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To: Jonathan Bishop, Chief Deputy Director, California State Water Resources Control Board

From: Matthew Landon, Program Chief-California Oil, Gas, and Groundwater Projects Group; Kimberly Taylor, Program Officer; California Water Science Center, U.S. Geological Survey

Subject: Summary of U.S. Geological Survey scientific methods used for the Regional Monitoring Program

The purpose of this letter is to summarize the objectives, sample collection and analysis protocols, quality-assurance procedures, approaches, and reporting procedures used by the U.S. Geological Survey (USGS) for the California State Water Resources Control Board's (Water Board) Regional Monitoring Program of Water Quality in Areas of Oil and Gas Production. This summary has been prepared in response to requests by stakeholders to clarify technical approaches used in the program. This summary is not intended to be a comprehensive description or step-by-step manual for the methods used in the Regional Monitoring Program, which would require a much lengthier document and would duplicate available technical resources and future publications that will describe results for specific areas based on data. Rather, this overview document cites published and publicly available information to summarize the scientific methods used for the Regional Monitoring Program. This letter augments a significant amount of material already provided to the Water Board and stakeholders, including a series of public presentations on study design which have been available as a published web page since September, and the Discussion Paper which outlined the study strategy in December 2014 (both are linked to the Water Board web page).

Thank you for sharing this information with Program Stakeholders. We look forward to further discussions and to the upcoming Program Stakeholder meeting.

Overview of methodology, quality-assurance, and reporting of regional monitoring of water quality in areas of oil and gas production, January 2018

Objectives, Scope, and Components of Regional Monitoring Program

The regional monitoring program is working to answer the following questions about oil and gas development and groundwater resources (https://ca.water.usgs.gov/projects/oil-gas-groundwater/index.html):

1. Where are protected groundwater resources?
2. How close are oil and gas operations and protected groundwater, and what geologic materials separate them?
3. Where is there evidence of fluids from oil and gas sources in protected groundwater? Where does evidence indicate no connections?
4. When fluids from oil and gas sources are present in protected groundwater, what pathways or processes are responsible for observed transport?
5. Have oil and gas operations as a whole contributed to water-quality changes in groundwater basins?

The overall scientific plan for answering these questions and then designing field-specific monitoring plans was outlined in the Dec 4, 2014 Discussion Paper beginning on p 38 (Taylor and others, 2014). The program's framework was developed and adopted by the California State Water Resources Control Board (Water Board) in July 2015. Subsequently, the USGS published a series of web pages based on the Water Board-USGS cooperative agreement scopes of work, the Discussion Paper, and public presentations of program plans. This letter augments all that material by specifically providing more detail on methods.

The current geographical focus of the program are 115 onshore oil and gas fields identified as being of highest priority with respect to implementing regional groundwater monitoring (Davis and others, in press; Discussion Paper, p.42). Maps of where different components of the regional monitoring program are being conducted are available at https://ca.water.usgs.gov/projects/oil-gas-groundwater/index.html. Using the prioritization information, each year the Water Board staff, in consultation with the USGS and Regional Water Quality Control Board staff, select which oil fields regional monitoring work will take place in.

Because each of the three major components of the regional monitoring program, regional groundwater sampling, produced water characterization, and subsurface salinity mapping, include unique methodology, each is described in a separate section below. Aspects of the program that are common to all components are described in the regional groundwater sampling design section.

Regional Groundwater Sampling Design

The purpose of this analysis is to determine if there is fluid movement from zones where oil and gas production activity is occurring into the zone of protected groundwater and to identify where best to monitor.

Site Selection & Network Design

The program uses a conceptual model as the starting basis for collecting information on groundwater quality in each study area. That model includes 1) sampling groundwater at different depths along regional flow paths from oil and gas infrastructure and activities to protected groundwater, and 2) incorporating a robust understanding of features such as regulated cleanup sites, faults and other hydrogeologic features, and historical chemistry data. Water well locations and completion depths (obtained from DWR driller logs) are then mapped over the target areas, and permissions sought to access appropriate wells. The end result is a sampling design for regional groundwater sampling in each study area that initially utilizes existing wells. These designs are not prepared as separate documents by the USGS. In some oil fields, such as the Fruitvale oil field on the east side of the Central Valley, the currently used groundwater resources directly overly the oil field. In other fields, such as on the west side of the Central Valley, groundwater is sparse within oil field boundaries but is extensive adjacent to the oil fields. Examples of the application of the general conceptual model and resulting study area specific designs of groundwater sampling near the Fruitvale and Lost Hills oil fields are provided at: https://ca.water.usgs.gov/projects/oil-gas-groundwater/science/design/.

The conceptual model for regional monitoring includes trying to characterize oil-field end-member or potential source water compositions, which are many and complex, and potential sources of groundwater outside of oil fields that may be mixing with groundwater near oil fields. It is also important to recognize that some groundwater and surface-water sources have been used as sources of water injected into oil fields. A simplified conceptual model and a diagram summarizing some of the source fluids we attempt to sample are further described at: https://ca.water.usgs.gov/projects/oil-gas-groundwater/science/geochem/.

The USGS briefs Water and Regional Board staff on both groundwater and produced water site-specific sampling plans to ensure agreement prior to initiating contact with well owners. During the process of requesting site access, the USGS and Water Board communicate with well owners and local water agencies regarding groundwater wells in the study area, including making presentations on the sampling design to entities owning or managing many wells to facilitate obtaining supporting site information, permission to sample, and logistical arrangements.

Site characteristics are documented during onsite visits following standard USGS procedures (Wilde, 2005; Cunningham and others, 2011).

Sample Collection

Groundwater samples are collected following standard and modified U.S. Geological Survey (USGS) protocols from the National Water Quality Assessment (NAWQA) Program (Koterba and others, 1995) and the National Field Manual (NFM; U.S. Geological Survey, variously dated). Samples are collected either from monitoring wells or from water-production wells (irrigation or drinking-water 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. Monitoring wells are sampled with submersible, positive-pressure pumps. For monitoring wells without pumps installed, portable USGS Bennett or Grundfos pumps equipped with Teflon tubing are used to collect samples. For monitoring wells with pumps installed, the existing pump is used to collect the sample. Some pumps may not be suitable for collection of all kinds of samples. Water-supply wells generally have permanently installed turbine pumps. Water-supply wells are sampled using Teflon® tubing and stainless steel fittings attached to a sampling point on the well discharge pipe that is as close to the well head as possible, and upstream of any treatment system (filtration or chlorination) or water-storage tank. All wells are pumped continuously to purge a minimum of three casing volumes of water from the well (Wilde, 2006) and are sampled after the field parameters collected at the sampling point have stabilized. Field measurements are determined using instruments in a flow-through chamber and a spectrophotometer. Samples are collected adjacent to the sampling point in a sampling chamber or inside of a mobile laboratory (Wilde, 2004). Temperature-sensitive samples are stored on ice prior to and during shipping. Temperature-sensitive or time-sensitive samples are shipped daily or weekly, as recommended by laboratory holding time protocols. All sampling equipment is cleaned between sample sites following USGS protocols (U.S. Geological Survey, variously dated).

Detailed sampling protocols for groups of analytes are described in the references listed in **table 1**. Standard methods have EPA method numbers, have been used in the SB4 local-area monitoring or Regional Board regulatory monitoring programs, or have been conventionally used in groundwater quality investigations. Research methods are not widely used in regulatory monitoring but have been selected to provide additional insight regarding water chemistry and processes affecting water chemistry. The standard and research method protocols used are included in **table 1**.

Sample Analysis

Analytes for regional groundwater monitoring samples include constituents with different transport characteristics; for example dissolved gases, dissolved inorganic constituents, dissolved organic constituents, water and solute isotopes, and groundwater age tracers. These analytes were selected based on a literature review of potential tracers used in oil, gas, and groundwater studies (https://ca.water.usgs.gov/projects/oil-gas-groundwater/science/geochem/; McMahon and others, 2017). Some of these analytes are also collected in SB4 local-area sampling. Analytes unique to the regional monitoring include noble gases, solute isotopes (Sr, B, Li, C, and sometimes SO_4 isotopes), groundwater age-dating tracers (^3H, ^{14}C, ^4He, ^3He, and SF_6), low molecular weight organic acids, and dissolved organic carbon concentrations and optical characteristics. These additional analytes provide information for understanding regional groundwater chemistry and potential relations to various sources and pathways of constituents dissolved in groundwater and expand on information available from regulatory datasets (see Interpretation).

Multiple USGS, University, and commercial laboratories are analyzing groundwater samples for the regional monitoring program (**table 2**). The laboratory analyzing the largest set of analytes is the USGS National Water Quality Laboratory (NWQL). Results for analyses made at the NWQL or by laboratories contracted by the NWQL are uploaded directly to the USGS National Water Information System (NWIS) database. Results of analyses done at other laboratories are subject to the USGS Laboratory Evaluation process to ensure program quality standards can be met, and when verified, the results are compiled in a project database and uploaded from there to the USGS NWIS database.

Quality Assurance/Quality Control

Procedures used to collect and assess quality-control (QC) data and quality-assurance (QA) data follow standard and modified U.S. Geological Survey (USGS) protocols from the National Water Quality Assessment (NAWQA) Program (Koterba and others, 1995), and the NFM (U.S. Geological Survey, variously dated). Recent published examples of USGS QA/QC, which ensures appropriate reporting levels for trace level constituents measured in groundwater samples, include reports from the Groundwater Ambient Monitoring and Assessment (GAMA) program (Fram and others, 2012; Davis and others, 2014) and exploratory sampling efforts for the regional monitoring program (Dillon and others, 2016 [see quality-assurance and quality-control methods and results]). Data that don't meet USGS quality standards will not be included in analysis or manuscripts.

Quality Assurance

The purpose of quality assurance is to describe the precision and accuracy of the data and to determine if the environmental data had been affected by contamination or bias during sample collection, processing, storage, transportation, or laboratory analysis. Quality control samples are collected and analyzed routinely evaluated as part of the regional monitoring

program including: (1) blank samples collected to assess positive bias as a result of contamination introduced by equipment or during sample handling or analysis; (2) replicate samples collected to assess variability; (3) VOC matrix-spike tests done in the lab to assess potential matrix effects from the chemical composition of each groundwater sample; and (4) surrogate compounds added in the laboratory to samples analyzed for organic constituents to assess potential positive or negative bias due to matrix interferences and to assess potential bias due to instrument performance and calibration. The regional monitoring program collects replicates for all constituents at about 10% of the sites sampled, blanks at about 10% of the sites sampled for those constituents for which blanks are appropriate, and VOC matrix spikes at 10% of the sites. Blanks are collected by using water certified by the NWQL to contain less than the reporting levels of selected constituents investigated in the study. Field and equipment blanks are collected by pumping blank water through the groundwater-sampling equipment (fittings, tubing, and filters).

Groundwater and produced water (see produced water section for details) samples are analyzed for the same analytes but sometimes require use of different laboratories because some laboratories are not equipped to analyze produced water samples with higher dissolved constituent concentrations. For analyte groups where different laboratories are used to analyze groundwater and produced water samples, split groundwater samples are collected at about 20% of the sampling sites and sent to laboratories analyzing produced water samples. The analytical results for these split samples sent to different laboratories are compared to evaluate variability between different laboratories. Split groundwater samples were sent to produced water laboratories analyzing samples for VOCs, major and minor ions and trace elements, and noble gases.

Quality assurance results will be reported in the appendix of interpretative manuscripts describing the sampling results and the QC data will be provided in supporting USGS data releases (see below).

Laboratory Evaluation Process

USGS Water Mission Area projects are required to evaluate the quality of laboratory results that they receive by obtaining and reviewing laboratory performance data (U.S. Geological Survey, 2014). This policy is known as the Laboratory Evaluation Policy. The USGS Data Management policies (Faundeen and others, 2013) state that projects must “Manage quality… [and] plan quality-assurance measures for data at the project’s inception, and then undertake ongoing quality-control monitoring and adjustment at subsequent lifecycle stages to verify that those measures perform as expected as the project proceeds.” As part of this process, a series of Laboratory Evaluation Packages (LEPs) will be prepared for each dataset (a set of environmental sample results and corresponding laboratory and project quality control and performance data for specific analytes analyzed by one laboratory during a specified time period) and an evaluation of that dataset relative to project-specific data requirements. The QA plan followed by the National Water Quality Laboratory (NWQL), the primary laboratory used

to analyze groundwater samples for this study, is described by Stevenson (2013). QA plans and procedures for other laboratories are available in references or online links shown in table 2. The USGS Laboratory Evaluation process requires project-specific data requirements, typically specifying criteria for method blanks, spike recovery, and replicate precision. Multiple USGS personnel are involved in the preparation and review of LEPs including a laboratory liaison, project laboratory-evaluation lead, QC-data specialist, and data reviewer or data-validation lead. Once sufficient QC data have been collected from each laboratory, an LEP will be generated for each laboratory and submitted for review and approval (U.S. Geological Survey, 2014).

Compilation of Existing Data

Large amounts of data from scanned oil/gas well records from DOGGR and water well completion reports records from DWR are being put into numerical records in databases to be used in analysis. The USGS has a cooperative agreement with the California State University Sacramento (CSUS) Geology Department, which is deploying large teams of students to extract data from oil and gas well records into databases. The data compiled include oil well perforation depths and borehole geophysical log data (see Subsurface salinity mapping-compilation and analysis of borehole geophysical log data). USGS has been compiling groundwater and produced water chemistry data from multiple sources. Most compiled water-quality data come from electronic data bases, including the following: NWIS, GeoTracker (Water Board), the USGS National Produced Waters Geochemical Database, California Department of Water Resources (DWR) water-quality data, DOGGR, and local sources such as counties and water districts. Some data, including oil and water well perforation depth data from DWR, and some water-chemistry records from GeoTracker and DOGGR are only available as scanned images and the data have to be manually entered into numerical data sets. In those instances, the transcribed data are spot checked against the original data source. In addition, charge balances are calculated for the compiled data and only those historical chemistry data having a charge balance closure <10% are used in analysis. Because some of these sources have chemistry data but no corresponding well perforation depth data there has been a substantial effort to populate the chemistry databases with well perforation depths from scanned well records.

This data compilation supports regional groundwater monitoring, produced water characterization, and subsurface salinity mapping. All of the compiled data will be publicly available as data releases after completion and review.

Reporting, Interpretation, Communications

Data Reporting

Well Owner Report

Once the laboratory data for individual sites sampled are quality-assured, the data will be sent to the owner of that well or site. This “Well Owner Report” will be sent in advance of presentations at public conferences or meetings. Because data are returned from different

laboratories at different times, in some cases multiple well owner reports may be sent. In general, well owner reports will be sent 6 to 18 months after sampling; the timing depends upon how long it takes to collect a complete set of samples from a study area and the time for laboratory data to be returned to the project. The well owner reports will be sent at least two months before presentations of results based on the data at public stakeholder meetings.

USGS Data Release

Digital datasets from federally funded research including datasets used to support scholarly publication must be made available to the public. Refer to Office of Science and Technology Policy (OSTP) from February 22, 2013 "Increasing Access to the Results of Federally Funded Scientific Research". The data releases undergo review through USGS Fundamental Science Practices (refer to IM OSQI 2015-03-Fundamental Science Practices: Review and Approval of Scientific Data for Release for full policy details) and are published in USGS Data Releases. The data from environmental samples collected by USGS will also be available to the public through the Water Board's GeoTracker) and USGS NWIS.

Interpretation

Interpretative Manuscripts

For most regional monitoring study areas, a manuscript describing the synthesis of existing information, study area specific design, results of analysis of newly collected and/or historical data, and answers to the program questions that can be determined based on the collected information will be published. These interpretative manuscripts may be journal articles or USGS reports. In some cases, a manuscript may summarize results from multiple study areas or on a particular topic or set of constituents. In addition to technical manuscripts, some USGS Fact Sheets summarizing results for the general public will be prepared. Manuscripts will also be linked to the regional monitoring websites (https://www.waterboards.ca.gov/water_issues/programs/groundwater/sb4/, https://ca.water.usgs.gov/projects/oil-gas-groundwater/).

All published manuscripts undergo review and approval by the USGS following Fundamental Science Practices (FSP) (https://www2.usgs.gov/fsp/). These practices are designed to ensure the USGS provides unbiased, objective, and impartial scientific information. FSP guidelines include that organizations/individuals with job-related, economic or political conflicts cannot be involved in the peer review process. Articles submitted to journals also undergo peer review by anonymous reviewers selected by the Journal in addition to USGS review and approval.

Data supporting interpretative manuscripts will be published coincidentally in publically accessible USGS Data Releases.

Interpretative Process

The process of interpreting water chemistry data to identify the potential presence of fluids from oil and gas sources, if any, and to gain insight on pathways these fluids could follow

and processes that could affect water quality is founded on several principles: (1) spatial analysis of geochemical data; (2) analysis of co-occurrence patterns of geochemical constituents (3) a conceptual end-member mixing model; (4) awareness of potential pathways; (5) physical context for fluid movement; (6) multiple lines of evidence; (7) objectivity/neutrality and consideration of uncertainties, (8) identifying gaps and approaches to fill gaps.

Spatial analysis: a key first step is to describe spatial patterns of water chemistry data in relation to potential explanatory factors such as proximity to and density of oil and gas infrastructure, position in the hydrogeologic flow system, geology, land use, and other potential other human and natural sources. This spatial analysis of water chemistry data includes new sample data with an extensive analyte list but limited spatial coverage combined with typically more widespread historical data with limited analytes. Spatial patterns in water chemistry may suggest relations to explanatory factors that require further evaluation.

Co-occurrence Patterns of Constituents: The different constituent groups have different transport characteristics and sources. Analysis of co-occurrence patterns of the different types of constituents are used to assess processes and pathways that may explain the observed patterns. McMahon and others (2017) provided several examples of analyzing the co-occurrence of petroleum hydrocarbons, solvents, groundwater age, methane concentrations and methane isotope signatures, water isotopes, and saline brine indicators such as major and minor ions, trace elements, and strontium isotopes to distinguish groundwater affected by mixing with produced water, groundwater containing thermogenic gas without co-occurring produced water, and groundwater affected by biogenic sources of methane unrelated to oil and gas sources. These exploratory data were collected as a field test of the co-occurrence approach in multiple areas of California to determine that approaches used elsewhere would be useful in this program; samples were not collected following the study areas design outlined above and thus did not represent a conclusive assessment of any particular area. The field test successfully identified different co-occurrence patterns of constituents that indicated different processes affecting water chemistry. This approach depends on having a wide array of tracers with different characteristics to enable co-occurrence analyses.

End-member mixing model: By characterizing different potential source waters (end-members) and groundwater compositions for an array of different tracers, it is possible to identify mixing curves that are or are not consistent with groundwater compositions. The end member mixing model is further described at: https://ca.water.usgs.gov/projects/oil-gas-groundwater/science/geochem/. After collection and comparison of a suite of endmember samples and a suite of groundwater samples, standard mixing model tools are used to evaluate a) if oil and gas signatures are present in the groundwater and b) if we can explain why. Other potential end-members in addition to potential oil and gas source fluids considered include background ancient groundwater, modern recharge beneath current land use, and surface water that may serve as a water source to agricultural regions.

Potential pathways: A discussion of potential pathways between oil and gas activities and protected groundwater is provided at https://ca.water.usgs.gov/projects/oil-gas-groundwater/science/pathways/. Data on proximity and density of potential pathways assembled from multiple sources are analyzed for relations to groundwater chemistry. A relation does not indicate causality but the identified relations can contribute to the multiple lines of evidence considered. The regional monitoring program is assembling extensive potential explanatory data for use in statistical analysis of water quality.

Physical Context: water chemistry data need to be interpreted within the hydrogeologic framework of the study area. Current and historical regional groundwater flow directions based on water-level/pressure data are evaluated to determine if fluid gradients are consistent with geochemical data. Compiled well depth data are being used to identify where oil and water well perforations are located in relation to the subsurface geology to provide physical context for understanding fluid movement in groundwater zones and water quality.

Multiple Lines of Evidence: We use multiple lines of evidence (Discussion Paper, p.23) to evaluate the risk that groundwater could be affected by oil/gas development versus other sources. We are sampling for a wide array of constituents, including several hundred compounds. All constituents in groundwater potentially have multiple sources. For example, chloride is a constituent of concern that can be influenced by sources including oil and gas reservoir fluids or agricultural and industrial activities unrelated to oil and gas. To evaluate sources of chloride in a water sample, one would use a variety of different constituent groups to try to unravel sources, including the whole set of major ion concentrations, ratios of ions, water isotopes, and groundwater age. In another example, evaluating whether methane is derived from oil and gas reservoirs rather than microbial production in shallow aquifers, one could potentially use many different geochemical tools including major ion data, hydrocarbon gas concentration and isotopic data, water and noble gas isotope data, and groundwater age information. Water chemistry interpretation involves using different chemical signals to figure out sources in different situations. These patterns have to be evaluated in light of what mechanisms are physically plausible. There is no silver bullet, no one signal that is always going to uniquely indicate the presence of oil and gas signatures in all settings. Rather a matrix of geochemical tracers, information on the chemical characteristics of different sources, and understanding of the hydrogeologic context and physical mechanisms for fluid movement are used to describe possible sources and processes affecting groundwater quality at regional scales.

Objectivity/Uncertainties: USGS standards of scientific analysis require that data be evaluated and results reported objectively. The FSP review and approval process is designed to assure that reported results are clear and supported and that uncertainties in interpretations are appropriately described. The regional monitoring program is designed to address the questions described in the first section and to provide data in areas of oil and gas development for understanding regional water quality beyond local Well Stimulation Treatment (WST)

projects. Monitoring around local WST, UIC, or contamination sites is included in the local-area monitoring conducted under the guidelines of the Water Board for the SB4 program, Water Board UIC monitoring programs, or existing Regional Board monitoring programs, respectively.

Identifying gaps and approaches to fill gaps: The regional monitoring program is designed to use lower cost methods first, including compilation and analysis of existing data, and sampling of existing wells, before deploying more expensive approaches such as drilling new monitoring wells (Discussion Paper, p. 18 and p. 38). Selection of new sample locations is based on analysis of existing information. After analyzing the results from sampling existing wells, drilling new monitoring wells at selected locations to help fill key data gaps may be considered. New monitoring well sites could include collection of water level, temperature, and borehole geophysical data over time that supports analysis of water chemistry data. Given the cost of drilling and installing multiple well monitoring sites at the expected depth ranges necessary, a limited number of high priority sites will be installed. An additional outcome of the initial round of regional monitoring in individual study areas will be to identify priorities for additional monitoring over time, if such monitoring is not already occurring.

Publications & Stakeholder Communication Process

The USGS has well-established rules and procedures in place for conducting robust, independent, scientific-based studies for use by resource managers. The Water Board recognizes that the USGS is an independent scientific agency with the organizational policies and practices in place that will ensure the sampling and results are credible.

The mission of the USGS California Water Science Center is *"to collect, analyze and disseminate the impartial hydrologic data and information needed to wisely manage water resources for the people of the United States and the State of California".* As a result, in the analysis of the data the USGS will operate as an independent entity to maintain the integrity of the regional monitoring program (RMP). The USGS interpretive efforts do not to involve input from outside entities, including operators who have provided access to sampling locations. The USGS's Fundamental Science Practices limits sharing draft information to Water Board staff.

The USGS works independently to: select field methods, analytical methods, and synthesize and interpret information done according to the USGS's Fundamental Science Practices and in consultation with Water Board staff. These practices require that data collected using adjusted and/or experimental field and analytical methods meet the same standard as published methods in order to be used as the basis for interpretation.

Steps & Typical Timeline for Delivery, Presentation and Publication of Water Quality Information Collected from Well Owners:

1. The USGS will send an individual well owner data from their well(s) (Well Owner Report). The Well Owner Report includes final data that has gone through the USGS's quality control/quality assurance procedures.

2. The USGS will present the results of the sampling at a Water Board staff hosted stakeholder briefing no sooner than two months after the Well Owner Reports have been forwarded to the individual well owners.
3. A USGS publication of interpreted results and the electronic release of all data will occur a few to several months after the stakeholder briefing.

Produced Water Characterization

The purpose of this work is to characterize and build a library of oil-field source water chemistry for comparison with groundwater chemistry. Oil-field source fluids sampled include injectate (water injected into the subsurface for enhance recovery or waste disposal), produced water and casing gas from oil/gas wells representing predominant oilfield management practices and formations in an oil field, surface ponds, and fluid sources mixed with produced water in injectate such as water source wells or surface water. The chemistry of oil field waters is highly variable, differing naturally by field, pool, geologic formation, and in response to field management practices such as enhanced recovery. Understanding this variability in oil-field fluid chemistry helps to better recognize contrasts and overlap between produced water and regional groundwater in complex environments.

Historical produced water data available from DOGGR records on well finder and underground injection control records, the USGS National Produced Waters Geochemical Database, and GeoTracker are more numerous and widespread than newly collected produced water data. These historical data provide key sources of data for analysis and are being compiled, when not already done so, into numerical datasets. Although the historical data typically have a limited set of analytes, often only major and minor inorganic ions and selected trace elements, these data are critical for spatial mapping. New produced water chemistry sample data collected for the regional monitoring program is intended to augment these historical data and provide additional analytes (particularly noble gases, solute (Sr, B, Li, SO4, and C) isotopes, dissolved organic carbon characteristics, and low molecular weight organic acids) that can help provide insight on fluid chemistry and processes affecting chemistry.

This produced water chemistry sampling and analysis is closely linked to regional groundwater analysis in the same study areas.

This section describes only those protocols and practices that differ from groundwater sampling described in the previous section.

Site Selection & Network Design

The objective of oil-field sampling is to collect samples representing major water types and the largest water flows in an oil field study area. Locations selected for sampling are designed to span a range of anticipated variations in fluid chemistry in context of oil field development history and hydrogeologic setting. Some active oil wells are selected to represent a range of formations. Some active oil wells are selected to represent reservoir fluids affected by the primary oil field management practices used, such as injections for enhanced recovery.

Injectate fluids will also be sampled, and surface ponds may be sampled, particularly if these represent relatively large volumes in the fluid balance of an oil field. In some cases, we seek to sample water source wells and/or surface water that is or has been used as a source of water injected into the oil field. Because of the complexity of oil field operations over time, many samples collected in oil field settings may represent mixtures of fluid reflecting multiple sources and activities.

During the process of requesting site access, the USGS and Water Board communicate with oil companies in each study area, including making presentations on the sampling design to facilitate obtaining supporting site information, permission to sample, and logistical arrangements. In the future, USGS will prepare a site history summary and will request review and input from oil companies on characteristics of the sites requested for sampling.

Sample Collection

Produced water sampling protocols are less standardized than groundwater sampling protocols because of the range of oil well characteristics; multiphase mixtures of water, oil, and gas issuing from sample ports on wells; sometimes elevated temperatures; and hazardous characteristics of the fluids being collected. The protocols followed to collect produced water samples include those used in previous USGS studies by Engel and others (2016), Karaka and Lico (1983), as well as other publications (Harkness and others, 2017, 2018; Ballentine and others, 1996; Barry and others, 2016, 2017). Samples can be largely divided into two categories (**table 3**): (1) samples for gases or volatile compounds dissolved in the produced water that are collected at the wellhead and (2) dissolved organic and inorganic solutes and isotopic tracers in produced water that are subsampled from 5 gallon or other large sample containers filled at the wellhead; these large sample containers are transported to a nearby sample processing area where the oil, gas, and water are allowed to separate so that aliquots of produced water without oil and gas phases can be collected.

Detailed sampling protocols for groups of analytes are described in the references listed in **table 3**. Standard methods are those that have EPA method numbers, have been used in the SB4 local-area monitoring, or have been conventionally used in historical produced water monitoring. Research methods are those not widely used in historical monitoring but selected to provide additional insight regarding water chemistry and processes affecting water chemistry. The standard and research method protocols used are included in **table 3**.

USGS employees follow all oil company safety protocols and policies when sampling oil wells or other sites in oil fields and are vigilant observing and reacting to changing conditions that could be potentially dangerous. The minimum required personal protection equipment worn by USGS employees working at the well head include: safety glasses or face shield, hard hats, steel-toe boots, fire resistant (FR) clothing, and individual hydrogen sulfide meters. A photoionization detector (PID) is utilized to monitor volatile organic compounds and other gases.

Sample Analysis

Produced water samples are analyzed for most of the same analytes as groundwater samples (**table 4**). However, some of the analytical laboratories differ from the groundwater laboratories used for the same analyte, because some laboratories or instrumentation are not equipped to handle the more concentrated and hazardous produced water samples. The laboratories differ for produced water and groundwater samples for VOCs; major and minor ions, trace elements, and alkalinity; carbon isotopes; and noble gases.

Subsurface Salinity Mapping

The objective of subsurface salinity analysis is to determine the distribution of protected groundwater near studied oil fields. Protected groundwater is defined as that having a total dissolved solids of less than 10,000 milligrams per liter. Understanding the location of protected groundwater resources in relation to oil and gas resources and production activities is a key step in determining what lies between oil and gas operations and protected water? We are using a number of different approaches (https://ca.water.usgs.gov/projects/oil-gas-groundwater/science/salinity/): (1) compiling water-quality sampling data from existing records and plotting them in three dimensions (3D); (2) expanding spatial coverage by using borehole geophysical measurements made when oil and water wells are drilled to calculate salinity; (3) expanding spatial coverage beyond drilled wells and oil fields using airborne and surface geophysical measurements.

This section only describes elements of the program unique to subsurface salinity mapping. Refer to the regional groundwater sampling design section for information on data releases, interpretative manuscripts, fundamental science practices, and stakeholder communications.

Compilation and analysis of existing water sample data

Groundwater and produced water sample salinity data (TDS and/or fluid specific conductance) near oil fields are being compiled from many sources including the USGS, Department of Water Resources (DWR), Water Board (GeoTracker, Division of Drinking Water), County and Local Water Agencies, and Department of Oil, Gas, and Geothermal Resources (DOGGR). Approximately half of the TDS values lack corresponding well perforation depths; these well depths need to be extracted manually from scanned DWR well completion reports or oil well records from the DOGGR well finder. Duplicate records for wells appearing in more than one data set also need to be removed. The data are being plotted spatially and with depth to identify regional 3D variations in salinity in proximity to oil fields. These existing water chemistry data are useful for large scale salinity mapping, but limited spatially and temporally (e.g. Gillespie and others, 2017; Stanton and others, 2017). In some cases, these gaps in existing sample data can be filled using other approaches (borehole geophysical log and/or airborne geophysical analysis).

Compilation and analysis of borehole geophysical log data

Analysis of borehole resistivity, porosity, self potential, and other supporting logs from oil and water wells can be used to estimate salinity for clean saturated sand intervals using petrophysical equations such as the Archie (1942) equation (e.g. Gillespie and others, 2017; Hamlin and de la Rocha, 2015). It is essential to calibrate these methods to available water sample salinity data. Calibration of these methods are needed because of uncertainties related to setting the parameters in the Archie equation. To ensure correct parameterization, we set these values using optimization methods with the sample salinity data. Borehole geophysical logs are available for many oil wells in the state in scanned form from DOGGR and for some water wells from local water agencies or DWR. Borehole geophysical log data are being analyzed to estimate salinity using both scanned log images and logs converted to numerical data using digitizing software. Through a cooperative agreement with USGS, the California State University Sacramento (CSUS) Geology Department has student teams digitizing and quality-assuring selected borehole geophysical logs in selected oil field study areas. As part of the log selection process, the CSUS team have been compiling numerical catalogs of geophysical log type and depth intervals in study fields. Data on depths of oil shows and water saturated sands are being compiled to identify zones where it is feasible to estimate salinity. As standard petrophysical methods require estimates of porosity to calculate salinity, wells with borehole porosity logs have been a high priority for digitizing so that porosity models of study areas can be developed. Borehole resistivity values are also temperature dependent and the CSUS team has been compiling a database of borehole bottom temperatures and temperature logs in selected fields. Steamed areas within oil fields affect the temperature profile. Currently, we have developed methods to identify and avoid steamed areas in space and time. This allows us to continue subsurface salinity mapping while other methods to account for steaming are being developed.

All data extracted from well records are reviewed by a quality control team following guidelines described in CSUS & USGS quality-assurance plans. For digitized geophysical logs, this QA analysis includes that digital data are spot checked and overlain with the original images to verify that digitizing was done appropriately. The original and digitized logs, summary interpreted lithologies, and calculated fluid salinity from petrophysical and statistical methods are preserved in digital project archival files that will be publicly available in USGS data releases.

Collection and analysis of airborne and surface electromagnetic data

Airborne and surface electromagnetic (EM) methods measure the distribution of bulk resistivity in the subsurface. Bulk resistivity is controlled by a combination of factors including the properties of geologic materials (e.g. lithology, clay content, mineralogy, etc…), fluid saturation and salinity, and subsurface temperature. The interpretation of changes in bulk resistivity within a study unit relies on a foundational framework of known geology and salinity observations from independent borehole and water quality sampling data. A combination of complementary airborne and ground-based time domain EM approaches are being used to

develop spatially extensive 3D maps of resistivity. These maps, in conjunction with water-quality and borehole log analyses being conducted as other components of the regional monitoring program, are being used to interpret groundwater salinity and to identify likely regions of protected groundwater adjacent to selected oil and gas fields. Use of these geophysical methods is limited in zones with intense infrastructure, which interfere with interpretation of EM data, and as such, these geophysical mapping approaches are being used primarily in rural areas adjacent to selected oil fields. This geophysical mapping process helps extend our spatial understanding of fluid salinity (mapping protected aquifers) and lithologic features like clay layers that affect groundwater flow beyond the existing network of wells. There are numerous examples of the use of airborne and surface geophysical approaches to map salinity and/or lithology distributions in many other locations (e.g. Bedrosian and others, 2014; Thamke and Smith, 2014; Christensen and Halkjaer, 2014; Fitterman and Deszcz-Pan, 1998; Kirkegaard and others, 2011; Mullen and Kellett, 2007; Paine, 2003). To date, airborne and surface geophysical surveys have been conducted in the fall 2016 and 2017 in the San Joaquin Valley in Kern County adjacent to the Lost Hills, North Belridge, South Belridge, Poso Creek, Elk Hills, North Coles Levee, and South Coles Levee oil fields. The airborne EM work is being conducted by the USGS Geology, Geophysics, and Geochemistry Center in Denver, CO and the surface EM work is being conducted by the USGS Water Mission Area Branch of Hydrogeophysics in Storrs, CN.

Interpretative Process – Additional Considerations & Elements

Within study areas, estimates of salinity determined from borehole, airborne, or surface resistivity and water sample data are spatially interpolated using geostatistical approaches. Geostatistical analysis incorporates uncertainties in data and in some cases is used to quantify probabilities that modeled salinity values exceed a specified threshold value such as 3,000 or 10,000 mg/L TDS. These geostatistical approaches help provide information on confidence of the interpolated result given the data available to constrain the spatial estimates.

Changes over time in salinity, temperature, water saturation in sand layers, and water chemistry type could introduce uncertainties in spatial mapping of fluid salinity based on sample, borehole, airborne, and surface data spanning different time periods. For this reason, salinity mapping efforts are including analysis of available time-series and borehole geophysical log data to identify areas where changes in subsurface conditions are occurring over time.

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Table 1. Regional monitoring program groundwater sample analytical methods and references.

[Abbreviations: **Elements:** H, hydrogen; O, oxygen; B, boron; Sr, strontium; C, carbon **Abbreviations:** UV, ultraviolet; VIS, visible; SUVA, specific ultraviolet-absorbance; δ, delta notation, the ratio of a heavier isotope of an element (^{i}E) to the more common lighter isotope of that element relative to a standard reference material, expressed as per mil; USGS, U.S. Geological Survey; EPA, U.S. Environmental Protection Agency; NRP, National Research Program; NWQL, USGS National Water Quality Laboratory, Denver, CO; filtered, sample water passed through 0.45 micrometer pore size filter; HDPE, High Density Polyethylene; L, liter; ml, milliliter;]

Category	Analyte Group	Sampling Method	Bottle(s)	Rinse	Filter	Preservative	Storage	Sampling Method Citation(s)
	Water-quality indicators							
Standard	Field parameters: temperature, dissolved oxygen, specific conductance, pH, turbidity, sulfide	Monitor until stability criteria reached during well purging	none	3 casing volumes	none	none	none	Wilde (variously dated)
	Organic constituents							
Standard	Volatile organic compounds	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	3 40 ml amber glass, no headspace	3 vols., bottom fill	none	1:1 HCl to pH<2	Chill	Connor and others (1998); Wilde (2009)
Standard	Dissolved organic carbon (DOC)	Collected from short non-methanol rinsed teflon tubing in a chamber bag at the wellhead	250 ml baked amber glass	1 vol., bottom fill	0.45 uM	H_2SO_4	Chill	Bird and others (2003); Wilde (2009)
Research	UV-VIS-absorbance	Collected from short non-methanol rinsed teflon tubing in a chamber bag at the wellhead	250 ml baked amber glass	1 vol., bottom fill	0.45 uM	None	Chill	Hanson and others (in press)
Research	Fluorescence							
Research	DOC fractionation [1]	Collected from short non-methanol rinsed teflon tubing in a chamber bag at the wellhead	3 1-L baked amber glass	1 vol., bottom fill	0.45 uM	none	Chill	Aiken and others (1992)
Research	Dissolved organic carbon (DOC) [1]	Collected from short non-methanol rinsed teflon tubing in a chamber bag at the wellhead	1 L baked amber glass	1 vol., bottom fill	0.45 uM	none	Chill	Bird and others (2003); Wilde (2009)
Research	UV-absorbance [1]	Collected from short non-methanol rinsed teflon tubing in a chamber bag at the wellhead	1 L baked amber glass	1 vol., bottom fill	0.45 uM	none	Chill	Poulin and others (2014)
Research	Low molecular weight organic acids [2]	Collected from short non-methanol rinsed teflon tubing in a chamber bag at the wellhead	2 40 ml clear glass vials, 2/3 full	yes	None	None	Freeze on dry ice on side	https://water.usgs.gov/nrp/biogeochemical-processes-in-groundwater/analytical-services.html

Table 1. Regional monitoring program groundwater sample analytical methods and references.

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Category	Analyte Group	Sampling Method	Bottle(s)	Rinse	Filter	Preservative	Storage	Sampling Method Citation(s)
Standard	Semi volatile organic compounds/ polycyclic aromatic hydrocarbons [2]	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	2 1-L amber glass	yes	none	none	chill	Wilde (2009)
	Inorganic constituents							
Standard	Major and minor ions, trace elements, alkalinity	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	250 ml clear HDPE	yes	none	none	chill	Wilde (2009)
			250 ml clear HDPE	yes	0.45 uM	HNO3 to a pH<2	chill	
			250 ml clear HDPE	yes	0.45 uM	none	chill	
Standard	Nutrients	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	125 brown HDPE	yes	0.45 uM	none	chill	Wilde (2009)
Research	Iron species	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	125 ml opaque HDPE	yes	0.45 uM	6 M HCl to a pH<2	chill	To and others (1999)
	Isotopic tracers and radioactive constituents							
Standard	Stable isotopes of hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) in water	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	60 ml glass with polyseal cap, 2/3 full	none	none	none	ambient, tape cap	Révész and Coplen (2008a,b)
Research	Stable isotopes of sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) of sulfate dissolved in water	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead. If H_2S present, purge with nitrogen gas.	1 L HDPE	None	0.45 uM	1M HCl to pH of 3-4	Chill	Carmody and others (1998); Revesz and others (2012)
Research	$\delta^{11}B$ of boron dissolved in water	Collected from short methanol rinsed teflon tubing in a chamber	125 ml clear HDPE	None	0.45 uM	None	Chill	Harkness and others (2017, 2018)
Research	$^{87}Sr/^{86}Sr$ of strontium dissolved in water							

Table 1. Regional monitoring program groundwater sample analytical methods and references.

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Category	Analyte Group	Sampling Method	Bottle(s)	Rinse	Filter	Preservative	Storage	Sampling Method Citation(s)
Research	δ^{7}Li of lithium dissolved in water							
Research	δ^{11}B of boron dissolved in water	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	250 ml clear HDPE	yes	0.45 uM	None	Ambient	Bayless and others (2004); Buscka and others (2007)
Research	^{87}Sr/^{86}Sr of strontium dissolved in water	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	250 ml clear HDPE	yes	0.45 uM	HNO3 to a pH<2	Ambient	Bullen and others (1996); Bayless and others (2004); Buscka and others (2007)
Research	δ^{13}C of inorganic carbon dissolved in water and carbon-14 abundance	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	1 L coated clear glass with polyseal cap, no headspace	3 vols., bottom fill	0.45 uM	None	Chill	Wilde (2009)
Research	Tritium	Collected from short non-methanol rinsed teflon tubing in achamber bag at the wellhead	1 L HDPE with polyseal cap, no headspace	Bottom fill	None	None	Ambient	Wilde (2009)
Standard	Radium-224 and radium-226	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	1 L HDPE	yes	0.45 uM	HNO3 to a pH<2	Ambient	Wilde (2009)
Standard	Radium-228	Collected from short methanol rinsed teflon tubing in a chamber bag at the wellhead	2 1 L HDPE	yes	0.45 uM	HNO3 to a pH<2	Ambient	Wilde (2009)

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Category	Analyte Group	Sampling Method	Bottle(s)	Rinse	Filter	Preservative	Storage	Sampling Method Citation(s)
	Dissolved gases							
Research	Dissolved noble gases	Collected at the wellhead	2 copper tubes, no bubbles, crimped	10 tubing volumes	None	None	Ambient	Poreda and others (1988); Solomon and others (1992)
Research	Dissolved sulfur hexafluoride	Collected from short non-methanol rinsed teflon tubing in achamber bag at the wellhead	2 1 L amber glass with polyseal caps, no headspace	3 vols., bottom fill	None	None	Ambient	Busenberg and Plummer (2000)
Standard	Dissolved standard and light hydrocarbon gases	Collected from short non-methanol rinsed teflon tubing in achamber bag at the wellhead	Isoflask	None	None	None	Ambient	Isotech (2018)
Standard	$\delta^{13}C$ & $\delta^{2}H$ of methane, $\delta^{13}C$ of ethane, propane dissolved in water							

[1] A subset of groundwater samples were analyzed for DOC fractions, with supporting DOC concentration and UV-absorbance measurements, at the USGS NRP Carbon Research Lab in Boulder through March 2017.

[2] All groundwater samples were analyzed for low molecular weight organic acids and semivolatile organic compounds beginning in June 2017. A subset of groundwater samples were analyzed for these constituents prior to this time.

[3] Groundwater samples were analyzed for strontium and boron isotopes at Duke University through 2017, at a USGS Menlo Park laboratory beginning in 2018.

Table 2. Regional monitoring program groundwater sample analytical methods and references.

[Abbreviations: **Elements:** H, hydrogen; O, oxygen; B, boron; Sr, strontium; C, carbon **Abbreviations:** UV, ultraviolet; VIS, visible; SUVA, specific ultraviolet-absorbance; δ, delta notation, the ratio of a heavier isotope of an element (^{i}E) to the more common lighter isotope of that element relative to a standard reference material, expressed as per mil; USGS, U.S. Geological Survey; EPA, U.S. Environmental Protection Agency; NRP, National Research Program; NWQL, USGS National Water Quality Laboratory, Denver, CO; filtered, sample water passed through 0.45 micrometer pore size filter; HDPE, High Density Polyethylene; L, liter; ml, milliliter;]

Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Analytical Method Citation(s)
	Water-quality indicators			
Standard	Field parameters: temperature, dissolved oxygen, specific conductance, pH, turbidity, sulfide	Calibrated field meters and test kits	USGS field measurement	Wilde (variously dated)
	Organic constituents			
Standard	Volatile organic compounds	Purge and trap capillary gas chromatography/mass spectrometry (EPA Method 524.2)	NWQL, Schedule 2020	Connor and others (1998)
Standard	Dissolved organic carbon (DOC)	High-temperature combustion catalytic oxidation (EPA 415.3 rev 1.2)	USGS Organic Matter Research Laboratory, Sacramento, California	Bird and others (2003); Potter and others (2009); Hansen and others (2016)
Research	UV-VIS-absorbance	Spectrophotometry	USGS Organic Matter Research Laboratory, Sacramento, California	Weishaar and others (2003); Helms and others (2008), Jaffe and others (2008); Hansen and others (2016)
Research	Fluorescence	Spectrofluorometry	USGS Organic Matter Research Laboratory, Sacramento, California	Coble (1996); Coble and others (2014); Stedmon and others (2003); Hansen and others (2016)
Research	DOC fractionation [1]	Resin fractionation	USGS NRP Carbon Research Laboratory, Boulder, Colorado	Aiken and others (1992)
Research	Dissolved organic carbon (DOC) [1]	UV-Promoted persolfate oxidation and infrared spectrometry	USGS NRP Carbon Research Laboratory, Boulder, Colorado	Aiken (1992)
Research	UV-absorbance [1]	Spectrophotometry	USGS NRP Research Laboratory, Boulder, Colorado	Poulin and others (2014)
Research	Low molecular weight organic acids [2]	Ion chromatography (EPA method 300)	USGS Biogeochemical Processes in Groundwater Laboratory, Reston, VA	U.S. Environmental Protection Agency (1993); Akob and others (2015); https://water.usgs.gov/nrp/biogeochemical-processes-in-groundwater/analytical-services.html

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Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Analytical Method Citation(s)
Standard	Semi volatile organic compounds/ polycyclic aromatic hydrocarbons [2]	Gas chromatography/ mass spectrometry (EPA method 8270D)	RTI Laboratories, Livonia, Michigan, Lab Method SW_8270A-LL (USGS contract)	U.S. Environmental Protection Agency (EPA) (1986)
	Inorganic constituents			
Standard	Major and minor ions, trace elements, alkalinity	Atomic absorption spectrometry, colorimetry, ion-exchange chromatography, inductively-coupled plasma atomic-emission spectrometry and mass spectrometry	NWQL, Schedule 1948	Fishman and Friedman, 1989; Faires, 1993; Fishman, 1993; McLain, 1993; American Public Health Association, 1998; Garbarino, 1999; Garbarino and others, 2006
Standard	Nutrients	Alkaline persulfate digestion, Kjedahl digestion, colorimetry by enzymatic reduction	NWQL, Schedule 2755	Fishman, 1993; Patton and Kryskalla, 2003, 2011
Research	Iron species	Ultraviolet visible (UV-Vis) spectrophotometry	USGS Trace Metal Laboratory, Boulder, Colorado (USGSTMCO)	Stookey, 1970; To and others, 1999; McCleskey and others, 2003
	Isotopic tracers and radioactive constituents			
Standard	Stable isotopes of hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) in water	Gaseous hydrogen and carbon dioxide--water equilibration and stable-isotope mass spectrometry	USGS Stable Isotope Laboratory, Reston, Virginia (USGSSIVA), NWQL Schedule 1142	Epstein and Mayeda, 1953; Coplen and others, 1991; Coplen, 1994; Révész and Coplen (2008a,b)
Research	Stable isotopes of sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) of sulfate dissolved in water	Barium sulfate precipitation with continuous-flow isotope-ratio mass spectrometry	USGS Stable Isotope Laboratory, Reston, Virginia (USGSSIVA), NWQL Lab Codes 1951, 891	Carmody and others (1998); Böhlke and others (2003); Revesz and others (2012)
Research	$\delta^{11}B$ of boron dissolved in water	Thermal-ionization mass spectrometry (TIMS)	Duke University TIMS Laboratory [3]	Vengosh and others (1989); Dwyer and Vengosh (2008); Warner and others (2014)

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Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Analytical Method Citation(s)
Research	$^{87}Sr/^{86}Sr$ of strontium dissolved in water	Chemical separations of thermal-ionization mass spectrometry	Duke University TIMS Laboratory [3]	Bullen and others (1996)
Research	$\delta^{7}Li$ of lithium dissolved in water	Thermal-ionization mass spectrometry (TIMS)	Duke University TIMS Laboratory [3]	Warner and others (2014)
Research	$\delta^{11}B$ of boron dissolved in water	Thermal-ionization mass spectrometry (TIMS)	USGS Menlo Park Isotope Laboratory [3]	Bayless and others (2004); Buscka and others (2007)
Research	$^{87}Sr/^{86}Sr$ of strontium dissolved in water	Chemical separations of thermal-ionization mass spectrometry	USGS Menlo Park Isotope Laboratory [3]	Bullen and others (1996); Bayless and others (2004); Buscka and others (2007)
Research	$\delta^{13}C$ of inorganic carbon dissolved in water and carbon-14 abundance	Stable isotope ratio mass spectrometry and accelerator mass spectrometry	Woods Hole Oceanographic Institution, National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS), Woods Hole, Massachusetts (MA-WHAMS), NWQL Schedule 2255 (USGS contract)	Vogel and others, 1987; Donahue and others, 1990; McNichol and others, 1992; Gagnon and Jones, 1993; McNichol and others, 1994; Schneider and others, 1994
Research	Tritium	Electrolytic enrichment and gas counting	USGS Menlo Park Stable Isotope and Tritium Laboratory	Ostlund and Dorsey 1977
Standard	Radium-224 and radium-226	Alpha spectroscopy (EPA method 903.1)	ALS Laboratories, Fort Collins, Colorado NWQL Lab Code 1364 (USGS contract)	U.S. Environmental Protection Agency (EPA), 1980
Standard	Radium-228	Gas proportional counting (EPA method 904.0)	ALS Laboratories, Fort Collins, Colorado NWQL Lab Code 2164 (USGS contract)	U.S. Environmental Protection Agency (EPA), 1980

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Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Analytical Method Citation(s)
	Dissolved gases			
Research	Dissolved noble gases	Mass spectrometry	USGS Noble Gas Laboratory, Denver, CO	Hunt (2015)
Research	Dissolved sulfur hexafluoride	Purge and trap gas chromatography with electron capture detector	USGS Groundwater Dating Laboratory, Reston, VA	Busenberg and Plummer (2000); Law and others (1994)
Standard	Dissolved standard and light hydrocarbon gases	Gas chromatography/thermal conductivity detection and flame ionization detection	Isotech Laboratories, Inc., Champaign, Illinois, Lab Schedule DG-1	U.S. Environmental Protection Agency (EPA) (1994); Isotech (2018)
Standard	$\delta^{13}C$ & $\delta^{2}H$ of methane, $\delta^{13}C$ of ethane, propane dissolved in water	Stable-isotope mass spectrometry	Isotech Laboratories, Inc., Champaign, Illinois, Lab Schedule DG-1, DG-2	Dai and others (2012); Isotech (2018)

[1] A subset of groundwater samples were analyzed for DOC fractions, with supporting DOC concentration and UV-absorbance measurements, at the USGS NRP Carbon Research Lab in Boulder through March 2017.

[2] All groundwater samples were analyzed for low molecular weight organic acids and semivolatile organic compounds beginning in June 2017. A subset of groundwater samples were analyzed for these constituents prior to this time.

[3] Groundwater samples were analyzed for strontium and boron isotopes at Duke University through 2017, at a USGS Menlo Park laboratory beginning in 2018.

Table 3. Regional monitoring program produced water sample collection methods and references.

[Abbreviations: **Elements:** H, hydrogen; O, oxygen; B, boron; Sr, strontium; C, carbon **Abbreviations:** UV, ultraviolet; VIS, visual; SUVA, specific ultraviolet-absorbance; δ, delta notation, the ratio of a heavier isotope of an element (^{i}E) to the more common lighter isotope of that element relative to a standard reference material, expressed as per mil; USGS, U.S. Geological Survey; EPA, U.S. Environmental Protection Agency; NRP, National Research Program; NWQL, USGS National Water Quality Laboratory, Denver, CO; filtered, sample water passed through 0.45 micrometer pore size filter; HDPE, High Density Polyethylene; L, Liter; ml, milliliter]

Category	Analyte Group	Sampling Method	Bottle(s)	Rinse	Filter	Preservative	Storage	Sampling Method Citation(s) [1]
	Water-quality indicators							
Standard	Field parameters: temperature, specific conductance, pH, sulfide, alkalinity.	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to beaker(s), field parameters measured with probes/spectrophotometer	none	none	0.45 uM	none	none	*Wilde (variously dated)*
	Organic constituents							
Research	Volatile organic compounds	Collected at wellhead. Bottom fill 1L baked amber bottle. Immediately remove subsample of water with syringe and Teflon tubing.	3 20 ml clear glass, no headspace	bottom fill	none	none	Chill	New method
Research	Dissolved organic carbon (DOC)	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	250 ml baked clear glass	1 vol., bottom fill	0.45 uM	H_2SO_4	Chill	Engle and others (2016)*; Bird and others (2003); Wilde (2009)*
Research	UV-VIS-absorbance	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	250 ml baked clear glass	1 vol., bottom fill	0.45 uM	None	Chill	*Hanson and others (in press)*
Research	Fluorescence	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	250 ml baked clear glass	1 vol., bottom fill	0.45 uM	None	Chill	
Research	DOC fractionation [2]	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	3 500mL baked amber glass	1 vol., bottom fill	0.45 uM	none	Chill	*Aiken and others (1992)*
Research	Dissolved organic carbon (DOC) [2]	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	3 500mL baked amber glass	1 vol., bottom fill	0.45 uM	none	Chill	*Bird and others (2003); Wilde (2009)*
Research	UV-absorbance [2]	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	3 500mL baked amber glass	1 vol., bottom fill	0.45 uM	none	Chill	*Poulin and others (2014)*
Research	Low molecular weight organic acids	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	2 20 ml clear glass vials, 2/3 full	yes	None	None	Freeze on dry ice on side	https://water.usgs.gov/nrp/biogeochemical-processes-in-groundwater/analytical-services.html
Standard	Semi volatile organic compounds/ polycyclic aromatic hydrocarbons [2]	Collected at wellhead. Bottom fill 4L baked amber bottle. Subsample water from 2L to bottle(s) using Teflon tubing.	2 1-L baked amber glass	yes	none	none	chill	*Wilde (2009)*

Table 3. Regional monitoring program produced water sample collection methods and references.

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Category	Analyte Group	Sampling Method	Bottle(s)	Rinse	Filter	Preservative	Storage	Sampling Method Citation(s) [1]
	Inorganic constituents							
Standard	Alkalinity	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	2 40 ml clear glass vials with septa, no headspace	Yes	0.45 uM	None	Chill	Engle and others (2016)
Standard	Major and minor ions, selected trace elements	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	125 ml HDPE	Yes	0.45 uM	HNO3 to pH<2	Chill	Engle and others (2016)
			125 ml HDPE	Yes	0.45 uM	None	Chill	
Standard	Selected trace elements, major and minor ions	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	60 ml HDPE	None	0.45 uM	10% HNO3 (bottles pre-acidified)	Chill	Engle and others (2016); Harkness and others (2017, 2018)
			60 ml HDPE	None	0.45 uM	None	Chill	
Research	Iron species	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	125 ml opaque HDPE	yes	0.45 uM	6 M HCl to a pH<2	chill	*To and others (1999)*
	Isotopic tracers and radioactive							
Standard	Stable isotopes of hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) in water	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	60 ml glass with polyseal cap, 2/3 full	none	none	none	ambient, tape cap	Engle and others (2016)*; Révész and Coplen (2008a,b)*
Research	Stable isotopes of sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) of sulfate dissolved in water	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s). If H_2S present, purge with nitrogen gas.	1 L HDPE	None	0.45 uM	1M HCl to pH of 3-4	Chill	*Carmody and others (1998); Revesz and others (2012)*
Research	$\delta^{11}B$ of boron dissolved in water	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	125 ml clear HDPE	None	0.45 uM	None	Chill	Engle and others (2016); Harkness and others (2017, 2018)
Research	$^{87}Sr/^{86}Sr$ of strontium dissolved in water							
Research	$\delta^{7}Li$ of lithium dissolved in water							
Research	$\delta^{13}C$ of inorganic carbon dissolved in water	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	250mL glass with polyseal cap	bottom fill	0.45 uM	ammoniacal strontium chloride	Ambient	*Singleton and others (2012)*
Standard	Radium-224 and radium-226	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	1 L HDPE	yes	0.45 uM	HNO3 to a pH<2	Ambient	*Wilde (2009)*
Standard	Radium-228	Collect fluids in 5 gal carboy at wellhead. Subsample water from carboy to bottle(s)	2 1 L HDPE	yes	0.45 uM	HNO3 to a pH<2	Ambient	*Wilde (2009)*

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[Abbreviations: **Elements:** H, hydrogen; O, oxygen; B, boron; Sr, strontium; C, carbon **Abbreviations:** UV, ultraviolet; VIS, visual; SUVA, specific ultraviolet-absorbance; δ, delta notation, the ratio of a heavier isotope of an element (^{i}E) to the more common lighter isotope of that element relative to a standard reference material, expressed as per mil; USGS, U.S. Geological Survey; EPA, U.S. Environmental Protection Agency; NRP, National Research Program; NWQL, USGS National Water Quality Laboratory, Denver, CO; filtered, sample water passed through 0.45 micrometer pore size filter; HDPE, High Density Polyethylene; L, Liter; ml, milliliter]

Category	Analyte Group	Sampling Method	Bottle(s)	Rinse	Filter	Preservative	Storage	Sampling Method Citation(s) [1]
	Dissolved gases							
Research	Dissolved noble gases in produced water	Collect at wellhead	2 copper tubes, no bubbles, crimped	10 tubing volumes	None	None	Ambient	Ballentine et al. (1996)
Research	Dissolved noble gases in casing gas	Collect at wellhead	2 copper tubes, crimped	10 tubing volumes	None	None	Ambient	Barry et al. (2016, 2017)
Standard	Dissolved standard and light hydrocarbon gases	Collect at wellhead	Isoflask	None	None	None	Ambient	Isotech (2018)
Standard	$\delta^{13}C$ & $\delta^{2}H$ of methane, $\delta^{13}C$ of ethane, propane dissolved in water							
Standard	$\delta^{13}C$ & $\delta^{2}H$ of methane, $\delta^{13}C$ of ethane, propane in casing gas	Collect at wellhead	Isoflask	None	None	None	Ambient	Isotech (2018)

[1] Method references for processing groundwater samples adapted for use for processing produced water samples are shown in italics. References that are not italized pertain directly to methods of sampling produced waters.

[2] Produced water samples were analyzed for DOC fractions, with supporting DOC concentration and UV-absorbance measurements, at the USGS NRP Carbon Research Lab in Boulder through March 2017.

Table 4. Regional monitoring program produced water sample analytical methods and references.

[Abbreviations: **Elements:** H, hydrogen; O, oxygen; B, boron; Sr, strontium; C, carbon **Abbreviations:** UV, ultraviolet; VIS, visual; SUVA, specific ultraviolet-absorbance; δ, delta notation, the ratio of a heavier isotope of an element (^{i}E) to the more common lighter isotope of that element relative to a standard reference material, expressed as per mil; USGS, U.S. Geological Survey; EPA, U.S. Environmental Protection Agency; NRP, National Research Program; NWQL, USGS National Water Quality Laboratory, Denver, CO]

Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Citation(s)
	Water-quality indicators			
Standard	Field parameters: temperature, specific conductance, pH, sulfide, alkalinity.	Calibrated field meters and test kits	USGS field measurement	Wilde (variously dated)
	Organic constituents			
Research	Volatile organic compounds	Purge and trap capillary gas chromatography/mass spectrometry with headspace autosampler (EPA Methods 524.2 and 8260C)	USGS Maryland Water Science Center Research Laboratory, Baltimore, MD	U.S. Environmental Protection Agency (1995, 2006); Majcher and others (2007); Lorah and others (2014)
Research	Dissolved organic carbon (DOC)	High-temperature combustion catalytic oxidation (EPA 415.3 rev 1.2)	USGS Organic Matter Research Laboratory, Sacramento, California	Bird and others (2003); Potter and others (2009); Hansen and others (2016)
Research	UV-VIS-absorbance	Spectrophotometry	USGS Organic Matter Research Laboratory, Sacramento, California	Weishaar and others (2003); Helms and others (2008), Jaffe and others (2008); Hansen and others (2016)
Research	Fluorescence	Spectrofluorometry	USGS Organic Matter Research Laboratory, Sacramento, California	Coble (1996); Coble and others (2014); Stedmon and others (2003); Hansen and others (2016)
Research	DOC fractionation [1]	Resin fractionation	USGS NRP Carbon Research Laboratory, Boulder, Colorado	Aiken and others (1992)
Research	Dissolved organic carbon (DOC) [1]	UV-Promoted persolfate oxidation and infarared spectrometry	USGS NRP Carbon Research Laboratory, Boulder, Colorado	Aiken (1992)
Research	UV-absorbance [1]	Spectrophotometry	USGS NRP Research Laboratory, Boulder, Colorado	Poulin and others (2014)

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Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Citation(s)
Research	Low molecular weight organic acids	High Performance Liquid Chromatography	USGS Biogeochemical Processes in Groundwater Laboratory, Reston, VA	U.S. Environmental Protection Agency Report 40 CFR 136 (1984); https://water.usgs.gov/nrp/biogeochemical-processes-in-groundwater/analytical-services.html
Standard	Semi volatile organic compounds/ polycyclic aromatic hydrocarbons	Gas chromatography/ mass spectrometry	RTI Laboratories, Livonia, Michigan, Lab Method SW_8270A-LL	U.S. Environmental Protection Agency (EPA) (1986)
	Inorganic constituents			
Standard	Alkalinity	Automatic Titrator (TIM900 Titration Manager and ABU901 Autoburette).	USGS Biogeochemical Processes in Groundwater Laboratory, Reston, VA	Cozzarelli and others (2016)
Standard	Major and minor ions, selected trace elements	Ion-exchange chromatography, inductively-coupled plasma optical-emission spectrometry (U.S. EPA Methods 300.0 and 6010D)	USGS Biogeochemical Processes in Groundwater Laboratory, Reston, VA	U.S. Environmental Protection Agency (EPA) (1993; 2014)
Standard	Selected trace elements, major and minor ions	Inductively coupled plasma mass spectrometry	Duke University Laboratory	Warner and others (2014)
Research	Iron species	Ultraviolet visible (UV-Vis) spectrophotometry	USGS Trace Metal Laboratory, Boulder, Colorado (USGSTMCO)	Stookey, 1970; To and others, 1999; McCleskey and others, 2003

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Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Citation(s)
	Isotopic tracers and radioactive constituents			
Standard	Stable isotopes of hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) in water	Gaseous hydrogen and carbon dioxide--water equilibration and stable-isotope mass spectrometry	USGS Stable Isotope Laboratory, Reston, Virginia (USGSSIVA), NWQL Schedule 1142	Epstein and Mayeda, 1953; Coplen and others, 1991; Coplen, 1994
Research	Stable isotopes of sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) of sulfate dissolved in water	Barium sulfate precipitation with continuous-flow isotope-ratio mass spectrometry	USGS Stable Isotope Laboratory, Reston, Virginia (USGSSIVA), NWQL Lab Codes 1951, 891	Carmody and others (1998); Böhlke and others (2003); Revesz and others (2012)
Research	$\delta^{11}B$ of boron dissolved in water	Thermal-ionization mass spectrometry (TIMS)	Duke University TIMS Laboratory	Vengosh and others (1989); Dwyer and Vengosh (2008); Warner and others (2014)
Research	$^{87}Sr/^{86}Sr$ of strontium dissolved in water	Chemical separations of thermal-ionization mass spectrometry	Duke University TIMS Laboratory	Bullen and others (1996)
Research	$\delta^{7}Li$ of lithium dissolved in water	Thermal-ionization mass spectrometry (TIMS)	Duke University TIMS Laboratory	Warner and others (2014)
Research	$\delta^{13}C$ of inorganic carbon dissolved in water	Strontium carbonate precipitation with duel-inlet isotope-ratio mass spectrometry	USGS Stable Isotope Laboratory, Reston, Virginia (USGSSIVA), NWQL Lab Code 1710	Singleton and others (2012)
Standard	Radium-224 and radium-226	Alpha spectroscopy	ALS Laboratories, Fort Collins, Colorado NWQL Lab Code 1364	U.S. Environmental Protection Agency (EPA), 1980
Standard	Radium-228	Gas proportional counting	ALS Laboratories, Fort Collins, Colorado NWQL Lab Code 2164	U.S. Environmental Protection Agency (EPA), 1980

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Category	Analyte Group	Analytical Method	Laboratory and analytical schedule	Citation(s)
	Dissolved gases			
Research	Dissolved noble gases in produced water	Mass spectrometry	Noble Gas Laboratory, Univ. of Oxford, Oxford, U.K.	Ballentine et al. (1996)
Research	Dissolved noble gases in casing gas	Mass spectrometry	Noble Gas Laboratory, Univ. of Oxford, Oxford, U.K.	Barry et al. (2016, 2017)
Standard	Dissolved standard and light hydrocarbon gases	Gas chromatography/thermal conductivity detector and flame ionization	Isotech Laboratories, Inc., Champaign, Illinois, Lab Schedule DG-1	U.S. Environmental Protection Agency (EPA) (1994); Isotech (2018)
Standard	$\delta^{13}C$ & $\delta^{2}H$ of methane, $\delta^{13}C$ of ethane, propane dissolved in water	Stable-isotope mass spectrometry	Isotech Laboratories, Inc., Champaign, Illinois, Lab Schedule DG-1, DG-2	Dai and others (2012); Isotech (2018)
Standard	$\delta^{13}C$ & $\delta^{2}H$ of methane, $\delta^{13}C$ of ethane, propane in casing gas	Stable-isotope mass spectrometry	Isotech Laboratories, Inc., Champaign, Illinois, Lab Schedule NG-2	Dai and others (2012); Isotech (2018)

[1] A subset of groundwater samples were analyzed for DOC fractions, with supporting DOC concentration and UV-absorbance measurements, at the USGS NRP Carbon Research Lab in Boulder through March 2017.