Oil, Gas, and Groundwater Quality in California—a discussion of issues relevant to monitoring the effects of well stimulation at regional scales

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Introduction

The California State Water Resources Control Board (SWRCB) is in the process of considering how to effectively monitor and manage the potential effects of oil and gas development on groundwater quality and in particular, the effects of well stimulation practices. Over the course of the next few months, a group of experts convened by Lawrence Livermore National Laboratory (LLNL) will prepare a set of recommendations to the SWRCB about appropriate model criteria for these new programs. The SWRCB will then hear comments on the recommendations and after a course of deliberations, define new model criteria for regional and site-specific monitoring programs.

The purpose of this discussion paper is to provide the public, the SWRCB, and the experts convened by LLNL with a synthesis of information on key policy issues, a potential scientific approach for the regional monitoring element, and potential strategies for implementation. It is intended to facilitate comments and discussion by all parties and includes the factors raised during public workshops held by the SWRCB in August, 2014 in Bakersfield and Los Angeles. Ultimately, the SWRCB will determine the nature of the scientific program.

This discussion paper is organized into two sections. The first section summarizes issues which should be addressed by the experts convened by LLNL. These issues are grouped into four categories: a) the policy issues which have a direct bearing on the scope and organization of monitoring programs, b) key considerations for the design and implementation of a regional monitoring program, c) discussion of specific elements in SB4, and d) a summary of how a regional program might interface with site-specific characterization. The second section presents a more detailed scientific proposal for a regional monitoring effort, beginning with a set of working hypotheses and anticipated findings.

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SECTION 1: Summaries of Issues for Discussion

Key Policy Questions for the SWRCB Which Affect the Design of Monitoring Programs

There are three key policy issues which will define the scope of regional and site-specific programs for which the SWRCB needs to provide guidance to ensure that any scientific program design will meet state goals:

- What groundwater resources are to be protected?
- How should areas that have already been affected by oil and gas development be managed? and
- How should the programs address the fact that potential effects of well stimulation on groundwater resources are occurring in the context of effects from other oil and gas development practices?

These elements represent the standard policy elements of monitoring program design and cover the process of determining where standards are met, where waters are impaired, and identifying causes and sources of water quality impairments whether it be at the site-specific scale, or statewide scale (USEPA 1988, 2003).

What Groundwater Resources are to be Protected?

In order to define the scope of regional and site-specific monitoring programs, an operational definition of groundwater requiring protection is needed. Currently, State water quality laws and regulations provide for the protection of groundwater resources that are or may be useable for purposes including drinking water, irrigation, and industrial supplies, and SWRCB policy currently targets 3,000 mg/l TDS as a general threshold for protection (SWRCB, 2014). Federal laws target the protection of groundwater resources for drinking water supplies and define these as resources containing less than 10,000 mg/l TDS. The same laws provide for an exemption to regulations governing injection of waste into aquifers if a) the zone does not currently serve as a drinking water sources, b) the zone cannot serve as a source in the future because it produces hydrocarbons, is too deep to be economically or technically practical, it is so contaminated that treatment would be impractical, or c) the groundwater contains between 3,000 mg/l and 10,000 mg/l TDS and is not reasonably expected to serve a public water system (summarized from 40 CFR 144.7).

Historically, groundwater resources that are relatively close to the land surface and of the highest quality have been tapped for consumptive use. The location, extent, and quality of those resources already being used in California are relatively well-understood.

Californians have been expanding their use of groundwater resources into deeper zones and areas containing poorer quality water over the past several decades as a means of improving local water supply reliability. Cooley and others (2006) reviewed desalination practices in California and noted that 43% of the desalination capacity at the time was in plants using brackish groundwater as a source. More than a dozen water agencies, primarily in the San Diego, greater Los Angeles, and San Francisco Bay

regions, currently operate desalters for groundwater with TDS concentrations ranging from 1,000 to 3,800 mg/L (City of Corona, 2012; WCVC, 2011; City of Menifee, 2014; Leitz and Boegli, 2011; ACWD, 2011; GWI, 1997; CSWSME, 1999; City of Camarillo, 2009; Lynch, 2009; EMWD, 2013; USBOR, 2006).

Two urban water agencies are currently planning for systems that would treat waters containing between 12,000 and 18,000 mg/L TDS to achieve local water supply reliability goals (BARDEP, 2011; EMWD, 2013). Desalination of these lower quality waters is projected to cost on the order of \$900-\$1400 per acre-foot (BARDP, 2011). The Panoche Water District in the western San Joaquin Valley has pilot plant in operation to desalinate agricultural drainage water containing up to 16,000 mg/L TDS (WaterFX, 2014). The primary goal is to help the District meet salt loading requirements

The USEPA regulates underground injection wells and allows states to take on the oversight role (described as "primacy") when USEPA determines that the state program meets certain quality objectives; California was granted permission to do this in 1983. As part of the primacy application process, CADOGGR identified aquifers where oil and gas waste disposal had occurred in the past, where hydrocarbons were present whether or not they could be commercially producible, and where TDS levels were between 3,000 and 10,000 mg/l TDS (Walker, 2011). These zones are called "exempt aquifers" because they are exempt from protection as sources of drinking water under federal law. CADOGGR (1981) defined the surface footprint of these exempt aquifers using township and range plots and the depth in terms of formations. The depth to "base of fresh water" for most of the oil and gas fields in the state is also recorded in field descriptions (CADOGGR, 1982, 1992, and 1998). No definition of what is meant by "fresh" is provided in the documents, however 3,000 mg/L of TDS or specific conductance of 3,000 μS/cm is generally used (Page, 1973).

In summary, guidance from the SWRCB on operational definitions for potentially useable groundwater will have a major impact on study designs for both the regional and well-specific programs. Much more is known about groundwater resources containing up to 3,000 mg/l TDS and less work would be required to characterize the extent and quality of this resource. In contrast, there is little information about groundwater resources containing between 3,000 mg/L and 10,000 mg/L TDS, and even less information about the intervening zones between these groundwater resources and oil and gas activities.

How Would Areas Already Affected by Oil and Gas Development be Managed?

One core working hypothesis presented in this discussion paper is that potentially useable groundwater resources in near-surface aquifers located near waste disposal ponds have already been affected by past oil and gas activities, while most of the groundwater currently being used for public supply has been affected to a minor degree if at all. This hypothesis is based on a number of factors, including past exemption of aquifers containing over 3,000 mg/l TDS and allowance of waste injection into them (CADOGGR, 1981; Walker, 2011), documented effects of surface waste disposal on near-surface groundwater quality (Brown and others, 1961; Bean and Logan, 1983; and Mitchell, 1989), and scientific information from the GAMA Program showing that geologically derived benzene is present in very few public supply wells (Landon and Belitz, 2012).

The scope and scientific design of the regional and site-specific programs will depend on how the SWRCB decides groundwater resources that have already been affected by oil and gas development activities should be managed. Much more detailed information will be needed if remediation or mitigation is being considered than if the focus will be on monitoring a boundary between useable and unusable groundwater resources. Similarly, the risk-based science management approach is based on estimating future risks to useable resources and may not be appropriate where legacy issues persist.

Well Stimulation in the Context of Other Potential Effects of Oil and Gas Development on Groundwater Resources

One requirement of the new regional and event/ site-specific monitoring programs is that they specifically identify the effects of well stimulation practices. Our working hypothesis is that it will be challenging to separate out the effects of well stimulation practices from the effects of other oil and gas development practices. Detailed background and hydrogeologic process information will be required to distinguish the effects of well stimulation in this complicated and highly managed hydrogeologic environment.

First, the pathways by which fluids associated with well stimulation practices can affect potentially useable groundwater can be the same as those by which all oil and gas operations, including enhanced recovery practices, can have effects. New pathways can be created when injection pressures are applied during well stimulation but they can also be created during enhanced recovery operations. There are many instances where enhanced recovery projects have resulted in significant land deformation and subsidence, causing well shearing and surface blowouts (for example, de Rouffignac, 1995; Jordan and Benson, 2008). Because the pathways are the same, it is likely to prove difficult to distinguish between what we expect are larger signals associated with long-term enhanced recovery practices and isolated current well stimulation events.

Second, the chemical additives used in well stimulation activities can include the same/ same type of additives used in water- and steam-flooding enhanced recovery operations and the latter are applied in volumes that are two orders of magnitude greater than in well stimulation. The following table adapts information presented in CCST (2014) and developed by NYSDEC (2011) and demonstrates the overlap.

Additive Type	Description of Purpose	Use in Well	Use in
		Stimulation (CCST,	Enhanced
		2014; NYSDEC,	Recovery
		2011)	
Proppant	"Props" open fractures and allows gas / fluids to	Yes	Typically no ¹
	flow more freely to the well bore.		
Breaker	Reduces the viscosity of the fluid in order to	Yes	Yes (SPE, 2011)
	release proppant into fractures and enhance the		

¹ Historically the well stimulation and enhanced recovery processes were separate. However there has been at least one recent patent filed which combines both steps into a single process http://www.google.com/patents/CA2648017A1?cl=en

	recovery of the fracturing fluid		
Bactericide / Biocide / Antibacterial	Prevents biofouling	Yes	Yes (McIlwaine, 2005)
Agent			
Buffer / pH Adjusting Agent	Adjusts and controls the pH of the fluid in order to maximize the effectiveness of other additives such as crosslinkers	Yes	Yes (Fink, 2012)
Clay Stabilizer / Control /KCl	Prevents swelling and migration of formation clays which could block pore spaces thereby reducing permeability.	Yes	Yes (Zhou, Gunter, and Jonasson, 1995)
Corrosion Inhibitor	Reduces rust formation on steel tubing, well casings, tools, and tanks (used only in fracturing fluids that contain acid).	Yes	Yes (SPE, 2011)
Crosslinkers and gelling agents	Increases fluid viscosity using phosphate esters combined with metals. The metals are referred to as crosslinking agents. The increased fluid viscosity allows the fluid to penetrate more into the fractures.	Yes	Yes (Alvarado and Manriquez, 2010)
Friction Reducer	Allows fluids to be injected at optimum rates and pressures by minimizing friction.	Yes	Yes (Ottot, 1996; Duane and Dauben, 1983)
Iron control	Prevents the precipitation of metal oxides which could plug off the formation.	Yes	
Scale inhibitor	Prevents the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, barium sulfate) which could plug off the formation.	Yes	Yes (SPE, 2011)
Solvent	Additive which is soluble in oil, water and acid- based treatment fluids which is used to control the wettability of contact surfaces or to prevent or break emulsions	Yes	Yes (Alvarado and Manriquez, 2010)
Surfactant	Reduces fluid surface tension thereby aiding fluid recovery.	Yes	Yes (Alvarado and Manriquez, 2010)

Third, flowback waters from individual well stimulation events are mixed into the overall produced water waste stream (CCST, 2014). Marginal changes in water quality associated with well stimulation would thus be found within the envelope of water quality changes associated with the much larger waste stream from oil and gas activities in general.

Fourth, current well stimulation in California takes place against a backdrop of historic well stimulation going back to the 1950s (California Research Bureau, 2014), extensive reworking of existing reservoirs (CCST, 2014) and existing wells (CADOGGR, 2014), and cycling of large volumes of fluids though hydrocarbon zones as much of the produced water waste stream is recycled and used as a source for enhanced recovery fluids (WSPA, undated; CADOGGR, 2014).

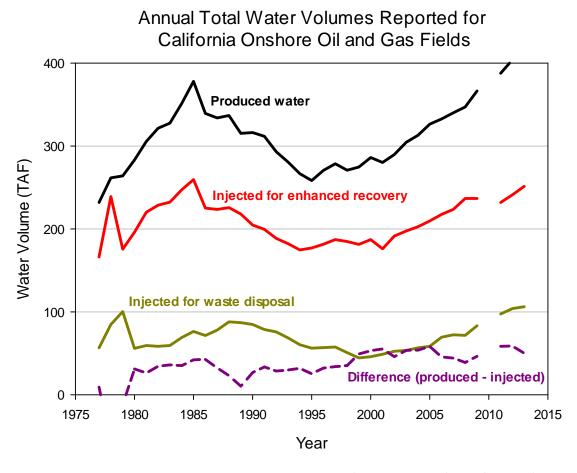


Figure 1 shows the statewide aggregated water volumes (in thousands of acre-ft or TAF) injected for enhanced recovery and as waste in comparison to the volume of produced waters reported each year in CADOGGR's annual production/injection databases between 1977 and 2013. The database for 2010 was not available at the time this report was prepared. Injections for enhanced recovery include water-flooding, steam-flooding, cyclic steaming, and pressure maintenance. The total volume injected for well stimulation events is estimated at less than 1 TAF per year (CCST, 2014). The reported volume of produced water is up to 50 TAF greater than the total reported volumes injected on an annual basis. One large project accounts for a significant percentage of this difference. The Chevron Kern River oil field project redirects an average of 25 TAF/yr to a local irrigation district and is currently permitted to

redirect up to 45 TAF/yr (CVRWQCB, 2012; Waldron, 2005). The remainder of the difference may either be disposed of in municipal wastewater sewer systems or in surface sump ponds. The same patterns can be seen using field-by-field data.

Total Produced and Injected Water 2009-2013 for Onshore California Fields

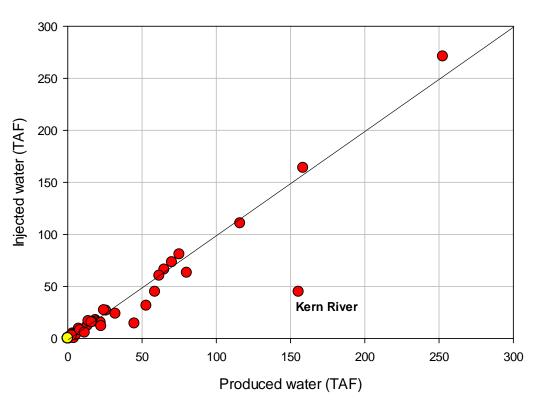


Figure 2 shows a comparison between the total volume of produced water and total volume of injected fluids on a field-by-field basis from the onshore oil and gas fields reporting on-site injection during the four years of CADOGGR data available from 2009-2013. Injection includes waste disposal (WD), water flooding (WF), steam flooding (SF), cyclic steam (SC), and pressure maintenance (PM). Oil fields are denoted by red symbols and gas fields by yellow symbols; gas fields have lower volumes of produced water than do most oil fields. The line represents the graphical location if produced water volumes were exactly the same as injected fluid volumes. The Kern River field plots off of this line because of the produced water redirected for use by a local irrigation district.

Most of the produced water is recycled within the oil fields, either by injection in enhanced recovery operations (water flood, steam flood, cyclic steam, pressure maintenance) or by injection into waste disposal zones (CADOGGR, 2014; WSPA, undated). This means that well stimulation is most likely to occur in fields that fluids have been cycling through at high volumes and for a long time.

Fifth, the fracturing of material in oil and gas reservoirs does not just occur during well stimulation practices. There have been cases documented where waste disposal and enhanced recovery practices also cause fractures initiated by thermal stress that grow with time and changes in pore pressure. Minner and others (2002) conducted a detailed study of this phenomenon in the Lost Hills area for the purposes of refining hydraulic fracturing operations, noting that "water injection and reservoir fluid production result in poroelastic stress changes that can dramatically alter the created fracture geometry on infill wells. This basic conclusion is not new. It has been documented in many different environments, and is supported by theoretical modeling." Another mechanism which can create fractures around water and waste injection wells is the slow clogging of pores by particles in the fluid. One indication of fracture propagation in these cases is "injectivity," which should decrease over time; if it does not, it is an indication that fractures are forming (Suarez-Rivera and others, 2002, and Gadde and Sharma, 2001). There have been documented cases in California where injection wells were intentionally fractured to solve this problem (Hainey and others, 1997, Sipple-Srinivasan and others, 1998). One key policy question is whether the State seeks to manage the effects of anthropogenically driven fracturing, regardless of the causal mechanism.

As in other parts of the country (Davies and others, 2014; Dusseault and others, 2014), movement of constituents from oil and gas development activities towards potentially useable groundwater resources through well bore pathways is likely to be found true in California as well. These pathways are likely to prove more prevalent conduits than fracture propagation. Older wells are more likely to be pathways because they were constructed before current well-integrity regulations, wells deteriorate over time, and because they have had more exposure to stresses from land deformation and subsidence. In addition to well age, the factors likely to drive wellbore transmission are cross-linking between new activities and old wells, local land deformation and subsidence, loss of pressure control during injections, and well density. Ramifications for monitoring programs include legacy effects on water quality in the vicinity of existing well bores, and the question of constituent transport long after well stimulation activities have ceased.

As a consequence of the factors described above, the proposed scientific approach is designed to determine the broader extent of water-quality patterns related to oil and gas activities, define current baseline conditions across oil fields, and identify how the affected zones relate to potentially useable groundwater. It is only within this broader context that more detailed site-specific determination of impacts can be achieved. Thus, the regional program provides context for understanding well-specific results.

Key Considerations for the Design and Implementation of the Regional Monitoring Program

SB4 requires the SWRCB to adopt "model criteria" for regional and well-specific monitoring; the working definition of model criteria and how they will function as part of a plan to implement SB4 will be decided by the SWRCB as part of the current regulatory process. In this section we use the concept of "design criteria" as a tool for summarizing the principles scientists use to design study approaches relevant to the interaction between oil and gas development activities and groundwater quality.

In situations where a great deal is already known about environmental systems, existing information can be analyzed and synthesized to answer questions like what constituents should be sampled, where, and for how long in order to conclusively link effects to causes. In the case of determining the effects of oil and gas development practices on groundwater resources in California, basic information, such as the locations of potentially useable groundwater resources, is incomplete. Therefore, preliminary scientific work is needed before detailed studies can be designed to detect effects and determine likely causes. Two specific examples illustrate this. Identifying exact locations needed for new monitoring wells before knowing the location of potentially useable resources can carry its own environmental risk because well bores are known to be dominant transport pathways (Davies and others, 2014, Dusseault and others, 2014), and the utility of existing wells cannot be determined until existing well log data has been analyzed. Another example where more research is needed is the question of whether isotopic tracers can be used as precise indicators of hydraulic fracturing processes. Warner and others (2014) determined that lithium and boron isotopic ratios could be used as tracers for well stimulation in West Virginia. These ratios are formed as the result of geochemical reactions between the shale matrix and fluids used for stimulation. California oil and gas reservoirs are typically in a sandstone matrix and it is unclear whether the same geochemical processes would exist. In addition, the number of laboratories that can reliably test for lithium isotopes is extremely limited. Studies similar to Warner and others in scope and detail would need to be carried out across the range of conditions expected in California before it could be determined whether specific tracers would be appropriate for use in these monitoring programs.

While it is not possible to precisely define many study design elements at the moment, it is possible to describe the process of <u>how</u> monitoring and scientific assessments could be conducted to deliver the required information. This section describes several organizing principles and implementation steps that could be considered as design criteria for a regional program.

Using Vulnerability to Determine Level of Effort

The concept of "vulnerability" can be used as a tool for organizing the regional monitoring effort. It supports a tiered study design in which areas where groundwater resources are less vulnerable are monitored with less intensity than areas where the resources are more vulnerable. In addition, vulnerability can change over time as a result of natural and anthropogenic factors, and a tiered study design can be adapted in response to those changes.

California has a diverse geology, and throughout the state, oil and gas deposits are found in different geologic settings as a result of varying amounts of deformation, uplift, faulting, and different depositional environments. Hence the thicknesses of geologic strata separating useable groundwater from oil and gas reservoirs vary throughout the state. Generally, in the absence of other controlling factors such as preferential pathways, the thickness of this layer of separation is inversely proportional to the vulnerability of groundwater to contamination. As such, an assessment of groundwater vulnerability for the regional monitoring program could be based on the proximity of the useable water to oil and gas deposits in each field. However, additional factors such as the number of abandoned oil and gas wells, number of active oil and gas wells, a history of waste injection, a history of well

stimulation, surface waste disposal or spills, or significant faulting in each field, also may increase the probability of groundwater contamination.

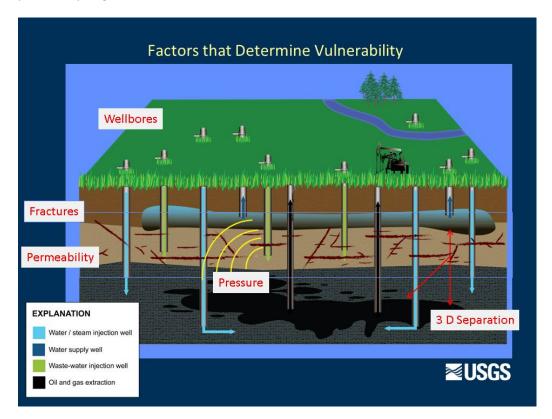


Figure 3 Graphical presentation of factors affecting the vulnerability of potentially useable groundwater resources to constituents transported away from oil and gas development activities.

Vulnerability would be used as an organizing concept in the following way:

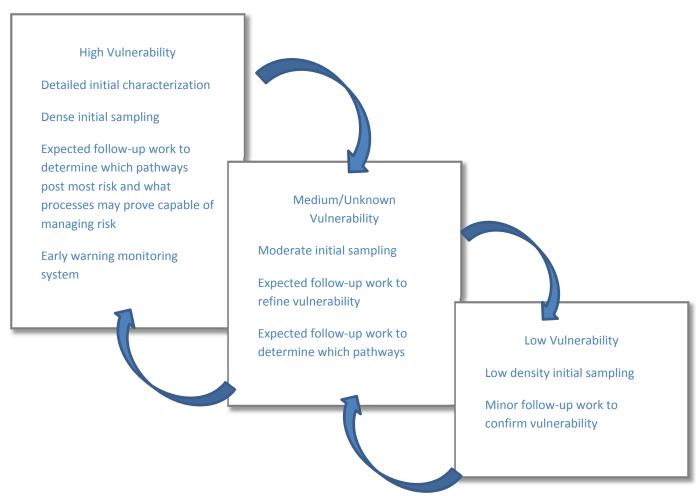


Figure 5. Conceptual model of how vulnerability would be used to determine level of effort

Each area would be assigned a level of vulnerability based on an initial assessment. High and low vulnerability categories should be reserved for those areas where classification is clear. The moderate/ unknown vulnerability category can then be comprised of everything that does not clearly fit into the high or low categories. As more detailed information is collected during the phased program and as the SWRCB and Regional Boards make site-specific determinations about the level of protection, those assignments would be subject to change.

It is important to note that vulnerability categories are intended as a means of organizing the science and not as an end in themselves. It is more important to design follow-up studies based on questions which arise from data and findings than to design follow-up work in order to more precisely categorize an area or move an area into a different vulnerability category. Consequently, decision guidelines for all of the different factors which could affect vulnerability are not proposed at this time. Instead, we propose an initial determination based on three-dimensional (3D) separation between currently used groundwater resources and oil and gas development activities.

An example of the method for determining 3D separation is presented below using the Kern River and Rose oil fields as cases. The USGS is in the process of extracting and synthesizing information from all

the water well logs within the surface footprint of oil and gas fields and will present a 3D separation analysis early next spring.

Location of Kern River and Rose Oil Fields

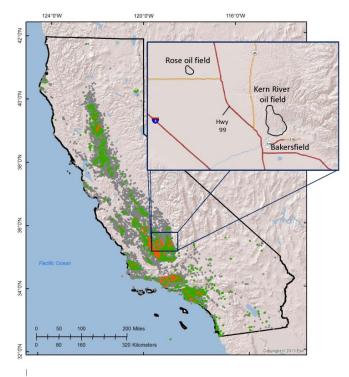


Figure 6A

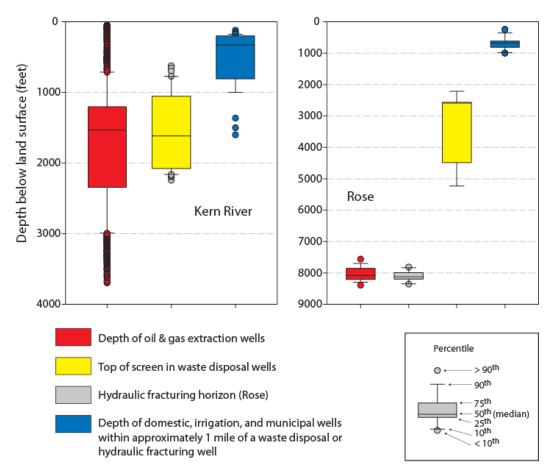


Figure 6 B,C

Figure 6A, B, and C. In the Kern River oil field, most oil extraction wells (red) are less than 2,000 feet deep. The tops of the screened intervals in many of the injection wells used for waste disposal (yellow) also are less than 2,000 feet deep, and some are as shallow as about 600 feet deep. Irrigation, domestic, and public supply wells (blue) located within approximately 1 mile of waste injection wells are up to 1,500 feet deep. These data suggest that oil and gas development activities in the Kern River oil field may be occurring in relatively close proximity to groundwater resources suitable for beneficial use. (B) In the Rose oil field, oil extraction wells (red) are approximately 8,000 feet deep, and recent and proposed hydraulic fracturing activity (grey) also is targeting a zone approximately 8,000 feet deep. Irrigation, domestic, and public supply wells (blue) located within approximately 1 mile of wells with hydraulic fracturing are up to 1,000 feet deep. These data suggest that the separation between oil and gas development activities and groundwater resources suitable for beneficial use is relatively large in the Rose oil field. [Data for depths of irrigation and drinking water wells obtained from DWR well completion reports, and data for depths of wells associated with the oil fields obtained from CADOGGR].

Following this initial assessment, a more thorough review of the lithologic and stratigraphic information for each oil field (CADOGGR 1982, 1992, and 1998) to determine permeability in the layers between oil and gas producing and waste disposal zones and useable groundwater resources. This review may result in reassignment of vulnerability categories.

Using Existing Information Before Developing New Information

Reviewing, compiling, synthesizing, and interpreting existing data from multiple sources prior to collecting new samples and installing new monitoring locations is generally the most cost effective approach to any scientific project. It is highlighted as a potential design criteria here because an assessment of data from existing wells within the study unit footprints is needed before effective choices about new monitoring locations can be made.

The following generally describes known information sources relevant to the broad question of how potentially useable groundwater resources might be affected by oil and gas development activities and how they would be used in the proposed regional monitoring approach.

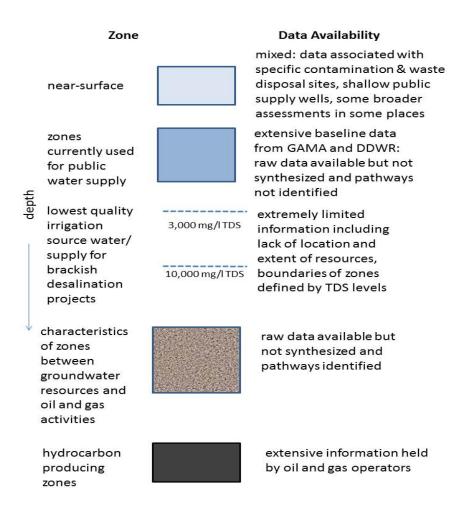


Figure 7. Conceptual model of availability of data regarding location and extent of useable groundwater resources, water quality, and geohydrological characteristics of zones lying between oil and gas activities and potentially useable groundwater resources.

Driller/ well logs for water wells

These are archived at CADWR for all water wells within study units: these sources have been used extensively by USGS scientists and methods have been established for efficiently extracting information needed to characterize aquifer properties and geohydrologic conditions within and around them. Interpretive information developed using these logs can be made public even though the precise location of the data sources cannot be. Most of these logs are in PDF form and data need to be extracted and recorded in electronic databases to be useful for mapping or any analyses.

Technical records for individual oil and gas wells

These records are archived at CADOGGR and include drillers/ well logs, e-logs and other geophysical logs, cross sections, Isopach maps, formation names and contacts, structures, and types of oil traps—and the vast majority of records are in PDF/ paper formats. To be useful, information will need to be extracted from these paper records and recorded in electronic format in databases.

Information in these archives can be used to create a number of core information products including the 3d surface at the base of waters containing 10,000 mg/l TDS or less, more precise quantification of the separation between oil and gas production and waste disposal activities and useable groundwater, geohydrologic characteristics of intervening material for use in refining vulnerability determinations and identifying constituent transport pathways, and if needed, the basis for extending existing flow models to greater depths. More detailed information about specific approaches for using these data is discussed in other sections.

These logs also contain information about well integrity, including documentation of cement bond logs, pressure tests, and injection tests with tracers.

Geological framework characterization data in electronic format

Oil and gas operators have already transferred a large amount of historical data from paper to electronic files, augmented it with new electronically captured data, and used these data to construct geological framework and flow models. Reviews of publicly available information suggest that the majority of this work has focused on deeper zones and there is much less coverage of the areas below currently used groundwater and above the shallowest waste disposal zone. Collection of data in electronic format will greatly reduce the amount of time required to make use of existing data.

Water quality data

There are several sources of groundwater quality information for assessing the relation of groundwater quality to oil and gas development activities. First, the Regional Boards and local water management agencies and oil companies are currently and have historically required or conducted monitoring of the effects of legacy surface disposal of produced waters on groundwater quality above or adjacent to oil fields where beneficial uses are being affected (Bean and Logan, 1983; Mitchell, 1989; Crosby and Schymiczek, 1990; CADOGGR website; SWRCB CIWQS website). Second, even though the definition of "fresh water" used in oil and gas field descriptions is not documented, the estimates of the base of fresh water contained in the CADOGGR oil and gas field reports (1982, 1992, and 1998) and maps for some fields (for example, Page, 1973) provide first-cut estimates. Third, water-quality data and assessments from groundwater resources used for public, domestic, and irrigation are available from several sources.

Data from the used resources are available regionally from the GAMA program, and data from regulatory sampling of public-supply wells are available from the SWRCB's Division of Drinking Water (SWRCB DDW) database and Geotracker website includes these data as well as data from regulatory investigations of contamination sites. USEPA and USGS also have databases of groundwater quality data. County, city, and local water districts sometimes have databases of water quality. Fourth, water-quality information about zones below those currently tapped for public drinking water supplies can be extracted from oil and gas well records kept by CADOGGR, although the records require extensive interpretation to transform scanned paper records into digital format. Borehole electric logs (e-logs) are also widely available for oil and gas wells from CADOGGR and some e-logs can and have been analyzed to estimate the base of freshwater.

There are several critical gaps in groundwater quality data and understanding to assessing the effects of oil and gas activities. Currently, the distribution of groundwater having TDS between 3,000 and 10,000 mg/L has not been systematically mapped. Available groundwater quality databases are likely to have limited information on groundwater quality at depths greater than those currently used for water supply. Groundwater data from existing databases may not extend deep enough to map the base of freshwater (depth at which TDS is greater than 10,000 mg/L). Additional data can be compiled from other sources, such as DOGGR records that are only available in PDF format, however, it is likely that the coverage will still be incomplete. These existing data will analyzed to develop preliminary threedimensional salinity maps, with emphasis on defining the locations of the 1,000 mg/L, 3,000 mg/L, and 10,000 mg/L contours. [1,000 mg/L is the SMCL, considered the limit of groundwater drinkable without treatment; 3,000 mg/L is groundwater that may be usable with minimal treatment and also a current approximate definition of freshwater; 10,000 mg/L is the limit of protected water]. These threedimensional salinity maps will be refined and updated as new data is acquired. A prioritization scheme for extracting water quality data from CADOGGR well files can be developed for the purpose of water quality mapping. For example, the prioritization scheme might include identifying oil and gas wells with high quality records of lithology and geophysical logs with corresponding water chemistry data from different depths as a top priority for analysis. Borehole electric logs (e-logs) typically available from oil and gas wells, resistivity and spontaneous potential, should be analyzed in comparison with water chemistry data, other geophysical log data used to independently estimate porosity and lithology, and lithologic records from boreholes. These data and supplemental data sets from other sources could be used to develop regression relations to calculate TDS from e-logs from oil and gas wells as part of a systematic regional analysis.

Complexities in the characteristics of potential source waters associated with oil and gas activities need to be recognized as part of a regional monitoring program but do not necessarily preclude using geochemical and hydrologic data to discern effects of oil and gas development on groundwater quality. Keys to addressing the complexities are: an inventory of historical sources and practices, analysis of available historical data to discern changes in the chemistry of potential source waters through time, and use of ratios of constituents such as chloride, iodide, bromide, boron, and lithium that may be diagnostic of solute sources even as they are diluted. For example, understanding the distribution and chemical signatures of groundwater affected by legacy surface disposal of produced waters may help to

discern these effects from water quality effects of well stimulation and secondary recovery activities and provide information on end-member source waters that may mix in modern groundwater.

Geophysical data: temperature, water level (pressure), and land deformation sensing

Geophysical measurements are an important component of both a regional and well-specific monitoring effort. Many oil and gas operators deploy geophysical sensors in monitoring networks covering large portions of oil fields to assess physical changes in reservoir systems on a near-real time basis during well stimulation and enhanced recovery operations. At the Belridge oil field, for example, Aera Energy uses distributed temperature sensing technology to precisely manage subsurface liquid injection and minimize local subsidence (Rahman and others, 2011). In the Kern River oil field, Coburn and Gillespie (2002) developed pressure gradient information from open-hole formation pressure tests, nuclear logs and temperature surveys, and static fluid levels in idle wells. As these data are not publicly available, it is not possible to determine what gaps may exist. The monitoring program objective would be to measure geophysical changes in the zones between oil and gas activities and potentially useable groundwater as an early warning of potential constituent transport. The characterization phase of the effort could use these to constrain interpretations.

Geophysical information is also collected under current CADOGGR regulations.

Known Major Data Gaps

Based on reviews of publicly available data, the biggest data gaps are:

- a) Extraction of information from paper records into electronic format. While not technically a "gap," a great deal of work is needed to make this information useful;
- b) 3D locations of useable groundwater resources and oil and gas waste injection zones;
- c) Salinity gradients below zones currently tapped by public drinking water supply wells;
- Detailed chemistry (see discussion on parameters elsewhere) of useable groundwater within study units, formation waters (single formations and unaffected by water/ steamflood operations), flowback waters, and control sites;
- e) Detailed geological characteristics of material and pathways lying between producing and waste disposal zones and potentially useable groundwater resources; most is available in general but not at scales that would permit a definitive assessment of zonal isolation; and
- f) Making geophysical measurement data collected by oil and gas operators, including water levels and temperature data from idle monitoring wells and tiltmeters, available to support evaluations of pathways and flow gradients.

Pilot Testing Each Element Before Scaling Up Work

The USGS makes extensive use of pilot scale efforts during virtually all aspects of a scientific effort. We have found this practice increases the quality of resulting scientific products and avoids wasted effort. Pilot testing is done on everything from whether temperature can be maintained in sample bottles

during shipment to the national laboratory and field testing new equipment to make sure the measured signal is performing as expected, to developing methods for abstracting data from large repositories and the mechanics of data transfer and storage between instruments and archival systems. An example of pilot work relevant to this effort is the process by which geological information is abstracted from existing well records to support the creation of framework models. First, a set of variables is drafted which would fully support the intended analyses, such as depth of the wells (not length), perforation intervals, electric logs, and driller's logs. Then, the contents of a small number of records is examined to learn how information pertaining to the desired variables is recorded, whether the desired information is consistently listed in one place and in every file, how the desired information might be constructed from presented data (for example, finding well depth information when only length is listed in a summary field), and whether the file contains robust information that can be analyzed in more detail later (such as driller's logs). The third step is the design of a database to record the abstracted information, and the fourth step is beta testing the abstracting methodology making corrections where needed.

Using Both Probability-Based and Process-Based Study Designs

The regional monitoring program element could have different purposes that will require different types of sampling network designs to achieve. The two main classes of sampling network designs are probability-based designs and "knowledge-based" or "process-based" designs (USEPA, 2002). Probability-based designs incorporate randomized selection of sampling sites within an area following a sampling theory. The strengths of this approach are a) a relatively small number samples can be used to make statistical inferences about the entire study unit, b) statistically robust comparisons also can be made between study units, allowing assessment at scales ranging from regional to statewide assessments. Probability-based designs do not track the effects of specific processes that occur within study units, such as the migration of a contaminant plume. The GAMA Program is an example of a probability-based design. A first step in the regional monitoring program would be to use a probabilistic sampling design to determine the prevalence of constituents associated with oil and gas activities in potentially useable groundwater. The characterization phase focuses on collecting enough locations in 3D to define the distribution of oil and gas effects rather than monitoring for temporal changes at only a few points along a specific pathway. Collection of a comprehensive and statistically representative set of synoptic samples in high vulnerability oil and gas areas, followed by reduced density sets of samples in medium and low vulnerability oil and gas areas across California could span several years.

In contrast, process-based designs use sampling locations selected on the basis of knowledge about the system and process being monitored. Examples of this approach include a network of carefully chosen 'sentinel' sites used to detect when contaminants associated with oil and gas activities are about to enter an area designated as protected groundwater, or sampling along a flow path to investigate a specific mechanism by which contaminants may be degraded as they move away from oil and gas activities. The strengths of this approach are a) it tracks a known causal relationship, and b) the underlying physical and geochemical factors driving the effect can be precisely determined. Weaknesses include the fact that new pathways can emerge over time outside the targeted design area, information gleaned at the site can not necessarily be used to support interpretive studies in other

places. Both probability-based and knowledge-based sampling designs are needed at the regional scale and can be scaled using the vulnerability concept.

The characterization phase of the program will use a wide variety of process-based factors to interpret the geochemical data collected using a probability-based design and end-member mixing model. Because this sampling design does not target specific pathways, a second phase of the regional program would need to develop additional monitoring approaches specific to those pathways. A particular focus of additional monitoring would be to better distinguish between the various anthropogenic pathways transporting basically the same fluids. For example, understanding whether well shear as a result of subsidence or old well integrity failure was the mechanism behind observed well bore transport would be important to the State but may not be discernable during the characterization phase. At the same time, the second phase could confirm areas with low vulnerability where water quality could be tracked with a modification of the initial sampling design.

Using Multiple Lines of Evidence

Many environmental monitoring programs go through a design stage where a conceptual model of the links between environmental stressors and receptors is developed, and then the links considered to be the clearest indicators of cause and effect which are both practical and cost effective to implement are selected for long-term monitoring. This approach works well when the level of knowledge supporting the initial conceptual model is robust, and a great deal is known about the relative importance of different factors causing change in the indicator at relevant spatial and temporal scales. When that is not the case, indicators can result in false positives and negatives, and can mask other sources of environmental stress that may be significant.

Several factors make using multiple lines of evidence a robust approach that will yield definitive information for managing future degradation of potentially useable groundwater. First, little is known about the relative importance of different constituent transport pathways. Second, oil and gas reservoir systems are highly managed and have a long legacy of effects in the production and waste disposal zones from conventional production, well stimulation, and enhanced recovery practices. Third, constituents found in producing formations can migrate independently of human activity.

An example of a successful project using multiple lines of evidence to determine effective mitigation programs for water quality problems is the case of fecal bacteria found on Santa Barbara's East Beach (Izbicki and others, 2009). Concentrations of fecal bacteria above water quality standards were found in this popular recreational area and residents variously attributed the problem to the homeless population living near local creeks, leaking sewer lines in the city transporting waste through shallow groundwater, urban runoff, boat owners illegally pumping waste overboard at the nearby marina, and birds gathering on the beach attracted to food waste. The research team used a broad, multiple lines of evidence approach which included geochemical characterization of surface and groundwater including specific analysis of multiple tracers for sewage, DNA analysis of the bacteria, and time-intensive sampling across tidal cycles. The study determined that the dominant source of fecal bacteria on the beach were shorebirds, and that the other potential sources did not contribute to the problem. This

determination would not have been possible without the multiple lines of evidence and the result allowed the city to focus resources on the most important causal factor.

Multiple lines of evidence were also used by Landon and Belitz (2012) in their study of geologically derived benzene in groundwater currently used for public supply in California. In that work, they were able to differentiate between benzene derived from anthropogenic sources like gasoline and from geologic sources and determine that many of the cases where benzene was detected in public supply wells were attributable to geogenic benzene. The study did not delve into the question of how geogenic benzene reached the used groundwater zone, which could have been through natural pathways or through pathways created anthropogenically.

The proposed approach for the regional monitoring program uses a multiple-lines-of-evidence approach to assess and quantify the effects of oil and gas activities on groundwater quality. Using a wide variety of constituents will provide the opportunity to better constrain and validate interpretations of monitoring data. Because all constituent signals are subject to limitations and uncertainties, use of many potential constituents in the scientific analysis provides greater confidence in the conclusions than if only a single constituent or signal is used as the basis of geochemical analysis.

Geochemical data need to be analyzed in conjunction with ancillary data that constrain understanding of plausible contaminant pathways and processes. Water-quality data cannot be interpreted in isolation from other physical hydrogeologic data. Ancillary data include water-level, temperature, lithologic, and geophysical data within a hydrogeologic framework that yields understanding of plausible fluid flows within the subsurface. In some high vulnerability oil and gas areas, framework and groundwater flow models may be necessary to use as tools for understanding of the interactions of oil and gas operations with potentially useable groundwater.

To discern potential effects of oil and gas activities on groundwater quality, water-quality data from protected groundwater will need to be compared to that of potential source waters, referred to as end-members, which could mix in aquifers. Because there are other sources of constituents to protected groundwater than oil and gas sources, the sampling of end-members needs to include some of the prevailing potential sources unrelated to oil and gas activities including:

- a) produced waters from oil and gas production; wastewaters from oil and gas production injected into the subsurface for disposal or for secondary recovery purposes, especially waters that have been treated or amended;
- b) other water used as a source of water flooding or steam injection into oil and gas reservoirs;
- c) flowback and produced waters from well stimulation sites;
- d) shallow groundwater recharge beneath oil and gas wastewater storage sites;
- e) shallow groundwater recharge beneath areas of predominant land use such as agricultural, urban, or natural areas that are not affected by oil and gas activities; and
- f) deep and/or old groundwater in the same or similar hydrogeologic setting that is unaffected by oil and gas activities (background or control samples).

These end-member samples represent only a basic list for relatively simple systems (see discussion below). The end-member samples are necessary to evaluate the mixing of waters from different sources in protected groundwater resources and to discern the effects of oil and gas activities from other sources that affect groundwater quality, including irrigation return flow and natural rock/water interactions. Understanding the mixtures and contributions from different sources to groundwater requires some characterization of the sources likely to be contributing. The source waters would need to be sampled for the same suite of analytes as the groundwater samples.

It is important to note that the sources of water and solutes potentially affecting protected groundwater are likely complex and variable over time, because most California oil and gas fields are highly engineered. Enhanced recovery using water and/or steam flooding is widely used in California oil fields and currently accounts for over 80% of oil produced onshore (CADOGGR 2010); these methods have been in use since the late 1950s and many oil fields have gone through multiple flooding cycles. The source of water used in enhanced recovery is predominately produced waters from oil and gas extraction (Loomis ,Fried, and Crowell, 1952a, 1952b), but can also include local groundwater (USDOE, 1994), and imported surface water (West Kern Water District, 2011). Water injected for water and steam flooding generally contains additives used to facilitate flushing or limit deleterious effects such as corrosion and clogging, and may be treated before injection, particularly for source water for steam flooding (Alvarado and Mangriquez, 2010; SPE, 2011). Apart from sources of waters injected for secondary recovery purposes, fluids (liquid or gas) are also injected into some petroleum reservoirs to maintain pressure in the field.² There are currently 12 depleted oil and gas fields in California that have been used for storage of natural gas from other locations (USEIA, 2008). If the fields are re-opened for production, these stored natural gas sources may have chemical and isotopic compositions that differ from native oil and gas hydrocarbon signatures, and although it is theoretically possible to discern native from non-native gases (for example, Revesz and others, 2012), it may not be practically possible because discrete samples of gases injected in the past are not now available.

Studies have noted that the ratio of produced water to oil tends to increase through time (Clark and Veil, 2009) and that the chemistry of produced waters can change over time (Bean and Logan, 1983). The changes can occur even if secondary recovery methods involving introduction of new fluids into the reservoir are not used. The concentrations in produced waters also change as a result of reservoir management activities such as steam and water flooding (CCST, 2014).

These complexities in the characteristics of potential source waters associated with oil and gas activities need to be recognized as part of a regional monitoring program, but do not necessarily preclude using geochemical and hydrologic data to discern the effects of current and legacy oil and gas activities on protected groundwater. Keys to addressing the complexities are: an inventory of historical sources and practices, analysis of available historical data to discern changes in the chemistry of potential source waters through time, identifying relations between chemical and isotopic signatures in current samples

² Pressure maintenance projects are listed in each CADOGGR Annual Report of the State Oil and Gas Supervisor (for example, CADOGGR, 2010).

to more limited data types available in historical data, and use of ratios of constituents such as chloride, iodide, bromide, boron, and lithium that may be diagnostic of solute sources even as they are diluted.

Identifying Controlling Factors

Environmental assessments typically begin with long lists of causal factors, but the most valuable information for resource managers is often documentation on which of the factors can be ignored and which factors are controlling. The process of determining the relative importance of different causal factors is never straightforward and often iterative. However, establishing a programmatic goal of determining the relative importance of causal factors and using that information to discard studies targeting the least important factors may facilitate this practice.

The first example of how this principle could be applied is the use of an end-member mixing model and measurement of a broad suite of water quality constituents in potentially useable groundwater and all oil and gas-related sources. When there is enough difference in chemical composition between the various sources and target resource, these tools can identify which pathways control constituent transport and which ones are negligible. Monitoring can then focus on the controlling pathways.

A second example of this principle involves using hydraulic gradients to determine if there is any reasonable chance of constituents moving from areas affected by oil and gas development towards potentially useable groundwater resources. If there is no flow towards these resources, then further study of how the gradient might be managed to prevent transport would not be needed. On the other hand, if flow gradients are favorable for transport, a water budget model might be the right tool to determine where and how much pumping could shift water flows and avoid contamination, and an optimum strategy for doing this.

Study planning needs to balance this concept against the need to use multiple lines of evidence when the relationship between causal factors is not well understood.

The extensive characterization phase of this proposal is designed to rigorously sort through the wide range of potential factors and deliver robust information on those which are controlling.

Using Geophysical and Hydraulic Monitoring to Complement Water Quality Sampling

Assessment of the potential impacts of oil and gas activities on potentially useable groundwater quality can be greatly aided through the collection, compilation, and analysis of other types of data besides groundwater chemistry data. This section describes a number of geophysical monitoring techniques and their potential use in a water quality assessment program.

Water level data should be collected from wells sampled where possible. In addition, water level data should be assembled and/or measured for the subsurface zones spanning from the water table to the oil and gas production reservoirs. Hydraulic head profiles and the resulting hydraulic gradient from these data will indicate the direction of potential water flow and indicate whether direct flow from oil and gas production zones and overlying formations to potentially useable groundwater is physically plausible. In the absence of hydraulic flow gradients towards potentially useable groundwater, detections of oil and

gas indicators in potentially useable groundwater may imply that contamination results from wastewater management at the land surface.

High-resolution temperature gradient logs should be collected as part of the regional monitoring program to fill gaps in available data (see discussion above on existing information). High-resolution temperature logs are a cost-effective tool for evaluating horizontal and vertical groundwater flow patterns through potentially usable groundwater zones and into underlying buffer and oil and gas production zones. The density of temperature gradient log data will need to be determined on a study unit basis. However, the high-resolution temperature logs will be of most value when located in close proximity to vertical profiles of water quality, pressure, and other geophysical logs that can be used to discern salinity and lithology. Therefore, it is likely that the design of temperature gradient log data collection will partially be a function of the density and location of other types of data in vertical profiles that can be used for comparison.

Pressure monitoring, geophysical logging, and high-resolution temperature logging as part of wellspecific monitoring efforts would provide physical hydrologic data to constrain interpretations of water quality data. As previously stated, vertical and horizontal pressure gradients indicate which direction fluids would be expected to move. Whenever possible, water levels should be measured when waterquality samples are collected. Pressure data should be collected before and during well stimulation and production phases of oil operations. Similarly, high-resolution temperature gradient logs should be collected in wells drilled through potentially usable groundwater to oil and gas zones. The temperature gradient logs could be used to identify zones where horizontal or vertical groundwater flow is occurring. If there are idle wells not being used for production, measurements at different times could be used to evaluate changes in groundwater flow in response to production. Distributed Temperature Sensing (DTS), which utilizes scattering of laser light in fiber optic cables to estimate temperature along the cable with a resolution of about 3 feet, has been used to determine temperature changes as a result of fluid injection into oil reservoirs (for example, Allan and Lalicata, 2011) and for hydrologic applications (for example, Becker and others, 2012). In selected areas, deployment of DTS to understand changes in subsurface conditions as a result of well stimulation could be considered as heat could be a low cost tracer as a result of the likely contrast in fluid temperatures between injected fluids, oil reservoirs, and potentially useable groundwater. Sequential borehole geophysical logging could also be considered as part of well-specific monitoring in some cases where practical as a cost-effective monitoring technique. For example, electromagnetic induction logs can be used to determine changes in salinity profiles over time in wells with PVC casing (for example, Metzger and Izbicki, 2013).

Measuring pressure gradients and high-resolution temperature gradient logs as part of monitoring of the effects of specific well stimulation activities would contribute to local-scale understanding as well as regional understanding of the relations between potentially usable groundwater and oil and gas zones. Collection of pressure and temperature data as part of well-specific monitoring would allow for integration and direct comparison with the regional monitoring efforts, which provide regional context for the results of the well-specific monitoring efforts. Specifically, the regional monitoring data could provide baseline information on pressure and temperature conditions that well-specific data could be compared to.

CADOGGR requires operators to notify the State when pressures are different from those expected or modeled during injection projects, but does not currently require follow up to determine if and where wells have been breached and constituents may have entered potentially useable groundwater. Follow-up monitoring, which includes geophysical logging of nearby wells, could be used to evaluate if the vertical distribution of these borehole geophysical signals indicates unusual profiles consistent with vertically distributed sources of relatively warm conductive fluids.

Control Sites

Any monitoring network should include some monitoring of control or background sites unaffected by potential oil and gas effects but in similar groundwater settings. The number of background or control sites is typically a small fraction of total wells monitored.

Data Quality

Data collection needs to follow rigorous quality-assurance/quality control protocols to ensure that the data are collected without bias, and with appropriate precision and accuracy. The sample collection needs to include sufficient numbers of field and laboratory blanks to evaluate if there are constituent detections that are an artifact of the sampling process rather than concentrations of target constituents in the groundwater samples (for example, Fram, Olsen, and Belitz, 2012). Field replicate samples need to be collected to determine the variability of measured concentrations between samples collected at the same location and time. For selected constituents, primarily organic constituents, field spikes should be collected to evaluate the recovery of target analytes in samples. The quality-assurance/quality-control results need to be documented and publicly available so that users of the data can evaluate potential sample bias, precision, and accuracy to determine if the data meets data quality objectives.

Specific Regional Monitoring Program Elements Defined in SB4 and in Public Workshops

This section presents an executive summary of potential program elements specifically called out in SB4 and in comments made during SWRCB public workshops. The concepts are discussed in more detail in a systemic framework in the following Detailed Regional Monitoring Program Plan section.

Water Quality Constituents for Regional Scale Monitoring

A review of scientific literature indicates that multiple constituents are potentially useful for discerning the effects of oil and gas development on groundwater quality. Although most literature is from locations outside of California, similar sources and geochemical processes result in many of these constituents being potentially useful as tracers of oil and gas effects on groundwater in California. Much of the recent literature concerning the effects of oil and gas activities on groundwater concerns the effects of recent unconventional development of shale gas in the eastern and central U.S. However, there is a large body of literature predating the recent expansion of unconventional recovery techniques including well stimulation, that also provides insight regarding constituents that are useful tracers of oil and gas activities, including some literature from California.

Review of the scientific literature indicates that an ensemble of constituents would be most useful for determining the extent and distribution of effects of oil and gas activities on groundwater. It is generally

not advisable to rely on only one set of tracers because all tracers have limitations and processes affecting their utility for identifying sources and mixing of waters and solute sources in groundwater.

At this time, the collection of samples for analysis of constituent groups presented in Table X should be considered for the regional monitoring program.

Constituent	Reason
Field parameters including pH, temperature,	Used to help determine geochemical
conductivity, turbidity, alkalinity, dissolved oxygen,	conditions
oxidation reduction potential, dissolved sulfides	
Dissolved hydrocarbons and other volatile organic	Association with well-stimulation or waste-
compounds (VOCs) using the low-level detection	injection activities
methods	
Dissolved combustible gases – short-chain	Combustible gases can serve as early warning
hydrocarbons containing up to six carbons in a	indicators for impacts of oil and gas operations
hydrocarbon molecule and their isotopic ratios	on groundwater resources because the gases
	can move faster through aquifer systems than
	dissolved constituents
Dissolved inorganic constituents, including major and	Used to determine the source of salinity in
minor ions and trace elements	groundwater, which is necessary to separate
	the effects of oil and gas activities from other
	anthropogenic and natural sources of salinity
	in groundwater
Dissolved noble and atmospheric gases	Tracers of groundwater age, recharge area and
	sources, and flowpaths used to understand the
	relation of water quality to groundwater flow
	within an aquifer system
Isotopic tracers, such as stable isotopes of water,	Used to determine sources of water and salts
dissolved carbon, strontium, and boron	and groundwater ages; new tracers specific to
	oil and gas development in California may
	emerge as part of characertization phase.
Naturally occurring radioactive materials	Tracers of fluids from oil and gas zones
	compared with other sources
Semi-volatile organic compounds, including polycylic	Potential indicators of dissolved petroleum
aromatic hydrocarbons (PAHs)	products in groundwater
Dissolved organic matter (DOM) characterization	DOM from difference sources has different
	optical fluorescence and absorbance
	properties and chemical compositions. These
	data are used to distinguish DOM from
Tillia	different sources.

Table 1

A core set of constituents needs to be collected and analyzed in samples of: (1) groundwater from different depths in protected groundwater resources overlying or adjacent to oil and gas areas and in background areas with similar hydrogeologic settings where no oil and gas activity occurs (background samples); and (2) sources waters potentially affecting water quality of protected groundwater resources, such as produced and flowback waters from oil and gas production, wastewaters disposed in injection

wells, wastewaters stored at the land surface, and other water sources unrelated to oil and gas activities.

To have a consistent, systematic, and comprehensive program that can be used to analyze data at Statewide, regional, and local scales, use of a consistent set of core analytes across all areas is desirable. Analysis of existing data and systematic collection of data for these constituents in selected oil and gas areas of California as part of a pilot or reconnaissance effort will yield refined information on which constituents are most valuable as tracers. Consequently, some refinement in the constituents measured to assess the effects of oil and gas activities on water quality may occur as the monitoring program evolves. However, it is recommended that a consistent set of core analytes be measured at all sites monitored as part of the regional program regardless of the classification of the vulnerability of groundwater in a particular oil and gas area. Rather than change the analyte list in areas with differing vulnerability, it is recommended that a consistent analyte list be used everywhere with adjustments in the density and frequency of monitoring in less vulnerable areas compared to more vulnerable areas.

Water Quality Constituents in the Well-Specific Program

The conceptual approach is to use the regional monitoring program to define baseline water quality across all study units with a detailed, consistent core suite of constituents that includes isotopes not typically available in commercial labs. Site-specific monitoring programs can then use a more limited set of constituents commonly supported by commercial laboratories and be collected at a much higher frequency that in the regional program.

Constituents:

- 1. Field parameters including pH, discharge temperature, conductivity, turbidity, alkalinity, dissolved oxygen, oxidation reduction potential, dissolved sulfides;
- Chemical constituents that are representative of the well stimulation treatment fluid composition;
- Total dissolved solids, inorganic chemicals listed under California Code of Regulations, title 22, Table 64431-A, organic chemicals listed under California Code of Regulations, title 22, Table 64444-A;
- 4. Hydrocarbon gas composition (methane through hexane);
- 5. Major and minor cations (including sodium, potassium, magnesium, calcium and strontium);
- 6. Major and minor anions (including chloride, sulfate, carbonate, and bromide);
- 7. Trace elements (including lithium, barium and boron); isotopic composition of water (hydrogen and oxygen); and
- 8. Radioactivity (including gross alpha, gross beta, uranium isotopic, radon and radium 226+228).

The constituents in common with the proposed regional program include: field parameters, selected major and minor ions, trace elements, nutrients, VOCs, semi-volatile organic compounds, hydrocarbon gas composition (methane through hexane), isotopic composition of water, and radioactive constituents (radium isotopes).

The regional program includes some constituents not on the well-specific list presented above, including: carbon isotopic values of methane through propane and hydrogen isotopic values of methane for evaluating sources of hydrocarbon gases, noble gases, tritium, and carbon-14 for groundwater age dating and water and gas source delineation purposes, dissolved organic carbon fractions for evaluating sources of organic carbon, and stable isotopes of strontium, boron, lithium, and carbon for use in evaluating sources of solutes. These additional constituents collected for the regional monitoring are essential to evaluate sources of constituents, gases, and water at the regional scale where the density of data will be less than at the well-specific scale and need to be collected at all regional monitoring sites to have a consistent set of data for regional analysis. It may not be necessary to include these additional tracers at the well-specific scale unless the initial results indicate that oil and gas related constituents are present and sources need to be determined through follow-up monitoring at the well-specific scale.

Determining Where New Monitoring Wells are Needed

Determining the location, depth, and number of wells for monitoring will involve a multiple step process that includes: (1) assessing the volume of protected groundwater resources that needs to be monitored in oil and gas areas at statewide, regional, and local scales and assessment of the appropriate density of monitoring points to attain sufficient statistical mass for assessing the effects of oil and gas activities on groundwater quality at regional to oil-field scales; (2) identifying the primary vertical zones within this volume requiring unique monitoring data; assessing the preferred spatial distribution of monitoring points; (3) assessing the location, depth, and number of existing wells that can be used for monitoring in relation to the desired number, with gaps being filled by drilling of new wells or collecting samples from discrete depths within existing wells; and (4) refining the design of monitoring networks as monitoring efforts evolve, to adapt monitoring network design to answer additional questions based upon refined understanding from previous data collection. Following these general principles, the design will be refined through pilot monitoring efforts in selected oil and gas areas. The results of these pilot efforts will inform the monitoring design in subsequent areas. For temporal sampling, the monitoring design needs to retain some common monitoring points for time-series analysis while permitting adaptation of other parts of the design to address new questions based on previous monitoring data.

Drilling New Monitoring Wells

The drilling, instrumentation, and sampling of multi-depth monitoring wells represents an important tool for monitoring protected groundwater near oil and gas fields. In some areas, where groundwater wells do not exist, it may be necessary to drill, instrument, and sample monitoring wells to provide the data necessary to evaluate for the effects of oil and gas development on groundwater resources. In addition, existing or newly drilling multiple well monitoring sites would be productive locations for high frequency monitoring in highly vulnerable areas

To fill gaps in existing well coverage within protected groundwater resources in proximity to oil and gas fields, drilling and installation of additional deep multiple well monitoring sites should be considered. Relatively short-screened monitoring wells would be installed at multiple depths within a single or multiple boreholes, spanning a depth range from the water table to the buffer zones between protected groundwater and oil and gas production zones. Multiple well monitoring sites permit collection of vertical profiles of groundwater quality and head and detailed lithologic and geophysical logs for characterizing subsurface conditions, all of which contribute to understanding relations of oil and gas zones to protected groundwater quality.

Installation of monitoring well sites also permit collection of detailed data at these locations in the future. For example, if 2-inch diameter or greater PVC cased wells are installed, the deepest well at each site can be used to collect Electromagnetic (EM) Conductance logs, which can be used in combination with water quality data from the monitoring wells and the lithologic and other geophysical logs at the site to determine a continuous profile of salinity to the bottom of the deepest monitoring well. Repeat EM conductance logging measurements over time can be used to determine if salinity is changing within the profile (Metzger and others, 2012), which could be an early warning indicator of changes in water quality that could reach supply wells in protected groundwater resources in the future.

Where only long-screened wells that integrate groundwater flow from multiple aquifer layers are present, another option for collecting data on groundwater quality from discrete depths within existing wells could be use of depth-dependent sampling techniques (Izbicki and others, 1999; Izbicki, 2004). Methods to collect, analyze, and model water chemistry and wellbore flow profiles within long-screened wells under pumping and ambient (un-pumped) conditions have been developed and extensively used in California (Gossell and others, 1999; Izbicki and others, 1998; 2003; 2005a; 2005b; 2006; 2008; Danskin and Church, 2005; Landon and others, 2010). These depth-dependent techniques permit the use of existing wells to obtain vertical profiles for monitoring for effects of oil and gas development on protected resources.

Frequency and Duration of Sampling - When Should Samples Be Collected?

The frequency and duration of monitoring will vary depending upon the vulnerability of usable groundwater resources to oil and gas activities. Areas classified as having high vulnerability based upon proximity, intensity and type of development, connectivity of oil and gas and groundwater resources, and historical data should have more frequent monitoring; areas with low vulnerability can have less frequent monitoring.

The duration of monitoring should extend beyond the end of the oil and gas activities. This is particularly the case for well-specific scale monitoring of the effects of particular well stimulation efforts. The effects of oil and gas activities can take time to be detected because of large depths and slow groundwater flow, the regional monitoring should also extend beyond the end of oil and gas activities in a particular oil and gas area to allow time for the effects to be detected.

Public Access to Data

Groundwater quality data collected for the regional, site-specific, and owner-notification programs will be submitted to the SWRCB in electronic format compatible with the SWRCB's web-based groundwater information system, GeoTracker GAMA. Wells should be identified with available identification codes (for example, PS-CODE, USGS STAID, State Well Number, GAMA ID, DWR WCR number, etc.) to facilitate cross-linking of records. To protect the privacy of participating well owners and users, well owner information should be kept confidential and not transferred to GeoTracker GAMA. Well locations (latitude/longitude) will be measured and reported, however, the locations of some types of wells, such as public supply wells, may be generalized for public GeoTracker GAMA users not authorized to receive precise location information. Basic well information, including well depth, depth to the top of the shallowest screened or open interval, well type (monitoring well, pumping well, or spring), and water level on the date of sampling should be reported. Well use (monitoring, domestic, irrigation, public-supply, industrial supply, elc.) should also be reported, but will only be released to authorized users.

Groundwater quality data should be released on GeoTracker GAMA as soon as possible after the data are acquired and quality-control checks have been completed, however, results for individual wells should be communicated to the participating well owner/user prior to public release. GeoTracker GAMA is designed to hold discrete water quality data from groundwater wells. The monitoring programs will likely include collection of data that do not meet those criteria. Such data should also be made publicly accessible to the extent possible, either through other publicly accessible database systems or in the form of reports. Reports resulting from water quality and other data collected for the monitoring programs will be made publicly available on the SWRCB's website after a rigorous scientific peer-review process.

When Might Existing Oil and Gas Wells be Repurposed for Groundwater Quality Monitoring?

Oil and gas wells that have been used for injection or production cannot be used because they already contain chemicals the monitoring is intended to track in surrounding groundwater. Existing wells may be appropriate for some geophysical monitoring that can help provide early warning of possible water quality changes.

Relationship Between Regional and Site-Specific Monitoring

There are three types of site-specific monitoring currently being undertaken in California to determine the effects of oil and gas development on groundwater resources. The first is the well- and event-specific monitoring that is a new requirement for well stimulation under SB4. The second is monitoring required at locations where surface disposal of combined waste streams in sump ponds has affected the quality of near-surface groundwater; these are conducted under WDRs issued by the Regional Boards. The third is mechanical integrity testing of waste and water injection wells using radioactive tracers, temperature, and/or spinner surveys carried out under CADOGGR regulations; these tests demonstrate that injected fluids are moving appropriately through wells and into intended locations in formations but do not track the long-term effects of injection on surrounding water quality because the aquifers are presumed to be isolated from other potential uses. Regional information developed at the oil field scale can support each of these site-specific monitoring programs in several ways.

First, geochemical data developed for end members at oil field scales (described in detail in the characterization phase discussion in Section 2) accomplishes the first step of any site-specific analysis of groundwater to determine where a complex mixture originated. Second, concentration information sampled on a probabilistic basis at the field scale can be used as an estimate of baseline conditions for specific sites. Third, pressure, temperature, and flow gradient information developed at oil field scales/scales larger than injection zones can be used to determine if there is a risk of constituent transport at specific sites as long as data are collected at temporal scales matching site-specific questions. For example, real-time geophysical data collected during well stimulation activities in a network of idle oil and gas wells surrounding the injection site can provide an initial screen for constituent transport potential. Fourth, tracers are dependent on geochemistry in injection zones and determining the validity of their use at a boarder scale requires studies that include a range of expected geochemical conditions within similar formations and across formation types. Finally, any studies designed to determine if waste injection zones are indeed isolated from potentially useable groundwater are most appropriately done at the oil field scale and require mapping of the resource.

The monitoring for well-by-well activities, designed to identify local effects of well stimulation activities, should occur more frequently than regional monitoring and should include samples collected before, during, after well-stimulation activities. Some studies of the effects on unconventional gas extractions in the Marcellus Shale in the northeastern U.S. have noted a significantly higher occurrence of stray (combustible) gas detections in water wells located within one kilometer of oil and gas drill sites and have suggested that wells within this radius should be monitored (Vengosh et al., 2014).

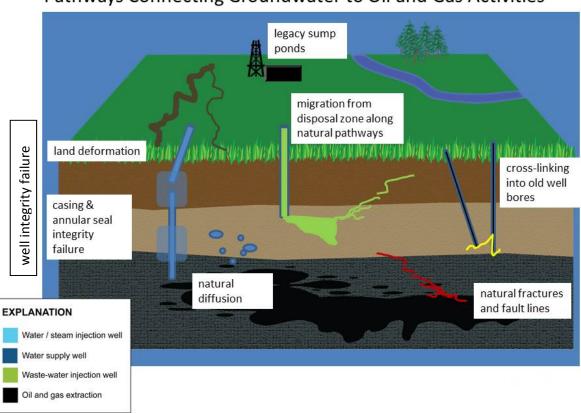
SECTION 2: Potential Detailed Regional Monitoring Program

Introduction

In California, relatively little is known about the interaction between oil and gas development and groundwater resources, in part because conventional wisdom has held that oil and gas resources and groundwater resources are sufficiently separated in California that interaction is unlikely. However, as California's reliance on groundwater has increased, the range of groundwater resources considered potentially suitable for beneficial uses has expanded, thereby increasing the spatial overlap between areas with groundwater resources suitable for present or future beneficial uses, and areas designated for oil and gas development. The expanded usage of well stimulation technologies also has potentially increased this spatial overlap by enlarging the viable oil and gas production zones and the intensity of oil and gas development activities. The geographic scope of a regional monitoring program would therefore comprises areas with past, present, or future oil and gas development activities and areas with groundwater resources that are currently, or may be in the future, used for beneficial purposes, statewide.

The connectivity between oil and gas resources and groundwater resources established by natural geologic pathways and by anthropogenic pathways (for example, well boreholes, induced fractures) may affect the vulnerability of usable groundwater to contamination from oil and gas activities.

The preservation of oil and gas deposits over geologic timescales implies that most oil and gas deposits have been relatively isolated in the subsurface. With the advent of oil and gas exploration and production, pathways for groundwater contamination may have been introduced, leading to communication between zones containing oil, gas, and associated formation water (often brines) and usable groundwater resources. The anthropogenic pathways for groundwater contamination include breaching of injection or production well integrity through multiple different mechanisms allowing flow of oil and gas-related constituents out of isolated zones; wastewater injection into zones hydrologically connected to groundwater resources; and the loss of fluids during injection projects into "thief" zones or old well bore holes which are also hydrologically connected to groundwater resources. All of these examples represent potential ongoing risks to groundwater quality. Surface waste disposal is another anthropogenic pathway but is generally considered a legacy practice in California, albeit with a potentially large footprint in near-surface groundwaters due to wide use of large evaporation ponds before the mid-1980s; the few remaining sump ponds are regulated by the CVRWQCB.



Pathways Connecting Groundwater to Oil and Gas Activities

Figure 8 presents a simplified conceptual model of the natural and anthropogenic pathways through which oil and gas-related constituents can migrate into potentially useable groundwater resources.

The most common pathway for contaminants from oil and gas activities to affect groundwater is movement of stray gases, brines, or dissolved petroleum compounds along leaky wellbores that provide preferential pathways for contamination to bypass subsurface layering and reach groundwater (Jackson and others, 2013, Davies and others, 2014, Darrah and others, 2014). Movement along wellbores can occur as a result of compromised annular seal or casing developing over time, incomplete annular seal of the borehole. Current CADOGGR regulations specify standards for well construction that are designed to promote well integrity and zonal isolation (California Code of Regulations Title 14 Chapter 4). The regulations specify include periodic testing of well integrity and in the case of injection wells, movement of injected fluid into the intended zone immediately adjacent to the well documented by radioactive tracer, spinner or similar surveys (Guerard, 1984). However, hundreds of thousands of wells have been drilled since the first oil well was drilled in California in 1859 (CADOGGR, undated), and many of the older wells certainly were not constructed to current standards. Moreover, oil fields generally have a high density of abandoned and active wellbores, so even a small percentage of compromised wellbores could correspond to a large number of transport pathways. Of the 168 currently active oil fields greater than 2 mi2 in size, 31 contain more than 100 known wellbores per square mile (CADOGGR data).

Extraction and injection of fluids may result in deformation in the subsurface and land subsidence. For example, groundwater pumping in the San Joaquin Valley has resulted in up to 30 feet of land surface subsidence (Galloway, Jones, and Ingebritsen, 1999) due to compaction of subsurface layers after groundwater was extracted from them. Differential subsidence and subsurface deformation associated with groundwater pumping has caused shearing of wellbores in water wells (Sneed, Brandt, and Solt, 2013). Similar amounts of land surface subsidence have been observed in areas with oil extraction (for example, Fielding and others, 2005, Bawden and others, 2003, and Poland and Davis, 1969), and well bore shearing has been documented as a major stress mechanism in at least one of them (Belridge; Frederich and others, 2000) and extensive pressure maintenance operations to minimize subsidence (Doornhof and others, 2006).

Natural pathways for groundwater contamination also exist. Oil, gas, and associated formation water may migrate to the surface along faults and fractures; factors which control and enhance this flow are complex. Eichhubl and Boles (2000), for example, describe processes controlling fluid flow along faults in the Monterey formation. The geology of a basin may constrain or increase the mobility of hydrocarbons and/or formation water from oil and gas deposits to shallower groundwater aquifers. In basins with impermeable "cap" formations, the deeper oil and gas deposits are effectively isolated from shallower aquifers. However, in basins with relatively porous overlying strata, hydrocarbons and formation water may migrate from deep deposits to shallower aquifers. Similarly, the character and density of faults within a basin may greatly impact the mobility of deeper hydrocarbons and formation water by acting as conduits by which these materials can be transported through cap formations into shallower aquifers. Groundwater overlying naturally permeable basins or basins with numerous active faults may contain elevated concentrations of dissolved gases (methane), increased salinity, and elemental isotopic ratios characteristic of deep hydrocarbon deposits.

Anticipated Findings

There are several working hypotheses which have significantly influenced the approaches proposed in this discussion paper. To summarize them:

- Near-surface groundwater resources located under waste disposal ponds have already been affected by past oil and gas activities; this has been documented in several studies (Brown and others, 1961; Bean and Logan, 1983; and Mitchell, 1989). Some of these legacy sites are being monitored under Waste Discharge Requirements (WDRs) issued by the Central Valley Regional Water Quality Control Board;
- 2. Deeper groundwater currently tapped by public supply wells is affected more by constituents from geological formations than by near-surface contamination sources such as leaking gasoline tanks. Landon and Belitz (2012) found low concentrations of geologically derived benzene statewide, although three public supply wells in the southwestern San Joaquin Valley tapping into deep, old, reducing groundwater had benzene concentrations that were over the Maximum Contaminant Level (MCL). The study did not delve into the question of whether the geogenic benzene reached the used resource through natural diffusion from formations bearing

- hydrocarbons, or whether oil and gas development activities played a role in bringing these natural constituents into contact with the used resource.
- 3. New monitoring in aquifer zones containing over 3,000 mg/l TDS is likely to show legacy effects of oil and gas development near oil and gas fields due to the allowance of waste injection into these zones (CADOGGR, 1981; Walker, 2011) and because geologically derived benzene is more frequently detected in the deeper public supply wells in proximity to oil and gas fields (Landon and Belitz, 2012).
- 4. Differentiating well stimulation-related fluid effects from produced water effects is likely to be extremely difficult for a number of reasons. First, fluids used in well stimulation are combined with the main produced water waste stream and the latter volumes are roughly two orders of magnitude greater. Second, the same types of additives used in hydraulic fracturing fluids also seem to be commonly used in water and steam injected into the production zone (with the exception of proppants); these enhanced recovery fluids make up a large fraction of produced water volumes. The mixed waste stream thus contains recycled produced water with additives, and well stimulation fluids with additives. Since a majority of the waste stream is reused in ongoing enhanced recovery or disposed of in waste injection wells, pathways between enhanced recovery and waste injection operations and potentially useable groundwater resources are relevant to the ultimate fate of well stimulation fluids. Chemical differentiation may be possible when imported surface water is used as the source of well stimulation fluids, but in situations where recycled produced water is used, differentiation will likely be challenging. The end-member mixing model/ multiple tracer approach is one of the best tools in such situations.
- 5. **Well bore flow is likely to be a dominant cause of any observed constituent transport.** This pattern has been found in other parts of the country (Davies and others, 2014; Dusseault and others, 2014).
- 6. Time is likely to be a critical factor in assessing the condition of potentially useable groundwater resources and future risks to them. The time scales involved in constituent transport are long, the full extent of water quality changes associated with past practices may not have fully manifested themselves, and changes associated with isolated current events may also take a long time to manifest themselves in water quality characteristics.

Three Phases

The primary tasks of a Statewide program to monitor the effects of oil and gas development on groundwater resources are to identify the extent and magnitude of effects, identify the primary pathways through which effects occur, and develop understanding of the factors affecting the vulnerability of usable groundwater resources to oil and gas activities. We propose that the regional program be divided into three phases.

The first phase would focus on **characterization** of the relationships between oil and gas development activities and potentially useable groundwater resources and determine where three controlling factors,

pathways, flow gradients, and geochemistry combine to pose potential risks to further water quality degradation. One of the basic tasks of the characterization phase is to develop 3D maps of potentially useable groundwater and "exempted" aquifer zones. The other tasks use the following multiple lines of evidence:

Type of Information Used in Characterization Phase	Rationale
Geological information on material lying between potentially useable groundwater and oil and gas activities	Supports identification of pathways
Probabilistic sampling of current water quality condition in and around potentially useable groundwater	3D baseline water quality conditions at regional scale and information to support end-member geochemical mixing analysis
End-member water quality sampling	Support end-member geochemical mixing analysis and identification of pathways
Geophysical information on pressure and temperature gradients	Supports identification of 3D flow gradients
Inclusion of isotopes in water quality analyses of samples	Supports identification of potential tracers specific to California conditions

The characterization phase results would be the identification of pathways where constituent transport is a concern.

The second phase of the program would focus on designing follow-up monitoring of specific pathways identified in the first phase, better distinguishing between different causal mechanisms of problematic pathways such as well bore integrity, and establishing low-intensity networks in areas without current pathways to monitor for new pathway formation. The second phase essentially requires significant changes to the characterization study design with new study units and sampling approaches.

Products from this phase would include:

- In cases where there is no evidence of transmission exist, a monitoring plan which uses the probabilistic sampling design in the characterization phase to track change over time from the established baseline;
- In cases where there is transmission and the source and pathways are known (other than well bores and waste injection zones), a monitoring plan using a sentinel network can track changes in risk to potentially useable groundwater quality over time;
- In cases where well bore transmission is determined to be a pathway of concern, follow-on studies designed to help distinguish which of the various mechanisms that could affect well integrity are most important;
- In cases where injected waste water has been found or is likely to interact with potentially
 useable groundwater, a monitoring plan constructed around 3D maps of zones that connect

waste disposal areas and useable waters and/or detailed tracer studies could confirm whether these areas are appropriate for future waste injection;

- In cases where a geochemical signal associated with oil and gas development has been detected
 and there are ongoing risks to water quality, but more information is needed to characterize the
 specific source and pathways, , additional studies would be designed and implemented before
 appropriate monitoring plans developed; and
- Identification of areas where a hydrologic model is needed to support management where complex flow paths exist;

The third phase of the program would focus on **implementing trend monitoring**, **conducting follow-up** studies, developing hydrologic models, and modifying data archiving systems.

Phase 1: Characterization

Effective monitoring plans require understanding the resource to be protected and the pathways by which undesirable constituents can be transported into that resource. Currently, the location and extent of potentially useable groundwater is, and there is no systematic assessment of the importance of different pathways by which constituents associated with oil and gas development can be transported into the resource of concern. This characterization phase is designed to provide the State with robust information about both.

The scientific steps needed in the characterization phase are:

- a) Delineation of the areas of the State that need to be evaluated and monitored and organization into study units;
- b) A reconnaissance-level step to define the separation between the used groundwater and zones used for oil and gas development;
- Prioritization of study units using the reconnaissance-level separation distance as an initial vulnerability determination and locations where well stimulation is currently taking place or planned for the near future;
- d) A more detailed mapping step to identify 3D subsurface volumes where potentially useable groundwater exists, the precise locations of "exempted" aquifers, and injection wells;
- e) Characterization of the geological material and features in the intervening volume to determine the thickness of material, its permeability, and potential pathways for constituent transport;
- f) Probabilistic sampling of current water quality conditions in the 3D volumes containing potentially useable groundwater, installing new monitoring wells where needed and none currently exist.
- g) Additional sampling of end-member sources including produced water, groundwater associated with legacy surface sumps, water/ steam injected for enhanced recovery purposes, formation

water, ancient deep groundwater, and control samples from areas without nearby oil and gas activities;

- h) Collection of geophysical information [injection wells] and analysis to determine 3D flow gradients;
- i) Where possible, an analysis of salinity changes over time within study areas using oil and gas well record data; the goal would be to determine if there is evidence of past changes in water quality at the oil and gas field scale
- j) An extensive analysis of basin geology, new monitoring data, and historical data, within a framework that examines the proximity of groundwater to oil and gas zones, intensity and type of oil and gas development, connectivity of oil and gas and groundwater resources, and hydraulic gradients within oil and gas zones and groundwater aquifers, to determine the sources and pathways of potential contamination and baseline water quality conditions of potentially useable groundwater.

Steps a) through c) take place at the beginning of this phase. Steps d) and e) follow, and steps g) through i) can take place concurrently. Step j) requires all others to be completed first.

Delineation of Study Units

The first step is to delineate, characterize, and prioritize the areas of the State that need to be evaluated and monitored by a regional program. The core concept for the regional program is vulnerability, the potential for interaction between oil and gas development activities and usable groundwater resources. The concept of vulnerability is important because it supports development of a tiered study design in which areas where groundwater resources are less vulnerable are monitored with less intensity than areas where the resources are more vulnerable. In addition, vulnerability can change over time as a result of natural and anthropogenic factors, and a tiered study design can be adapted in response to those changes. The use of vulnerability as a guiding concept for design and implementation of a regional program is consistent with the principles of a Conceptual Site Model approach to project design and implementation and with guidance developed by US EPA for state water monitoring and assessment programs (USEPA, 1988; 2003).

California contains over 500 active and inactive oil and gas fields (CADOGGR 1982, 1992 and 1998). The regional groundwater monitoring program sampling design is based on assessing water quality in and around oil and gas fields, designated as study units. Each study unit will contain one or more oil and gas fields, and a buffer zone around each oil field; the combined area will represent a study unit. The size of the buffer could be:

- a) fixed, such as a 3-km buffer similar to that used by the GAMA program around public-supply wells, or
- b) variable, determined based on estimated groundwater velocities near the edge of the oil field Study units may be grouped together for sampling efficiency or on the basis of geology.

It is expected that study unit configuration will change after the initial characterization phase. Low vulnerability areas can be monitored with low frequency using a probabilistic sampling design like GAMA with units aggregated accordingly. Areas with confirmed pathways between oil and gas development activities and potentially useable groundwater resources would require monitoring approaches specific to those pathways and study units recast accordingly.

Reconnaissance-Level Determination of Separation Between Used Groundwater and Oil and Gas Activities

The separation between groundwater that is or has been used for public supply, domestic, and irrigation purposes and oil and gas activities is in the process of being determined by the USGS in cooperation with the SWRCB. Data on public drinking water supply wells are kept by the SWRCB's Division of Drinking Water (DDW). The Department of Water Resources (DWR) has compiled a library of over 700,000 scanned images of well completion reports (WCRs). Johnson and Belitz (2014) extracted information from a statistical subsampling of about 40,000 of these WCRs to map the distribution of individual domestic wells at a 1 square mile section scale statewide, demonstrating that this library of WCRs can be used effectively. The 99,770 oil and gas wells in California (active, inactive and new; CADOGGR, 2014) are located in 2,534 of the 158,678 1-mi2 sections in the State. Approximately 14,723 of the 635,736 water well completion reports (WCRs) that can be plotted are located in these 2,534 sections, and about another 35,372 WCRs are located in sections adjacent to sections where active oil and gas wells are located. Data from these 35,372 WCRs including well location, type, and depth are being compiled in a database and will be the primary data used to identify the depths and locations of groundwater currently or historically used for public supply, domestic supply, or irrigation in and directly adjacent to currently active oil and gas fields.

Oil and gas activity locations will be determined using CADOGGR oil and gas field summaries (CADOGGR, 1982; 1992; 1998) and subsamples of wells within each field. The USGS is currently developing a methodology for extracting information needed for multiple steps from the CADOGGR well files.

Initial Vulnerability Categorization and Prioritization of Study Units

Numerical thresholds for categorizing study units based the preliminary determination of vulnerability using linear separation need to be defined by the SWRCB. Once applied, study units can be grouped accordingly. Thresholds should represent the depths of intervening material through which natural flows will probably not/ will likely/ and may occur, rather than fracture propagation distances (for example, Davies and others, 2012, Flewelling and others, 2013). Vulnerability will then be used to determine the density of probability-based sampling described below, and the order in which scientific work is carried out across study units.

The location of current and planned well stimulation projects can be used as an additional factor in determining the order in which study units are characterized.

Detailed Mapping of Potentially Useable Groundwater, "Exempt" Aquifer Zones, and Injection Wells

Defining the depths and locations of potentially usable groundwater in and directly adjacent to currently active oil and gas fields requires a definition of what constitutes potentially usable groundwater. As

discussed in Section 1 of this document, this definition is based on regulatory considerations, not on scientific ones, and ultimately the SWRCB will need to establish the definition that will be used for the regional monitoring program. For this exposition of a potential design for the regional program, we use the definition provided by the USEPA for operational purposes: potentially usable groundwater is groundwater containing less than 10,000 mg/L TDS (USEPA, 2001).

To the extent possible, existing data will be used to map the 3-D spatial distribution of groundwater containing less than 10,000 mg/L TDS in and adjacent to oil and gas fields. The data used to estimate 3-D spatial distribution of groundwater containing less than 10,000 mg/L TDS could include the following sources: 1) CADOGGR oil and gas field summaries, 2) existing maps of the depths to the base of freshwater compiled by previous studies, 3) existing digital groundwater quality databases, 4) non-digital water quality data collected during oil and gas activities in CADOGGR files, and 5) analysis of geophysical logs to estimate salinity. Given the short timeline for implementation of the regional monitoring program (must be implemented by January 1, 2016), the initial preliminary characterization of potentially usable groundwater may only include data from the first two sources; data from the other three sources will be used to refine characterization. It is likely that there will be gaps in the existing data such that collection of new data during the probabilistic sampling step may be necessary to adequately map groundwater salinities in some areas.

CADOGGR summary descriptions of oil and gas fields include notes on depths to the base of fresh water (CADOGGR, 1982; 1992; 1998). The salinity at the base of fresh water is not defined, but likely corresponds to a TDS content of 2,000 – 3,000 mg/L, on the basis of how fresh water has been defined elsewhere. For example, Page (1973) and Williamson and others (1989) define fresh water as having a specific conductance of less than 3,000 uS/cm, which corresponds to a TDS content of approximately 2,000 mg/L. This information can be used to compile reconnaissance data for constraining the depth of the base of freshwater for oil and gas fields in California and for comparison with other estimates. For example, Page (1973) mapped the base to the depth at which groundwater with a specific conductance of about 3,000 micromhos occurs in the San Joaquin Valley using a variety of data sources, including geophysical logs from oil and gas wells.

For more detailed characterization, available groundwater sample data for total dissolved solids (TDS) within areas overlying and adjacent to each oil and gas field will be compiled and mapped. Data sources will include USGS, Geotracker, CADOGGR, SWRCB, USEPA, and easily accessible local sources. From each well, the most recent data available will be used in mapping groundwater salinity distributions. For wells with specific conductance (electrical conductance) or major ion data without reported TDS values, TDS values will be calculated based on regression relations with these measured parameters. Available well depth and well perforation data for wells with TDS data will be compiled. The ensemble of TDS data will be used to map in three-dimensions the depths of threshold values of TDS such as 3,000 and 10,000 mg/.

Included in the TDS mapping effort will be the use of groundwater level elevations to discern the effect of isolated groundwater zones, with little connection to the regional flow system, on TDS patterns. The intent is to identify groundwater zones that do not fit within regional patterns, are not representative of

the aquifer system in general, and contribute to anomalous TDS values that distort broader depth vs. TDS relations in the groundwater system. High TDS can result in these zones because of restricted groundwater flow rates and salt accumulation from water/rock reactions. Identifying the association of anomalous TDS and water-level data could allow for anomalous TDS values to be screened out of the TDS maps, resulting in more accurate understanding of the distribution of usable resources. These analyses will be done first with existing data. Subsequently, targeted collection of groundwater level and electrical conductance (field measured) data will occur in sub-areas to clarify relations of TDS to water levels.

It is likely that the existing water quality databases will not contain extensive data that is deep enough to include groundwater having TDS > 10,000 or even 3,000 mg/L. Consequently, in these situations, these maps will be limited and show that the base of freshwater is below the maximum depth of the available freshwater data.

A potential source of more extensive water-quality data from deeper zones where salinity is higher is data collected as part of oil and gas assessment activities and stored in CADOGGR files for individual oil and gas wells. The basic approach is to use borehole electric logs (e-logs), resistivity and spontaneous potential, lithologic records, and other geophysical data typically included in the oil and gas well records to independently estimate porosity and lithology. These data and supplemental high quality data sets from other sources can then be used to develop regression relations to calculate vertical salinity profiles. In locations where this method is not sufficient to map depths to groundwater containing less than 3,000 mg/l and between 3,000 mg/l and 10,000 mg/L, collection of additional geophysical log data (gamma or neutron logs) in steel cased wells may allow the effects of vertical changes in lithology, temperature, or porosity that effect e-log signals to be filtered out so that the corrected e-log profile can be used to estimate salinity. Where existing wells cannot be used, data gaps will be filled by collecting salinity profiles in new wells needed for the probabilistic sampling step described below.

Extracting water-quality data available in hard copy may be necessary to provide sufficient information. A methodology for extracting this information is being developed by the USGS in collaboration with the SWRCB. The methodology will likely include identifying the oil and gas wells with high quality records of lithology and geophysical logs with corresponding water chemistry data from different depths as a top priority for analysis. The products from this effort will be study area-scale maps of the depths (or minimum depths if poorly constrained) to the base of groundwater salinity thresholds such as 3,000 mg/L and 10,000 mg/L. These 3D maps will be used to define the volumes to be sampled for during the probabilistic sampling step.

Exempted aquifer zones were defined by CADOGGR (1981) using a surface footprint based on township and range plots and operational descriptions of depth based on geologic formations. The precise location of these zones in relationship to potentially useable groundwater has not been documented with precise mapping and recent discoveries of injection wells located in aquifers zones currently used for drinking water supply has highlighted the need for better mapping.

Most oil and gas fields in California contain injection wells. These injection wells are used for several purposes, including: enhanced extraction by water- or steam-flooding as a secondary recovery method for extracting addition hydrocarbons from fields, maintaining pressure in oil and gas reservoirs, and disposing of produced waters extracted with oil and gas (wastewaters). As discussed in Section 1 of this document, the volumes of water injected for water-flood, steam-flood, and cyclic-steam operations can be very large, and in many fields, these operations have been going on for decades. The primary source of water for these operations is recycled produced water.

In the context of the large amounts of water injected for water-flood, steam-flood, and cyclic-steam operations, and the amounts injected for waste disposal, the volumes of water used for SB4 well stimulation operations (hydraulic fracturing and acid matrix) are quite small. Furthermore, the waste stream from well stimulation operations is mixed into the overall produced water stream (CCST, 2014), meaning that any unique tracers of flowback water from well stimulation activities will be spread into waste injection wells and back into the hydrocarbon reservoir during enhanced recovery practices in most fields.

Because of the potential impact of oil and gas injection activities on groundwater quality, the locations and depths of all injection wells need to be compiled and analyzed as part of the 3D detailed mapping step to better assess the vulnerability of usable groundwater resources to underground injection. Of particular importance is assessing the relation between the location of injections and potential pathways that could allow injected fluids to reach usable groundwater resources. Additional data on the volumes injected, chemical characteristics of the injection fluids, and periods of operation are available through CADOGGR and are part of the information collected as part of their regulatory program. The broader effects of injections on subsurface pressure distribution need to be ascertained using a combination of oil and gas field geophysical monitoring data collected as a routine part of reservoir management, and augmented monitoring requirements. These will be analyzed in the final step of the characterization phase to determine if injections could result in pressure gradients that could drive fluids into potentially usable groundwater.

Refining Vulnerability Categorization: Characterization of Geologic Material and Features in Intervening Zones

The first steps of estimating the vulnerability of potentially useable groundwater resources to oil and gas development activities covered only the linear separation. The next step is to refine that reconnaissance-level work by adding information on permeability and known fault properties. As an additional step or refinement to relative vulnerability classifications, the estimated properties (permeability, porosity) of formations separating oil and gas fields would be combined with the thickness to calculate an effective vertical hydraulic conductivity or permeability for the zone separating useable groundwater from oil and gas production zones. Williamson and others (1989) and Faunt and others (2009) describe methods for calculating effective vertical hydraulic conductivities. The properties of the intervening formations would be estimated from lithologic data and geophysical logs within ranges of literature values of properties for particular lithologies. Once combined with estimates of hydraulic gradients across these formations, volumetric flux rates of fluids can be estimated. These calculations would yield estimates of the vulnerability of useable groundwater to natural seepage of

fluids from underlying formations and could serve as a refined indicator for vulnerability compared to proximity alone. However, as noted elsewhere, natural seepage is not expected to be the predominant mechanism influencing the vulnerability of useable groundwater to contamination from underlying oil and gas extraction activities; rather, the presence of preferential pathways such as leaky wellbores are expected to be the predominant pathway for contaminant transport. Consequently, the utility of refined estimates of vulnerability based on the properties of formations separating useable groundwater and oil and gas zones should be evaluated through pilot studies. This will result in a need for a second vulnerability criterion to be established by the SWRCB.

In high vulnerability areas where evidence is found of a transmission pathway from the water quality sampling in Phase 1, a more detailed geological framework model will likely be needed to investigate pathways and controlling factors in more detail.

Probabilistic Sampling of Current Water Quality Conditions in Potentially Useable Groundwater

Probabilistic study design

The basic monitoring network will be established using an approach that selects wells that are spatially distributed in three dimensions within the volume of potentially useable groundwater mapped in the first task. An element of randomization will be included in the site selection process (Scott, 1990) to provide a statistical representation of the resource. This probabilistic study design enables

- a) the regional assessment to be used as a baseline for well- and site-specific monitoring, and
- b) aggregated and/or comparisons of different study units to produce regional and statewide assessments.

The number and density of wells to be sampled in this volume needs to be sufficient to allow for assessment of water quality within study areas. The USGS NAWQA program provides guidelines for broad-scale assessments of ground-water quality and for detailed studies of the effects of land-use on ground-water quality. For both types of studies, the guidelines suggest that at least 20 to 30 wells be sampled to provide statistical confidence (Gilliom and others, 1995). The USGS NAWQA program also provides guidelines for well density: no less than 1 well per 39 mi2 for a broad-scale assessment (Gilliom and others, 1995), and no greater than 1 well per 0.39 mi2 for a detailed assessment (Squillace and others, 1996). These densities correspond to surface spacing between wells of 6 and 0.6 mi, respectively.

Groundwater quality is expected to vary with depth and, as a consequence, the initial water quality characterization should include samples from more than one depth zones. For example, the characterization could include three depth zones: shallow groundwater reflecting recent recharge, groundwater from the depths most commonly used for irrigation or drinking water supply, and deep groundwater from below the zone most commonly used for supply. The number of depth zones required for characterization of a study unit would depend on the characteristics of the groundwater resource and the vulnerability classification of the study unit.

Once the number and depth of samples for each study units has been determined using the process described above, existing public supply, agricultural, monitoring, and industrial wells will be screened to determine if they can be used for sampling purposes. Wells that have been used for oil and gas production or injection in the past are not suitable for assessing baseline water quality (though they may be useful for geophysical measurements). Wells with long screens that integrate groundwater flow from multiple aquifer layers will be considered in this review, as there are methods to collect, analyze, and model water chemistry and wellbore flow profiles within long-screened wells under pumping and ambient (un-pumped) conditions that have been extensively used in California (Gossell and others, 1999; Izbicki, Danskin, and Mendez, 1998; Izbicki and others, 2003; 2005a; 2005b; 2006; 2008; Danskin and Church, 2005; Landon and others, 2010). It is likely that wells will not be present and/or available for sampling in all parts of the volume of potentially useable groundwater, and we expect to find very few if any wells providing access to the deeper zones not currently tapped for beneficial uses.

The total number of wells that would be required to complete a statewide probabilistic sampling network can be estimated by considering the size of the area to be included in the network and the desired sampling density. For example, the area to be included in the network could be defined as all areas within a specified distance of an active oil and gas well. Such an area would be delineated as the collective area covered by circles of the specified radius drawn around every oil and gas well. This is referred to as the 'well-buffer' approach to defining the statewide study area. If a 1-mile distance is used, the well-buffer approach yields a total area of 3,000 mi2 statewide that is within 1 mile of an oil or gas well. For a probabilistic sampling network, this total area would be divided into study units, and each study unit divided into equal-area grid cells. One sampling site is then randomly selected in each grid cell. Study units assigned high priority will have a greater density of samples collected to provide a higher resolution than lower priority areas. The number of sampling sites would be estimated as:

$$N = 3000 \times \left(\frac{f_{high} D_{high}}{G_{high}} + \frac{f_{low} D_{low}}{G_{low}} \right)$$

Where f_{high} and f_{low} are the fractions of the total area that are high and low priority,

D_{high} and D_{low} are the number of depth zones to be sampled in high and low priority areas and,

G_{high} and Gl_{ow} are the grid cell sizes in the high and low priority areas.

If $\frac{1}{2}$ of the total area is defined as high priority ($f_{high} = 0.25$ and $f_{low} = 0.75$), the high priority areas have a grid cell size of 2 mi2 and three depth zones, and the low priority areas have a grid cell size of 5 mi2 and one depth zone, then the total number of sampling sites would be 1,575.

Water-Quality Constituents

Water quality samples should be analyzed for a variety of constituents to support identification of the influence of formation water and hydrocarbons in potentially useable groundwater. There is a large body of literature that provides insight regarding constituents that are useful tracers of oil and gas activities, including Jackson and others, 2013; Orem and others, 2014; Vengosh and others, 2014, and some literature from California (for example, Bean and others, 1983; Izbicki and others, 2005; Landon

and others, 2012). More recent studies focus on exposure of new geologic formations bearing shale gas in the eastern and central U.S. through unconventional oil and gas development techniques including Darrah and others, 2014; Vengosh and others, 2014, 2013).

We suggest that a multi-parameter analytical approach would be most useful for determining the extent and distribution of effects of oil and gas activities on groundwater. It is generally not advisable to rely on only one set of tracers because all tracers have limitations and the geochemical processes affecting their utility for identifying sources and mixing of waters and solute sources in groundwater may prove different in California than other places, or even differ between study units or over time as enhanced recovery practices change geochemical conditions.

Based on the existing literature, the following constituent groups should be considered for the characterization phase of the regional monitoring program:

- (a) A suite of dissolved hydrocarbons and other volatile organic compounds (VOCs) using the low-level detection methods. The VOCs include constituents that could be associated with well-stimulation, waste-injection activities, or naturally occurring hydrocarbon deposits;
- (b) Dissolved short-chain hydrocarbon gases (one to six carbons in a molecule), their proportions and isotopic ratios. These properties of short chain hydrocarbons are diagnostic for determining the source of the gases, whether thermogenic or biogenic, and provide a means of identifying leaking well casings;
- (c) Dissolved inorganic constituents, including major and minor ions and trace elements. These salts and metals, and the ratios of selected constituents can be used for determining sources of salinity in groundwater, which is necessary to distinguish the effects of oil and gas activities from other anthropogenic and natural sources of salinity in groundwater;
- (d) Dissolved noble and atmospheric gases can be used to calculate groundwater age, recharge location, and subsurface flow regimes. These tracers are essential ancillary data used to understand the relation of water quality to groundwater flow within an aquifer system;
- (e) Isotopic tracers, such as stable isotopes of water, dissolved carbon, strontium, boron, and lithium used for determining sources of water and salts and groundwater ages;
- (f) Naturally occurring radioactive materials, which can be effective tracers of fluids from oil and gas zones.
- (g) Semi-volatile organic compounds, including polycyclic aromatic hydrocarbons (PAHs), which are potential indicators of dissolved petroleum products in groundwater,
- (h) Organic carbon fractions, separation of dissolved organic carbon in groundwater into different fractions on the basis of polarity and molecular weight yields different signatures for petroleum sources compared with other sources of organic carbon

(i) Field parameters including pH, water temperature, specific conductance, turbidity, alkalinity, dissolved oxygen, and dissolved sulfide.

For a systematic and comprehensive program to analyze data at Statewide, regional, and local scales, a consistent set of core analytes across all areas is desirable. Rather than change the analyte list in areas based on vulnerability, it is recommended that a consistent analyte list be used everywhere with adjustments in the density and frequency of monitoring in less vulnerable areas compared to more vulnerable areas.

Sampling End-Members to Support Identification of Pathways

In addition to sampling water quality from the volume of potentially useable groundwater resources, chemical analyses of "end-member" samples will provide the most robust opportunity to determine what fractions of the constituents detected in potentially useable groundwater are derived from specific sources, including those related to oil and gas. The end-members define a range of possible compositions that could mix and move to produce groundwater quality found in the aquifer volumes defined by the 3D mapping described above.

The figure below provides a conceptual illustration of the primary sources of water (end-members) and constituents that need to be considered in evaluating the sources of constituents in samples of groundwater. Conceptually, the end-members shown on the figure are classified into those that are unique sources that are not mixed (unmixed) with other sources and sources that are likely to be comprised of mixtures of other end-members. The chemical compositions of end-members can be temporally or spatially variable. If these variations within end-member compositions are less than the variations between different end-members and the groundwater of interest, geochemical mixing analysis can be successful in identifying source waters. If there are not unique chemical compositions for different end-members, geochemical mixing analysis will not be able to determine sources of chemical constituents in groundwater resources. Samples need to be collected of each end-member to determine the range of compositions at the scale of the regional analysis.

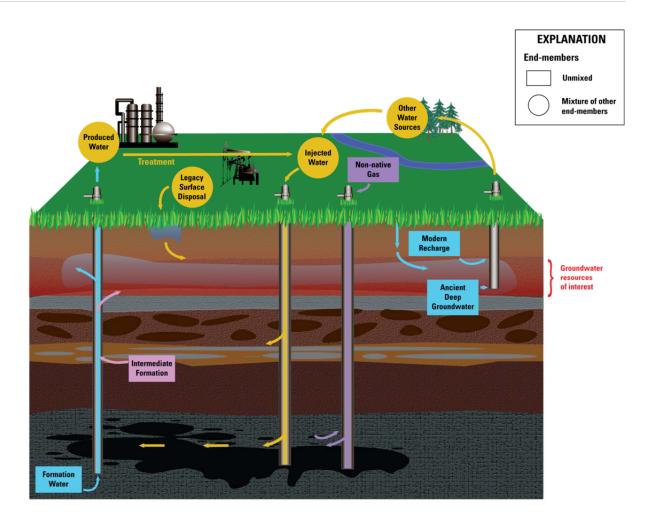


Figure 9. Conceptual diagram showing potential end-member sources that may mix in groundwater resources of interest.

The end-members discussed below represent conceptual classifications. The primary end-members to consider are:

Unmixed:

Formation water: water originally present within the oil and gas production reservoirs that is withdrawn with the oil. The composition of formation water can vary spatially, particularly between different petroleum pools and depths, and can vary over time at the same location as more mobile formation waters are drained and replaced with fluid from less permeable portions of the formation (Orem and others, 2014). Formation waters typically are highly saline (brines) and have chemical compositions that are distinct from other end-members. Formation waters are a primary component of produced waters, which include a mixture of formation waters and injected water (see below). Formation waters can potentially reach groundwater resources by leakage from wellbores or by spills and leaks from produced waters managed at the land surface.

Samples of oil-field seepage will also be collected as part of efforts to characterize formation waters from oil and gas fields. The compositions of oil-field brines from seeps can be used to evaluate the chemical signatures of oil-field fluids that follow natural pathways to reach the surface. These natural seepage end-member samples could help distinguish natural seepage of oil-field fluids from fluids that follow short-circuit pathways such as leaky wellbores.

Intermediate Formation: fluids present within formations overlying the oil and gas reservoirs and below groundwater resources that move upward to groundwater along wellbores. Most commonly, intermediate formation effects on groundwater have been detected as stray hydrocarbon gases that moved upward along wellbores. However, brines or connate fluids from intermediate formations could also potentially move upward along wellbores and influence groundwater. As with formation water, chemical compositions from intermediate formations could be spatially variable but may have compositions that are unique and distinguishable from other end-members despite that variability. Because intermediate formations are younger than deeper oil and gas source rocks, hydrocarbons in intermediate formations may be less mature and have chemical and isotopic compositions that are distinct from formation water.

Non-native gas: natural gas from other gas fields that is temporarily stored in oil and gas fields to help maintain reservoir pressure until recovered for use. Storage of non-native gas has been practiced in 12 oil and gas field in California (USEIA, 2008). The non-native natural gas may have hydrocarbon gas ratios and isotopic signatures distinct from native natural gas and hydrocarbon gases associated with native oil. Some stored gas may not be recovered and could persist in hydrocarbon reservoirs.

Modern recharge: groundwater recharge from precipitation, irrigation return, or canal leakage unaffected by oil and gas activities. Groundwater recharge in the last few decades generally has altered composition in comparison with pre-development recharge as a result of changes in land use, atmospheric compositions, and water management. Groundwater recharge in the last half century has concentrations of age tracers and noble gases, as well as some dissolved constituent concentrations, which are distinct from groundwater recharged before the widespread anthropogenic changes to the landscape and atmosphere. The category of modern recharge represents a category of sources, as recently recharged groundwater compositions vary with land use and water source. Sampling of shallow groundwater in areas unaffected by oil and gas near oil and gas regions is necessary so that any effects of oil and gas activities can be evaluated in comparison.

Ancient deep groundwater: groundwater in aquifers recharged during pre-modern times typically has different chemistry than modern recharge because of different hydrologic conditions near the land surface. Ancient deep groundwater has also generally been affected by rock/water interactions in the subsurface. Ancient deep groundwater end-members would be selected from areas where effects of oil and gas activities would not be expected, but from a similar hydrogeologic setting. More broadly, groundwater compositions are expected to fall along a continuum between modern recharge and ancient deep groundwater end-member compositions. Characterizing young and old groundwater end-members constrains estimates of groundwater compositions that may mix with water affected by oil and gas activities.

Mixtures of other End-Members: these represent major sources of water within oil and gas areas that are often mixtures of other types of water. These include:

Produced water: water mixed with hydrocarbons withdrawn from petroleum reservoirs. The produced water is a mixture of formation water and injected water from secondary recovery operations. During initial stages of hydrocarbon extraction, produced waters are formation waters. Once secondary recovery practices such as water-flooding, steam-flooding, and well stimulation occur, produced waters can include some of the fluids injected into the petroleum reservoir. Produced water compositions can change through time in response to reservoir management and secondary recovery activities (CCST, 2014; Orem and others, 2014). Analysis of historical data on produced water compositions in comparison with current compositions for a wider array of potential tracers can be useful to constrain the range of produced water compositions. Produced water is currently predominantly treated and reinjected for secondary recovery purposes or, less commonly, for disposal. Produced waters, once exposed to the atmosphere, may obtain noble and atmospheric gas signatures reset to the modern atmosphere, while retaining chemical compositions of dissolved constituents consistent with diluted oil field brines. These combined signals may be distinctive relative to other potential sources.

Legacy surface disposal: produced water historically disposed of in surface pits, ponds, or sumps. Percolation of fluids from these legacy disposal sources has been found to influence groundwater quality in some oil and gas areas in California. Recharge from produced water surface disposal sites could be modified by treatment, evaporation, biodegradation, and sorption, perhaps resulting in chemical and isotopic characteristics that differ from the produced water. Groundwater-quality monitoring related to legacy surface disposal is managed by Regional Boards and is not currently planned to be part of the regional oil and gas groundwater monitoring program. However, some samples of groundwater affected by legacy surface disposal should be collected to characterize signatures of this source for comparison with other potential sources.

Injected water: water injected into the subsurface for secondary recovery of hydrocarbons and/or maintaining fluid pressures in petroleum reservoirs or injected into other subsurface formations for waste disposal. Injected water consists of produced waters, commonly modified by treatment or amendment, sometimes mixed with other water sources such as water from wells or surface-water allocations. Amendments may include chemicals that allow water to be injected without clogging injection wells or the nearby formation (see earlier discussion). Injected water could include injections for steam- or water-flooding or can include well stimulation fluids. As with other end-member categories, there is spatial and temporal variability in chemical compositions. Characterization of injected water end-member(s) for the regional monitoring program would involve sampling an ensemble of injected water sources in an attempt to identify chemical or isotopic signatures that would distinguish these sources from other potential sources.

Other water sources: other sources of water used for injection include groundwater pumped from wells or surface-water, including canals, streams, and reservoirs. In some cases, multiple other water sources may be used or the mix may change over time. If other water sources comprise a substantial fraction of the injected water, these other water sources should be characterized. For many constituents, these

other water sources may have the effect of diluting constituents associated with produced waters but may have isotopic values or ratios of constituents distinctly different from oil field brines.

These end-member samples represent a basic list for conceptually simple systems. The source waters would need to be sampled for the same suite of analytes as the groundwater samples. Given the complexity of hydrologic systems and changes in the management practices of highly engineered oil and gas reservoirs, it should be recognized that end-member signatures do not necessarily stay constant with time. For this reason, mining of historically available data to evaluate changes in end-member concentrations should be included in the data analysis as part of this element.

It is important to note that the sources of water and solutes potentially affecting usable groundwater could be complex and variable over time, particularly in some California oil and gas fields that are highly engineered. Water and/or steam flooding are widely used in most California oil and gas fields (CADOGGR, 2014). The sources of water used for these purposes are dominated by produced waters from oil and gas extraction but can vary over time and also include local groundwater and surface water, imported water, and other brackish or saline water pumped from the subsurface. Water injected for water and steam flooding typically contains additives used to facilitate flushing or limit deleterious effects such as corrosion and clogging and may be treated before injection, particularly for source water for steam flooding. Apart from sources of waters injected for secondary recovery purposes, fluids (liquid or gas) are also injected into some petroleum reservoirs to maintain pressure in the field and have also been used for pilot tests of gas-driven enhanced recovery (for example, Sullivan 1963). A number of depleted oil and gas fields in California have been used for storage of natural gas from other locations (CADOGGR, 2014; USEIA, 2008). These stored natural gas sources may have chemical and isotopic compositions that differ from native oil and gas hydrocarbon signatures. The stored gases may be discerned from native sources using chemical and isotopic analyses (for example, Revesz and others, 2012; Darrah and others, 2014). However, if the gas storage occurred in the past, it may not be possible to characterize the composition of the imported gas.

Many studies have noted that the ratio of produced water to oil tends to increase through time (Clark and Veil, 2009) and that the chemistry of produced waters can change over time (Orem et al., 2014; CCST, 2014). The changes can occur even if secondary recovery methods involving introduction of new fluids into the reservoir are not used. The concentrations in produced waters also change as a result of reservoir management activities such as steam and water flooding. Usually waters added for secondary recovery are the same produced waters removed or are diluted with fresher waters. In the latter case, the concentrations of constituents in produced waters decrease.

These complex characteristics of potential source waters associated with oil and gas activities need to be recognized as part of a regional monitoring program, but do not necessarily preclude using geochemical and hydrologic data to discern the effects of oil and gas activities on usable groundwater. Keys to addressing the complexities are: an inventory of historical sources and practices, analysis of available historical data to discern changes in the chemistry of potential source waters through time, identifying relations between chemical and isotopic signatures in current samples to more limited data

types available in historical data, and use of ratios of constituents such as chloride, iodide, bromide, boron, and lithium that may be diagnostic of solute sources even as they are diluted.

If there is little differentiation between the general chemical characteristics (dissolved solids, inorganic major, minor, and trace elements) of petroleum production zone water and groundwater, for example, if both are freshwater, discerning the effects of fluid movement from oil and gas zones to groundwater could focus on the abundance of constituents uniquely associated with petroleum production zones, secondary recovery fluids, or well stimulation, including dissolved hydrocarbons, short-chain hydrocarbon gases, or semi-volatile organic compounds. Moreover, fluids from petroleum formations reaching groundwater by fast-pathways such as wellbores would typically have noble gas signatures and possibly water and solute isotopic values that would contrast with those of shallower groundwater. Given analysis of samples for a wide array of potential tracers, it is likely that some constituents having contrasting concentrations would be identified that would allow tracing of fluids from petroleum zones. Note that water samples from long-screened production wells could be highly mixed and might not indicate clear water and solute source signals but a collection of samples from different depths in the wellbore. Samples from discrete depths in the wellbore, coupled with wellbore flow profiles, could yield more detailed information on the vertical distribution of water quality that would allow sources to be discerned.

If the presence of petroleum zone fluids in groundwater is suspected but unresolved based on sampling results, temperature could serve as potential tracers of fluids from production zones entering groundwater. Fluid temperatures are generally expected to be higher in petroleum production zones than in overlying groundwater. Groundwater temperature data can typically be collected at many locations at relatively low cost. The presence of anomalously elevated temperatures in profiles in groundwater wells could provide an indication of fluids from deeper zones that could be further investigated with detailed sampling in zones with temperature anomalies. Temperature could potentially be used a reconnaissance tool for identifying wells to sample according to a knowledge-based sample design.

Alternatively, if no ambient tracers for distinguishing petroleum production zone fluids from overlying or adjacent groundwater are identified unique tracers could be added to fluids injected into production zones. These artificial tracers would need to be conservative with fluid movement (non-reactive), non-hazardous, inexpensive, and easily detected. Because gases can move faster vertically along preferential pathways than dissolved constituents, addition of a unique gas with injected fluids and subsequent detection in monitoring samples could serve as an early-indicator of fluid exchanges that could affect groundwater quality. Because the volume of tracer introduced would be very small in comparison with the volumes of recycled fluids injected, the tracer tests might need to continue for an extended period of time and over a large area, such as at a whole oil-field scale.

Geophysical and Hydraulic Information to Determine Flow Gradients

As part of characterization, water-level/pressure data from groundwater aquifers, oil and gas production zones, and injection zones need to be compiled and analyzed to determine whether fluids potentially affected by oil and gas activities are expected to move towards or away from usable groundwater

resources. Vertical and lateral head gradients indicate which direction fluids are expected to move and, in conjunction with estimated hydraulic properties, can be used to estimate groundwater velocities. The water-level/pressure data will need to be compiled from a variety of sources, including CADWR (including CASGEM), CADOGGR, USGS, local agency, and private company data). Vertical head profiles from the water table through usable groundwater resources to oil and gas production zones need to be determined wherever possible. Understanding head gradients provides the physical context for assessing whether it is physically plausible that fluids affected by oil and gas activities could impact groundwater resources, either from activities at the land surface or in the deep subsurface.

Head gradient profiles need to be constructed with recognition of what data may be missing. For example, studies in Pennsylvania and Western Canada concluded that, on the basis of chemical and isotopic signatures and other data, the source of methane and other stray hydrocarbon gases in groundwater aquifers overlying oil and gas fields was not the petroleum production zones, but rather natural gas from formations between the production zones and aquifer moving up wellbores (Harrison, 1983; 1985; Muehlenbachs, 2012; Tilley and Muehlenbachs, 2013). Similar situations could exist in California. In this case, head data in the formations between oil and gas reservoirs and groundwater aquifers would be necessary to understand the head gradients driving fluid flow towards the aquifer. An understanding of the complexities of the subsurface will be required to carefully assess whether the available head data is sufficient to characterize the important hydrologic gradients and flows in the system.

In addition to compiling and/or collecting profiles of pressure and geophysical logs to evaluate salinity, temperature logs should also be compiled from existing records and collected in new monitoring wells drilled as part of the probabilistic sampling step. The temperature logs are an effective tool for evaluating horizontal and vertical groundwater flow patterns through usable groundwater zones and into underlying buffer and oil and gas production zones. Perturbations in the geothermal gradient in temperature logs can provide information about lithology changes as well as horizontal and vertical groundwater-flow patterns (Keys and MacCary, 1971; Beck, 1976; Michalski, 1989; Williams et al., 1994; Hurwitz et al., 2010). Generally, groundwater temperature increases with depth, and the global average is about 25 degrees Celsius (°C) per kilometer. The geothermal gradient in sedimentary basins generally exceeds this average because of the relatively low thermal conductivity of sedimentary materials (Ingebritsen and Sanford, 1998). Groundwater temperature is related to factors such as lithology (which affects thermal conductance), depth, recharge source, and residence time within the aquifer. Measured temperature logs, when expressed as a measured vertical temperature gradient and compared with the geothermal gradient, can be used to identify potential zones of groundwater flow. Depth intervals exhibiting greater temperature perturbation can be interpreted as zones of greater flow (Everett and others, 2013). For example, horizontal flow in the aquifer may appear as a deflection or an interval of constant temperature in the temperature log. Moreover, temperature logs can be useful for evaluating flow patterns related to injection of waste fluids because of the temperature differences between injection water and the surrounding formations (Land and others, 2004). Consequently, for study unit characterization analyses, available temperature logs should be compiled and analyzed to determine if they are suitable for evaluating temperature gradient anomalies.

The products for this characterization task will be maps and profile plots that show the distribution of pressure, and temperature and the insights that it provides regarding potential interactions between oil and gas activities and groundwater quality.

Past Subsidence

Land deformation can be a major factor in compromising well integrity, which can facilitate well bore transmission of constituents between zones where oil and gas activities are occurring and potentially useable groundwater resources.

Subsidence can occur as a result of oil and gas field operations (citations) and is generally managed by injecting fluids in a manner which maintains pressure in the depleted reservoir. In diatomite fields, subsidence is an ongoing management challenge and has historically caused a significant number of well failures and damaged on-site infrastructure. The spatial relationship between areas of potential subsidence and potential useable groundwater resources is key to determining whether these processes might pose a risk. However, subsidence due to local groundwater pumping above zones where oil and gas development and waste disposal is taking place is also a potential mechanism by which oil and gas well integrity can be breached.

Land deformation and subsidence are thus expected to be directly linked to groundwater quality in and near oil and gas fields and map overlays of past deformation may provide explanatory variables for pathway identification.

Salinity Distribution Time Series

A time series of 3D salinity distributions can be developed from geophysical logs taken during sequential well installations. Evidence of change in salinity distributions would indicate groundwater flow over time, which would in turn help support further risk assessments.

Analysis Step

Wells sampled as part of the regional monitoring would be attributed with a large ensemble of explanatory variables related to the process by which constituents might have been transported and/or formed, many of which will be developed during characertization of geologic features. Explanatory variables would include source (proximity and density of a variety of potential sources), transport (geochemical and physical characteristics of the groundwater system surrounding the well), and receptor (characteristics of the wells sampled) variables. Statistical analysis of the relations of water quality measures (dependent variables) to potential explanatory variables (independent variables) at local, regional, and statewide data sets would provide an opportunity for understanding factors influencing potentially useable groundwater quality in oil and gas areas.

The general process for determining predominant pathways for groundwater quality degradation as a result of oil and gas activities using geochemical data consists of:

- Comparing groundwater chemical and isotopic signatures to end-members to identify potential sources that could explain the detected signatures, while excluding other potential sources that are not consistent with the detections.
- Evaluate all available information on potential pathways that could allow the detected signatures to move from the potential sources to sampled groundwater, including analysis of spatial patterns in detected groundwater signatures and potential pathways.
- Refine the list of potential pathways by identifying those consistent with multiple chemical and isotopic signatures in groundwater.
- Evaluate whether hypothesized pathways are physically plausible on the basis of all available ancillary data such as well construction, hydrogeologic, and pressure distribution data.

An example illustrates the process of interpreting pathways. Darrah and others (2014) conducted a study of mechanisms of hydrocarbon gas contamination in drinking-water wells overlying the Marcellus and Barnett shale's. The study determined that specific clusters of groundwater contamination were due to "hydrocarbon gas leakage from intermediate-depth strata through failures of annulus cement, faulty production casings from the target gas zone production, and underground gas well failure". The study drew these conclusions utilizing hydrocarbon gas concentrations, ratios, and isotopic signatures, noble gas analyses, and dissolved inorganic constituents. Groundwater supersaturated with methane in the absence of high chloride, indicative of background natural brine seepage from deep formations, but associated with deep geogenic noble gas signatures occurred less than 1 km from gas drilling sites. Hydrocarbon gas detection and geogenic noble gas signatures detected in groundwater in the absence of natural brine seepage signatures were deduced to occur by movement of gases along fast paths (leaky wells). Hydrocarbon gas ratios and isotopic signatures were used to separate intermediate and production zone sources of stray hydrocarbon gases.

Another example is the use of end-member mixing to distinguish between formation water leaking through a failed casing, surface spills/disposal percolating down, waste injection, and reinjected steam flooding, because the isotopic and chemical composition of native formation water changes during the various production steps. When the formation water is undisturbed, it has noble gas concentrations and isotopic ratios characteristic of a deep crustal reservoir that has been isolated from the atmosphere for tens to hundreds of thousands of years. When these fluids are pumped and brought to land surface (now produced waters), their dissolved gases equilibrate with the atmosphere, shifting the gas ratios and concentrations. Produced waters reinjected as waste have atmospheric characteristics (Darrah et al. 2014). When produced waters are recycled and heated for steam flooding (~300 F), atmospheric gases are lost and these new high temperature fluids will have unique isotopic and chemical characteristics. Based on these shifts in dissolved gas characteristics, it is possible to distinguish between formation water leaking through a failed casing, surface spills/disposal percolating down, injected wastes, and reinjected steam flooding.

Summary

In summary, the products of the characterization phase would include:

- 3d maps of potentially useable groundwater resources and currently used groundwater in spatial relationship to oil and gas development activities with geological framework information for intervening material
- Initial vulnerability categorization of every oil and gas field
- Baseline water quality characteristics of used and potentially useable groundwater that can serve as context for well- and event-specific monitoring
- Identification of pathways along which constituents from oil and gas development activities have traveled into potentially useable groundwater

Phase 2: Designing Follow-Up Monitoring Plans

The primary tasks of a Statewide program to monitor the effects of oil and gas development on groundwater resources are to identify the extent and magnitude of effects, identify the primary pathways through which effects occur, and develop understanding of the factors affecting the vulnerability of usable groundwater resources to oil and gas activities. The second phase of the program is designed to use information produced during the characterization phase to designing follow-up monitoring of specific pathways identified in the first phase, better distinguish between different causal mechanisms of problematic pathways such as well bore integrity, and establishing low-intensity networks in areas without current pathways to monitor for new pathway formation using trend analysis. During this phase, study units will be reconfigured and sampling approaches tailored to conditions found within each oil and gas field.

The discussion which follows uses a set of hypothetical case examples to articulate the design concepts for monitoring different situations we expect to emerge as a result of the characterization phase. Cases are described in the most simple terms, but real-world cases will likely involve a combination of approaches because environmental settings are more complex. We use the word "concept" here instead of "criteria" because each situation will have unique conditions that can't be pre-judged, but there are still basic principles at work in any design process. The five cases discussed below address situations where 1) no connection is found between oil and gas development activities and potentially useable groundwater, 2) both the source and pathways are defined well enough to establish sentinel wells and geophysical monitoring for early warning of transmission, 3) well bore integrity is identified as a problem and detailed linkages between structural integrity and water quality need to be examined to distinguish between potentially manageable issues (for example, adopting the use of material more flexible than cement) and unmanageable issues (leaking abandoned wells), 4) injected waste is not confined to the exempted zone and has been moving into or towards potentially useable groundwater resources, and 5) a geochemical signature is identified but the source and pathways need to be better characterized.

Case 1: No Transmission Pathways

In this hypothetical case, the characterization phase of the regional program has found little evidence of oil and gas-related constituents in potentially useable groundwater, no anthropogenic pathway can be

linked to observed concentrations in groundwater. Such a situation would be indicated when groundwater samples contain deep formation tracers (such as hydrocarbon gases and noble gases) co-occurring with dissolved solutes because all of the constituents are moving slowly through porous natural formations and flow occurs over geologic time periods. The long-term goal in this case is to determine if new pathways emerge. That goal can be met by a) periodically resampling using the probabilistic design and well network to changing water quality, and b) periodically collecting new end-member samples of fluids used in well stimulation and enhanced recovery projects, produced water. New end-member samples are needed to account for any major changes in oil and gas development practices, that is to say end-member compositions, that may occur after the characterization phase is complete.

The same methods described in the characterization phase section will be used to determine if there is evidence of a new transmission pathway.

Case 2: Source and Pathways Known and Sentinel Monitoring Network Can Be Established

This hypothetical situation would exist when pathways and contaminant transport have been identified as causal factors in water quality conditions in or near potentially useable groundwater. The basic monitoring design principles in this case are to establish a network of sentinel water quality monitoring wells along pathways, geophysical monitoring wells across the entire pathway including a buffer zone beyond it, and continue collecting samples of end-member sources. If new tracers specific to the situation are discovered as part of the characterization phase, they should be included in the water quality analyses.

An example of such a monitoring situation involves a contaminant plume emanating from a known source, migrating in a known direction, and of known extent at the time the sentinel site plan is designed. In this example, the objective is containment of the plume, to prevent it from crossing a predefined spatial boundary into a zone of usable groundwater. The zone within the plume at the time the boundary is defined as having unusable groundwater. At the minimum, a sentinel site design for this case would consist of a monitoring well installed downgradient of the plume at the pre-defined spatial boundary at the edge of potentially useable resources. A more thorough sentinel site design would consist of a multiple monitoring wells installed downgradient of the plume at different distances between the plume and the boundary, plus a few monitoring wells installed at the boundary on the other sides of the plume. This would allow for monitoring of the rate at which the plume is moving towards the boundary and also provide a safety margin in case the plume does not moved exactly in the direction predicted. As the desired degree of confidence that the plume is indeed contained increases, the number of monitoring wells required decreases. Careful planning and application of prioritization criteria must be used when scaling-up a sentinel site design to avoid the enormous costs that would be associated with installing a network of monitoring wells over the entire 3,000 mi2 that may be within the areal scope of the regional monitoring program.

Case 3: Well Bore Transmission Identified as Important Pathway

This hypothetical situation would be indicated when work in the characterization phase determined that water quality in or near potentially useable groundwater was affected by well bore transmission. Such a

situation would be indicated when samples are observed containing stray hydrocarbon gases with deep subsurface noble gas signatures but no dissolved hydrocarbon or brine solutes (Darrah and others, 2014). Well bore leakage can be correlated with specific well construction practices, well age, and the history of well use, known integrity problems, known pressure anomalies discovered during injection that may indicate cross-linking, and/or external factors such as land deformation. Determining which factors are associated with observed well bore transmission and which are not, or only present to a small degree, is necessary to design a long-term monitoring program based on those factors. For example, wells constructed under modern regulations may only be associated with changes in water quality when they are subjected to stress they were not designed for. Another potential finding is that integrity failure also correlates with the history of well use.

One basic principle for designing studies where external factors such as land deformation may play a major role in moving constituents beyond isolated zones is to find study sites where wells have similar histories and land deformation has occurred in one part of the area and not another (control set). A second basic principle is that detailed well integrity information needs to be gleaned from the well records and interpreted in the context of local forces. Frederich and others (2000) did this to determine what kind of forces were causing past well integrity problems in Belridge diatomite fields. The team was able to identify shear as the main forcing mechanism and document that most of the shear occurred at the boundary between the diatomite and the Tulare formation.

There are many examples of methods pertinent to this hypothetical case. Davies and others (2014) review past studies involving identification of casual factors in oil and gas well integrity problems. Others have investigated specific causes of failures in California (for example, Jordan and Benson, 2008). CADOGGR has indicated that oil and gas operators use the federal UIC program guidance (Engineering Enterprises, 1985) as a method for proactively identifying which wells may be potential contamination pathways as part of "Area of Review" requirements for underground injection projects and a similar approach may be useful in grouping wells in follow-up monitoring designs. Dusseault (2014) outlines steps for canvassing wells for leakage. In California, active wells and gas pipelines are regularly sampled by operators for gas leaks and monitored for pressure anomalies, abandoned wells are sampled before final closure and land use restrictions are attached to surface property when leaks are found, and injection wells undergo a periodic battery of integrity tests. The USGS is currently pilot testing a method for sampling methane, ethane, and CO₂ above abandoned wells to determine the utility of the method for distinguishing well bore leakage from abandoned compared to operational wells.

Case 4: Injected Waste Water Found Interacting With Potentially Useable Groundwater

CADOGGR and the SWRCB are currently reviewing elements of the UIC program and in particular where waste injection into and near useable groundwater has been documented (Bishop, 2014). The extent of changes in water quality caused by these practices is not known. Our working hypothesis is there may be additional cases where "exempt" aquifers do have a hydrologic connection to the larger aquifer systems and where ongoing waste injection may pose a future risk. One approach would be to review injection data for all waste disposal wells and identify those where there was no decline in "injectivity" due to pore clogging. The result would be an initial set of locations where zones may not be isolated from the surrounding system. Another approach might be to organize an oil-field scale tracer test.

CADOGGR currently requires periodic integrity tests of waste disposal wells and use of a tracer with a long enough life to be detected in subsequent water quality sampling might prove to be a more definitive diagnostic tool.

Case 5: Geochemical Signal Detected But More Information Needed to Characterize Sources and Pathways

The end-member mixing model approach using multiple tracers and the level of detail of information developed during Phase 1 may not be precise enough to distinguish between some of the source: pathway combinations. For example, the fluid injected into waste disposal wells has generally the same geochemical fingerprint as the fluid source for most water flood operations (if recycled produced water is the source). Leaks from inside these wells and from waste disposal areas might not have enough geochemical differences to conclusively determine which pathway was responsible. In these situations, approaches from cases 2) through 4) and the use of additional tools described below such as a detailed geological framework model may be needed to achieve more certainty about sources and pathways before a monitoring program can be designed.

Additional Monitoring Tools For High Vulnerability Areas

Additional monitoring may be useful in areas classified as high vulnerability in order to identify the processes and pathways for the transfer of fluids from oil and gas zones into shallower groundwater. Techniques for detailed characterization include high frequency monitoring of potentially useable groundwater chemistry, fluid pressures and dissolved gases, measuring temperature profiles (with depth), and the use of electromagnetic sensing devices to characterize well enhancement techniques.

High Frequency (Real-time) Gas Monitoring

Within high vulnerability areas, collection of high frequency data could provide insight on the effects of well stimulation on potentially useable groundwater systems. High frequency data could provide an early warning for changes in hydrologic conditions that could signal the effects of oil and gas development. High frequency or real-time data collection, relayed by telemetry, could provide data on conditions such as the vertical distributions of fluid pressure, temperature, electrical conductance, or total-gas pressure in multiple well monitoring sites.

To assess the impact of active oil and gas development on usable zones, it is possible to monitor the arrival of tracers in deep aquifer wells in real time (5-minute intervals). Generally, the speed of transport from a source to detection at a monitoring location, from fastest to slowest, is: pressure, volatiles (dissolved gases), dissolved constituents in water, and temperature. Monitoring multiple signals helps constrain understanding of the sources, mechanisms, and rates at which the effects of oil and gas activities could affect highly vulnerable potentially usable groundwater. Monitoring of faster signals, pressure and volatiles, could help provide early warning for signals that would arrive later, such as increased concentrations of dissolved constituents.

High frequency data could provide insight into changes in vertical gradients within potentially usable groundwater resources in proximity to oil and gas zones, which could change in response to oil and gas development activities. In addition, high frequency data collection could include monitoring volatiles (combustible or stray hydrocarbon gases) in deep aquifer wells in real time as a direct measure of oil and

gas effects. The transport of volatile gases can occur at rates orders of magnitude greater than transport of dissolved constituents through diffusion or advection. As such, the identification of volatile gases associated with oil and gas deposits, and specifically the unique isotopic ratios characteristic of oil and gas deposits, provide information about the impacts of oil and gas development and the possibility of an increase in vulnerability of usable waters.

Electromagnetic (EM) Sensing Techniques

Conductance information provides a powerful tool for discrimination of resistors (oil, gas & CO₂) from conductors (water, steam & chemicals). Improved knowledge about such fluid distribution and movement can improve characterization of the potential interactions between these reservoirs. Electromagnetic techniques utilize EM induction processes to measure one or more electric or magnetic field components resulting from transient or artificially-generated alternating current sources. The term 'electromagnetic' applies toward techniques which use low-frequency induction. Low frequency EM fields are primarily sensitive to the electrical resistivity of the earth.

Magnetotellurics (MT) is an electromagnetic geophysical method of imaging the Earth's subsurface by measuring natural variations of electrical and magnetic fields at the Earth's surface. Investigation depth ranges from 300m below ground by recording higher frequencies down to 10,000m or deeper with long-period soundings.

The application of these new EM technologies at selected sites, such as high vulnerability sites with thin separating units between potentially useable groundwater and oil zones, may allow for the characterization of the vertical and lateral extent of hydraulic fracking. Repeat EM conductance logging in PVC cased wells also could be used to identify changes in potentially useable groundwater salinity over time (Metzger et al., 2012). The electromagnetic induction tool (EM tool) is used to construct a continuous profile of electrical conductivity of the geologic formation penetrated by a borehole. The EM tool induces eddy currents that produce secondary magnetic and electrical fields. The receiver coil on the tool senses both secondary fields. The magnitude of the fields sensed is proportional to the conductivity of the surrounding media or bulk electrical and magnetic conductivity (McNeill and others, 1990). Natural variability in the EM-log conductivity is caused by physical properties of the geologic deposits. Coarser deposits are much more resistive than are the finer grained deposits when the pore water is not saline. Clay and silt material is intrinsically conductive. In addition, finer grained layers have the ability to retain chloride from evaporative salts long after salts have been flushed from adjacent coarser grained layers. This retention can cause EM-log conductivity in the finer-grained layers to remain high. When combined with other data, such as gamma-ray logs, the EM data can be used to identify and monitor zones of high-salinity water, such as formation water, through both blank and perforated PVC casing. EM logs therefore may reveal the relation between potentially usable groundwater, formation water, and stratigraphy at depths at which a well is not perforated.

Geological Framework Models

Geologic framework models are tools used to help determine how fluids can move through complex subsurface systems and are often the first step in creating a flow model. Oil and gas operators construct detailed framework models of petroleum-bearing formations and hydrologists do the same for

groundwater basins. A detailed description of an approach for constructing a framework model is described by Sweetkind, Faunt, and Hanson (2013). Figure 10 is extracted from that report and depicts how information can be extracted from water and oil well logs as the first step in constructing geologic framework models.

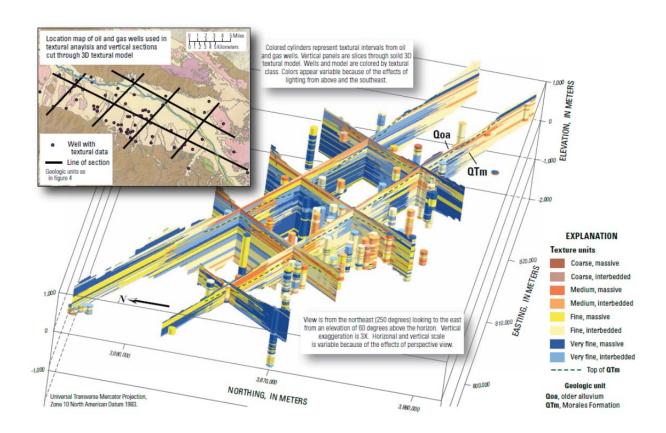


Figure 10. Perspective view showing results of 3-D textural modeling from oil and gas well data (Sweetkind, Faunt, and Hanson, 2013).

The process of building the 3-D framework will yield critical information for the characterization phase including the location and extent of potentially usable groundwater resources, the location and extent of waste disposal zones, characteristics of intervening material, and the distribution of existing wells. This information is needed to support the analysis of which combination of anthropogenic activity and transport pathways are most likely responsible for any observed oil and gas-related constituents found in the geochemical sampling work done in the first phase of the program.

Phase 3: Implementing Long-Term Monitoring Plans and Follow-up Study Phase

The third phase of the regional monitoring program would focus on:

- Implementing long-term trend monitoring to identify when new pathways are created;
- Implementing follow-up studies and modeling in high vulnerability areas; and

• Updating the State's electronic data collection, processing, and archiving system to include new monitoring

Hydrologic Models

There are many different types of models that can be used to simulate different hydrologic processes, that are relevant on different scales, and that can be used to address a wide variety of questions. The general approach to modeling is to start with the simplest systems and then add complexity if they leave major questions unanswered. The simplest is a conceptual model that estimates flow potential through intervening material by assigning transmissivity values to different geologic units based on material and thickness and by estimating flow gradients. If the conceptual model shows travel times that would pose moderate or high risks, then more a more detailed study of what is controlling the flow pathways and rates, gradients, whether there are preferential pathways involved, and what it would take to manage flow is warranted. At this point, more sophisticated modeling could be considered.

Specific characteristics of the area in question will determine whether a model based on water flow properties could provide flow rate estimates at a level of precision sufficient for system management, or whether models that are based on water, gas, and oil (multiphase flows are needed. MODFLOW is an example of the first type (Harbaugh, 2005). If heat and/or multiphase flow need to be considered, there are a number of options available from a variety of sources, including the USGS and the National Labs. For example, the fully compositional and thermal reservoir simulation based on a combination of the Automatic Differentiation-General Purpose Research Simulator (AD-GPRS) and multiphase equilibrium has recently been developed (Zaydullin and others, 2014). Predicting geochemical transformation of constituents along a transport path is yet another layer of complexity.

Pressure gradients in the vicinity of oil and gas fields are heavily managed as part of production operations, but these also exist in the context of basin-scale pressure forces (McPherson and Garven, 1999). At this time, we are assuming these basin-scale forces would not need to be accounted for in much smaller scale models of high vulnerability areas.

Some questions that modeling in general can help answer include identifying the appropriate locations and depth for monitoring wells, and predicted rates and extent of plume migration.

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Acronyms

AD-GPRS Automatic Differentiation-General Purpose Research Simulator

CADOGGR California Department of Conservation, Division of Oil, Gas, and Geothermal Resources

CADWR California Department of Water Resources

CASGEM California Statewide Groundwater Elevation Monitoring Program

CIWQS California Integrated Water Quality System Project

DDW State Water Resources Control Board Division of Drinking Water

DTS Distributed Temperature Sensing

DNA Deoxyribonucleic acid

EM Electromagnetic

ESRI Environmental Science Research Institute

GAMA Groundwater Ambient Monitoring Program

GAMA PBP Groundwater Ambient Monitoring Program Priority Basin Project

LLNL Lawrence Livermore National Laboratory

MT Magnetotellurics

MCL Maximum Contaminant Level

PDF Portable Document Format

PAHs Polycylic aromatic hydrocarbons

PVC Polyvinyl chloride

SB4 Senate Bill 4, California State Senate

SWRCB California State Water Resources Control Board

TAF Thousand Acre-Feet

TDS Total dissolved solids

U.S. United States

USDOE United States Department of Energy

USEIA United States Energy Information Agency

USEPA United States Environmental Protection Agency

USGS United States Geological Survey

USGS NAWQA United States Geological Survey National Water Quality Assessment Program

VOCs Volatile organic compounds

WDRs Waste Discharge Requirements

WCRs Well completion reports

WSPA Western States Petroleum Association