infrastructure in 2008 noted water seeping around the outside of the heavily corroded casing (California Department of Conservation, 2020b).

Among the oil and gas wells within 500 m of the RMP sampled groundwater wells, well reports (California Department of Conservation, 2020b) were reviewed to assess the occurrence of reported well integrity issues, including casing damage or collapse at depth (well construction integrity issue) and water or gas leaks around the casing or from the wellhead at the surface (surface expression). Of the 15 oil wells, six had well integrity issues at depths potentially intersecting the groundwater resource zone; these included one well with a well construction integrity issue, one well with a surface expression, and four wells with both well construction integrity issues and surface expressions (table S3). All six of these wells were installed during 1901–1907 and plugged and abandoned between 1946 and 2012. Well construction integrity issues also were noted in four of the oil wells at depths within oil and gas producing zones below fresh groundwater; however, three of these wells had cement in the wellbore annulus and/or cement plugs installed in the casing during well abandonment in overlying zones, indicating that well integrity issues in producing zones would be unlikely to provide a potential transport pathway to groundwater (the cement distributions in overlying zones in the fourth well were not recorded) (table S3). The losses of water or gas from target zones during the installation and development of injection and production wells have been noted in other cases outside of those reported within 500 m of sampled water wells but have not been systematically documented across the field; the magnitude of these subsurface releases is unknown. A connection between the thermogenic methane and/or water from oil-bearing formations in groundwater wells and nearby oil wells with possible integrity issues cannot be ruled out or conclusively established.

Another potential source/pathway for thermogenic gas are oil and gas shows that naturally occur in places in sediments overlying the Orcutt Oil Field. Analysis of 33 mud logs within the administrative boundary of the oil field indicates that shallow oil and gas shows are present in sediments at shallow depths overlying the oil field in upland portions of the field, where oil zones are closest to land surface (table S4; Figs. 2, 9a, b). At these locations, oil and gas shows can occur at depths of as little as 16.8 m below land surface (bls) and 15.2 m bls, respectively, in some upland areas (table S4; Fig. 9a, b). In the closest mud log to OR-2 (and OR-3), the first appearance of oil and gas shows are reported (API 08322543) at elevations of 220 and 258 m, respectively, compared with top of perforation elevations for OR-2 and OR-3 of 147 and 165 m, respectively, located 912 m to the south. It is presumed that oil/gas shows in mud logs reflect the natural distribution over geologic time and not redistribution following oil development activities and that oil-bearing formation water would co-occur with oil/gas shows. The sampled wells OR-2 and OR-3 are located within an alluvial valley incised into the sometimes oil-bearing basal layer of the Careaga Formation and the underlying Sisquoc Formation (Kuuskraa et al., 1987), which generally dip to the south (fig. S3; California Department of Conservation, 1992). Although the density of the data is low, it is possible that the occurrence of thermogenic gas and oil-bearing formation water in groundwater at these sites may reflect lateral or vertical transport of these constituents from geologic sources (oil-bearing formations) in the oil-bearing sediments overlying the oil field.

Mixtures of oil-bearing formation water with groundwater are indicated for sample OR-13 collected from outside the boundary of the oil field. Groundwater age tracers (^{3}H and ^{14}C) indicate the groundwater was at least recharged prior to 1953 and is likely ancient (^{3}H not detected, ^{14}C = 2.8 pmC). The notion of ancient groundwater existing adjacent to the oil field is further supported by noble gas data (^{4}He = 4.05 $\times 10^{-7}$ cm^{3} STP/g (where STP is standard temperature and pressure)) and may preclude a historical produced-water disposal pond or dump site from being the source of the oil-bearing formation water. Instead, potential sources/pathways for oil-bearing formation water include lateral movement from nearby oil fields (Orcutt or Casmalia to the west) along natural flow paths through formations or faults or anthropogenic pathways such as wells/wellbores, which may/may not be influenced by oil-field development activities such as injection. However, the nearest oil wells are located > 470 m away from OR-13 and areas of dense oil wells and injections are located almost 1000 m to the east (Fig. 2, table S2). Another possible source/pathway for oil-bearing formation water to groundwater is unidentified oil and gas shows in the aquifer adjacent to the oil field. However, the absence of mud logs and oil exploration test holes means there are no data for assessing shallow oil and gas occurrence in this area but that previous oil exploration did not regard this area as target for economic quantities of hydrocarbons.

Finally, the areas of the Orcutt Oil Field having the highest injection volumes co-located with plugged and abandoned wells are in the northern part of the field (Fig. 2). These areas may have the highest risk of water, gas, and oil from oil-bearing formations reaching overlying zones. Because of the absence of groundwater wells in these areas, the effects of these factors, if any, cannot be evaluated without additional data. Additional discussion on the movement of water from oil-producing formations to groundwater along potential anthropogenic or natural pathways is presented in the Supplementary Information.

3.4. Multiple lines of evidence for oil-bearing formation water and/or thermogenic gas in groundwater

Identification of the presence of oil-bearing formation water and thermogenic gas in some groundwater wells required the use of analytes with little or no historical data, including light hydrocarbon gas concentration and isotopic data, carbon isotopic values of dissolved inorganic carbon, dissolved organic carbon, groundwater age tracers, and noble gases. These analyses provide multiple lines of evidence for the presence of oil-bearing formation water and/or thermogenic gas in three of the 15 groundwater wells sampled. Other groundwater samples collected as part of the RMP, along with available historical data, showed no evidence of mixing with water from oil-bearing formations. Results of the groundwater sampling to investigate the occurrence of water and thermogenic gas from oil-bearing formations in groundwater are summarized in table S7.

In two wells available for sampling within the boundary of the Orcutt Oil Field and in relative proximity to historical dense oil development, OR-2 and OR-3, the following relevant indicators of water and gas from oil-bearing formations detected in groundwater near the Orcutt Oil Field were: (1) thermogenic light hydrocarbon gas (CH_4, C_2H_6, C_3H_8) mixed with microbial CH_4; (2) elevated concentrations of TDS and Cl, minor-ion ratios (Br/Cl), NH_3 and DOC potentially indicating small amounts of oil-bearing formation water present; and (3) depletion of lighter noble gases and enrichment of heavier noble gases in these samples, particularly OR-2, indicating the sampled groundwater has been affected by gas migration independent of water movement. The source and pathways of the thermogenic gas in groundwater at these wells cannot be determined conclusively from the available data. Possibilities include: (1) upward movement from underlying oil and gas producing formations along; (a) natural flow paths through formations or faults; or (b) anthropogenic pathways such as wells/wellbores and/or influenced by oil-field development activities such as injection; and (2) oil and gas shows that occur in water-bearing sediments overlying the Orcutt Oil Field.

At OR-13, elevated concentrations of TDS, Cl, NH_3, and DOC, minor-ion ratios (Br/Cl and I/Cl), and enriched δ^{13}C-DIC and δ^{13}C-C_2H_6 values are consistent with mixing of oil-bearing formation water and thermogenic gas from a subsurface source but could also be partially explained by old brackish groundwater interacting with aquifer sediments in a reducing environment with appreciable nitrogen and organic matter. Undetectable tritium, low uncorrected ^{14}C activity (2.8 pmC) and noble gas ratios indicate the groundwater is ancient. Although there is historical evidence of legacy disposal of produced water in surface ponds affecting groundwater in this area (EnviroManagement, Inc, 2016a, 2016b), the age tracer and noble gas data are incongruent with OR-13 being affected by a surface pond source.

3.5. Limitations and uncertainties

The initial phase of the RMP uses existing infrastructure to achieve coverage across many oil-field areas in California. As a result, sampling locations and depths for more precise determination of pathways were non-ideal and limited by the small number of wells available for sampling groundwater overlying and near the edge of the Orcutt Oil Field. Due to the low sampling density, a definitive analysis of relations to potential anthropogenic and natural explanatory factors was not possible. As a result, the sources and pathways of the thermogenic light hydrocarbon gas and/or water from oil-bearing formations detected in some groundwater wells overlying and near the Orcutt Oil Field cannot be confirmed at present. In order to further evaluate the source and pathways at local scales, we suggest: (1) a higher density of groundwater observational data located at various vertical and horizontal distances from oil and gas production including water sample data and analysis of available temperature and borehole resistivity data, which are available in some areas of oil development where groundwater wells are absent; (2) additional data on potential end-member compositions, including oil-production zones and samples from discrete depths where oil and gas shows in aquifer sediments overlying the zones of oil production occur; (3) additional data collection and analysis to determine pressure gradients between oil production and groundwater zones and their relations to groundwater withdrawals and oil and gas reservoir production and injection: and (4) expanded analysis of oil-well seals across the oil field to document the incidence of potential pathways. A more detailed description of suggested future analysis is provided in the Supplementary Information.

4. Conclusions

The California State Water Resources Control Board, in cooperation with the U.S. Geological Survey, implemented the Oil and Gas Regional Monitoring Program (RMP) near the Orcutt Oil Field to address concerns about groundwater quality in regions of oil and gas development activities. The findings of this study indicate most groundwater in the area of the Orcutt Oil Field appears to be of good quality with respect to the constituents analyzed since most groundwater samples, as well as available inorganic historical chemistry data, showed no indication of water from oil-bearing formations in groundwater. These results support previous water-quality studies which have noted irrigation return flow, natural-occurring water-rock interaction, and lateral seepage from the surrounding outcrops of marine rocks are the predominant processes contributing to the salinity in groundwater in the study area.

The chemical and isotopic composition of three of the 15 groundwater samples obtained as part of the study indicated potential mixing with water and/or hydrocarbon gas from oil-bearing formations. The relevant indicators used to identify the presence of oil-bearing formation water and thermogenic gas in groundwater included three or more of the following: (1) elevated salinity tracers (TDS, Cl, Br), NH_3, and DOC); (2) enriched δ^{13}C-DIC values; (3) higher methane concentrations with trace amounts of propane and isobutane; (4) δ^{2}H-CH_4 and δ^{13}C-CH_4 values intermediate between thermogenic hydrocarbon and microbial gas; (5) δ^{13}C-C_2H_6 values consistent with a thermogenic source; and (6) depletion of light noble gases relative to heavier noble gases in combination with elevated ^{4}He concentrations. The potential sources/pathways for the occurrence of water and thermogenic gas in groundwater near the Orcutt Oil Field included: (1) upward movement from oil-producing formations due to, a) anthropogenic activity such as injection

and/or movement along leaky wells/wellbores, or b) natural migration through formations and/or faults; and (2) non-producing oil-bearing formations overlying and adjacent to the oil field.

Determination of oil-field sources and pathways affecting groundwater were limited by the small number of wells available in areas of oil development. Future insight on sources and pathways for thermogenic gas and water from oil-bearing formations could be provided by denser data on groundwater and potential end-member compositions from new and existing wells, analysis of borehole temperature and resistivity data, and assessments of the potential for upwelling of water and thermogenic hydrocarbon gas from vertical head gradients between oil and groundwater zones and more comprehensive analysis of pathways related to oil infrastructure.

CRediT authorship contribution statement

Robert Anders: Writing – original draft preparation, Conceptualization, Formal analysis. **Matthew K. Landon:** Writing – review & editing, Conceptualization, Supervision. **Peter B. McMahon:** Writing – review & editing, Formal analysis. **Justin T. Kulongoski:** Writing – review & editing, Formal analysis. **Andrew G. Hunt:** Writing – review & editing, Formal analysis. **Tracy A. Davis:** Formal analysis.

Declaration of Competing Interest

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

Acknowledgments

Funding for this study was provided by the California State Water Resources Control Board Oil and Gas Regional Monitoring Program. The authors are grateful to many individuals for their technical insights as well as many USGS colleagues for their assistance in identifying, collecting, collating, reviewing, and preparing the data presented here. Their collective contribution to the study cannot be overstated. We also thank the reviewers who provided helpful comments on earlier versions of the manuscript. Any use of trade, firm, or product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ejrh.2022.101065.

References

Aravena, R., Wassenaar, L.I., Plummer, L.N., 1995. Estimating ^{14}C groundwater ages in a methanogenic aquifer. Water Resour. Res. 31, 2307–2317. https://doi.org/10.1029/95WR01271.

Arnold, R., Anderson, R., 1907. Geology and oil resources of the Santa Maria Oil District, Santa Barbara County, California U. S. Geol. Surv. Number Ser., 332, 161 doi: 10.3133/b322.

Baldassare, F.J., Mccaffrey, M.A., Harper, J.A., 2014. A geochemical context for stray gas investigations in the Northern Appalachian Basin: implications of natural gases from Neogene- through Devonian-age strata. Am. Asssoc. Pet. Geol. Bull. 98 (2), 341–372. https://doi.org/10.1306/06111312178.

Blondes, M.S., Gans, K.D., Engle, M.A., Kharaka, Y.K., Reidy, M.E., Saraswathula, V., Thordsen, J.J., Rowan, E.L., and Morrissey, E.A., 2018, U.S. Geological Survey National Produced Waters Geochemical Database (ver. 2.3, January 2018): U.S. Geological Survey data release. ⟨https://doi.org/10.5066/F7J964W8⟩.

Brantley, S.L., Yoxtheimer, D., Arjmand, S., Grieve, P., Vidic, R., Pollak, J., 2014. Water resource impacts during unconventional shale gas development: the Pennsylvania experience. Int. J. Coal Geol. 126, 140–156.

California Department of Conservation, 1992, Division of Oil, Gas, and Geothermal Resources, California Oil and Gas Fields Volume II-Southern, Central, and Offshore California, 645 p.

California Department of Conservation, 2019, Division of Oil, Gas, and Geothermal Resources, California statutes and regulations for the Division of Oil, Gas, and Geothermal Resources: April 2019, accessed January 2020 at: ⟨https://www.conservation.ca.gov/calgem/pubs_stats/Documents/DOGGR-Statutes-Regs.pdf⟩.

California Department of Water Resources, 2018, Water quality data reports: California Department of Water Resources web page, accessed April 2018 at: ⟨http://www.water.ca.gov/waterdatalibrary/waterquality/index.cfm/⟩.

California State Water Resources Control Board, 2019, Water quality in areas of oil and gas production – regional groundwater monitoring, accessed January 2019 at: ⟨https://www.waterboards.ca.gov/water_issues/programs/groundwater/sb4/regional_monitoring/index.shtml⟩.

California Department of Conservation, 2020a, Oil and gas online data: Geologic Energy Management Division, accessed January 8, 2020 at: ⟨https://www.conservation.ca.gov/calgem/Online_Data/Pages/Index.aspx⟩.

California Department of Conservation, 2020b, Well Finder: Geologic Energy Management Division, Well Finder, accessed January 8, 2020 at: ⟨https://www.conservation.ca.gov/calgem/Pages/WellFinder.aspx⟩.

California Department of Conservation, 2020c, Idle well program, Geologic Energy Management Division, accessed May 2020 at: ⟨https://www.conservation.ca.gov/calgem/idle_well⟩.

California Department of Water Resources, 2003, California's groundwater: California Department of Water Resources Bulletin 118, 246 p., accessed April 2018 at: http://www.water.ca.gov/pubs/groundwater/bulletin_118/california's_groundwater_bulletin_118_-_update_2003_/bulletin118_entire.pdf.

California Geological Survey, 2021, Geological Map of California. California Geological Survey, California Department of Conservation, accessed January 2021 at: ⟨https://maps.conservation.ca.gov/cgs/gmc/⟩.

California State Water Resources Control Board, 2018, Geotracker GAMA, accessed April 2018 at: ⟨https://geotracker.waterboards.ca.gov/gama/⟩.

Chapelle, F.H., McMahon, P.B., Dubrovsky, N.M., Fujii, R.F., Oaksford, E.T., Vroblesky, D.A., 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. Water Resour. Res. 31, 359–371.

Coleman, D.D., Liu, C.-L., Riley, K.M., 1988. Microbial methane in the shallow Paleozoic sediments and glacial deposits of Illinois, U.S.A. Chem. Geol. 71, 23–40.

Collins, A., 1975. Geochemistry of Oilfield Waters, 1. Elsevier.
Crain, E.R., 2010, Crain's Petrophysical Handbook, Mud Logging and Mud Gas Logging webpage version, accessed September 2019 at: ⟨https://www.spec2000.net/08-mud.htm⟩.
Darling, W.G., Gooddy, D.C., 2006. The hydrogeochemistry of methane: evidence from English groundwaters. Chem. Geol. 229, 293–312. ⟨https://www.spec2000.net/08-mud.htm⟩.
Darrah, T.H., Vengosh, A., Jackson, R.B., Warner, N.R., Poreda, R.J., 2014. Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. Proc. Natl. Acad. Sci. U.S.A. 111, 14076–14081.
Davis, T.A., Landon, M.K., Bennett, G.L., 2018, Prioritization of oil and gas fields for regional groundwater monitoring based on a preliminary assessment of petroleum resource development and proximity to California's groundwater resources: U.S. Geological Survey Scientific Investigations Report 2018–5065, 115 p. ⟨https://doi.org/10.3133/sir20185065⟩.
DiGiulio, D.C., Jackson, R.B., 2016. Impact to underground sources of drinking water and domestic wells from production well stimulation and completion practices in the Pavillion, Wyoming, Field. Environ. Sci. Technol. 50 (8), 4524–4536.
California Department of Conservation, 2017, Division of Oil, Gas, and Geothermal Resources, GIS Mapping, DOGGR, Sacramento, CA, accessed May 2017 at: ⟨http://www.conservation.ca.gov/dog/maps/Pages/GISMapping2.aspx⟩.
Dillon, D.B., Davis, T.A., Landon, M.K., Land, M.T., Wright, M.T., and Kulongoski, J.T., 2016, Data from exploratory sampling of groundwater in selected oil and gas areas of coastal Los Angeles County and Kern and Kings Counties in southern San Joaquin Valley, 2014–15: California Oil, Gas, and Groundwater Project: U.S. Geological Survey Open-File Report 2016–1181, 24 p. ⟨http://dx.doi.org/10.3133/ofr20161181⟩.
Eltschlager, K.K., Hawkins, J.W., Ehler, W.C., Baldassare, F., 2001, Technical measures for the investigation and mitigation of fugitive methane hazards in areas of coal mining. U.S. Dept. Interior, Office of Surface Mining Reclamation and Enforcement, Appalachian Regional Coordinating Center, 124 pp.
Engle, M.A., Reyes, F.R., Varonka, M.S., Orem, W.H., Ma, L., Ianno, A.J., 2016. Geochemistry of formation waters from the Wolfcamp and "Cline" shales: insights into brine origin, reservoir connectivity, and fluid flow in the Permian Basin, USA. Chem. Geol. 425, 76–92.
EnviroManagement, Inc, 2016a, Report of findings: Construction of groundwater monitoring wells, Biely property, 7325 Graciosa Road, Santa Barbara County, California (SMU-2 No. 20189), accessed December 2017 at: ⟨https://geotracker.waterboards.ca.gov/map/?global_id=T10000005135⟩.
EnviroManagement, Inc, 2016b, Report of findings: Second, third, and fourth quarters 2015, groundwater monitoring events, Biely property, 7325 Graciosa Road, Santa Barbara County, California (SMU-2 No. 20189), accessed December 2017 at: ⟨https://geotracker.waterboards.ca.gov/map/?global_id=T10000005135⟩.
Flewelling, S.A, Sharma, M., 2014. Constraints on upward migration of hydraulic fluid and brine. Groundwater 52 (1), 8–19. https://doi.org/10.1111/gwat.12095.
Gillespie, J., Davis, T., Stephens, M., Ball, L., Landon, M., 2019. Groundwater salinity and the effects of produced water disposal in the Lost Hills–Belridge oil fields, Kern County, California. Environ. Geosci. 26, 73–96. https://doi.org/10.1306/eg.02271918009.
Harkness, J.S., Darrah, T.H., Warner, N.R., Whyte, C.J., Moore, M.T., Millot, R., Kloppmann, W., Jackson, R.B., Vengosh, A., 2017. The geochemistry of naturally occurring methane and saline groundwater in an area of unconventional shale gas development. Geochimica et Cosmochimica Acta 208, 302–334. https://doi.org/10.1016/j.gca.2017.03.039.
Harkness, J.S., Dwyer, G.S., Warner, N.R., Parker, K.M., Mitch, W.A., Vengosh, Avner, 2014. Iodide, bromide, and ammonium in hydraulic fracturing and oil and gas wastewaters: environmental implications. Environ. Sci. Technol. 49 (3), 1955–1963. https://doi.org/10.1021/es504654n.
Haynes, William M. (Ed.), 2016. CRC Handbook of Chemistry and Physics, 97th ed. CRC Press. ISBN 9781498754293.
Hein, F.J., 2013, Overview of heavy oil, seeps, and oil (tar) sands, California. In F.J. Hein, D. Lekie, S. Larter, and J.R; Sutter, *eds*., Heavy oil and oil-sand petroleum systems in Alberta and beyond: AAPG Studies in Geology, 64, 407–435.
Heizer, R.F., 1940. Aboriginal use of bitumen by the California Indians. In: Geological Formations And Economic Development of the Oil and Gas Fields of California, 118. State Division of Mines Bulletin, p. 74.
Hughes, J.L., 1977, Evaluation of groundwater quality in the Santa Maria Valley, California: U.S. Geological Survey Water Resources Investigation Report 76–128, 72 p.
Hornafius, J.S., Quigley, D., Luyendyk, B.P., 1999. The world's most spectacular marine hydrocarbon seeps (Coal Oil Point, Santa Barbara Channel, California): Quantification of emissions. J. Geophysical Res. 104, 20703–20711. https://doi.org/10.1029/1999JC900148.
Hunt, A.G., Darrah, T.H., Poreda, R.J., 2012. Determining the source and genetic fingerprint of natural gases using noble gas geochemistry: a northern Appalachian Basin case study. Am. Assoc. Pet. Geol. Bull. 96 (10), 1785–1811. https://doi.org/10.1306/03161211093.
Hutchinson, C.B., 1980, Appraisal of groundwater resources in the San Antonio Creek Valley, Santa Barbara County, California: U.S. Geological Survey Water Resources Open-File Report 80–750, 48 p.
Isaacs, C.M., 1992, Petroleum geology of the Santa Maria Basin Assessment Province, California for the 1987 National Assessment of undiscovered oil and gas resources: U.S. Geological Survey Open-File Report 89–450-C, 43 p.
Isaacs, C.M., Rullkötter, J., 2001. The Monterey Formation: From Rocks to Molecules. Columbia University Press, New York, New York, p. 218.
Jackson, R.B., Vengosh, A., Darrah, T.H., Warner, N.R., Down, A., Poreda, R.J., Osborn, S.G., Zhao, K., Karr, J.D., 2013a. Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. Proc. Natl. Acad. Sci. U.S.A. 110 (28), 11250–11255. https://doi.org/10.1073/pnas.1221635110.
Jackson, R.E., Gorody, A.W., Mayer, B., Roy, J.W., Ryan, M.C., Van Stempvoort, D.R., 2013b. Groundwater protection and unconventional gas extraction; the critical need for field-based hydrological research. Groundwater 51 (4), 488–510. https://doi.org/10.1111/gwat.12074.
Johnson, T.D., Belitz, K., 2009. Assigning land use to supply wells for the statistical characterization of regional groundwater quality: correlating urban land use and VOC occurrence. J. Hydrol. 370, 100–108. https://doi.org/10.1016/j.jhydrol.2009.02.056.
Kang, M., Jackson, R.B., 2016. Salinity of deep groundwater in California: Water quantity, quality, and protection. Proc. Natl. Acad. Sci. U.S.A. 113 (28), 7768–7773. https://doi.org/10.1073/pnas.1600400113.
Karolytė, R., Barry, P.H., Hunt, A.G., Kulongoski, J.T., Tyne, R.L., Davis, T.A., Wright, M.T., McMahon, P.B., Ballentine, C.J., 2021. Noble gas signatures constrain oil-field water as the carrier phase of hydrocarbons occurring in shallow aquifers in the San Joaquin Basin, USA. Chem. Geol. 584, 120491 https://doi.org/10.1016/j.chemgeo.2021.120491.
Kreuzer, R.L., Darrah, T.H., Grove, B.S., Moore, M.T., Warner, N.R., Eymold, W.K., Whyte, C.J., Mitra, G., Jackson, R.B., Vengosh, A., Poreda, R.J., 2018. Structural and hydrogeological controls on hydrocarbon and brine migration into drinking water aquifers in southern New York. Groundwater 56, 225–244.
Koterba, M.T., Wilde, F.D., Lapham, W.W., 1995, Groundwater data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95–399.
Kulongoski, J.T., McMahon, P.B., Land, M., Wright, M.T., Johnson, T.A., Landon, M.K., 2018. Origin of methane and sources of high concentrations in Los Angeles groundwater. J. Geophys. Res. 123 https://doi.org/10.1002/2017JG004026.
Kuuskraa, V.A., Hammershaimb, E.C., Pague, M., 1987. Major tar sand and heavy-oil deposits of the United States, in Exploration for heavy crude oil and natural bitumen. AAPG Studies in Geology 25, 126–136.
Lackner, N., Hintersonnleitner, A., Wagner, A.O., Illmer, P., 2018. Hydrogenotrophic methanogenesis and autotrophic growth of *Methanosarcina thermophila*. Article ID 4712608 Archaea 2018, 7. https://doi.org/10.1155/2018/4712608.
Leck, L.V., 1921. Petroleum resources of California, with special reference to unproven areas. Bulletin 89, 69–101. ⟨https://digitalcommons.csumb.edu/hornbeck_usa_3_d/78⟩.
Leifer, I., 2010. Characteristics and scaling of bubble plumes from marine hydrocarbon seepage in the Coal Oil Point seep field. J. Geophys. Res. 115 (C11014), 20.
Marine Research Specialists, 2016, Orcutt Hill Resource Enhancement Plan Project FINAL Environmental Impact Report, 14EIR-00000–00001, 25 p.
McCarlson, A.J., Johnson, J.C., Marcusa, J.A., Qi, S.L., Davis, T.A., and Rosecrans, C.Z., 2021, Water chemistry data for samples collected at groundwater sites near the Orcutt Oil Field, September 2017–March 2018, Santa Barbara County, California: U.S. Geologic Survey data release. ⟨https://doi.org/10.5066/P90RCZ3T⟩.
McMahon, P.B., Caldwell, R.R., Galloway, J.M., Valder, J.F., Hunt, A.G., 2015. Quality and age of shallow groundwater in the Bakken Formation production area, Williston Basin, Montana and North Dakota. Groundwater 53 (S1), 81–94. https://doi.org/10.1111/gwat.12296.
McMahon, P.B., Chapelle, F.H., 2008. Redox processes and water quality of selected principal aquifers. Groundwater 46, 259–271.

McMahon, P.B., Barlow, J.R., Engle, M.A., Belitz, K., Ging, P.B., Hunt, A.G., Jurgens, B.C., Kharaka, Y.K., Tollett, R.W., Kresse, T.M., 2017a. Methane and benzene in drinking-water wells overlying the Eagle Ford, Fayetteville, and Haynesville Shale hydrocarbon production areas. Environ. Sci. Technol. 51 (12), 6727–6734. https://doi.org/10.1021/acs.est.7b00746.

McMahon, P.B., Kulongoski, J.T., Wright, M.T, Land, M.T., Landon, M.K., Cozzarelli, I.M., Vengosh, A., Aiken, G.R., 2017b. Preliminary results from exploratory sampling of wells for the California oil, gas, and groundwater program, 2014–15 (ver 1.1, January 2017). U.S. Geological Survey Open-File Report 2016–1100 8. https://doi.org/10.3133/ofr20161100.

McMahon, P.B., Kulongoski, J.T., Vengosh, A., Cozzarelli, I.M., Landon, M.K., Kharaka, Y.K., Gillespie, J.M., Davis, T.A., 2018a. Regional patterns in the geochemistry of oil-field water, southern San Joaquin Valley, California, USA. Appl. Geochem. 98, 127–140. https://doi.org/10.1016/j.apgeochem.2018.09.015.

McMahon, P.B., Landon, M.K., Davis, T.A., Wright, M.T., Rosecrans, C.Z., Anders, R., Land, M.T., Kulongoski, J.T., Hunt, A.G., 2021. Relative risk of groundwater-quality degradation near California (USA) Oil Fields estimated from ^{3}H, ^{14}C, and ^{4}He. Appl. Geochem. 131 https://doi.org/10.1016/j.apgeochem.2021.105024.

McMahon, P.B., Thomas, J.C., Crawford, J.T., Dornblaser, M.M., Hunt, A.G., 2018b. Methane in groundwater from a leaking gas well, Piceance Basin, Colorado, USA. Sci. Total Environ. 634 (1), 791–801.

Metzger, L.F., Herrera, P.J., 2020, Historical produced water chemistry data compiled for the Orcutt and Oxnard oil fields, Santa Barbara and Ventura Counties, southern California: U.S. Geological Survey data release. ⟨https://doi.org/10.5066/P9AYRXBD⟩.

McMahon, P.B., Vengosh, A., Davis, T.A., Landon, M.K., Tyne, R.L., Wright, M.T., Kulongoski, J.T., Hunt, A.G., Barry, P.H., Kondash, A.J., Wang, Z., Ballentine, C.J., 2019. Occurrence and sources of radium in groundwater associated with oil fields in the southern San Joaquin Valley, California. Environ. Sci. Technol. 53 (16), 9398–9406. https://doi.org/10.1021/acs.est.9b02395.

Molofsky, L.J., Connor, J.A., Wylie, A.S., Wagner, T., Farhat, S.K., 2013. Evaluation of methane sources in groundwater in northeastern Pennsylvania. Groundwater 51 (3), 333–349. https://doi.org/10.1111/gwat.12056.

Moritz, A., Helie, J.-F., Pinti, D.L., Larocque, M., Barnetche, D., Retailleau, S., Lefebvre, R., Gelinas, Y., 2015. Methane baseline concentrations and sources in shallow aquifers from the shale gas-prone region of the St. Lawrence lowlands (Quebec, Canada). Environ. Sci. Technol. 49, 4765–4771. https://doi.org/10.1021/acs.est.5b00443.

Muir, K.S., 1964, Geology and ground water of San Antonio Creek valley, Santa Barbara County, California: U.S. Geological Survey Water-Supply Paper 1664, 53 p.

Mullaney, J.R., Lorenz, D.L., Arntson, A.D., 2009, Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, northern United States: U.S. Geological Survey Scientific Investigations Report 2009–5086, 41 p.

Mulqueen, S.P., 2007, Petroleum seeps: Structural setting, energy drive and path migration, In: D. S. Kunitomi, S. P. Mulqueen, and B. H. Hesson, eds., Oil on their shoes: Famous and little known oil seeps of Los Angeles and Ventura counties. AAPG Pacific Section, 1–26.

Namson, J., Davis, T.L., 1990. Late Cenozoic fold and thrust belt of the southern Coast Ranges and Santa Maria Basin, California. Am. Assoc. Pet. Geol. Bull. 74, 467–492.

Osborn, S.G., McIntosh, J.C., 2010. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. Appl. Geochem. 25 (3), 456–471. https://doi.org/10.1016/j.apgeochem.2010.01.001.

Pacific Coast Energy Company, 2017, Project proposal for Pacific Coast Energy Co - Orcutt cyclic steam Diatomite - 2017–10, accessed October 2017 at: ⟨https://geotracker.waterboards.ca.gov/profile_report.asp?global_id=T10000011075⟩.

Planert, M., and Williams, J.S., 1995, Ground water atlas of the United States, chap. B, California, Nevada: U.S. Geological Survey Hydrologic Atlas (HA) 730–B, accessed at: ⟨http://pubs.usgs.gov/ha/ha730/ch_b/index.html⟩.

Quigley, D.C., Hornafius, J.S., Luyendyk, B.P., Francis, R.D., Clark, J., Washburn, L., 1999. Decrease in natural marine hydrocarbon seepage near Coal Oil Point, California, associated with offshore oil production. Geol 27, 1047–1050.

Rosecrans, C.Z., Landon, M.K., McMahon, P.B., Gillespie, J.M., Kulongoski, J.T., Stephens, M.J., Hunt, A.G., Shimabukuro, D.H., Davis, T.A., 2021. Groundwater quality of aquifers overlying the Oxnard oil field, Ventura County, California. Sci. Total Environ. 771, 144822 https://doi.org/10.1016/j.scitotenv.2020.144822.

Schenk, C.J., Brownfield, M.E., Charpentier, R.R., Cook, T.A., Gautier, D.L., Higley, D.K., Kirschbaum, M.A., Klett, T.R., Pitman, J.K., Pollastro, R.M., Tennyson, M.E., Wandrey, C.J., and Whidden, K.J., (World Conventional Resources Assessment Team), 2012, An estimate of undiscovered conventional oil and gas resources of the world, 2012: U.S. Geological Survey Fact Sheet FS-2012–3042. ⟨http://pubs.usgs.gov/fs/2012/3042⟩.

Schloemer, S., Elbracht, J., Blumenberg, M., Illing, C.J., 2016. Distribution and origin of dissolved methane, ethane, and propane in shallow groundwater of Lower Saxony. Ger. Appl. Geochem. 67, 118–132. https://doi.org/10.1016/j.apgeochem.2016.02.005.

Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. Geochim. Cosmochim. Acta 44, 649–661.

Seitz, N.O., Kulongoski, J.T., Marcusa, J.A., and Qi, S.L., 2021, Produced water chemistry data collected from the Orcutt oil field, 2018, Santa Barbara County, California: U.S. Geological Survey data release. ⟨https://doi.org/10.5066/P936ZEZW⟩.

Sherwood, O.A., Rogers, J.D., Lackey, G., Burke, T.L., Osborn, S.G. and Ryan, J.N., 2016a, Groundwater methane in relation to oil and gas development and shallow coal seams in the Denver-Julesburg Basin of Colorado: Proc. Natl. Acad. Sci. U.S.A., 113(30), 8391–8396. ⟨https://doi.org/10.1073/pnas.1523267113⟩.

Siegel, D.I., Azzolina, N.A., Smith, B.J., Perry, A.E., Bothun, R.L., 2015a. Methane concentrations in water wells unrelated to proximity to existing oil and gas wells in northeastern Pennsylvania. Environ. Sci. Technol. 49 (7), 4106–4112.

Siegel, D.I., Smith, B., Perry, E., Bothun, R., Hollingsworth, M., 2015b. Pre-drilling water-quality data of groundwater prior to shale gas drilling in the Appalachian Basin: the chesapeake energy corporation data set. Appl. Geochem. 63, 37–57.

Sherwood, O.A., Rogers, J.D., Lackey, G., Burke, T.L., Osborn, S.G., Ryan, J.N., 2016b. Groundwater methane in relation to oil and gas development and shallow coal seams in the Denver-Julesburg Basin of Colorado. Proc. Natl. Acad. Sci. U.S.A. 113 (30), 8391–8396. https://doi.org/10.1073/pnas.1523267113.

Swanson, R.G., 1981. Sample examination manual. Am. Assoc. Pet. Geol. 54. https://doi.org/10.1306/Mth1413.

Sweetkind, D.S., Tennyson, M.E., Langenheim, V.E., Shumaker, L.E., 2010, Digital tabulation of stratigraphic data from oil and gas wells in the Santa Maria Basin and surrounding areas, central California coast. U.S. Geological Survey Open-File Report 2010–1129, 11 p. ⟨https://doi.org/10.3133/ofr20101129⟩.

Taylor, S.W., Sherwood Lollar, B., Wassenaar, L.I., 2000. Bacteriogenic ethane in near-surface aquifers: Implications for leaking hydrocarbon well bores. Environ. Sci. Technol. 34, 4727–4732.

Tyne, R.L., Barry, P.H., Karolytė, R., Byrne, D.J., Kulongoski, J.T., Hillegonds, D.J., Ballentine, C.J., 2021. Investigating the effect of enhanced oil recovery on the noble gas signature of casing gases and produced waters from selected California oil fields. Chem. Geol. 584, 120540 https://doi.org/10.1016/j.chemgeo.2021.120540.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Report Technical Water Resources Investigation, book 9, chap. A1–A9. accessed January 2018a at: ⟨https://water.usgs.gov/owq/FieldManual/⟩.

U.S. Geological Survey, 2018b, National Water Information System: U.S. Geological Survey web interface, http://dx.doi.org/10.5066/F7P55KJN. accessed January 2018 at: ⟨http://waterdata.usgs.gov/nwis/⟩.

U.S. Geological Survey, 2019a, Active Quaternary faults, California, accessed August 2019 at: ⟨https://www.usgs.gov/natural-hazards/earthquake-hazards/faults?qt-science_support_page_related_con=4#qt-science_support_page_related_con⟩.

U.S. Geological Survey, 2019b, California Oil, Gas, and Groundwater (COGG) Program webpage, accessed April 2019 at: ⟨https://ca.water.usgs.gov/projects/oil-gas-groundwater/⟩.

U.S. Geological Survey, 2020, San Antonio Creek Water Availability- Monitoring Networks, accessed May 2020 at: ⟨https://ca.water.usgs.gov/projects/san-antonio-creek/san-antonio-creek-water-data.html⟩.

Vengosh, A., Jackson, R.B., Warner, N., Darrah, T.H., Kondash, A., 2014. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. Environ. Sci. Technol. 48 (15), 8334–8348. https://doi.org/10.1021/es405118y.

Warner, N.R., Jackson, R.B., Darrah, T.H., Osborn, S.G., Down, A., Zhao, K., White, A., Vengosh, A., 2012. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. Proc. Natl. Acad. Sci. U.S.A. 109 (30), 11961–11966. https://doi.org/10.1073/iti3012109.

Warner, N.R., Kresse, T.M., Hays, P.D., Down, A., Karr, J.D., Jackson, R.B., Vengosh, A., 2013. Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas. Appl. Geochem. 35, 207–220. https://doi.org/10.1016/j.apgeochem.2013.04.013.

Wen, T., Niu, X., Gonzales, M., Zheng, G., Li, Z., Brantley, S.L., 2018. Big groundwater data sets reveal possible rare contamination amid otherwise improved water quality for some analytes in a region of Marcellus Shale development. Environ. Sci. Technol. 52, 7149–7159.
Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chem. Geol. 161, 291–314.
Whyte, C.J., Vengosh, Avner, Warner, N.R., Jackson, R.B., Muehlenbachs, Karlis, Schwartz, F.W., Darrah, T.H., 2021. Geochemical evidence for fugitive gas contamination and associated water quality changes in drinking-water wells from Parker County, Texas. Sci. Total Environ. 780, 146555.
Woda, J., Wen, T., Yoxtheimer, D., Engelder, T., Clara Castro, M., Brantley, S.L., 2018. Detecting and explaining why aquifers occasionally become degraded near hydraulically fractured shale gas wells. Proc. Natl. Acad. Sci. U.S.A. 115, 12349–12358. https://doi.org/10.1073/pnas.1809013115.
Worts, G.F., Jr., 1951, Geology and groundwater resources of the Santa Maria Valley area, California: U.S. Geological Survey Water-Supply Paper 1000. 169 p.
Wright, M.T., McMahon, P.B., Landon, M.K., Kulongoski, J.T., 2019. Groundwater quality of a public supply aquifer in proximity to oil development, Fruitvale oil field, Bakersfield, California. Appl. Geochem. 106, 82–95. https://doi.org/10.1016/j.apgeochem.2019.05.003.