

A product of the California Oil and Gas Regional Groundwater Monitoring Program

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



Open-File Report 2016–1181

Cover. Photograph showing a well in Kern County, California. (Photograph taken by Michael Wright, U.S. Geological Survey).

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By David B. Dillon, Tracy A. Davis, Matthew K. Landon, Michael T. Land, Michael T. Wright, and Justin T. Kulongoski

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Prepared in cooperation with the California State Water Resources Control Board

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Tables

Tables are provided in a Microsoft Excel file.

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Volume		
gallon (gal)	3785	milliliter (mL)
gallon (gal)	3.785	liter (L)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

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

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Datum

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).

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Turbidity is given in nephelometric turbidity units (NTU).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$). Milligrams per liter is equivalent to parts per million (ppm) and micrograms per liter is equivalent to parts per billion (ppb).

Concentrations of noble gases are given as the atom ratio (for helium-3/helium-4) or as cubic centimeters of gas at standard temperature and pressure per gram of water ($\text{cm}^3\text{STP}/\text{gH}_2\text{O}$).

Concentrations of radioactive constituents in water are given in picocuries per liter (pCi/L).

Selected Terms and Symbols

$\text{cm}^3\text{STP/gH}_2\text{O}$ cubic centimeters of gas at standard temperature and pressure (0 degrees Celsius and 1 atmosphere of pressure) per gram of water

δc^iE delta notation, the ratio of a heavier isotope of an element (iE) to the more common lighter isotope of that element, relative to a standard reference material, expressed as per mil

Abbreviations and Acronyms

CSU	combined standard uncertainty
CCV	continuous calibration verification
GAMA	Groundwater Ambient Monitoring and Assessment Program
ICV	initial calibration verification
LM	lab methods
LRL	laboratory reporting level
LT-MDL	long-term method detection level
MDL	method detection limit
MRL	minimum reporting level
MU	method uncertainty
MWMS	multiple well monitoring sites
NFM	National Field Manual (USGS)
NWIS	National Water Information System (USGS)
PBP	Priority Basin Project
PCFF	Personal Computer Field Form program designed for USGS sampling
QA	quality assurance
QC	quality control
RSD	relative standard deviation
SD	standard deviation
SRL	study reporting level
ssL_c	sample-specific critical level
UV	ultraviolet
VPDB	Vienna Pee Dee Belemnite (the international reference standard for carbon isotopes)
VSMOW	Vienna Standard Mean Ocean Water (an isotopic water standard defined in 1968 by the International Atomic Energy Agency)

Organizations

COGG	California Oil, Gas, and Groundwater Program
NAWQA	National Water Quality Assessment Program (USGS)
NWQL	National Water Quality Laboratory (USGS)
SWRCB	California State Water Resources Control Board
USGS	U.S. Geological Survey
WRD	Water Replenishment District of Southern California

Selected Constituent Names

DOC	dissolved organic carbon
PAH	polycyclic aromatic hydrocarbons
PVC	polyvinyl chloride
SVOC	semi-volatile organic compound
TDS	total dissolved solids
TOC	total organic carbon
VOC	volatile organic compound

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Abstract

Exploratory sampling of groundwater in coastal Los Angeles County and Kern and Kings Counties of the southern San Joaquin Valley was done by the U.S. Geological Survey from September 2014 through January 2015 as part of the California State Water Resources Control Board's Water Quality in Areas of Oil and Gas Production Regional Groundwater Monitoring Program. The Regional Groundwater Monitoring Program was established in response to the California Senate Bill 4 of 2013 mandating that the California State Water Resources Control Board design and implement a groundwater-monitoring program to assess potential effects of well-stimulation treatments on groundwater resources in California. The U.S. Geological Survey is in cooperation with the California State Water Resources Control Board to collaboratively implement the Regional Groundwater Monitoring Program through the California Oil, Gas, and Groundwater Project.

Many researchers have documented the utility of different suites of chemical tracers for evaluating the effects of oil and gas development on groundwater quality. The purpose of this exploratory sampling effort was to determine whether tracers reported in the literature could be used effectively in California. This reconnaissance effort was not designed to assess the effects of oil and gas on groundwater quality in the sampled areas. A suite of water-quality indicators and geochemical tracers were sampled at groundwater sites in selected areas that have extensive oil and gas development. Groundwater samples were collected from a total of 51 wells, including 37 monitoring wells at 17 multiple-well monitoring

sites in coastal Los Angeles County and 5 monitoring wells and 9 water-production wells in southern San Joaquin Valley, primarily in Kern and Kings Counties.

Groundwater samples were analyzed for field water-quality indicators; organic constituents, including volatile and semi-volatile organic compounds and dissolved organic carbon indicators; naturally present inorganic constituents, including trace elements, nutrients, major and minor ions, and iron species; naturally present stable and radioactive isotopes; dissolved noble gases; dissolved standard and hydrocarbon gases, $\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane. In total, 249 constituents and water-quality indicators were measured.

Four types of quality-control samples (blanks, replicates, matrix spikes, and surrogates spiked in environmental and blank samples) were collected at approximately 10 percent of the wells. The quality-control data were used to determine whether the groundwater-sample data were of sufficient quality for the measured analytes to be used as potential indicators of oil and gas effects. The data from the 51 groundwater samples and from the quality-control samples are presented in this report.

Introduction

California Senate Bill 4 of 2013 (SB 4; State of California, 2013) mandated that the California State Water Resources Control Board (SWRCB) design and implement a groundwater-monitoring program to assess and track the potential effects of well-stimulation methods used to increase oil and gas reservoir permeability on groundwater resources.

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These well-stimulation methods include hydraulic fracturing and acid matrix dissolution. During 2014–15, the SWRCB gathered stakeholder and technical input to develop model criteria for groundwater monitoring in areas of oil and gas well stimulation, which concluded with the adoption of monitoring criteria on July 7, 2015 (California State Water Resources Control Board, 2016). The resulting monitoring program consists of two groundwater activities: area-specific monitoring by oil and gas well operators and regional groundwater monitoring by the SWRCB. The area-specific monitoring involves oil and gas companies submitting plans for monitoring groundwater quality near individual wells or groups of wells undergoing well stimulation. All fluids produced or introduced by the well-stimulation process, “produced-water” ponds (ponds containing water brought to the surface by oil and gas production wells), underground injection control wells, and other oil and gas activities are to be examined in the regional monitoring program.

The areas of California where well-stimulation methods are in use as of 2016 have had long histories of oil and gas development and are dominated by conventional extraction methods, including enhanced recovery through steam or water flooding (California Council on Science and Technology, 2014). In addition, oil and gas well-construction standards, extraction technologies, and field waste-management practices have changed over time. Consequently, the effects of well stimulation on groundwater resources can be difficult to distinguish from the effects of other past or present components of oil and gas development. As a result, the SWRCB’s Water Quality in Areas of Oil and Gas Production Regional Groundwater Monitoring Program (RGMP) plans to make an overall assessment of the effects of oil and gas development on groundwater resources. The U.S. Geological Survey (USGS) is collaborating with the SWRCB to fund the RGMP through the California Oil, Gas, and Groundwater (COGG) Project during 2015–17 along with other agencies or groups involved in managing groundwater and oil and gas resources, including the Division of Oil, Gas, and Geothermal Resources, the Regional Water Quality Control Boards, local water agencies, well owners, and stakeholders.

During 2014–15, the USGS collaborated with the SWRCB to provide technical information in support of the monitoring-design process. One of the key information gaps was the paucity of groundwater data for zones between oil and gas reservoirs and protected groundwater and for aquifer zones containing water with greater salinity than has generally been used in the past. To bridge that gap, the USGS undertook reconnaissance sampling of California groundwater to test the utility of suites of chemical tracers reported in the scientific literature as useful for determining the effects of oil and gas development on groundwater quality. The exploratory sampling of groundwater took place in selected oil and gas development areas of California between September 2014

and January 2015. The data from these exploratory sampling efforts are presented in this report.

The purpose of this report is to describe (1) the study design and methods, (2) the analytical results for groundwater samples collected in coastal Los Angeles County and Tulare Lake Basin of the San Joaquin Valley, and (3) the results of quality assurance and quality control (QA/QC) analyses of the groundwater sample data. Groundwater samples were analyzed for field water-quality indicators; organic constituents, including volatile and semi-volatile organic compounds and dissolved organic carbon indicators; naturally present inorganic constituents, including trace elements, nutrients, major and minor ions, and iron species; naturally present stable and radioactive isotopes; dissolved noble gases; and dissolved standard and hydrocarbon gases, $\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane. This reconnaissance sampling effort was not designed to be an assessment of the effects of oil and gas production activities on groundwater quality in the sampled areas, and this report does not include an assessment of whether detections of constituents were related to oil and gas development.

Methods

This section presents the objectives for data quality toward which the selected methods were aimed, the study design, and a brief overview of sample collection and analysis. The appendix contains detailed descriptions of the sample-collection protocols, analytical methods, quality-assurance (QA) methods, and results of analyses of quality-control (QC) samples.

Data-Quality Objectives

Methods used for the exploratory sampling were selected to achieve the following objectives: (1) to collect samples in a consistent manner, (2) to analyze samples by using proven and reliable laboratory methods, (3) to assure the quality of the groundwater data, and (4) to maintain data securely and with relevant documentation.

Study Design

Two regions in California, the coastal part of Los Angeles County and parts of Kings and Kern Counties in the southern San Joaquin Valley, were chosen for the exploratory sampling because they have had extensive historical oil and gas development, including areas where well-stimulation technologies are used at present (2016) or have been used in the past, and they have groundwater resources that are used for drinking water or irrigation supply.

Reichard and others (2003) provided an overview of the hydrogeologic setting for the coastal part of Los Angeles County (fig. 1). Coastal Los Angeles County has been an area of active oil and gas development for about 150 years and also is an area where groundwater is intensively used for municipal and industrial supply. The Water Replenishment District of Southern California (WRD) has a network of about 55 multiple-well monitoring sites (MWMS), including about 301 monitoring wells, and collects water samples from these sites once or twice annually to monitor changes in groundwater quality in the area (Water Replenishment District of Southern California, 2015). These MWMS have monitoring wells up to 3,000 feet (ft) deep, and sampling at greater depth was thought to make detection of oil and gas-related constituents more likely. This well network was installed by the USGS and the WRD during the last 20 years and includes extensive lithologic, borehole-geophysical, and aquifer-properties data (Reichard and others, 2003; Land and others, 2004). A subset of these monitoring wells, most within about 2 miles of an oil field, were selected for the COGG exploratory sampling.

At 17 locations in coastal Los Angeles County, 37 monitoring wells (fig. 1) were sampled for the COGG exploratory study. At 12 locations, 2 monitoring wells were sampled, including 1 in the primary zones used for water supply and 1 in deeper zones, below those pumped for water supply. The depth of primary water production was determined from analysis of water-level data and from vertical water-head gradients indicating aquifer zones that generally have the lowest water-levels and where water-levels are most responsive to nearby pumping; these data also are consistent with the perforation depths of supply wells. At four locations, a third monitoring well at relatively shallow depths above the primary zone of water production was also selected for sampling. One well (LA_8) was far from oil fields and served as a control site representing deep groundwater likely to be unaffected by oil and gas development (fig. 1).

Faunt (2009) described the hydrogeologic setting of the southern San Joaquin Valley. Western Kern County has the greatest number of oil wells undergoing well stimulation in California (California Council on Science and Technology, 2014). Because of the paucity of monitoring wells and water-quality samples collected during oil and gas well drilling, however, groundwater-quality data from western Kern County are relatively sparse, particularly data from discrete, short, vertical intervals in the aquifer. The southern San Joaquin Valley does not have a network of monitoring wells analogous to the WRD MWMS network of the coastal part of Los Angeles County; therefore, most of the wells available for potential sampling were irrigation or drinking-water supply wells.

In Kern and Kings Counties, 5 monitoring wells and 9 irrigation or drinking-water supply wells were sampled for

this study (fig. 2). These wells were selected for sampling either because of their close proximity to oil and gas fields or on the basis of historical water-quality data. Irrigation and drinking-water supply wells less than 3 miles downgradient from an oil and gas field were considered to be close to the field. The downgradient direction from oil and gas fields was estimated from Faunt (2009). Locations of wells were obtained from the USGS National Water Information System (NWIS) database and from the California Department of Water Resources' well-completion reports. Results from the California Groundwater Ambient Monitoring and Assessment (GAMA) Program Priority Basin Project had identified the presence of hydrocarbons from oil and gas fields in groundwater used for public drinking-water supply in western Kern County (Burton and others, 2012; Landon and Belitz, 2012). Public-supply wells for which there were historical water-quality data indicating the presence of benzene and other hydrocarbons potentially related to oil and gas fields were considered for sampling. The wells selected were those for which well-construction data were available and well-owner permission for sampling was granted. Most of the wells selected had relatively long screens integrating groundwater inflow to the well from different depths in the aquifer system. This type of well construction is typical of the majority of wells in the area. Data about the wells sampled can be found in table 1.

An extensive suite of chemical and isotope tracers for exploring hydrologic and geochemical processes were selected for the COGG exploratory sampling, including field water-quality indicators, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon (DOC), ultraviolet (UV) absorbance, DOC fractionation, trace elements, nutrients, major and minor ions, iron speciation, stable isotopes, naturally present radioactive isotopes, dissolved noble gases, dissolved standard and hydrocarbon gases, $\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane (table 2). This set of constituents, identified through review of the literature from other oil, gas, and groundwater studies, was selected to reflect inherent differences in chemical properties and in source signatures, so that together, they provide data that can be used to determine whether detections in groundwater are related to oil and gas development activities. The suite of data can also contribute to a better understanding of the pathways by which constituents related to oil and gas development activities are transported in groundwater.

Published and quality-assured data collected for the COGG Program are stored in the Web-based GAMA GeoTracker database, maintained by the SWRCB (<http://geotracker.waterboards.ca.gov/gama/>), and in the Web-based USGS National Water Information System (<http://waterdata.usgs.gov/nwis>).

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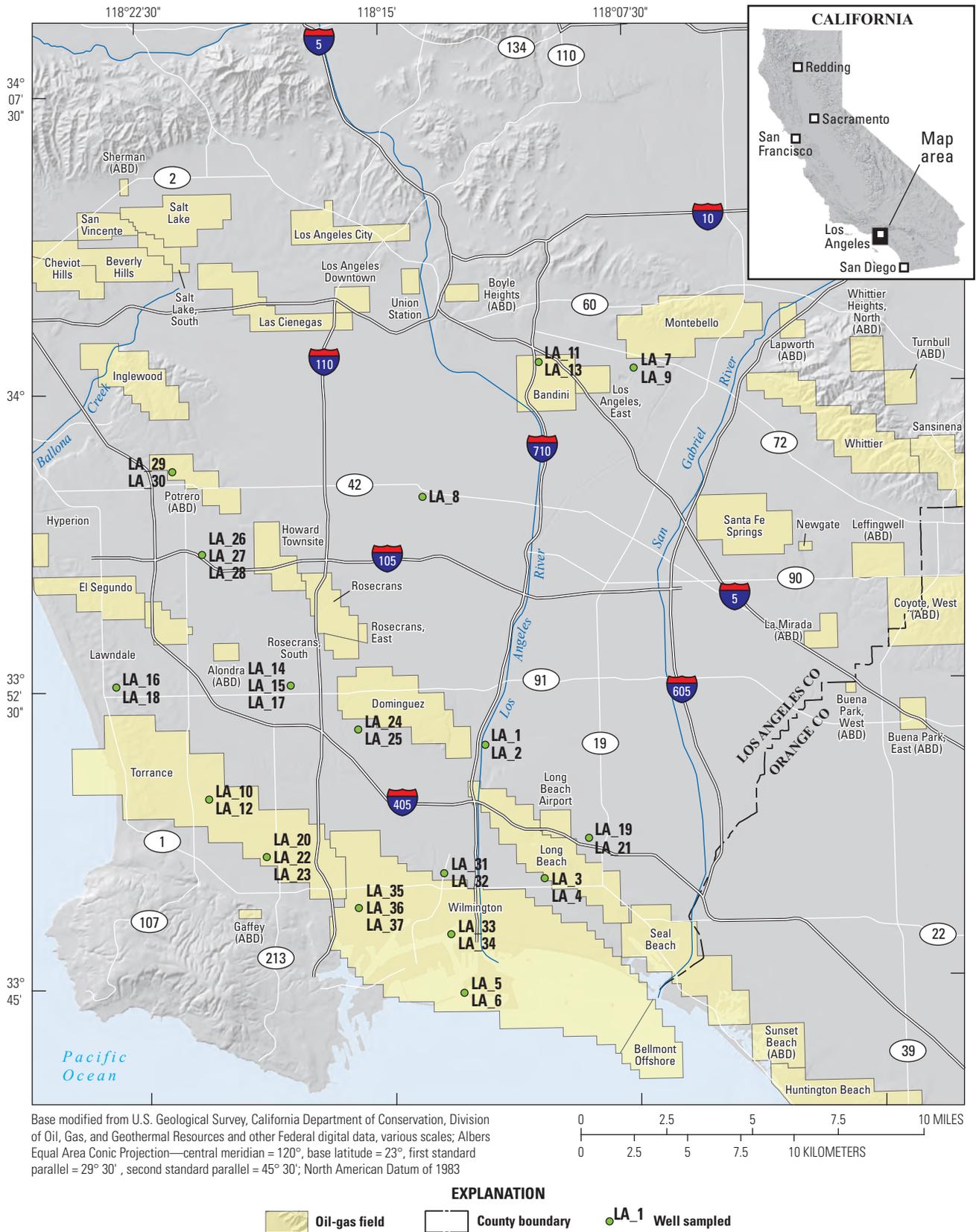


Figure 1. Relief, oil and gas fields, and wells sampled for groundwater in coastal Los Angeles County for the California Oil, Gas, and Groundwater Project.

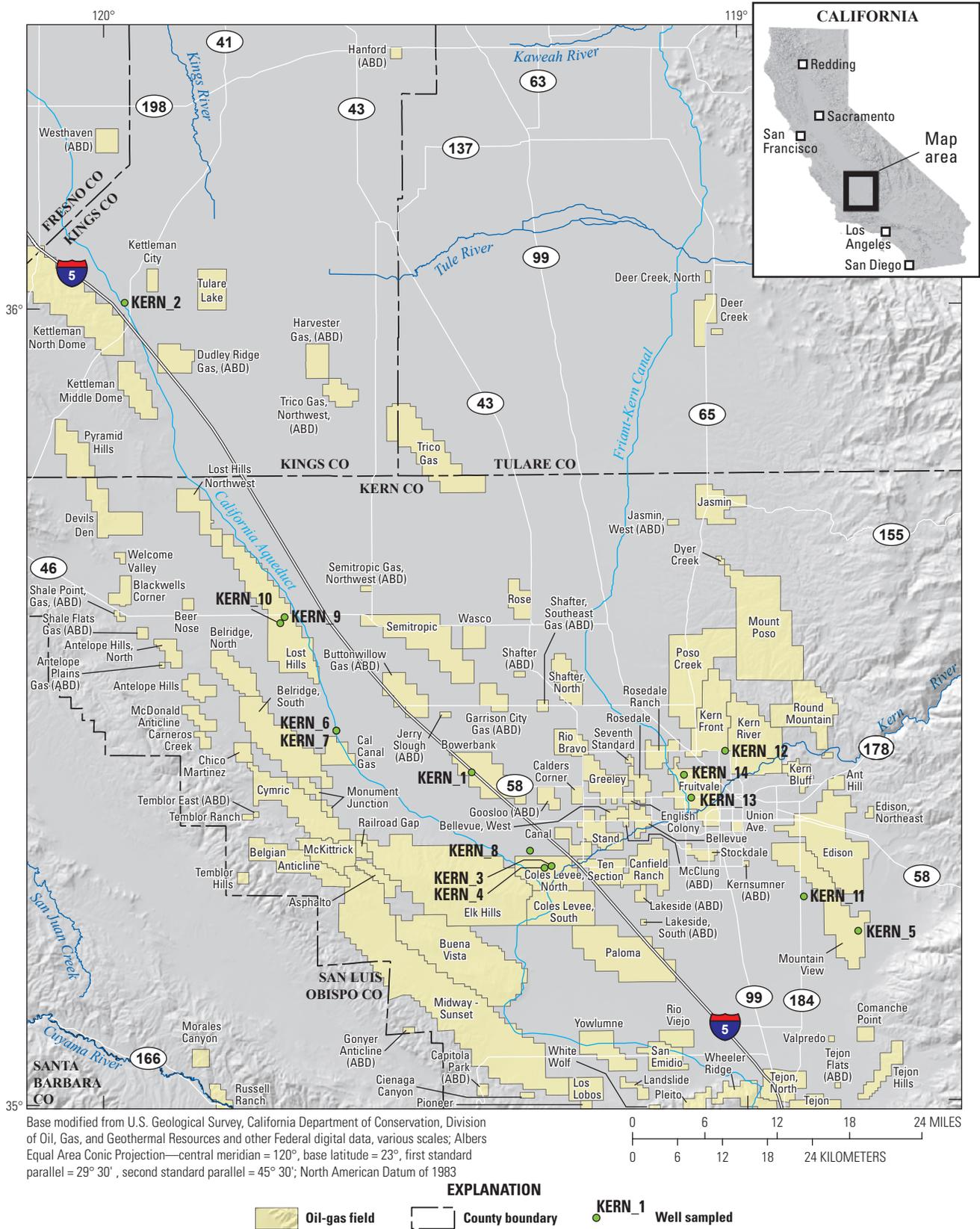


Figure 2. Relief, oil and gas fields, and wells sampled for groundwater in Kern and Kings Counties of the southern San Joaquin Valley for the California Oil, Gas, and Groundwater Project.

Sample Collection and Analysis

Samples were collected according to protocols established by the USGS National Water Quality Assessment (NAWQA) program (Koterba and others, 1995) and the USGS National Field Manual (U.S. Geological Survey, variously dated), except that a pump operated by WRD was used to sample some of the Los Angeles County monitoring wells for logistical reasons. 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 contamination. Use of the sampling protocols also allows data collected by the COGG exploratory sampling to be compared with data collected for other USGS projects in California and the Nation.

All 51 wells in the COGG exploratory reconnaissance were sampled for a standard set of constituents, except that samples for dissolved organic carbon fractionation were only collected at a subset of the sites. Groundwater samples were analyzed for 86 VOCs; 66 SVOCs and PAHs; 9 constituents of DOC, UV absorbance, and DOC fractionation; 23 trace elements; 5 nutrients; 11 major and minor ions; 2 iron species; 5 isotopic tracers and 5 radioactive constituents, including carbon-14 abundance, radium, and tritium activity; 6 dissolved noble gases; and 25 dissolved standard and hydrocarbon gases, $\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane. The methods used for sample collection and analysis are described in the “[Sample Collection](#)” appendix section.

Water-Quality Results

The data from the 51 groundwater samples and from the quality-control samples are presented in the “[Tables](#)” section of this report. The series of tables of results are organized by the purpose for sample collection and are briefly described in this section.

Quality-Control Results

Results of QC analyses (blanks, replicates, and matrix and surrogate spikes) were used to evaluate the quality of the data for the groundwater samples. On the basis of detections in field blanks collected for the COGG exploratory sampling and for the GAMA-Priority Basin Project (Fram and others, 2012; Davis and others, 2014), as well as a review of available QA/QC information, raised reporting levels were identified and applied for seven trace elements (copper, iron, lead, manganese, molybdenum, nickel, and zinc). These raised reporting levels are referred to as “study reporting levels” (SRLs). Detections of constituents at concentrations less than the SRLs were coded with a less than or equal to symbol (\leq) in this report and in the USGS NWIS database. Additionally, all groundwater results for cobalt, benzyl alcohol, benzyl *n*-butyl phthalate, bis(2-ethylhexyl) phthalate, diethyl phthalate,

di-*n*-butyl phthalate, and phenol were coded as “reviewed and rejected” because of low recoveries. The blank results from the COGG exploratory sampling and references for additional information are in [appendix table A-2A-B](#) and the appendix section “[Detections in Blank Samples and Application of Study Reporting Levels](#).”

Results from the replicates confirmed that the procedures used to collect and analyze the samples yielded consistent analytical results. Variability for about 98 percent of the replicate pairs of constituents detected in samples was within acceptable limits ([appendix table A-3A-C](#)). The criteria for acceptable replication are described in the appendix section “[Replicates](#).”

For the 85 VOCs analyzed, all VOC median matrix-spike recoveries were within an acceptable range of 70 to 130 percent ([appendix table A-4](#)). Matrix spikes of SVOCs and PAHs were generally within laboratory-defined acceptable limits for matrix-spike recoveries. These QC results are described in the appendix section “[Matrix Spikes](#).” Surrogates were analyzed in environmental samples and blank samples for VOCs, SVOCs, and PAHs. The VOC recoveries were generally very close to 100 percent, whereas the SVOC and PAH recoveries were consistently in the 60-percent range. The results are described in the appendix section “[Surrogate Compounds](#).”

Groundwater-Quality Data

Results from analyses of groundwater samples from the COGG exploratory sampling are presented in [tables 3–13](#). In each table, the results are presented by area (Los Angeles County and southern San Joaquin Valley). Groundwater samples were analyzed for 249 unique constituents; 102 of those constituents were not detected in any of the samples, and 131 constituents were detected in at least 1 groundwater sample.

For organic constituents, the results listed in the tables include only those constituents that were detected. For the inorganic, isotopic, radioactive, dissolved organic carbon, and dissolved standard and hydrocarbon gases, $\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane, the tables include all of the constituents that were analyzed, because all the constituents were detected in at least one groundwater sample. The VOC, SVOC, and PAH constituents that were analyzed, however, were not all detected, so a separate table is included for each constituent class that lists the non-detected constituents.

Water-quality indicators measured in the field and at the National Water Quality Laboratory (NWQL) are included in [table 3](#). The results of groundwater analyses, organized by constituent class, are presented in [tables 4–13](#):

- Organic constituents.
- VOCs ([table 4](#)).
- SVOCs and PAHs ([table 5](#)).

- DOC, UV absorbance, and DOC fractionation (table 6).
- Inorganic constituents.
 - Trace elements (table 7).
 - Nutrients (table 8).
 - Major and minor ions (table 9).
- Iron speciation (table 10).
- Isotopic tracers and radioactive constituents (table 11).
- Dissolved noble gases (table 12).
- Dissolved standard and hydrocarbon gases, $\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane (table 13).

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Tables

Tables are provided in a [Microsoft Excel file located here](#).

Appendix A. Methods and Water-Quality Results for the California Oil, Gas, and Groundwater Project

This appendix includes detailed discussions of the methods used to collect and analyze groundwater samples and reports the resulting water-quality data. These methods were selected to obtain representative samples of the groundwater from each well and to minimize the potential for contamination of the samples or bias in the data. Procedures used to collect and assess quality-control (QC) data and the results of the QC assessments also are discussed.

Groundwater samples were collected, and quality-assurance (QA) procedures followed standard and modified U.S. Geological Survey (USGS) protocols from the National Water Quality Assessment (NAWQA) Program (Koterba and others, 1995), the National Field Manual (NFM; U.S. Geological Survey, variously dated), and protocols described by Shelton and others (2001) and Wright and others (2005). The QA plan followed by the National Water Quality Laboratory (NWQL), the primary laboratory used to analyze samples for this study, is described by Stevenson (2013).

Sample Collection

Samples were collected either from monitoring wells or from water-production wells (irrigation or drinking-water supply wells). Sites classified as monitoring wells are drilled vertically into the ground, usually in a multiple-well monitoring site that has 2–3-inch polyvinyl chloride (PVC) well casings. Each well is screened for a specific interval (generally 20 feet [ft]) and is isolated from other wells by a low-permeability bentonite grout. All 37 wells sampled in coastal Los Angeles County and 5 of the wells sampled in the southern San Joaquin Valley were monitoring wells. For the KERN_10 well, a dedicated bladder pump was used to sample, pumping approximately 1 liter (L) per minute. Nine of the wells sampled in the southern San Joaquin Valley were drinking-water-supply or irrigation-supply wells. Unlike monitoring wells, water-supply wells generally have screened intervals open to several water-bearing units; consequently, water from such wells is a mixture of water from those units.

Samples were collected either outdoors in a sampling chamber or inside of a mobile laboratory (Wilde, 2004). Monitoring wells were sampled with one of four submersible, positive-pressure pumps: a 750-ft Bennett pump or a 300-ft Grundfos pump, which were owned and operated by the USGS, or two Grundfos Rediflo pumps, owned and operated by the Water Replenishment District (WRD) of southern California. The Bennett pump and Grundfos pump owned by the USGS were used to sample wells in the southern San Joaquin Valley, and the USGS Bennett pump and the WRD

Grundfos pump were used to sample wells in coastal Los Angeles County.

The water-supply wells had permanently installed turbine pumps, which operated at least daily. Water-supply wells were sampled using Teflon® tubing attached to a sampling point on the well discharge pipe with brass and stainless-steel fittings that was as close to the well head as possible and upstream of any treatment system or water-storage tank. Samples were collected before filtration or chemical treatment, such as chlorination. If a chlorinating system was attached to the well, the chlorinator was shut off at least 24 hours prior to purging and sampling the well to clear all chlorine out of the system.

Wells were pumped continuously to purge at least three casing volumes of water from the well (Wilde, 2006a) and were sampled after the field parameters stabilized. Field measurements were taken by pumping groundwater through a flow-through chamber that was attached to the sampling point and fitted with a YSI® multi-probe meter that simultaneously measures the field water-quality indicators dissolved oxygen, temperature, pH, and specific conductance. For all wells, field measurements of dissolved oxygen, water temperature, pH, and specific conductance were recorded at 3- to 5-minute intervals before sampling and then checked against the stabilization criteria described in the NFM to ensure the purging was sufficient (Wilde, 2008). Turbidity was measured with a Hach® 2100P turbidimeter (Anderson, 2005). Sulfide concentrations were measured one to two times prior to sampling with a Chemetrics V 2000, and any odor in the groundwater was noted. All field measurements were taken in accordance with protocols in the USGS NFM (Radtke and others, 2005; Lewis, 2006; Wilde, 2006b; Ritz and Collins, 2008; Wilde, 2008). All sensors on the YSI® multi-probe meter were calibrated daily.

Field measurements and instrument calibrations were recorded by hand on field record sheets and recorded electronically in the USGS's Personal Computer Field Form (PCFF) program and have been archived. Analytical service requests for the NWQL were generated by the PCFF, whereas analytical service requests for non-NWQL analyses were entered in laboratory-specific spreadsheets. Information from the PCFF was uploaded to the USGS National Water Information System (NWIS) database.

Prior to sample collection, polyethylene sample bottles were pre-rinsed three times with deionized water and then once with sample water before sample collection. Samples requiring acidification were brought to a pH of 2–1 using the appropriate acids from ampoules of certified, traceable, concentrated acids from the NWQL.

10 Data from Exploratory Sampling of Groundwater in Selected Oil and Gas Areas

Temperature-sensitive samples were stored on ice prior to and during shipping, which went out daily to the various laboratories. Temperature-sensitive or time-sensitive samples for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs) and polycyclic aromatic hydrocarbons (PAHs), dissolved organic carbon (DOC) and ultraviolet (UV) absorbance, DOC fractionation, trace elements, nutrients, major and minor ions, radium isotopes, and dissolved standard and hydrocarbon gases, $\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane were shipped weekly or daily, whenever possible. Time-sensitive samples of radium isotopes were shipped daily at room temperature because of the 3.6-day half-life of radium-224. Samples for the determination of isotopes of dissolved inorganic carbon were refrigerated and shipped when laboratory measurements of alkalinity were made available. The non-temperature-sensitive samples for tritium activity, stable isotopes of hydrogen and oxygen in water, isotopes of boron and strontium dissolved in water, and dissolved noble gases were shipped monthly.

Detailed sampling protocols for individual analyses and groups of analytes are described in Koterba and others (1995), the NFM (Wilde, 2009), and in the references for analytical methods listed in [table A-1](#); brief descriptions, in the order of sample collection, are given here.

Samples for the analysis of VOCs were collected in three 40-milliliter (mL) sample vials that were purged with three vial volumes of unfiltered groundwater before filling underwater to eliminate atmospheric contamination. One-to-one hydrochloric acid to water solution was added as a preservative to the VOC samples.

Samples for SVOCs and PAHs were collected by filling two 1-L amber-glass bottles to the shoulder with unfiltered groundwater. Samples for the analysis of tritium activity were collected by filling one 1-L polyethylene bottle with unfiltered groundwater, after first overfilling the bottle with three volumes of the unfiltered groundwater.

Samples for analysis of stable isotopes of hydrogen and oxygen in water were collected in a 60-mL clear-glass bottle filled with unfiltered groundwater, sealed with a conical cap, and secured with electrical tape to prevent leakage and evaporation.

Samples for the analysis of trace elements, major and minor ions, nutrients, and laboratory alkalinity required filling one 250-mL polyethylene bottle with unfiltered groundwater and one 500-mL and one 250-mL polyethylene bottle with filtered groundwater. Filtration was done using a 0.45-micrometer (μm) pore-size PALL® unvented capsule filter that was pre-rinsed with 2 L of deionized water and then rinsed with 1 L of groundwater prior to sampling. Each 250-mL filtered sample then was preserved with 7.5-Normal (N) nitric acid. Nutrient samples were collected by filtering groundwater into 125-mL brown polyethylene bottles.

Samples for iron species were filtered into one 125-mL brown-polyethylene bottle or one 250-mL polyethylene bottle that was wrapped with black plastic to prevent exposure to light and then preserved with 6-N hydrochloric acid.

Samples for the analysis of radium isotopes (Ra-224, Ra-226, Ra-228) were filtered into three 1-L polyethylene bottles to the shoulder, preserved with 7.5-N nitric acid, and secured with electrical tape to prevent leakage and evaporation.

Samples for the analysis of isotopes of dissolved boron and strontium were filtered into 250-mL polyethylene bottles and secured with electrical tape.

Samples for the analysis of stable isotopes of dissolved inorganic carbon and carbon-14 abundance were filled underwater with a silicone tube into 500-mL glass bottles that first were overfilled with three bottle volumes of filtered groundwater. Sample bottles for carbon isotope analysis had no headspace and were sealed with conical caps to avoid atmospheric contamination.

Samples for analysis of dissolved and standard hydrocarbon gases were collected by using a Teflon® tube sampling apparatus attached to a hose bib. Groundwater was flushed through the tubing and the flow was partially restricted with a control valve. An evacuated IsoFlask® pouch containing a bactericide capsule was attached to the tubing and filled with 600–700 mL of sample water.

Samples for analyses of DOC, UV absorbance, and DOC fractionation were collected using a Teflon® tube sampling apparatus attached to a hose bib. Each sample was collected by filling one previously baked 125-mL amber-glass bottle (for DOC and UV absorbance) and three previously baked 1-L amber-glass bottles (for DOC fractionation) underwater that had first been overfilled with filtered groundwater. These samples had no headspace or air bubbles inside the bottles and were sealed underwater to avoid atmospheric contamination.

Dissolved noble gases were collected in $\frac{3}{8}$ -inch-diameter copper tubes by using reinforced-nylon tubing connected to the hose bib at the wellhead. Groundwater was flushed through the tubing to dislodge bubbles before the flow was restricted with a back-pressure valve. Clamps on either side of the copper tube then were tightened, trapping a sample of groundwater for analyses of dissolved noble gases (Weiss, 1968).

Sample Analysis and Data Reporting

Thirteen laboratories performed chemical analyses for this study ([table A-1](#)), although most of the analyses were performed at the USGS National Water Quality Laboratory (NWQL) or by laboratories contracted by the NWQL. The NWQL maintains a rigorous QA program (Stevenson, 2013). Results for analyses made at the NWQL or by laboratories contracted by the NWQL are uploaded directly to the USGS NWIS database. Results of analyses done at other laboratories were compiled in a project database and uploaded from there to the USGS NWIS database. The data are available online through the USGS NWIS-Web interface (<http://waterdata.usgs.gov/nwis>).

Data for VOCs (table 4) are reported with a laboratory reporting level (LRL). The LRL is set to minimize the reporting of false negatives (not detecting a compound when it is present in a sample) to less than 1 percent (Childress and others, 1999). The LRL usually is set at twice the long-term method detection level (LT–MDL). The LT–MDL is derived from results for low-level spikes and laboratory set blanks analyzed during an extended period (Childress and others, 1999). The LT-MDL is the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the concentration was greater than zero (at the MDL there is less than 1-percent chance of a false positive; Childress and others, 1999; U.S. Environmental Protection Agency, 2002). Detections of concentrations less than the LRL are reported with “E” codes preceding the value. Detections of organic constituents at concentrations less than the LT-MDL are reported in table 4.4, but were not counted as detections.

The LT-MDL is generally the level used by the NWQL for reporting analytical results of inorganics, with some exceptions. The MDL is used by the NWQL for reporting bromide, nitrate, and nitrite and by the USGS Trace Metal Laboratory, Boulder, Colo. (USGSTMCO), which is a part of the USGS National Research Program (NRP), for iron species. The minimum reporting level (MRL) is used by the NWQL for reporting total dissolved solids. The MRL is the lowest measurable concentration of a constituent that can be reliably reported by using a given analytical method (Timme, 1995). Results for the SVOCs and PAHs analyzed by RTI Laboratories (table 5) were reported with censoring at the MDLs. Constituents not detected by the laboratories are listed as non-detections in this report and reported in the USGS NWIS database as less than the associated reporting level (less than the LT-MDL, less than the MDL, or less than the MRL).

The reporting levels listed in this report were in effect when analyses were done for this study. The USGS NWQL updates reporting level values for each constituent at least once a year. On October 1, 2014, reporting levels changed for two inorganic constituents—aluminum, from 2.2 to 3.0 micrograms per liter ($\mu\text{g/L}$), and vanadium, from 0.08 to 1.0 $\mu\text{g/L}$. The greater of the two values is reported with the groundwater results in table 7.

Results for some trace elements (copper, iron, lead, manganese, molybdenum, nickel, and zinc) were censored by using study reporting levels (SRL) derived from an assessment of the data from QC samples collected with groundwater samples as part of the California Oil, Gas, and Groundwater (COGG) Project and the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP; see the “Detections in Blanks and Application of Study Reporting Levels” section in this appendix).

Isotopic ratios of boron, strontium, carbon, hydrogen, and oxygen are reported with method uncertainties that indicate the precision of the analytical measurement. Carbon-14 abundance is reported with a counting error.

Tritium and radium activities are reported with combined standard uncertainties (CSU) and sample-specific critical levels (ssL_c). The ssL_c is defined as the minimum measured activity that indicates a positive detection of the radionuclide in the sample, with less than a 5-percent probability of a false-positive detection (McCurdy and others, 2008). Measured activities less than the ssL_c were reported as non-detections. The CSU was reported at the 68-percent confidence level (1-sigma; McCurdy and others, 2008).

Notation

Stable-isotope compositions of boron, carbon, hydrogen, and oxygen are reported as relative isotopic ratios in units of per mil using the standard delta (δ) notation (Coplen and others, 2002; Coplen, 2011):

$$\delta^i E = \left[\frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right] \times 1,000 \text{ per mil} \quad (1)$$

where

- i is the atomic mass of the heavier isotope of the element,
- E is the element (B for boron, C for carbon, H for hydrogen, O for oxygen),
- R_{sample} is the ratio of the abundance of the heavier isotope of the element (^{11}B , ^{13}C , ^2H , ^{18}O) to that of the lighter isotope of the element (^{10}B , ^{12}C , ^1H , ^{16}O) in the sample, and
- $R_{\text{reference}}$ is the ratio of the abundance of the heavier isotope of the element to that of the lighter isotope of the element in the reference material.

The reference material for boron is boric acid from the National Institute of Standards and Technology (NIST) reference material SRM 951, which is assigned a $\delta^{11}\text{B}$ value of 0 per mil (Coplen and others, 2002). The reference material for carbon is Vienna Pee Dee Belemnite, which is assigned a $\delta^{13}\text{C}$ value of 0 per mil (Coplen and others, 2002; Coplen, 2011). Oxygen and hydrogen reference material is Vienna Standard Mean Ocean Water, which is assigned $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of 0 per mil (note that $\delta^2\text{H}$ is sometimes written as δD because the common name of the heavier isotope of hydrogen, hydrogen-2, is deuterium) (Coplen and others, 2002; Coplen, 2011). Positive values indicate enrichment of the heavier isotope, and negative values indicate depletion of the heavier isotope, compared to the ratio observed in the standard reference material.

The isotopic composition of strontium is presented as the ratio (and therefore not based on a reference standard) of the abundance of atoms of the heavier isotope (^{87}Sr) to that of the lighter isotope (^{86}Sr) of the element.

Constituents on Multiple Analytical Schedules

Twenty-nine constituents targeted in this study were measured by more than one analytical method or by more than one laboratory. The preferred analytical methods generally were selected on the basis of better performance or sensitivity for the constituent.

The SVOCs and PAHs were analyzed by a combination of two different lab methods (LM) (LM 8270D-LL and LM 8270D-SIM) at RTI Laboratories. All SVOCs and PAHs were analyzed by LM 8270D-LL. Of the 64 compounds, 17 compounds plus 3 surrogates were analyzed by both methods, and results are reported using a lower reporting level for LM 8270D-SIM (reporting level is 0.02 µg/L) than for LM 8270D-LL (minimum reporting level is 0.2 µg/L). The 17 compounds analyzed by the lower level reporting limit are listed in [table 5A](#) (footnote 1) and [table 5B](#) (footnote 1). Results from LM 8270D-SIM are preferred and are reported in the NWIS database and this report. Four constituents were analyzed by the methods used for the VOCs and for the SVOCs. Naphthalene was also analyzed by the NWQL Schedule 2020 at a reporting level of 0.18 µg/L, which is lower than the reporting level of 0.2 µg/L for the RTI method 8270D-LL. Because of the better performance overall by the NWQL Schedule 2020 compared to the RTI methods (discussed in the “Blank Samples” and “Matrix Spikes” appendix sections), results from the NWQL schedule were preferred, and groundwater results from the RTI methods for naphthalene are not included in this report. Three additional compounds (hexachlorobutadiene, hexachloroethane, and 1,2,4-trichlorobenzene) were analyzed on NWQL Schedule 2020 and the RTI method 8270D-LL. Reporting levels for these compounds were about an order of magnitude less for the NWQL schedule than for the RTI method and were, therefore, preferred. Hexachlorobutadiene has two different parameter codes, however, so results from both laboratories are in the database.

Three standard or noble gases (argon, oxygen, and nitrogen) were analyzed both by Isotech Laboratories and by Lawrence Livermore National Laboratory. Each laboratory used different units and parameter codes to report the gases. All results are in the NWIS database and are in this report.

For total iron concentrations, the approved method used by the NWQL, Schedule 1948 ([table 7](#)), was preferred over the research methods used by the USGS Trace Metal Laboratory ([table 10](#)); however, results of both methods are in the USGS NWIS database and are presented in this report. The concentrations measured by the Trace Metal Laboratory were used to calculate ratios of redox species for iron as follows:

$$\frac{Fe(III)}{Fe(II)} = \frac{Fe(T) - Fe(II)}{Fe(II)} \quad (2)$$

where

$Fe(T)$	is the total iron concentration (measured),
$Fe(II)$	is the concentration of iron oxide (measured), and
$Fe(III)$	is the concentration of ferric oxide (calculated).

In addition, the field water-quality indicators pH and specific conductance were measured in the field and at the NWQL, and both sets of results are reported ([table 3](#)). Field measurements generally were considered more representative of groundwater conditions than laboratory measurements because the amount of time for reactions in the water sample after exposure to the atmosphere was limited (Hem, 1985).

Quality-Assurance and Quality-Control Methods and Results

The purpose of QA/QC is to describe the precision and accuracy of the data and to determine if the data had been affected by contamination or bias during sample collection, processing, storage, transportation, or laboratory analysis. Four types of QC measurements were evaluated in this study: (1) blank samples were collected to assess positive bias as a result of contamination during sample handling or analysis; (2) replicate samples were collected to assess variability; (3) matrix-spike tests were done for organic constituents to assess positive or negative bias; and (4) surrogate compounds were added to samples analyzed for organic constituents to assess potential matrix effects from the chemical composition of each groundwater sample as well as to assess potential bias of laboratory analytical methods.

Blank Samples

The primary purposes for collecting blanks are to evaluate the potential contamination of samples by compounds of interest during sample handling or analysis and to identify and mitigate the sources of sample contamination. Source solution, field, and equipment blanks were collected at 8 of the 51 (16 percent) COGG exploratory sampling sites. Results from these blanks were assessed and compared to blank results from the GAMA-PBP, which were collected with some of the same equipment as was used in this study. Raised SRLs based on these data were applied to some constituents detected in blanks.

Because of the high frequency of detections of the SVOCs and PAHs in blank samples collected by the USGS, internal QC set blanks maintained by the laboratory were also analyzed to pinpoint the source of contamination.

Collection of Blank Samples

Blanks were collected by using water certified by the NWQL to contain less than the reporting levels of selected constituents investigated in the study (James A. Lewis, USGS National Water Quality Laboratory, written commun., June 2014). Organic-free water, purged with nitrogen gas, was used for blanks of organic constituents (VOCs, SVOCs, PAHs, DOC, UV absorbance, and dissolved hydrocarbon gases), and inorganic-free water was used for blanks of some of the inorganic constituents (major and minor ions, trace elements, nutrients, and iron species). Blanks were not collected for radium-224, radium-226, or radium-228 because the laboratory determines the ssL_c value for each sample. The ssL_c is the minimum measured value that indicates a non-zero amount of the radionuclide in the sample or, in other words, an amount of the radionuclide that is significantly greater than the amount in a blank. Blanks were not collected for tritium activity, dissolved noble gases, dissolved standard gases, or carbon-14 abundance because these constituents are present in the atmosphere and would dissolve into any solution used to collect a blank. Stable-isotope ratios of carbon, boron, hydrogen, oxygen, strontium, and dissolved standard and hydrocarbon gases, $\delta^{13}C$ of methane, ethane, and δ^2H of methane are intrinsic to all of these constituents; therefore, a blank does not apply to these ratios.

One source-solution blank was collected at the beginning of the COGG exploratory sampling period by pouring blank water directly into the sample containers to assess potential contamination of samples during transport and analysis as well as potential contamination of the certified blank water obtained from the NWQL. The source-solution blank was analyzed for all constituents, except for dissolved standard and hydrocarbon gases, $\delta^{13}C$ of methane, ethane, and δ^2H of methane, because it was not feasible to pour blank water into the evacuated IsoFlask[®] pouch without a pump.

Three equipment blanks were collected at the start of the COGG exploratory sampling period to assess the potential sources and extent of contamination from the equipment. Equipment blanks were collected for the Bennett pump and for each of the two WRD Grundfos pumps by pumping blank water through the sampling equipment. Sampling equipment was conditioned with 69–94 liters of dilute Liquinox solution, tap water, deionized water, and NWQL certified blank water before the equipment blank was collected. Four field blanks were collected during the course of the study to assess potential contamination of samples during collection, processing, transport, and analysis. Field and equipment blanks were collected by pumping blank water through the groundwater-sampling equipment (fittings, tubing, and filters). Field blanks were collected at sites where an environmental sample was collected, whereas equipment blanks were

collected at either the USGS or WRD office. One field blank was collected using one of the WRD Grundfos pumps, two field blanks were collected using the Bennett pump, and one field blank was collected using a peristaltic pump. All pumps and sampling lines were first cleaned with a dilute Liquinox solution, then flushed with tap water, and finally conditioned with three equipment volumes of deionized water and certified blank water before each field blank was collected.

Detections in Blank Samples and Application of Study Reporting Limits

Tables A–2A–B presents a summary of detections in the blank samples collected for the COGG exploratory sampling. There were few detections in source-solution blanks, and only the detections are discussed in this section of the appendix. Following an initial discussion of the field and equipment blanks in relation to different pumps, the detections in blank samples are discussed by constituent group.

The field and equipment blanks collected using the two WRD Grundfos pumps are presented in this report separately from other blanks after analysis of QC data indicated that there were measurable differences among the equipment. The WRD Grundfos pumps were not cleaned after each groundwater sample was collected, but were rinsed with dilute Liquinox and tap water the night before a blank sample was collected. The blank results indicated that the water and possibly gas fumes that collected in the lines overnight were not thoroughly rinsed out during the conditioning of sample lines prior to the collection of blank samples. The sampling equipment used for the groundwater sampling, however, was rinsed with 3–6 well casing volumes of raw groundwater prior to the collection of groundwater samples, which, in general, was deemed sufficient for removing any carryover contamination from the previous sample. Detections in equipment blanks from the WRD Grundfos pumps are attributed to potential contamination from the sampling equipment and, in part, to non-standard collection and processing techniques (including use of a cracked collection vessel or not enough blank water used prior to sampling, for example). The VOCs, SVOCs, and PAHs, which have a much lower reporting level than other constituent groups, had significantly different blank results for equipment blanks than for field blank sets. Other groups of constituents were more frequently detected in the WRD Grundfos pump blanks than in other blanks. Most of the constituents that did not have SRLs established were detected in blank samples at concentrations several magnitudes lower than concentrations detected in environmental samples collected with the same equipment; therefore, no SRLs were set using the detections in the blank samples from the WRD Grundfos pumps.

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Fifteen VOCs constituents were detected in three blanks collected using the WRD Grundfos pumps (table A–2A). Only six of the detected VOCs (carbon disulfide, isopropylbenzene, tetrachloroethene, toluene, trichloroethene, and chloroform) were detected in groundwater samples collected at the coastal Los Angeles County monitoring-well sites where the Grundfos pumps were used. The blanks collected at these monitoring-well sites were not representative of the COGG sampling procedures used for collecting groundwater samples; therefore, these results were not used to establish SRLs for VOCs. There were no detections of VOCs in the five other source-solution, equipment, and field blanks that were collected using COGG sampling procedures.

In the equipment blanks collected with the WRD Grundfos pumps, five SVOCs were detected that were not detected in other blanks or in environmental groundwater samples: benzoic acid, benzyl alcohol, benzyl *n*-butyl phthalate, di-*n*-butyl phthalate, and phenol (table A–2A). Because these constituents were not detected in groundwater samples, it was not necessary to establish SRLs for them. Naphthalene was detected in equipment blanks collected with the WRD Grundfos pumps, in source-solution blanks, and in field blanks, and two other SVOCs—diethyl phthalate and 2-methylnaphthalene—were detected in other field blanks.

Because of the frequency of detections of SVOCs in the field blanks, data from an additional set of blanks were examined. The RTI Laboratories analyzed a laboratory set blank for each of the 30 sets of samples they analyzed for this project. The lower reporting level method, LM 8270D-SIM, and the higher reporting level, LM 8270D-LL were each used to analyze 15 different laboratory set blanks. Eight SVOCs were detected in the laboratory set blanks (table A–2B). Detections in laboratory set blanks indicated there was contamination of samples during laboratory processing. Because laboratory set blanks were processed using the same methods by which the environmental samples were processed, the environmental samples could have the same contamination frequency as the laboratory set blanks. For this study, a greater than 1-percent detection frequency of concentrations greater than or equal to the MRL was defined as an unacceptable frequency of contamination of laboratory set blanks. For constituents that had an unacceptable frequency of contamination of laboratory set blanks, all detections in groundwater samples were considered questionable and were coded as “reviewed and rejected.” Using these criteria, two detections of 2-methylnaphthalene and one detection of fluoranthene in groundwater samples were coded as “reviewed and rejected.” Anthracene was detected in laboratory set blanks for LM 8270D-LL, but the data reported for groundwater samples are from the LM 8270D-SIM, which did not have any detections in laboratory set blanks; therefore, no SRL was defined. Three SVOCs detected in the laboratory set blanks (diethyl phthalate, 2-methylnaphthalene, and naphthalene) also were detected in field blanks, indicating

that the detections in the field blanks could be the result of contamination during laboratory processing and analysis, not the result of contamination during sample collection in the field.

Seven SVOCs were each detected in one to two equipment or field blanks: benzoic acid, at 9.8 µg/L; benzyl alcohol, at 4.1 and 4.8 µg/L; benzyl *n*-butyl phthalate, at 24 and 41 µg/L; diethyl phthalate, at 0.20 µg/L; di-*n*-butyl phthalate, at 0.41 µg/L; 2-methylnaphthalene, at 0.053 µg/L; and phenol, at 4.1 and 28 µg/L (table A–2A). All detections of these compounds were in samples collected from monitoring-well sites using a plastic sample line. Most of these SVOCs are associated with plastics and PVC piping, which were materials used in the sampling equipment and casing for monitoring wells. Diethyl phthalate was also detected in laboratory set blanks at concentrations (0.3–0.73 µg/L, table A–2B) near those detected in groundwater samples (0.20–0.39 µg/L), including two samples analyzed in the same run as the laboratory set blank. One additional phthalate, bis (2-ethylhexyl) phthalate, was not detected in any blanks, but was detected at concentrations ranging from 0.29 to 1.8 µg/L in 10 groundwater samples collected from monitoring-well sites. Detections of these SVOCs were attributable to likely contamination from the sampling and well-casing materials, and some laboratory contamination was possible for diethyl phthalate. Because of the likelihood of sample contamination, the groundwater results for the phthalates benzyl *n*-butyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, and bis (2-ethylhexyl) phthalate and results for phenol and benzyl alcohol were re-classified as “reviewed and rejected” in the USGS NWIS database. The frequency and concentration of detections in blanks (including laboratory set blanks) indicated that laboratory procedures and sampling equipment could be the source of contamination, and detections of these SVOCs in environmental samples were not representative of groundwater conditions. Similarly, naphthalene was detected in the source-solution blank (0.029 µg/L). Groundwater results for 2-methylnaphthalene by LM 8270D-SIM and naphthalene by both RTI SVOC laboratory methods were not reported in the USGS NWIS database and are not included in this report.

The blank results for organic constituents showed that the USGS protocols for thorough and regular cleaning (U.S. Geological Survey, variously dated) and maintenance of sampling equipment are necessary to prevent low-level VOC, SVOC, and PAH contamination, so the protocols need to be applied to all equipment used for COGG regional monitoring in the future. No SRLs were established for other organic constituent groups.

In blanks collected with the Bennett pump and the WRD Grundfos pump, DOC and UV absorbance were both detected. Furthermore, DOC was detected in the source-solution blank at 0.3 mg/L. Concentrations measured in all the blanks were at least two times lower than detections in the environmental samples, so no SRLs were set.

Four major and minor ions (calcium, magnesium, fluoride, and silica) and twelve trace elements (antimony, arsenic, barium, boron, cobalt, copper, lead, molybdenum, nickel, strontium, vanadium, and zinc) were detected in blanks collected with the WRD Grundfos pumps (table A-2A). Chloride and five trace elements (cadmium, copper, iron, lead, and zinc) were detected in the Bennett pump blank sample set. Only lead, at 0.070 µg/L, was detected in field blanks collected at a water-production well through a peristaltic pump. Detections of major and minor ions and some trace elements (antimony, arsenic, barium, boron, molybdenum, and vanadium) in blanks were at concentrations typically one to two orders of magnitude less than the concentrations detected in groundwater samples. Any contamination of groundwater samples from the sampling equipment or processes by major and minor ions and by most trace elements (with the exception of those listed in the next paragraph) was considered small enough to not affect interpretation of results.

Seven of the trace elements detected in blanks had SRLs defined by Davis and others (2014) for data collected starting in October 2009 for the GAMA-Priority Basin Project (PBP): cobalt (all detections), copper (2.1 µg/L), iron (6 µg/L), lead (0.82 µg/L), manganese (0.66 µg/L), molybdenum (0.023 µg/L), nickel (0.21 µg/L), and zinc (6.2 µg/L). These SRLs were defined on the basis of statistical assessment of results from the field blanks collected for the GAMA-PBP study units from October 2009 through March 2013. The assessment used order statistics and binomial probabilities to construct an upper confidence limit (Hahn and Meeker, 1991; Olsen and others, 2010) for the maximum concentration of constituents potentially introduced when groundwater samples were collected, handled, transported, and analyzed. Concentrations of trace elements in blanks for the COGG exploratory sampling were near the SRL concentrations (table A-2A); therefore, the GAMA-PBP SRLs were applied to COGG groundwater results. Detections of trace elements at concentrations less than the SRLs are marked with a “less than or equal to” symbol preceding the reported value in table 7 to indicate that the true value could be less than or equal to the reported value (or could possibly be a non-detection). Applying the SRLs resulted in the re-classification of few to no groundwater results for four of the seven trace elements (copper, iron, nickel, zinc), because concentrations detected in groundwater were generally greater than the concentrations detected in COGG field blanks and the GAMA-PBP SRLs. The SRLs were applied to detections of lead and zinc, which are common materials used in equipment and fittings to collect groundwater samples. Concentrations of lead and zinc in the COGG field and equipment blanks were comparable to groundwater concentrations, resulting in the re-classification of several COGG groundwater detections with a less than or equal to symbol. Additionally, all results for cobalt were re-classified as “reviewed and rejected” because of potential contamination of the capsule filters used to filter COGG groundwater samples (Davis and others, 2014).

Ammonia was detected in all blanks at concentrations between 0.010 and 0.022 milligrams per liter (mg/L), and orthophosphate and total nitrogen were detected at 0.017 and 0.109 mg/L, respectively, in one field blank each from a coastal Los Angeles County monitoring-well site (table A-2A). Ammonia was detected at 0.01 mg/L in the source-solution blank and, therefore, in the inorganic blank water (USGS NWIS lot number 81404) from the NWQL used to collect blanks. The average concentration of ammonium in the inorganic blank water was 0.0084 mg/L, and the highest concentration was 0.0095 mg/L (James Lewis, USGS National Water Quality Laboratory, written commun., July 2014). Because the concentration of ammonia in the inorganic blank water was close to the LT-MDL (0.01 mg/L) and because of the frequency and concentration of ammonia in blanks, detections of ammonia in blanks were attributed, at least in part, to contamination of the inorganic blank water. Almost all detections in the environmental samples were at least an order or magnitude higher than the detections of ammonia in the blanks. An SRL is set as the highest detected blank (0.02 mg/L), however, so KERN_1, at a concentration of 0.015 mg/L, was changed to “reviewed and rejected.”

Iron was analyzed at the USGS NRP and was detected in most of the blanks, including the source-solution blank, at concentrations between 3 and 8 µg/L (table A-2A). Only two detections of total iron in groundwater samples were at concentrations less than 8 µg/L (both at 5 µg/L), and these two detections were in poor agreement with iron results from the NWQL Schedule 1948 of 37.6 µg/L and 9.88 µg/L. The results from the two laboratories for one other blank were in poor agreement: 28 µg/L from the USGS NRP and 57.1 µg/L from the NWQL. Iron-speciation results for three samples were re-classified as “reviewed and rejected” on the basis of blank results and comparison with NWQL iron results (table 10).

Dissolved hydrocarbon gases analyzed by Isotech Laboratories, Inc., were each detected in at least one blank from the WRD Grundfos pumps, whereas only methane and dissolved methane were detected in the other blanks (table A-2A). Concentrations of ethane, methane, and dissolved methane detected in blanks were several orders of magnitude less than the concentrations detected in the COGG groundwater samples, so were not considered meaningful. The detection of dissolved ethane in the blank sample from the WRD Grundfos pumps was very near the reporting level, so was not considered meaningful.

Replicates

Sequential replicate samples were collected to assess the precision of the water-quality data. Estimates of data precision are needed to determine whether differences in concentrations measured in samples reflect differences in groundwater quality or simply variability from collecting, processing and analyzing the samples.

If results from replicate sample pairs indicate that precision for a constituent is unacceptable and no specific reason can be identified, then this variability must be considered when interpreting the data. If measured concentrations are greater than a reporting level, then actual concentrations could be less than the reporting level. Similarly, if measured concentrations are less than the reporting level, then actual concentrations could be greater than the reporting level. Also, if a constituent concentration was highly variable between replicate samples, then a greater difference in concentrations between two independent samples is required to conclude that the two sampled populations had significantly different concentrations.

Two methods used for measuring variability between replicates were used to assess precision accurately for the range of measured concentrations. The variability between measured concentrations for pairs of sequential replicate samples was represented by the standard deviation (SD) for low concentrations and by relative standard deviation (RSD) for high concentrations (Anderson, 1987; Mueller and Titus, 2005). The RSD is defined as the SD divided by the mean concentration of each pair of replicate samples, expressed as a percentage. The boundary between concentrations for which variability was assessed by the SD and concentrations for which variability was assessed by the RSD was defined as five times the reporting level (RL) for each constituent. The RL may be an LRL, LT-MDL, SRL, MDL, or MRL for each constituent.

Replicate samples for all constituents, except radioactive constituents and isotopic ratios, were evaluated as follows:

- If both values were reported as detections, the SD was calculated if the mean concentration was less than five times the RL for the constituent, and the RSD was calculated if the mean concentration was greater than or equal to five times the RL for the constituent. Acceptable precision was defined as an SD of less than half the RL or an RSD of less than 10 percent. For comparison, an RSD of 10 percent is equivalent to a relative percentage difference (RPD) of 14 percent.
- If both values were reported as non-detections, the variability was set to zero, by definition.
- If one value for a replicate sample was reported as a non-detection and the other value was reported as a remarked value (“less than or equal to” code), or if both values are coded with a “less than or equal to” value, the SD was not calculated, because the values could be analytically identical. The “less than or equal to” code indicates that the value is a maximum potential concentration, and that the actual concentration could be low enough to be reported as a non-detection.

Replicate Samples Analysis

Tables A-3A–C summarizes the results of replicate analyses of constituents detected in groundwater samples collected for the COGG exploratory sampling. Replicate analyses were made at five sites, approximately 10 percent of all the groundwater samples collected.

Of the 1,134 replicate pairs of constituents analyzed, 806 pairs had no detections in either sample and, thus, had acceptable precision. Of the 328 pairs of constituents that had detections in either or both of the samples of the pair, 310 pairs had acceptable precision, and 18 pairs were outside the limits for acceptable precision (tables A-3A–C).

Three laboratory-analyzed water-quality parameters (alkalinity, pH, and specific conductance) were measured in 5 replicate pairs. All replicated measurements were within acceptable precision (table A-3A).

Most of the VOCs analyzed in replicate samples were below detection levels; however, 11 of the 85 VOCs analyzed were detected in at least 1 replicate sample. Detections for all 55 replicate pairs were within acceptable precision (table A-3A).

Six SVOCs and PAHs were detected in at least one replicate pair. Of these SVOCs and PAHs, 3—benzyl *n*-butyl phthalate, phenol, and bis (2-ethylhexyl) phthalate—were within acceptable precision in 15 replicate pairs (table A-3A). The three remaining SVOCs and PAHs (naphthalene, 2-methylnaphthalene, and diethyl phthalate) were coded as “reviewed and rejected” because of detections in laboratory set blanks (see the “Blank Samples” section of this appendix); therefore, replicate pairs were not evaluated and are not presented in table A-3A. All results for the remaining three SVOCs and PAHs were acceptable (table A-3A).

Dissolved organic carbon, UV absorbance, and DOC fractionation were detected in all 12 replicate samples analyzed, and all had acceptable precision (table A-3A).

Nutrients (total nitrogen, ammonia, nitrate, and phosphate, orthophosphate) were at detectable levels in most of the 20 replicate pairs. Of the 17 replicate pairs for which there was at least 1 detection of a nutrient, 16 were within acceptable precision. Only one replicate pair had unacceptable results: a pair for which there was a non-detection and a detection (nitrate) at a concentration close to the LT-MDL (table A-3A).

All 11 major and minor ions analyzed were detected in at least 1 replicate pair (table A-3A). Of the 55 replicate pairs analyzed, there was at least 1 detection in 52 of the pairs, and 51 of these were within acceptable precision. One replicate pair had unacceptable results for iodide (0.126 and 0.155 mg/L) with an RSD of 10.4 percent; the inconsistency was not significant (it was barely greater than the RSD) and no data were changed because of it.

In a total of 115 replicate pairs, 15 of the trace elements were detected. Of the 57 pairs that had at least 1 trace element detection, 54 of these were acceptable. The three replicate pairs that had unacceptable results consisted of a non-detection and a detection at a concentration close to the LT-MDL (arsenic, selenium, uranium). In one replicate pair, the environmental sample had a value of 114 $\mu\text{g/L}$ for aluminum, whereas the replicate sample was a non-detection (less than 55 $\mu\text{g/L}$). Both samples were re-analyzed by the NWQL, and the new results were both non-detections. A possible cause of the initial error was that the environmental sample was diluted, which increased the LT-MDL by 25 times the initial level; so either matrix interference, an error in the dilution calculation, or both could have caused the variability. Replicate samples of uranium and selenium had unacceptable results because one sample of the pair had a non-detect, whereas the other had a detection. Replicate pairs for arsenic and nickel had concentrations greater than five times the LT-MDL and unacceptable precision (table A-3A). The causes for these inconsistencies were not determined and no actions were taken in censoring data.

Four replicate pairs were collected for measurements of iron speciation, that is iron (II) and iron (II) plus iron (III). All eight replicate pairs had detections, and all had acceptable results (table A-3A).

Of the 20 dissolved analyzed hydrocarbon and standard gas constituents, 14 individual gases were detected in 34 replicate samples, and all but 1 were within acceptable range. Oxygen was the only constituent out of range (11.70 mole percent and 9.44 mole percent), which was barely out of acceptable precision with an RSD of 11 percent (table A-3A).

Isotopic ratios in water ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{11}\text{B}$, and $^{87}\text{Sr}/^{86}\text{Sr}$) and dissolved hydrocarbon gases ($\delta^{13}\text{C}$ of methane, $\delta^2\text{H}$ of methane, $\delta^{13}\text{C}$ of ethane, and $\delta^{13}\text{C}$ of propane) are reported with an absolute uncertainty (tables 11, 13), such that the result is expressed as the reported value plus or minus the uncertainty. A replicate pair of isotope ratios of water and dissolved hydrocarbon gas was considered acceptable if the reported values, plus or minus the uncertainty, for the environmental and replicate members of a replicate pair overlapped. Five replicate samples of isotopic ratios in water were collected, and all replicate pairs were acceptable (table A-3B). Four isotopes of dissolved standard and hydrocarbon gases ($\delta^{13}\text{C}$ of methane, ethane, and $\delta^2\text{H}$ of methane) were analyzed, composing six samples in total. All samples were within acceptable precision.

Carbon-14 is reported with a sample-specific counting error (table 11), such that the result is expressed as the reported value plus or minus the uncertainty. A replicate pair was considered acceptable if the reported values, plus or minus the uncertainty, for the environmental and replicate members of the replicate pair overlapped. Of the five replicate pairs, four were acceptable, and one was unacceptable (table A-3B).

Noble gas concentrations and $^3\text{He}/^4\text{He}$ ratios are reported with a percentage uncertainty (table 12), such that the result is expressed as the reported value plus or minus the percentage uncertainty of the reported value. Uncertainties ranged from 1 to 3 percent. A replicate pair was considered acceptable if the reported values plus or minus the uncertainty for the environmental and replicate members of the replicate pair overlapped. Of the 27 replicate pairs, 21 had acceptable precision (table A-3B). The reason for the lack of agreement between six of the replicate pairs is uncertain, and no data were censored. Four of the six replicate pairs of analyses were from the same replicate-sample pair, however, possibly indicating inconsistency in sample collection at one site.

Replicate pairs of analyses for radiochemical constituents were evaluated by using the following equation (McCurdy and others, 2008) to calculate the normalized absolute difference (NAD):

$$NAD = \frac{|R_1 - R_2|}{\sqrt{(CSU_1^2 + CSU_2^2)}} \quad (3)$$

where

R_1 and R_2 are the results for the two samples in the replicate pair, and

CSU_1 and CSU_2 are the combined standard uncertainties associated with the results.

Values less than 1.65 for the NAD correspond to a significance level (α) of 5 percent ($\alpha = 0.05$), indicating differences that are acceptably small and not statistically significant (McCurdy and others, 2008).

There were 16 replicate pairs for 4 radioactive constituents: radium-224, radium-226, radium-228, and tritium (table A-3C). Five replicate samples were collected for radium-224 analysis; however, four were marked as “failed” by the lab and were not reported (discussed further in the “Other Quality-Control Results” section of this appendix). Of the 16 replicate pairs, 5 were outside the limits of acceptable precision.

Matrix Spikes

The addition of a known concentration of a constituent (spike) to a replicate environmental sample enables the laboratory to determine the effect of the matrix, in this case groundwater, on the analytical technique used to measure the constituent. For this study, matrix spikes were added in the laboratory performing the analysis, rather than in the field. The known compounds added to matrix spikes are the same as those analyzed in the environmental samples. This enables an analysis of matrix interferences on a compound-by-compound basis. A low matrix-spike recovery can indicate that the compound potentially would not be detected in some samples in which it was present at low concentrations.

For the COGG exploratory sampling, matrix spikes were carried out for VOCs (NWQL Schedule 2020), SVOCs (RTI LM 8270D-LL), and PAHs (LM 8270D-SIM). For this project, the acceptable median matrix-spike recoveries were defined as 70 to 130 percent for VOCs and were variable and constituent-specific for SVOCs and PAHs. Only constituents for which median matrix-spike recoveries were outside of this range were flagged as having unacceptable recoveries. The acceptable range of 70 to 130 percent for median matrix-spike recovery is generally more restrictive than the acceptable control limits for laboratory set-spike recoveries. Laboratory set spikes are aliquots of laboratory blank water to which the same spike solution used for the matrix spikes was added. One set spike was analyzed with each set of samples. Acceptable control limits for set spikes were defined relative to the long-term variability in recovery. For example, for many NWQL analyses, acceptable set-spike recovery is within plus or minus 3 F-pseudosigma of the median recovery for at least 30 set spikes (Connor and others, 1998); the less the F-pseudosigma, the more precise the determinations (Hoaglin, 1983).

Table A-4 presents a summary of matrix-spike recoveries for VOCs analyzed for the COGG exploratory sampling. Samples for the addition of the spike mixtures for 85 VOCs were collected at 4 sites (3 in the coastal Los Angeles County study area and one in the Kern and Kings Counties of the southern San Joaquin Valley), approximately 10 percent of the wells sampled. Median matrix-spike recoveries were between 70 and 130 percent for all VOCs (table A-4). Because only about 2 percent (8 out of 340 samples) of the matrix-spike recoveries were just outside of the acceptable range, VOC detections in environmental samples were not reclassified on the basis of the matrix-spike recovery analysis.

Acceptable median-spike recoveries for SVOCs and PAHs were defined as the control limits set by RTI Laboratories (http://rtilab.com/wp-content/themes/rtilab/pdf/QAP-20120618_v1.pdf), which varied by constituent and were generally between 40 and 125 percent. Results for SVOC and PAH matrix spikes were reported as percentage recoveries from the laboratory and, therefore, were not stored in the USGS NWIS database. Matrix-spike recoveries for SVOCs and PAHs are not tabulated in this report; however, a summary of the results follows.

Samples for the spikes of 81 SVOCs and PAHs were collected at the same 4 sites as those for the VOCs and, generally, were within the acceptable range set by the laboratory. The RTI Laboratories ran an initial calibration verification (ICV) before a set of samples was analyzed and continued calibration verification (CCV) during the analysis using the same standard to make sure the instrument did not drift from the ICV (Gary Cottrell, U.S. Geological Survey, written commun., October 2014). Any analysis of benzoic acid

was omitted by the lab because it is a poor and inconsistent responder, as indicated by not meeting the ICV and CCV controls (Rachel Dear, RTI Laboratories, written commun., October 2014). The analytes that were measured using LM 8270D-LL were mostly within acceptable laboratory limits. Pentachlorophenol and hexachlorocyclopentadiene were the only two constituents for which more than one sample was outside of the laboratory's reporting limit: the upper limit of acceptance for pentachlorophenol is 138 percent, and two spike samples had recoveries of 159 percent and 163 percent, whereas two spike samples for hexachlorocyclopentadiene had recoveries of 23 percent and 46 percent, which were below the lower limit of acceptability of 50 percent. All the analytes that were measured with RTI method 8270D-SIM were within laboratory acceptability limits, except for samples from the well LA_31, which consistently had recoveries near or below the acceptable limit of recovery. Even though the recoveries for samples from LA_31 were low, the paucity of detections of SVOCs and PAHs in the rest of the environmental samples provided confidence that the non-detections in LA_31 were accurate. Values of detections of SVOCs and PAHs in all the environmental samples were not adjusted in this report.

Surrogate Compounds

Surrogate compounds were added to the COGG groundwater and blank samples in the laboratory prior to analyses of VOCs, SVOCs, and PAHs. Surrogates are used to evaluate the recovery of similar constituents in order to identify general problems that can arise during laboratory sample analysis and affect the results for all compounds in that sample. A potential problem includes matrix interferences (such as high levels of DOC) that produce a positive bias or incomplete laboratory recovery (possibly from improper maintenance or calibration of analytical equipment), which produces a negative bias. A 70 to 130 percent recovery of surrogates, in general, is considered acceptable; values outside this range indicate possible problems with the processing and analysis of samples (Connor and others, 1998; Sandstrom and others, 2001).

Table A-5 presents a summary of the surrogate recoveries for the COGG exploratory sampling. The table lists the surrogate compound, the analytical schedule for which each surrogate was used, the number of analyses of blanks and environmental samples, and the number of surrogate recoveries less than 70 percent and the number of surrogate recoveries greater than 130 percent for the blank and environmental samples. Field blanks and environmental samples were compared separately to assess whether the matrices in environmental samples affected surrogate recoveries.

Most surrogate recoveries for the blank and environmental samples were within the acceptable range of 70 to 130 percent. The total of 624 surrogate analyses comprised 537 environmental samples and 87 blanks. Of the surrogate samples collected, 177 were analyzed for VOCs (153 environmental and 24 blanks), and 447 were analyzed for SVOCs and PAHs (384 environmental and 63 blanks). For the VOC analyses, 96 percent of the blanks and 95 percent of the environmental surrogate recoveries were within the acceptable range. For the SVOC and PAH analyses, 62 percent of the blanks and 55 percent of the environmental surrogate recoveries were within the acceptable range (table A-5).

Detections of VOCs were outside of the acceptable range for 5 percent of the samples, which was considered acceptable recovery; therefore, VOC detections in environmental samples were not reclassified on the basis of surrogate recovery analysis. The surrogate samples for SVOCs and PAHs had low recoveries. Detections in environmental samples were not reclassified on the basis of the surrogate recovery analysis; however, sample results were still censored owing to the poor recoveries in laboratory set blanks.

Other Quality-Control Results

During the analysis of samples collected for the COGG exploratory sampling, there were three laboratory QC problems that affected four laboratory analysis runs: the effects of laboratory QC failures; holding-time violations for radium-isotope analyses; and matrix interference in analyses for iron speciation, noble gases, and UV absorbance.

Results for the analysis of radium isotopes in 17 groundwater samples were rejected because of holding-time violations, QC failures, or both. Holding time is specific to each constituent and method of analysis and refers to the time in which a sample should be analyzed after collection in order to protect sample integrity and give reliable results. For example, samples for analysis of radium-224, which has a half-life of 3.6 days, must be

shipped to the laboratory overnight to allow enough time for the analysis. Three radium-224 samples were delayed in shipment past the holding time, and the results could not be reported. For 12 other samples, results for radium-224 and radium-226 failed laboratory QC limits and were rerun after the radium-224 holding time; only the radium-226 results for these samples were reported. In addition, radium-228 results could not be reported for two samples owing to multiple laboratory QC issues (Ann Mullin, U.S. Geological Survey, written commun., November 2014).

Problems with iron speciation for eight samples from coastal Los Angeles County were due to matrix interference. Matrix interference is the bias created or masking of the constituent because of other factors in the matrix (in this case, groundwater). Because of a combination of relatively high conductance, natural water color, or high DOC content, the matrix interfered with the analysis of iron speciation (Blaine R. McCleskey, written commun., U.S. Geological Survey National Research Program, November 2014), and the results could not be reported. Results for these samples were coded in the USGS NWIS database with the null-qualifier code “u” for unable to determine—matrix interference.

Similarly, noble gas results for 15 groundwater samples from coastal Los Angeles County could not be reported. The analytical results for these samples were compromised either as a result of high concentrations of methane or of degassing. In an effort to reduce methane interference, sample temperatures were increased during analysis. This, in turn, increased water-influenced interference (Ate Visser, written commun., Lawrence Livermore National Lab, January 2015). The results were coded as “reviewed and rejected” in NWIS.

Absorbance scans were analyzed visually before interpreting the spectral properties. Results for UV absorbance and specific UV absorbance (SUVA) were reported with laboratory comments indicating that data could have a slight positive bias due to matrix interference (Kenna Butler, written commun., U.S. Geological Survey National Research Program, February 26, 2015).

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Appendix Tables

Tables are provided in a [Microsoft Excel file located here](#).

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