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Groundwater Quality Near the Placerita Oil Field, California, 2018

Scientific Investigations Report 2024–5042

U.S. Department of the Interior
U.S. Geological Survey

Cover. Google Earth image accessed 2019. Golden Valley Road (at right) did not exist in 1949. Lyons Avenue is the yellow line running diagonally in the upper left corner.

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By Jennifer S. Stanton, Matthew K. Landon, David H. Shimabukuro, Justin T. Kulongoski, Andrew G. Hunt, Peter B. McMahon, Isabelle M. Cozzarelli, Robert Anders, and Theron A. Sowers

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Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
	Area	
square kilometer (km^2)	247.1	acre
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
cubic meter (m^3)	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	0.2642	gallon (gal)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
liter (L)	61.02	cubic inch (in^3)
cubic meter (m^3)	0.0008107	acre-foot (acre-ft)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32.$$

Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Elevation, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Results for measurements of stable isotopes of an element (with symbol E) in water, solids, and dissolved constituents commonly are expressed as the relative difference in the ratio of the number of the less abundant isotope (iE) to the number of the more abundant isotope of a sample with respect to a measurement standard.

Tritium is given in tritium units (TUs), which is equal to 3.19 picocuries per liter.

Carbon-14 in dissolved inorganic carbon is given in percent modern carbon (pmc).

Dissolved light hydrocarbon gases are given in milligrams per liter (mg/L) or percentage of total dissolved gases (mole percent).

Oil-field terminology used throughout this report is defined in appendix 1.

Abbreviations

^{14}C-DIC	carbon-14 in dissolved inorganic carbon
δ^{13}C-DIC	stable isotopes of carbon in dissolved inorganic carbon
δ^{2}H-CH_4	stable isotopes of hydrogen in methane
δ^{13}C-CH_4	stable isotopes of carbon in methane
δ^{2}H	stable isotopes of hydrogen in water
δ^{18}O	stable isotopes of oxygen in water
^{3}H	tritium
API	American Petroleum Institute
BTEX	benzene, toluene, ethylbenzene, and xylenes
COGG	California Oil, Gas, and Groundwater program
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
PCE	tetrachloroethylene
RMP	California State Water Resources Control Board Oil and Gas Regional Monitoring Program
TDS	total dissolved solids
USGS	U.S. Geological Survey
VOC	volatile organic compound

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Abstract

Groundwater-quality data and potential fluid-migration pathways near the Placerita Oil Field in Los Angeles County, California, were examined by the U.S. Geological Survey to determine if oil-field fluids (water and gas from oil-producing and non-producing zones) have mixed with groundwater resources. Six of the 13 new groundwater samples collected for this study contained petroleum hydrocarbons, thermogenic gas, inorganic chemical signatures, and (or) isotopic values consistent with potential mixing with fluids from hydrocarbon-bearing formations.

For historical groundwater samples, benzene was the most detected petroleum hydrocarbon. The historical groundwater samples with a benzene concentration greater than 0.5 micrograms per liter were from environmental monitoring wells at industrial or commercial facilities unrelated to oil and gas development that, in many cases, have identified soil or groundwater contamination and were not typically analyzed for other constituents that could provide additional lines of evidence for potential mixing with oil-field fluids. Methane was not detected in any of the 12 historical samples with a reported measurement.

Reviewing historical data revealed factors that could potentially adversely affect groundwater quality in the study area. These factors include modified hydraulic gradients caused by large volumes of water extracted from the main production area and reinjected downgradient into nonproducing zones, well-barrier failures in wells constructed in the northern part of the oil field before the 1970s, well-barrier failures in produced-water disposal wells downgradient from the main production area, and naturally occurring hydrocarbons at shallow intervals. The groundwater samples most geochemically similar to samples from hydrocarbon-bearing formations were in areas where hydrocarbons are naturally occurring at shallow intervals and where oil development is at shallow depths. Additional data for hydraulic heads, water quality, and formation temperatures at multiple depths in areas with large injection volumes and well-integrity issues are needed to evaluate whether those factors have contributed to mixing between fluids from oil-producing or injection formations and groundwater resources.

Introduction

California produces substantial volumes of crude oil (U.S. Energy Information Administration, 2020) with almost 500 onshore oil fields. Fresh groundwater used for drinking water supply and other purposes typically is separated from hydrocarbon-producing zones (zones from which commercial quantities of oil or gas have been extracted) by low-permeability confining layers. However, oil and gas development can sometimes introduce pathways for migration of fluids from hydrocarbon-producing zones to groundwater resources (Richter and Kreitler, 1991; Darrah and others, 2014; Hammond and others, 2020; McMahon and others, 2023). In addition, natural features such as faults and discontinuous, low-permeability confining layers can allow upward movement of oil-field fluids (Jung and others, 2015; Eichhubl and Boles, 2000). Naturally occurring hydrocarbons at shallow intervals can also affect groundwater resources (Hodgson, 1987; Hornafius and others, 1999; Rosecrans and others, 2021). Where pathways are present, upward movement of water from injection zones can be driven by increased pressures caused by injecting produced water or steam into subsurface formations (Rosecrans and others, 2021; McMahon and others, 2023) or withdrawing water from supply wells with perforations close to deep formations (Izbicki and others, 2005a, b; United Water Conservation District, 2021).

The U.S. Geological Survey (USGS) is working in cooperation with the California State Water Resources Control Board (State Water Board), and other State and local agencies, to implement the Oil and Gas Regional Monitoring Program (RMP) as required by California Senate Bill 4 (California State Legislature, 2013). The objectives of the RMP are to assess the location of groundwater resources with less than 10,000 milligrams per liter (mg/L) total dissolved solids (TDS), the upper limit defined for potential sources of drinking water (U.S. Environmental Protection Agency, 2019), in proximity to oil and gas fields; assess evidence for

[1]U.S. Geological Survey.

[2]California State University.

the presence or absence of constituents potentially derived from hydrocarbon-bearing formations in groundwater, and, if present, identify potential migration pathways or processes; and determine how oil and gas development has affected groundwater quality relative to other anthropogenic activities and natural processes (U.S. Geological Survey, undated). The USGS serves as the technical lead of the RMP through the California Oil, Gas, and Groundwater program.

The Placerita Oil Field and surrounding areas in Los Angeles County, California (fig. 1) was selected in consultation with the State Water Board and Los Angeles Regional Water Quality Control Board as a priority oil field for study because of its high density of oil wells and its close vertical proximity of the oil-producing zones to land surface relative to other oil fields in California (Davis and others, 2018a). In addition, the Placerita Oil Field is at the upgradient end of a groundwater basin (fig. 2) that provides water for public supply and other uses.

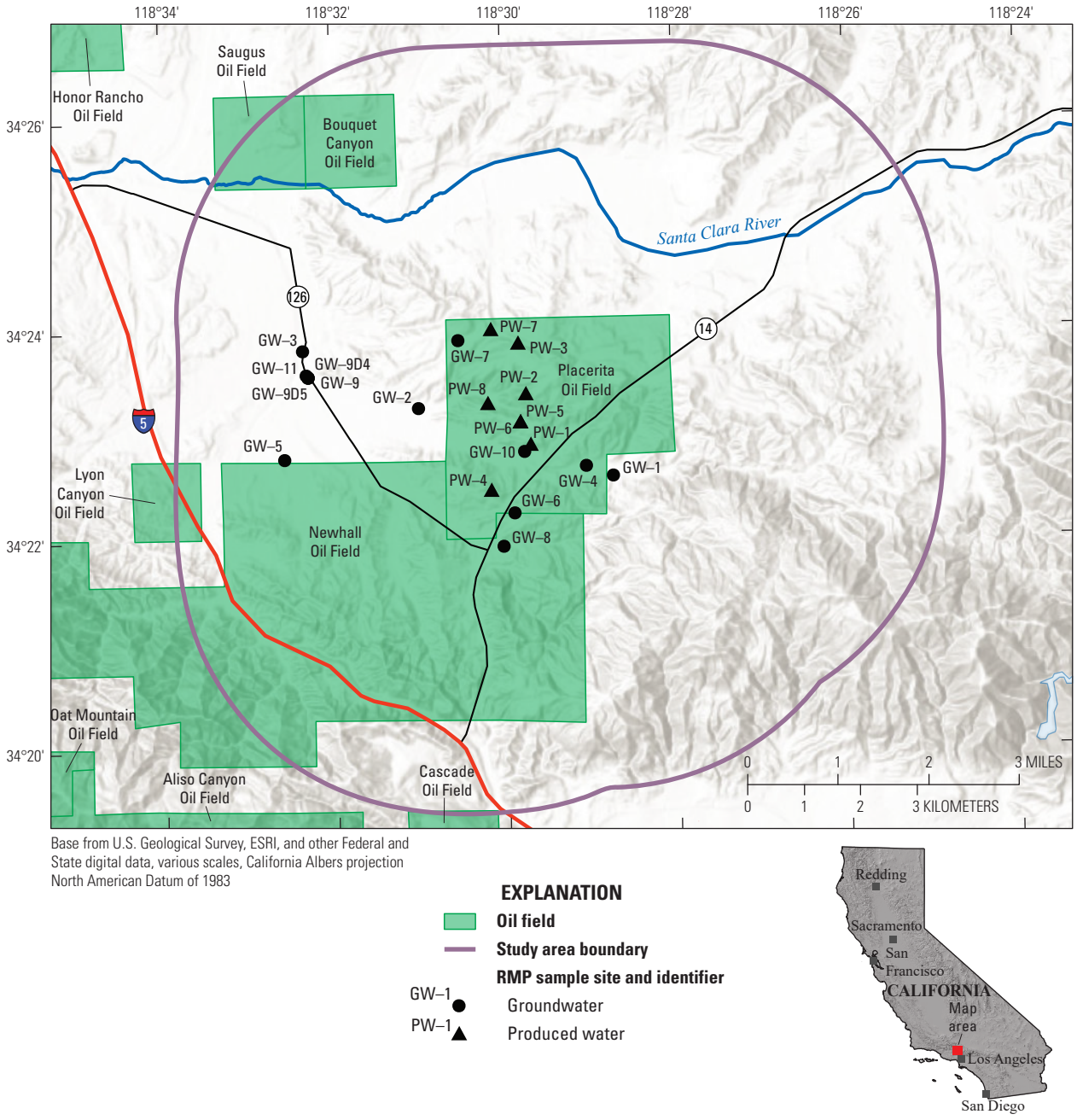
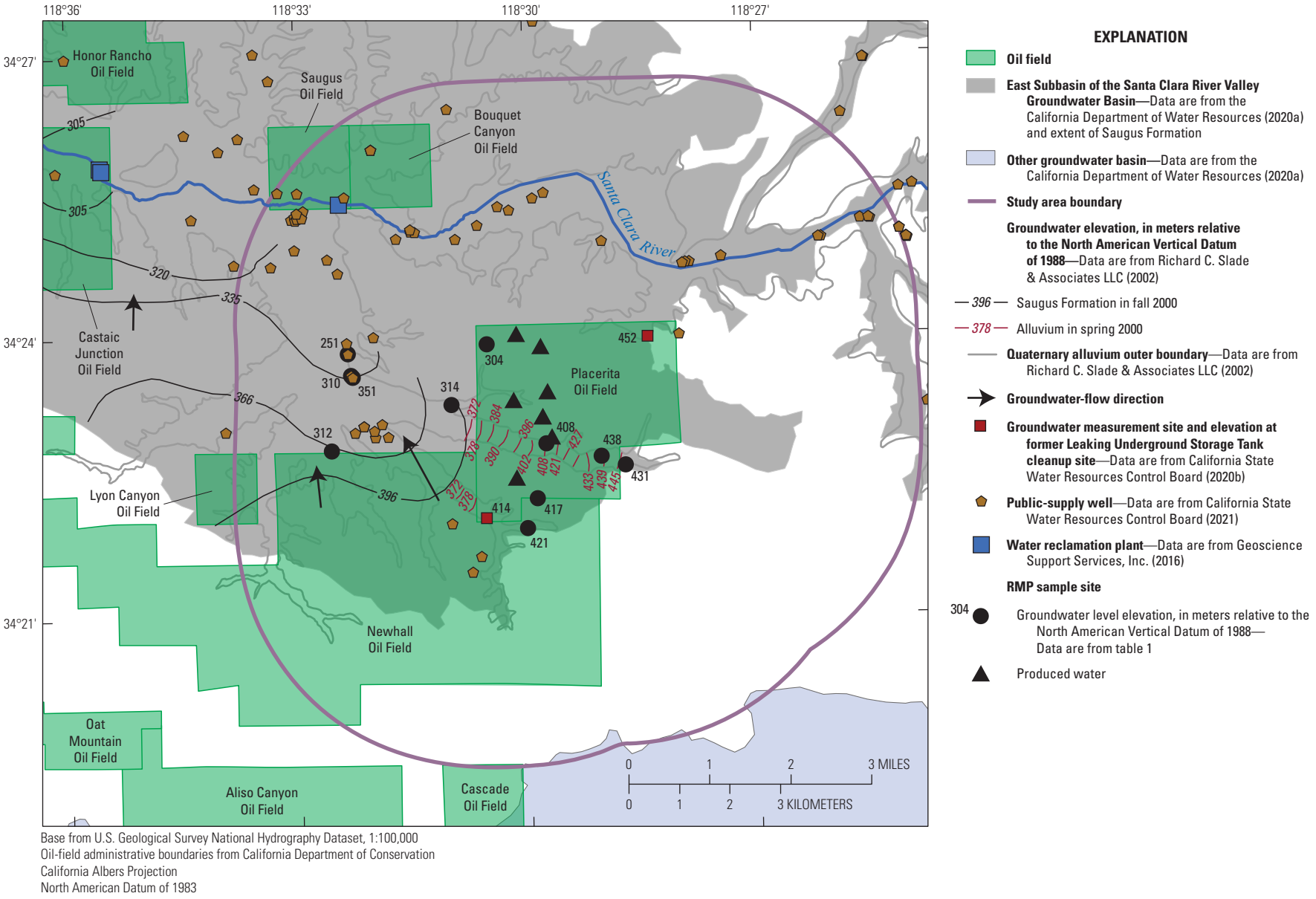


Figure 1. Map showing the Placerita Oil Field study area and California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) sample collection sites, California, 2018. Data are from Stanton and Marcusa (2024).



Base from U.S. Geological Survey National Hydrography Dataset, 1:100,000
Oil-field administrative boundaries from California Department of Conservation
California Albers Projection
North American Datum of 1983

Figure 2. Map showing the groundwater basins, public-supply wells, water reclamation plants, groundwater elevations, and other hydrogeologic features near the Placerita Oil Field study area and California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) sample collection sites, California, 2018.

Purpose and Scope

This report describes groundwater quality in the context of oil development, other anthropogenic activities, and natural processes near the Placerita Oil Field. Study results are provided in three sections: "Groundwater Quality", "Potential Fluid-Migration Pathways", and "Relation of Groundwater Quality to Pathways". The "Groundwater Quality" section discusses the primary chemical constituents most helpful for identifying potential effects of oil development on groundwater in the study area:

- volatile organic compounds (VOCs),
- light hydrocarbon gases and stable isotopes of methane,
- groundwater age-dating tracers,
- inorganic tracers,
- dissolved organic carbon,
- stable isotopes of water,
- noble gases, and
- stable isotopes of carbon in dissolved inorganic carbon.

Groundwater quality results were compared with the chemistry of oil field produced-water samples representing oil field formation water, water stored in tanks before injection, and water from wells that have been used for steam injection and disposal.

Information about potential sources and pathways of hydrocarbons and other chemical constituents that are associated with oil-field fluids are presented in the "Potential Fluid-Migration Pathways" section. Data about potential pathways were obtained from historical data, historical publications and documents, and new analyses conducted by this study. The potential pathways were assessed using a coarse-level examination of available information and more detailed reviews of data in selected parts of the study area where the coarse-level examination indicated the presence of potential pathways.

The "Relation of Groundwater Quality to Pathways" section includes detailed reviews of possible pathways near the California Oil, Gas, and Groundwater RMP groundwater samples with chemistry results that indicated potential mixing with fluids from hydrocarbon-bearing formations.

Data limitations that prevented a better understanding of the effects of anthropogenic activities and natural factors on groundwater quality were identified. The RMP groundwater chemistry data used for analyses within this report are published in Stanton and Marcusa (2024), and the RMP produced-water chemistry data are published in Seitz and others (2024).

Study Area Description

The study area includes the area within 4.8 kilometers (km) of the Placerita Oil Field administrative boundary. The Placerita Oil Field is about 3 km east of the town of Newhall in western Los Angeles County and is at the upgradient end of the East Subbasin of the Santa Clara River Valley Groundwater Basin, hereinafter referred to as the East Subbasin (fig. 2; California Department of Water Resources, 2020a). As of 2012, land use in the study area was designated as 30 percent low use (shrub or scrub or grassland), 28 percent urban, and 25 percent residential (Falcone, 2015; Multi-Resolution Land Characteristics Consortium, 2021). Smaller parts of the study area were used for commercial, industrial, transportation, and recreation purposes (17 percent).

Hydrogeologic Setting

The most prominent surface-water feature in the study area is the Santa Clara River, which intermittently flows and is north of the Placerita Oil Field (fig. 2). Several small tributaries of the Santa Clara River serve as drainage features within and downgradient from the Placerita Oil Field. Groundwater used for supply is stored in Quaternary alluvial deposits under the Santa Clara River and its tributaries and in the Pliocene to Pleistocene Saugus Formation (Richard C. Slade & Associates, LLC, 2002; Geoscience Support Services, Inc., 2016). Infiltration of water from the Santa Clara River and intermittently flowing tributary streams is the major source of recharge in the alluvial aquifer (Robson, 1972; Geoscience Support Services, Inc., 2016). Primary sources of water to the Saugus Formation are groundwater from the overlying alluvium, recharge from precipitation, and smaller amounts of subsurface inflow from upgradient geologic units (Geoscience Support Services, Inc., 2016).

The Saugus Formation is composed of two stratigraphic units (Richard C. Slade & Associates, LLC, 2002). The lower unit is composed of fine-grained sandstone and siltstone sediments that were deposited in shallow marine and terrestrial environments and is not widely used for public supply because of its brackish quality and low well yields (Richard C. Slade & Associates, LLC, 2002). Water from the lower unit could be a source of salinity in areas where hydraulic gradients favor upward movement of groundwater. The upper unit is composed of coarse-grained sediments that were deposited in a terrestrial environment. Sediments of the upper unit comprise aquifers that are used for public water supply at depths from about 90 to 760 meters (m) below land surface. The base of freshwater, commonly defined in California as having a TDS concentration of less than 3,000 mg/L, varies across the study area. The depth to base of freshwater has a maximum depth of about 460 m below land surface on the north side of the San Gabriel Fault (fig. 3) and more than 1,000 m below land surface south of the San Gabriel Fault (Richard C. Slade & Associates, LLC, 2002).

Within the Placerita Oil Field, the base of freshwater denoted in oil-field well drilling records is commonly at a depth of about 150 m below land surface (Davis and others, 2018b).

Few water levels were available from wells within the Placerita Oil Field for determining the depth to groundwater and local flow directions above the oil production and injection zones (California Department of Water Resources, 2020b). However, documentation for a produced-water spill indicated that groundwater is or has been within 15 m below land surface (corresponding to elevations of 452 and 414 m) at several locations near the far northeast and southwest edges of the Placerita Oil Field (GeoTracker Global ID T1000007342). Groundwater elevations in the alluvial valleys were also available in the southern part of the Placerita Oil Field and ranged from 378 to 445 m (fig. 2; Richard C. Slade & Associates LLC, 2002). The regional groundwater flow in the Saugus Formation downgradient of the Placerita Oil Field is generally toward the northwest (fig. 2), with local groundwater flow patterns in the alluvium toward the river and then westward (Richard C. Slade & Associates, LLC, 2002; Geoscience Support Services, Inc., 2016; Luhdorff & Scalmanini Consulting Engineers, 2021).

Water use exceeds local aquifer production, and in 2020, more than 60 percent of water supply was imported from the State Water Project and other sources, 22 percent was pumped from groundwater in alluvial deposits, 16 percent was pumped from groundwater in the Saugus Formation, and less than 1 percent was from recycled wastewater (Luhdorff & Scalmanini Consulting Engineers, 2021). Water has been imported from outside the study area since the 1980s and has been the primary source of freshwater since 2003. Three water reclamation plants are downgradient from the Placerita Oil Field and RMP sample locations (fig. 2). They are tertiary treatment facilities, primarily treating municipal wastewater for discharge into the Santa Clara River or for beneficial reuse downgradient from the study area (Geoscience Support Services, Inc., 2016). Unlike some oil field settings in California, such as the Fruitvale (Wright and others, 2019) and Oxnard (Rosecrans and others, 2021) Oil Fields, groundwater directly overlying the Placerita Oil Field is not used for purposes that require high quality water, such as for drinking (California Department of Water Resources, 2023). As of 2020, water in the region was primarily used for municipal supply with smaller amounts used for agriculture and other purposes (Luhdorff & Scalmanini Consulting Engineers, 2021).

Oil Field Geology and History

The geologic structures of the Placerita Oil Field consist of a series of Quaternary and Tertiary sedimentary deposits that lie on northwest dipping pre-Cretaceous crystalline rocks (Barton and Sampson, 1949; Oakeshott, 1950; Tudor, 1962; Winterer and Durham, 1962; California Department of Conservation, 1992). The extent of oil-producing zones in the Placerita Oil Field has been described as limited by an edge-water drive (groundwater flow into the oil-producing zones) on the west and geologic facies changes in other directions (Tudor, 1962; Berkman, 1994). Most oil development is west of the Whitney Canyon fault and south of the San Gabriel fault (fig. 3). Other than the bounding faults, faulting within the field is minor (Tudor, 1962). Oil is produced from three zones: the Pliocene-Pleistocene Shepard zone in the lower unit of the Saugus Formation, and the Pliocene Upper Kraft and Lower Kraft zones in the Pico and Repetto (Towsley) Formations (fig. 4). The Lower Kraft zone is the main producing interval (Berkman, 1994). The elevation of the top of the Shepard zone, the shallowest oil-producing zone, ranges from 46 to 411 m (fig. 4), corresponding with approximate depths of 400 to 60 m below land surface (California Department of Conservation, 1992). The oil-producing zones are overlain by younger intervals of the Saugus Formation, terrace deposits, and recent alluvium (Oakeshott, 1950; Tudor, 1962).

The Placerita Oil Field had two early periods of development. Four wells (York 1, 2, 3, 4) were developed to maximum depths of 487 m below land surface between 1920 and 1933 (Winterer and Durham, 1962). These first four wells only yielded small amounts of low gravity (11.8° American Petroleum Institute [API] gravity) oil; therefore, no further development commenced until the late 1940s when a well (Kraft 1) was constructed that yielded 10 cubic meters (m^3) a day of 16.4° API gravity oil from depths of 178 to 219 m below land surface (Winterer and Durham, 1962). In 1949, a period of rapid development in the northern part of the field was initiated by the completion of a well (Juanita 1) that produced 54 m^3 a day of 22.8° API gravity oil from 529 to 560 m below land surface (Winterer and Durham, 1962). By the end of November 1951, 1.8 million cubic meters (Mm^3) of high-gravity oil was produced from the northern part of the field, and 0.5 Mm^3 of lower gravity oil was produced in the southern part of the field (Winterer and Durham, 1962). Oil production declined substantially after 1950 and has remained below about 200,000 m^3 per year since 1959 (fig. 5; California Department of Conservation, variously dated). The field produced almost 11.7 Mm^3 of oil, 278,000 m^3 of gas, and 137 Mm^3 of water from 1949 to 2017 (California Department of Conservation, variously dated). Gas has not been extracted since 1990. Because gas extraction is relatively small in the study area compared to oil extraction, discussions throughout this report focus on oil development.

Enhanced oil recovery practices used since the mid-1950s in the Placerita Oil Field to help increase the flow of low gravity oil for extraction include waterflooding, steamflooding, cyclic steam, and fireflooding (California Department of Conservation, 1992, variously dated). Waterflooding began in 1954 but is no longer practiced. Steamflooding and cyclic steam activities began in 1964 and are still common in the Placerita Oil Field. Fireflooding was only used between 1964 and 1967. Hydraulic fracturing

was not reported as an enhanced oil recovery practice used within the Placerita Oil Field (California Department of Conservation, 2021).

As of 2018, the Placerita Oil Field had 978 wells (184 active, 261 idle, and 533 abandoned; fig. 3; California Department of Conservation, 2018). Among active wells, 2 were used for production without cyclic steam, 128 were used for production with cyclic steam, 40 were used for steam flood injection, 10 were used for produced-water disposal injection, and four wells were used for observation. About 142 Mm^3 of water and steam were injected in the Placerita Oil Field from 1954 to 2017 with about 55 Mm^3 injected for enhanced oil recovery and about 87 Mm^3 injected for disposal (fig. 5; California Department of Conservation, variously dated). The cumulative volume of water and steam injected between 1949 and 2017 is about 4 percent smaller than the volume of oil and water produced. More water and steam were injected than produced in the mid-1960s to late-1970s, implying that produced water was treated and used for enhanced oil recovery and sources of water in addition to produced water were injected. During the other times, more water was produced than injected, indicating that excess water was disposed of using methods other than injection, such as surface disposal ponds, before disposal through injection wells became more prevalent, or through export out of the oil field, or because excess water was generated by groundwater flow into the oil-producing zones. Production and injection are shallower, and volumes are generally smaller, in the southern part of the Placerita Oil Field (fig. 6*A*, *B*, *C*). Water and steam injection volumes are discussed in more detail in the "Hydraulic Gradients" section.

Other oil fields in the study area are the Newhall Oil Field, Bouquet Canyon Oil Field, Lyon Canyon Oil Field, and Saugus Oil Field. Oil development in these fields is much less extensive than in the Placerita Oil Field (California Department of Conservation, 2018, 2020). As of 2018, 27 idle and 294 abandoned oil-field wells in the study area were outside of the Placerita Oil Field; however, 186 of those were dry holes never used for production or injection. Between 1977 and 2018, 48,000 m^3 of oil were produced from 41 of those oil-field wells, mostly from the Newhall Oil Field.

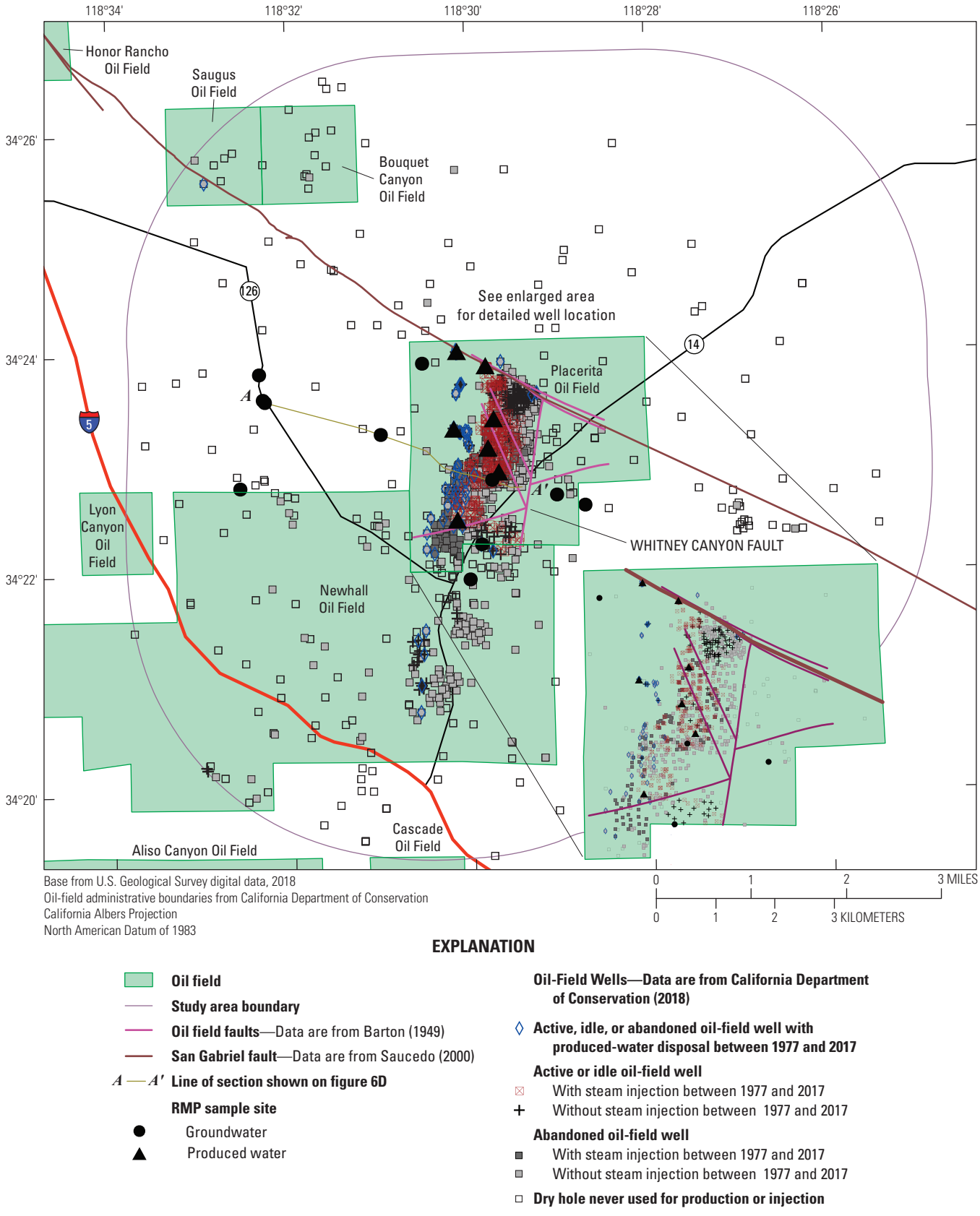


Figure 3. Map showing oil-field wells and faults in the Placerita Oil Field study area and California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) sample collection sites, California, 2018.

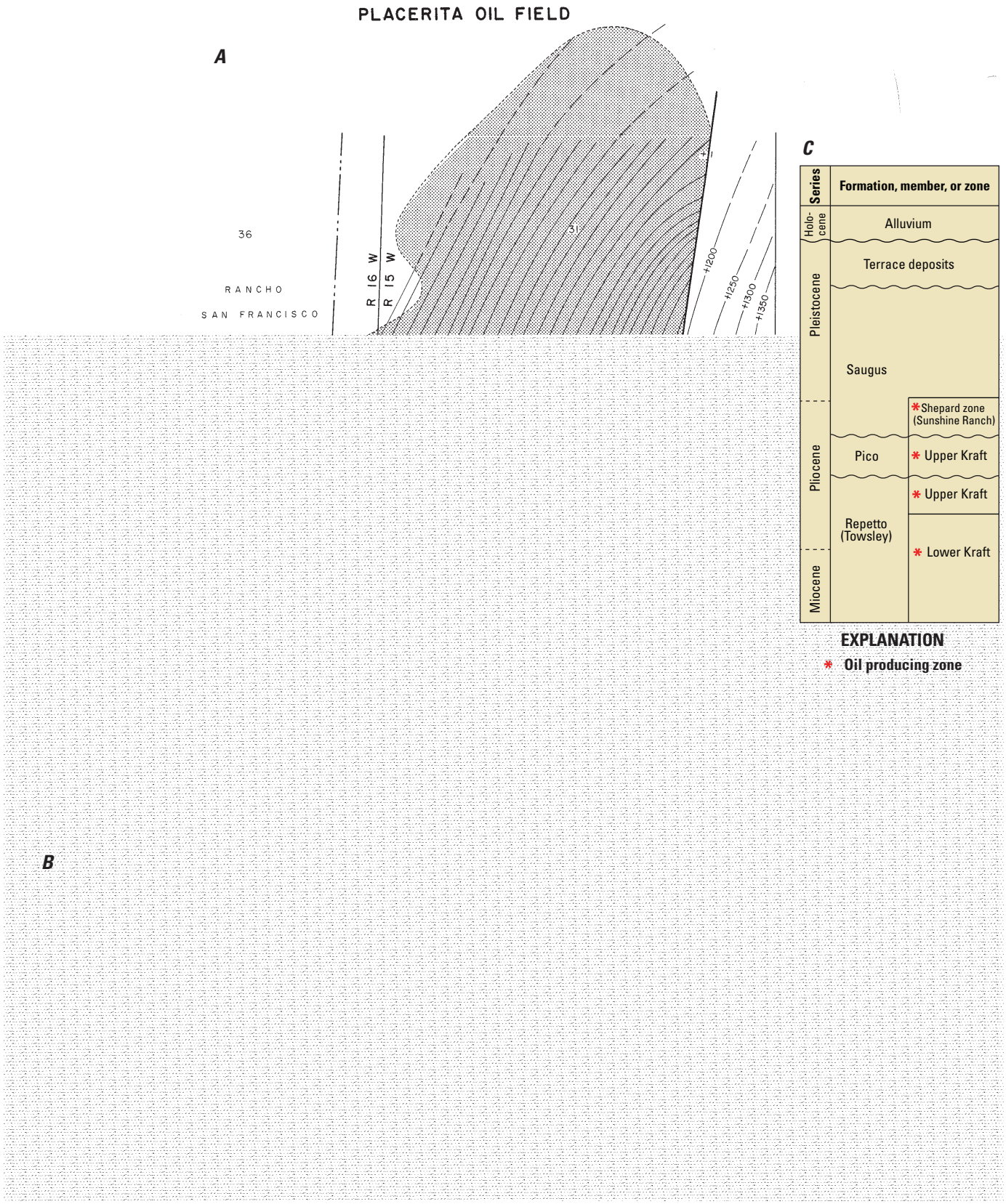


Figure 4. *A*, map showing elevation, in feet above sea level, of the top of the oil-producing zones (Shepard zone); *B*, cross section of oil-producing zones (California Department of Conservation, 1992, p. 386); and, *C*, stratigraphy of oil-producing zones (Tudor, 1962, table 1; Winterer and Durham, 1962) in the Placerita Oil Field, California.

Terms Related to Physical Formation or Zone

Hydrocarbon-bearing formations Oil- and gas-bearing formations, including those used for commercial oil and gas production and naturally occurring oil and gas shows in overlying sediments.

Hydrocarbon-producing zones Zones from which commercial quantities of oil or gas have been extracted.

Terms Related to Oil and Gas Development

Oil and gas development Commercial oil and gas extraction activities including production (withdrawal) from wells, injection, treatment, and disposal of excess water.

Oil and gas shows Gas or oil detected in the drilling mud or drilling cuttings and reported in mud logs or cores.

Oil-field well Any well constructed for oil-field activities including oil production, gas production, produced-water disposal, waterflood, steam flood, cyclic steam, observation, dry hole (never produced), and water supply.

Terms Related to Sources

Oil and gas sources of chemical constituents Include oil- and gas-development activities and naturally occurring (geologic) oil, gas, and saline water in sediments near oil fields. Synonyms: oil-production activities, oil-bearing formations, hydrocarbon-bearing formations.

Naturally occurring sources of hydrocarbons Naturally occurring oil and gas shows in sediments overlying or near oil fields; these do not yield commercial quantities of oil or gas.

Terms Related to Water

Oil-field fluids Water and gas from oil-producing zones and non-producing oil-bearing formations.

Water from oil-bearing formations Water having elevated salinity and concentrations of inorganic or organic solutes derived from oil- and gas-bearing formations, including those used for commercial oil and gas production and naturally occurring oil and gas shows in overlying sediments.

Water from oil-producing zones Water derived from an oil-field source. This can include produced water, oil-field formation water and injectate (water intended for disposal or injection for secondary recovery). Differs from produced water in terms of how the sample is accessed. This would not include water potentially derived from naturally hydrocarbon-bearing sediments overlying oil fields that do not yield commercial quantities of oil or gas.

Produced water Water withdrawn from an oil well and brought to the surface and may include oil, water, and gas from the geologic formation, and water or gas injected for enhanced recovery.

Oil-field formation water Water of original composition in the pore spaces of oil-producing zones that has not been altered by injection processes.

Injectate Water injected for disposal or for secondary recovery. Generally, consists primarily of recycled produced water, with treatments such as oil skimming (dehydrogenation), sometimes with treatment and (or) additives to limit biological activity, corrosion, and buildup of mineral deposits in injection wells. In some fields, injection for disposal occurs outside of oil-producing zones.

Water from non-producing oil-bearing formations Water from sediments containing naturally occurring oil and gas shows that overlie oil-producing zones.

Deep formation water unassociated with active oil fields Water having elevated salinity (concentrations of inorganic constituents and other dissolved solutes) derived from relatively deep formations not associated with oil and gas fields.

Idle well fluid level A fluid level measured in a well that has not produced oil or gas, produced water to be used in production stimulation, or been used for enhanced oil recovery, reservoir pressure management, or injection for a period of 24 consecutive months.

Terms Related to Gas

Thermogenic gas from oil-bearing formations Hydrocarbon gas of thermogenic origin derived from oil- and gas-bearing formations, including those used for commercial oil and gas production and naturally occurring oil and gas shows in overlying sediments.

Thermogenic gas from oil-producing zones Thermogenic gas derived from an oil-field source. This can include produced water, oil-field formation water, and injectate (water intended for disposal or injection for secondary recovery). This would not include water potentially derived from naturally occurring hydrocarbon-bearing sediments overlying oil fields that do not yield commercial quantities of oil or gas.

Thermogenic gas from non-producing oil-bearing formations Thermogenic gas from sediments containing naturally occurring oil and gas shows that overlie oil-producing zones.

Thermogenic gas Natural gas including methane and heavier light hydrocarbon gases derived from oil and gas generation processes including heating and high pressure, typically originally occurring at relatively large depths.

Microbial gas Natural gas, generally including methane with sometimes small amounts of ethane, derived from in situ production by microbe-facilitated reactions with organic carbon.

Terms Related to Enhanced Oil Recovery (EOR)

Cyclic steam Injecting steam into the oil-production zone through an oil-production well, allowing time for the heat energy of steam to reduce viscosity of the oil, and then producing oil from the well.

Waterflood The use of water injection to increase the reservoir pressure.

Steamflood Injecting steam into the oil-production zone through injection wells to reduce oil viscosity and drive oil toward oil-production wells.

Fireflood Igniting a fire in the oil-production zone to reduce oil viscosity and generate steam to drive oil toward oil-production wells.

Hydraulic fracturing A well stimulation treatment that, in whole or in part, includes the pressurized injection of one or more base fluids mixed with physical and chemical additives into an underground geologic formation in order to fracture the formation, thereby causing or enhancing the production of oil or gas from a well.

Appendix 2. Supplemental Tables for the Placerita Oil Field Study Area, California, 2018

Additional tables were prepared to provide supplemental oil well and geochemistry data used for assessing the potential for mixing of oil-field fluids with groundwater resources in the Placerita Oil Field study area. Oil field data were obtained from oil field operator records collected for the California Department of Conservation, Division of Geologic Energy Management (California Department of Conservation, 2020; 2022). Geochemistry data are available in Stanton and Marcusa (2024) and Seitz and others (2024) but are provided here to highlight and summarize the data used for analyses as a convenience for the reader.

Table 2.1. Oil-field well characteristics within 500 meters of California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) groundwater samples in the Placerita Oil Field study area, California.

[Table is available as a Microsoft Excel (xlsx) and a comma separated values (csv) format file for download at https://doi.org/10.3133/sir20245042]

Table 2.2. Volatile organic compounds detected in California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) groundwater samples, Placerita Oil Field study area, California, 2018.

[Table is available as a Microsoft Excel (xlsx) and a comma separated values (csv) format file for download at https://doi.org/10.3133/sir20245042.]

Table 2.3. Volatile organic compound concentrations, dissolved organic carbon concentrations, and age-dating results in California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) groundwater samples, Placerita Oil Field study area, California, 2018.

[Table is available as a Microsoft Excel (xlsx) and a comma separated values (csv) format file for download at https://doi.org/10.3133/sir20245042]

Table 2.4. Dissolved gases and other light hydrocarbon gas properties in California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) groundwater samples, Placerita Oil Field study area, California, 2018.

[Table is available as a Microsoft Excel (xlsx) and a comma separated values (csv) format file for download at https://doi.org/10.3133/sir20245042]

Table 2.5. Summary of selected inorganic constituent concentrations in California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) groundwater and produced-water samples, and historical produced-water samples, Placerita Oil Field study area, California.

[Table is available as a Microsoft Excel (xlsx) and a comma separated values (csv) format file for download at https://doi.org/10.3133/sir20245042]

Table 2.6. Well-barrier failures above top perforations of oil-field wells, Placerita Oil Field, California.

[Table is available as a Microsoft Excel (xlsx) and a comma separated values (csv) format file for download at https://doi.org/10.3133/sir20245042]

Table 2.7. Produced-water disposal wells downgradient from the main production area that have injected more than 500,000 cubic meters of produced water between 1977 and 2018, Placerita Oil Field, California.

[Table is available as a Microsoft Excel (xlsx) and a comma separated values (csv) format file for download at https://doi.org/10.3133/sir20245042]

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Appendix 3. Quality of Groundwater Samples Collected for the Placerita Oil Field Study Area, California, 2018

Quality-control samples were collected to assess the reliability of sampling procedures and analytical methods. These quality-control samples include equipment-blank, field-blank, replicate, and laboratory-matrix spike samples (table 3.1). Quality-control samples collected for all oil fields assessed by the Regional Monitoring Program during the general period (within three months) that samples were collected for the Placerita Oil Field study area were used to assess the quality of laboratory results used for this report. Quality-control sample results of constituents used for analyses in this report indicated that the laboratory results reasonably represent groundwater conditions. The following discussion is primarily for constituents used for analyses in this report. Additional results and details for quality-control samples are provided in Stanton and Marcusa (2024).

Field-blank samples were used to determine the occurrence and magnitude of sample contamination during sample collection, equipment cleaning, transport, and analysis. Sample bottles were filled with water that was specially prepared at the U.S. Geological Survey (USGS) National Water Quality Lab (NWQL) and certified to be free of the environmental sample analytes. Field-blank samples were otherwise collected using the same procedures and equipment as environmental samples. Small concentrations of several constituents analyzed for this study were detected in field blanks (ammonium, lead, manganese, and dissolved organic carbon [DOC]) but were not large enough to affect interpretations in this report. No volatile organic compounds (VOCs) were detected in field-blank samples.

One equipment-blank sample was used to assess the effectiveness of equipment cleaning protocols for a pump used to sample wells that did not have one permanently installed at the well. Like field-blank samples, the equipment-blank sample was collected using source-solution water that was specially prepared at the NWQL and circulated through the pump. Small amounts of DOC, copper, and orthophosphate were detected in the equipment-blank sample but did not affect interpretations for this study.

Table 3.1. Quality-control samples used for evaluating data quality of California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) groundwater samples collected for the Placerita Oil Field study area, 2018.

Chemical constituent group (number of constituents in the group)	Number of equipment blank samples	Number of field-blank samples	Number of replicate samples	Number of laboratory-matrix spike samples	Number of verification samples
Nutrients (9)	1	3	4	0	2
Major ions (11)	1	3	4	0	2
Trace elements (23)	1	3	4	0	2
Iron speciation (2)	1	2	4	0	0
Dissolved organic carbon and optical properties (21)	0	2	3	0	0
Volatile organic carbons (VOCs) (85)	1	3	4	3	2
Standard and hydrocarbon gases (23)	0	0	4	0	0
Radium isotope ratios (3)	0	0	4	0	1
Water isotope ratios (2)	0	0	4	0	0
Carbon isotope ratios (2)	0	0	4	0	0
Tritium	0	0	4	0	0
Sulfur hexafluoride (SF_6)	0	0	4	0	0
Noble gases (10)	0	0	4	0	0
Organic acids (5)	1	3	4	0	0
Strontium isotope ratio	0	0	4	0	0
Boron isotope ratio	0	0	4	0	0

The National Water Quality Laboratory follows a quality assurance plan described by Maloney (2005). It conducts internal testing as part of this plan to identify false positive and false negative results for VOCs. For the 22 VOCs detected in RMP groundwater samples, 18 had at least one false negative result and 9 had at least one false positive result (app. 2, table 2.2). The compound with the most false negative results was toluene (3.1 percent of the 65 spiked samples), and the compound with the most false positive results was tetrachloroethene (13.3 percent of the 150 blank samples).

Replicate samples were collected sequentially to determine data variability due to sampling and analytical procedures, or natural variation. Replicate pairs were compared for variability when both concentrations of a constituent were greater than the laboratory detection level (detected). Pairs were not assessed if one of the two concentrations was undetected. Pairs were considered to have a variability of zero when both constituents were undetected. Several methods were used to assess variability between replicate pairs at four wells and are described in Stanton and Marcusa (2024). Replicate sample results indicated that variability was generally less than 10 percent. Constituents with variability greater than 10 percent included

- barium (one replicate pair),
- boron (one replicate pair),
- lithium (one replicate pair),
- methane (two replicate pairs),
- ethane (one replicate pair),
- carbon-14 in dissolved inorganic carbon (^{14}C-DIC; one replicate pair),
- neon (one replicate pair),
- helium-4 (one replicate pair), and
- helium-3/helium-4 ratio (one replicate pair).

Laboratory-matrix spike samples were used to quantify the gain or loss of VOCs due to water-matrix properties or laboratory procedures. A spike recovery of 100 percent indicates no matrix interference and good analytical recovery. Of the 85 VOCs analyzed, 46 were within the range of from 70- to 130-percent recovery for all three spike samples. Of the 22 VOCs detected in environmental groundwater samples, 8 VOCs had acceptable recoveries in all three laboratory-matrix spike samples, 13 VOCs had one laboratory-matrix spike sample that was not within the acceptable range, and 1 VOC had 2 laboratory-matrix spike samples that were not within the acceptable range (app. 2, table 2.3). Most recovery values for the 22 VOCs detected in RMP environmental groundwater samples were greater than 100 percent, indicating that groundwater may have smaller VOC concentrations than what the laboratory analysis reports.

Samples GW–1 and GW–3 arrived at the laboratory above the recommended temperature for preventing degradation of VOCs and nutrients. Laboratory results for those constituents were verified by collecting new samples and resubmitting to the laboratory at the correct temperature. Comparison of results for sample GW–1 indicated that concentrations in the verification sample were the same as the original sample, except for the VOC styrene, which was 0.052 µg/L in the verification sample but undetected in the original sample. For sample GW–3, concentrations in the verification sample were smaller than the original sample, indicating that the original sample concentrations had probably not degraded. These results provided confidence that the original sample results were reliable and were used for interpretations in this report.

Four samples (GW–9, GW–9D4, GW–9D5, and GW–10) were not analyzed for DOC and its optical properties because bottles were lost or broken before arriving at the laboratory.

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Appendix 4. Noble Gas Compositions of Groundwater and Produced Water in the Placerita Oil Field Study Area, California, 2018

Noble gas concentrations and isotopic ratios can be used to identify groundwater that has interacted with hydrocarbons or is affected by other processes (Bosch and Mazor, 1988; Ballentine and others, 1991; Ballentine and others, 1996; Ballentine and others, 2002; Hunt and others, 2012; Barry and others, 2018; Tyne and others, 2019, 2021; Byrne and others, 2020; Karolytė and others, 2021). The composition of noble gases dissolved in groundwater is set during recharge by the partial pressure of the gas in the atmosphere and the temperature and salinity of the water. Partitioning of the gases from the atmosphere into the fluid produces a characteristic composition. During recharge, the composition of noble gas isotopes is preserved in groundwater isolated from the atmosphere and should plot along the calculated air saturated water values. Deviations from air saturated water values result from excess-air bubble entrainment during recharge (Heaton and Vogel, 1981) or light noble gas stripping and heavy noble gas enrichment during water, oil, or gas mixing (Hunt and others, 2012). The addition of atmospheric bubbles results in a characteristic positive slope from air saturated water values due to concentrations of noble gases above air saturated water values. One of the RMP produced-water samples (PW–4) and all the RMP groundwater samples except GW–10 show this characteristic addition of excess air bubbles (fig. 4.1).

Partitioning of the light noble gases neon-20 and argon-36 from water to the oil or gas phases results in a negative trend from the air saturated water values. This result was observed in groundwater sample GW–10 and all produced-water samples except for PW–4.

Elevated chloride concentrations, along with elevated helium-4 and the trend of concomitantly increasing helium-4 (driving low helium-3/helium-4) and chloride, and trace methane suggest a natural evolution of the groundwater in samples GW–2, GW–7, GW–9, and GW–9D4 likely due to exogenous crustal or radiogenic source of gases to the aquifer (Harkness and others, 2017; Stanton and Marcusa, 2024). Low tritium (^{3}H) and high helium-4 in those samples indicate isolation from the atmosphere for hundreds to thousands of years; thus, high chloride concentrations are likely from natural evolution of the water rather than the result of a surface spill of produced water. Noble gas data in combination with age-tracer data (table 2) also indicate samples containing modern groundwater were primarily derived from air equilibration during recharge with minor amounts of air bubble entrainment. Old groundwater, after equilibration during recharge, accumulated in situ produced (terrigenic) helium-4 and mantle helium-4 and helium-3 over long periods.

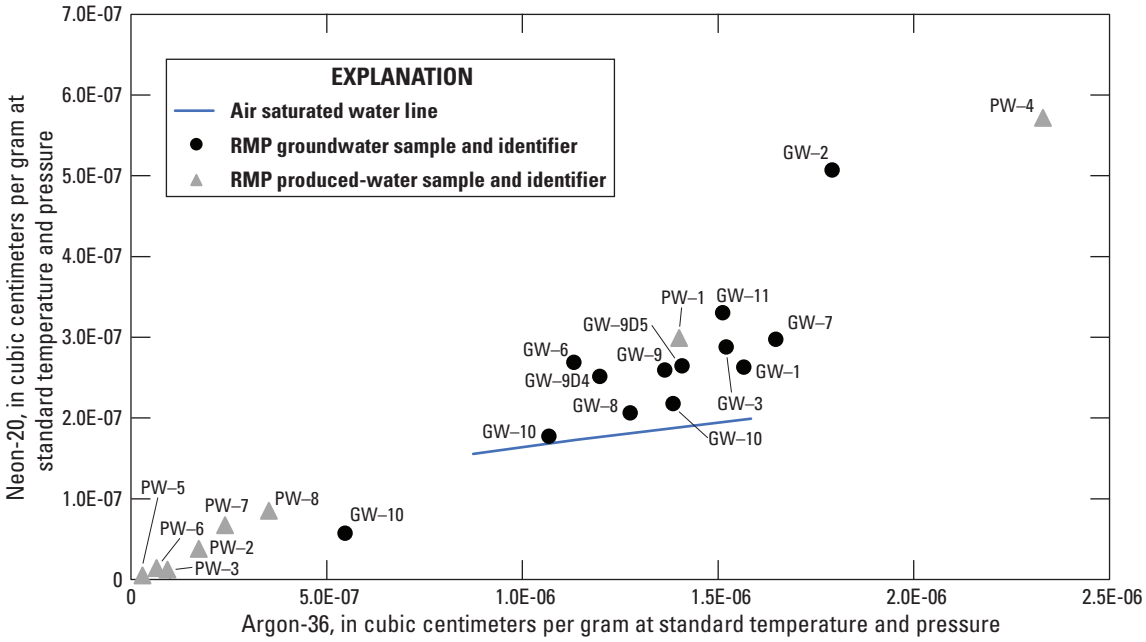

Figure 4.1. Neon-20 and argon-36 isotopes in California State Water Resources Control Board Oil and Gas Regional Monitoring Program (RMP) groundwater and produced-water samples with the air-saturated water line at 2–30 degrees Celsius.

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