

**CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD  
LAHONTAN REGION**

**MEETING OF JANUARY 8-9, 2014  
BARSTOW**

**ITEM:** 2

**SUBJECT:** **UNITED STATES GEOLOGICAL SURVEY (USGS)  
PRESENTATION OF A PROPOSAL TO INVESTIGATE  
THE OCCURRENCE OF NATURAL AND  
ANTHROPOGENIC HEXAVALENT CHROMIUM AND  
ESTIMATE BACKGROUND CHROMIUM  
CONCENTRATIONS IN HINKLEY, CA NEAR THE  
PACIFIC GAS AND ELECTRIC COMPANY'S AREA  
IMPACTED BY CHROMIUM CONTAMINATION**

**CHRONOLOGY:** This chronology lists Water Board actions related to establishing background chromium concentrations in groundwater in the Hinkley area.

August 8,  
2008

Cleanup and Abatement Order No. R6V-2008-0002 required PG&E to implement actions to achieve plume containment and propose a feasibility study to clean up groundwater to background water quality.

November 12,  
2008

Amended Cleanup and Abatement Order No. R6V-2008-0002A1 established maximum and average background chromium concentrations for total and hexavalent chromium based on results of PG&E's 2007 Groundwater Chromium Background Study Report.

- March 9, 2011 Water Board members heard public concerns related to the validity of the 2007 Background Study and its results. Water Board members directed staff to obtain scientific peer review of PG&E's 2007 Chromium Background Study Report.
- March 15, 2012 Water Board members heard a summary of peer review comments received. The peer reviewers' comments were primarily critical of the 2007 Background Study Report. The criticisms are grouped into four categories:
- 1) Lack of aquifer-specific sampling
  - 2) Statistical methods and assumptions
  - 3) Uncertainty regarding historic plume migration
  - 4) Sample analysis quality control procedures

**DISCUSSION:**

Since December 2012, Hinkley stakeholders have been meeting monthly to discuss a revised approach to determining background levels of chromium in groundwater following peer review criticism of PG&E's 2007 Background Study Report. This Background Study Technical Working Group (TWG) is comprised of Water Board staff, a sub-group of the Hinkley Community Advisory Committee, the CAC's consultant (Project Navigator), PG&E and its consultants, and Dr. John Izbicki of the US Geological Survey.

Dr. Izbicki is a recognized expert on chromium in the Mojave Desert. As a TWG member, he has developed a draft study proposal to evaluate the occurrence of natural and anthropogenic chromium, and estimate background chromium concentrations in the Hinkley Valley.

The revised study will begin in mid-2014 and end in 2018. The estimated budget for the proposal is \$4.5 million. There are federal matching funds available to offset this cost.

The USGS, as a federal agency, is generally restricted from accepting funds from private entities such as PG&E, but may accept funds from State agencies to conduct investigations. PG&E provided funding for Dr. Izbicki's participation in TWG to develop the study proposal, and Water Board staff worked with the State Water Board's contracting department to set up a holding account to execute a contract between the Lahontan Water Board and the USGS using those funds. Similarly, to execute a contract for the USGS to implement this proposal, staff would continue to work with State Board staff to develop and manage a new contract, pending PG&E's funding of the study. Water Board staff would also continue to participate in TWG as the study moves forward, including reviewing interim and final documents.

**RECOMMENDATION:**

The Water Board may provide direction to staff as appropriate, including indicating support for staff's continued involvement in the TWG.

**ENCLOSURES**

<b>Enclosure</b>	<b>Item</b>	<b>Bates Number</b>
1	Draft Proposal: Occurrence of Natural and Anthropogenic Chromium near a Mapped Plume, Hinkley CA. Dr. John Izbicki, US Geological Survey	2-7
Comments on USGS Draft Proposal by TWG members:		
2	PG&E	2-51
3	Project Navigator/Community Advisory Committee	2-57
4	Water Board Staff	2-65

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# **ENCLOSURE 1**

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## PROJECT PROPOSAL COVER SHEET

<b>USGS Area:</b> Southwest	<b>Number:</b> CA14 X
<b>CENTER:</b> California Water Science Center	<b>DATE (Initial):</b>
<b>PROJECT LONG TITLE:</b> Occurrence of natural and anthropogenic Cr VI near a mapped plume, Hinkley, CA	<b>DATE (Revised):</b>
<b>PROJECT CHIEF:</b> John Izbicki	<b>BEGIN DATE: (mo/yr):</b> 10/13
<b>Cooperator(s):</b> Lahontan RWQCB	<b>END DATE: (mo/yr):</b>
	<b>Cooperator Contact(s):</b> Anne Holden <a href="mailto:Anne.Holden@waterboards.ca.gov">Anne.Holden@waterboards.ca.gov</a> (530) 542-5450

ADMIN USE ONLY:  Research  Resource Appraisal  Basic Data Collection  Technical Support

### PROJECT TYPE:

<b>Standard:</b> X	<b>Monitoring Only:</b>	<b>Add-on or Extension of Current Work (include previous proposal name and number):</b>
<b>Proposals written for RFPs:</b>	<b>USGS-Funded Projects:</b>	<b>Other (repetitive work, technical advice, etc.):</b>

### PROPOSED PUBLICATION TYPE(S):

Scientific Investigative Report (SIR): \_\_\_\_\_ Open File Report (OFR):  Fact Sheet:  Data Series: \_\_\_\_\_  
 Journal Article:  Letter: \_\_\_\_\_ Professional Paper: \_\_\_\_\_ Book Chapter: \_\_\_\_\_  
 Abstract: \_\_\_\_\_ Poster: \_\_\_\_\_ Other (specify) \_\_\_\_\_

### ESTIMATED PROJECT FUNDING

Choose one:  firm  probable  questionable

FISCAL YEAR	2014	2015	2016	2017	2018	Total (FY-13 costs)
OFA/FEDERAL <sup>1</sup>	\$	\$	\$	\$	\$	\$
COOP REPAY <sup>2</sup>	\$	\$	\$	\$	\$	\$
COOP DIRECT <sup>3</sup>	\$	\$	\$	\$	\$	\$
COOP UNMATCHED <sup>4</sup>	\$	\$	\$	\$	\$	\$
COOP TOTAL <sup>5</sup>	\$	\$	\$	\$	\$	\$ 3,551,567
FMEs:	\$	\$	\$	\$	\$	\$ 997,500
<b>TOTAL FOR FY:</b>	\$	\$	\$	\$	\$	\$ 4,549,067

**NOTE:** Costs are estimated costs for FFY-13. After approval of the proposal scope by the TWG, cost will be distributed between fiscal years according to the project timeline, and burdened at a rate of 5 percent per year to account for inflation

## Project Proposal Summary

### Occurrence of natural and anthropogenic Cr VI near a mapped plume, Hinkley, CA

By: John A. Izbicki

**Problem:** The Pacific Gas and Electric Company (PG&E) Hinkley Compressor Station, 3 miles southeast of Hinkley, CA and 80 miles northeast of Los Angeles, is used to compress natural gas as the gas is transported through pipelines from Texas to California. Between 1952 and 1964, cooling water was treated with a compound containing chromium to prevent corrosion within the compressor station. This water was discharged to unlined ponds, resulting in contamination of soil and groundwater within the underlying alluvial aquifer. In 2007 a background study estimated average Cr VI concentrations in the area of 1.1 micrograms per liter ( $\mu\text{g/L}$ ). The normal 95 percent upper tolerance level of 3.1  $\mu\text{g/L}$  from the background study was adopted as the cleanup level for remediation at the site. The Water Board agreed to revisit the 2007 background Cr VI study given criticism of the 2007 study, and the increase in mapped extent of the plume between 2008 and 2011.

**Objectives:** The purpose of this study is to evaluate the occurrence of natural and anthropogenic Cr VI, and estimate background Cr VI concentrations upgradient, near the plume margins, and downgradient from a mapped Cr VI contamination plume near Hinkley, CA.

**Science Plan:** The cooperator for this study is the Lahontan Regional Water Quality Control Board. The scope of the study was developed by the U.S. Geological Survey in collaboration with the Technical Working Group (TWG) composed of local stakeholders (the Hinkley Citizens Action Committee, CAC), community advisors (Project Navigator, Inc.), State regulatory agencies (Lahontan Regional Water Quality Control Board), and Pacific Gas and Electric and their consultants. The scope includes the following tasks: 1) evaluation of existing data, 2) sample collection and analyses of rock and alluvium, 3) sample collection and analysis for water chemistry and multiple chemical and isotopic tracers to evaluate the potential occurrence of natural chromium and the potential occurrence of low fraction mixtures of water recharged when releases of Cr VI from the compressor station occurred, 4) data collection within western, northern, eastern parts of the study area to address specific issues relative to the occurrence of Cr VI within those subareas, 5) use of an existing model to evaluate historic and present-day groundwater movement, 6) evaluation of results to determine the occurrence of natural and anthropogenic chromium, and 7) estimation of background Cr VI concentrations. The study will begin in Federal Fiscal Year 2014 and end in 2018. An initial fact-sheet style report describing the study approach, an interim report describing selected preliminary results, and a final report will be produced.

**Relevance and Benefits:** Results of this study will be used to help establish clean-up goals for the Cr VI contamination plume near Hinkley, CA. This proposal will contribute to the U.S. Geological Survey's ability to "ensure adequate quantity and quality of water to meet human and ecological needs in the face of growing competition among domestic, industrial-commercial, agricultural, and environmental uses" as described in the U.S. Geological Survey Science Strategy (2007). The proposal is within the U.S. Geological Survey Water Resources Mission Areas to "define and better protect the quality of the Nation's water resources".

## Occurrence of natural and anthropogenic Cr VI near a mapped plume, Hinkley, CA

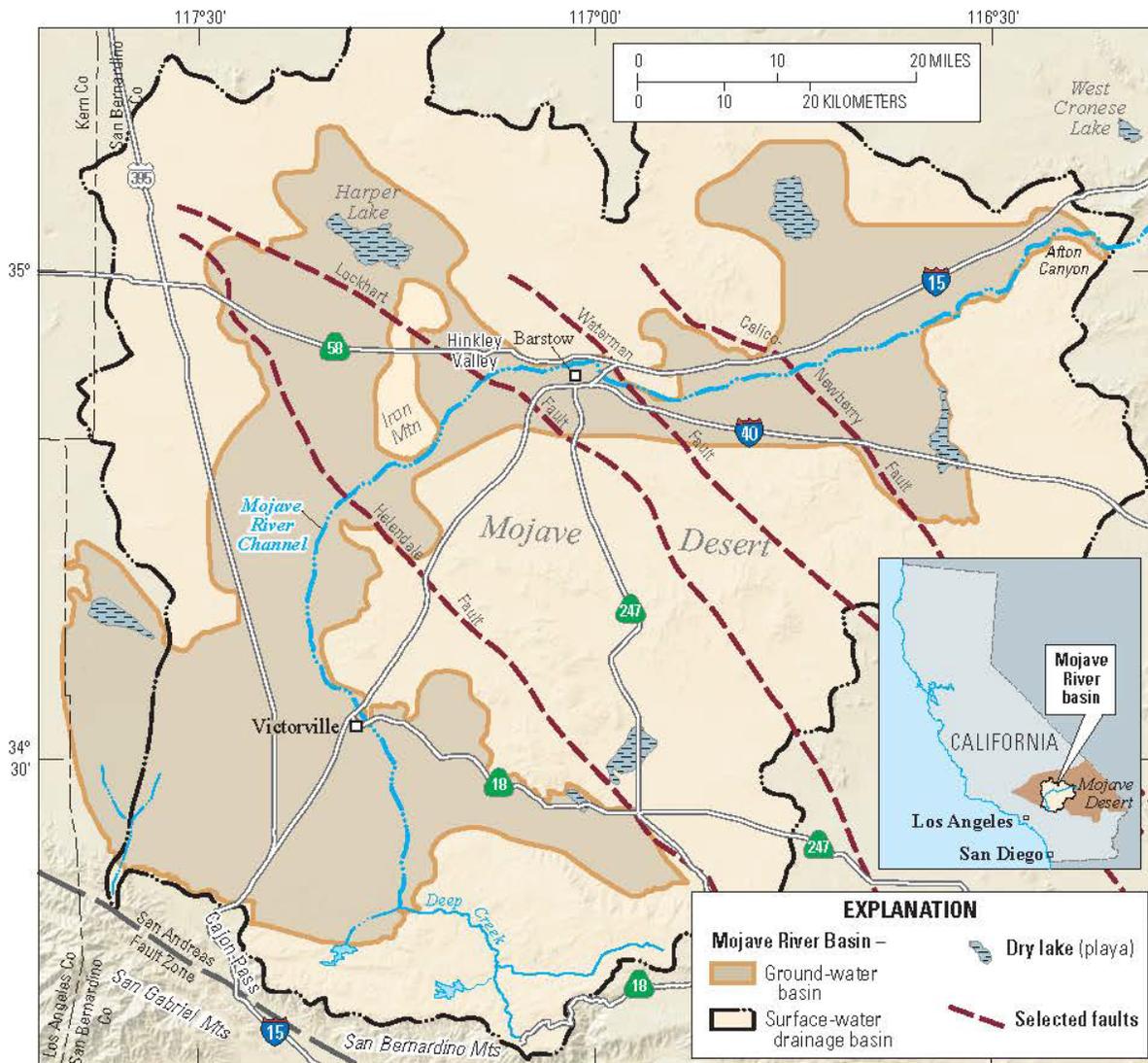
By: John A. Izbicki

**Problem:** The Pacific Gas and Electric Company (PG&E) Hinkley Compressor Station, 3 miles southeast of Hinkley, CA and 80 miles northeast of Los Angeles (fig. 1), is used to compress natural gas as the gas is transported through pipelines from Texas to California. Between 1952 and 1964, water treated with a compound containing chromium was used to prevent corrosion of pipes and machinery within the compressor station. This water was discharged to unlined ponds, resulting in contamination of soil and groundwater within the underlying alluvial aquifer with total and hexavalent chromium (Cr VI) (LRWQCB, 2012a).

The California Water Resources Control Board requires clean-up of discharges to either background water quality, or to the best water quality reasonably obtainable if background water quality cannot be restored. Background is defined as the water quality that existed before the discharge occurred (LRWQCB, 2012a). A 2007 background study (CH2M-Hill, 2007) estimated average Cr VI concentrations near the mapped plume of 1.1 micrograms per liter ( $\mu\text{g/L}$ ). The normal 95 percent upper tolerance level of 3.1  $\mu\text{g/L}$  from the 2007 background study was adopted as the cleanup level for remediation activities at the site. On the basis of those data, in 2008 the mapped extent of the plume was about 2 miles north of the compressor station and the plume was about 1 mile wide (LRWQCB, 2008). By 2011 the mapped extent of the plume increased to 5.4 miles long and 2.4 miles wide. The increased extent of the plume may have resulted from a combination of: 1) movement of Cr VI with groundwater (the plume is bigger), 2) more comprehensive sampling of areas surrounding the 2008 mapped plume extent (there are more data), and 3) improved understanding of the distribution of chromium in different layers within the aquifer and how to sample those layers to obtain maximum concentrations (the data are higher quality) (LRWQCB, 2012b).

The 2007 background study was criticized by independent reviewers for: 1) use of existing wells not specifically designed for groundwater monitoring and often having incomplete construction data, 2) inconsistent spatial and temporal distribution of data from wells used for the background study, 3) statistical handling of the data with respect to less than values, outliers, and representative concentrations from sampled wells, 4) uncertainty as to the historic extent of Cr VI contamination at the site, and 5) lack of a site conceptual model that includes the effects of pumping and ongoing remediation on groundwater flow and contaminant movement (Lahontan Regional Water Quality Control Board, 2012b). The Water Board agreed to revisit the background Cr VI given criticism of the 2007 background study and the increased mapped extent of the plume.

In response to criticism of the 2007 study, PG&E proposed a statically-based approach for a revised background study (Stantec, 2012). That proposal included installation of almost 30 wells, uniformly distributed near the center of township and range grids throughout the study area, with one-year of data collection from the wells. Although statistically unbiased and designed to estimate the average Cr VI concentrations within the volume of groundwater sampled, the proposed study design provided limited evaluation of the hydrologic history of the area with respect to historic groundwater movement relative to contamination from the compressor station, and limited evaluation of the potential geologic sources of natural chromium within the study area.



**Figure 1.**—Mojave River groundwater basin

**Hydrogeologic setting:** Hinkley Valley, within the Harper Valley Groundwater Basin (Department of Water Resources, 2004), is part of the Mojave River groundwater basin (Stamos and others, 2001) (fig. 1). The geologically recent development of the Mojave River is the result of movement along the San Andreas Fault and the subsequent opening of Cajon Pass between the San Bernardino and San Gabriel Mountains (Meisling and Weldon 1989). As the pass opened, increased precipitation within the Mojave Desert near the pass gave rise to the Mojave River. Transport of alluvium as the river extended farther into the Mojave Desert created interconnected alluvial aquifers, including Hinkley Valley, that extend from near Cajon Pass to Soda (dry) Lake more than 100 miles from the mountain front (Tchakerian and Lancaster, 2002; Enzel and others, 2003).

Hinkley Valley is bounded to the west by Iron Mountain composed of quartzite and marble, with smaller hills to the north composed of quartz monsonite. The valley is bounded to the east by Mount General composed of quartzite, marble, and Tertiary-age dacitic volcanics, with smaller hills to the north

composed of quartz monsonite (Dibblee, 2008). The northwest trending Lockhart and Mount General Faults are present along the southwest and northeast parts of the valley, respectively. To the north, there is a narrow gap separating Hinkley and Water valleys. The Mount General Fault passes through this gap and volcanic rocks are exposed within the gap (fig. 2).

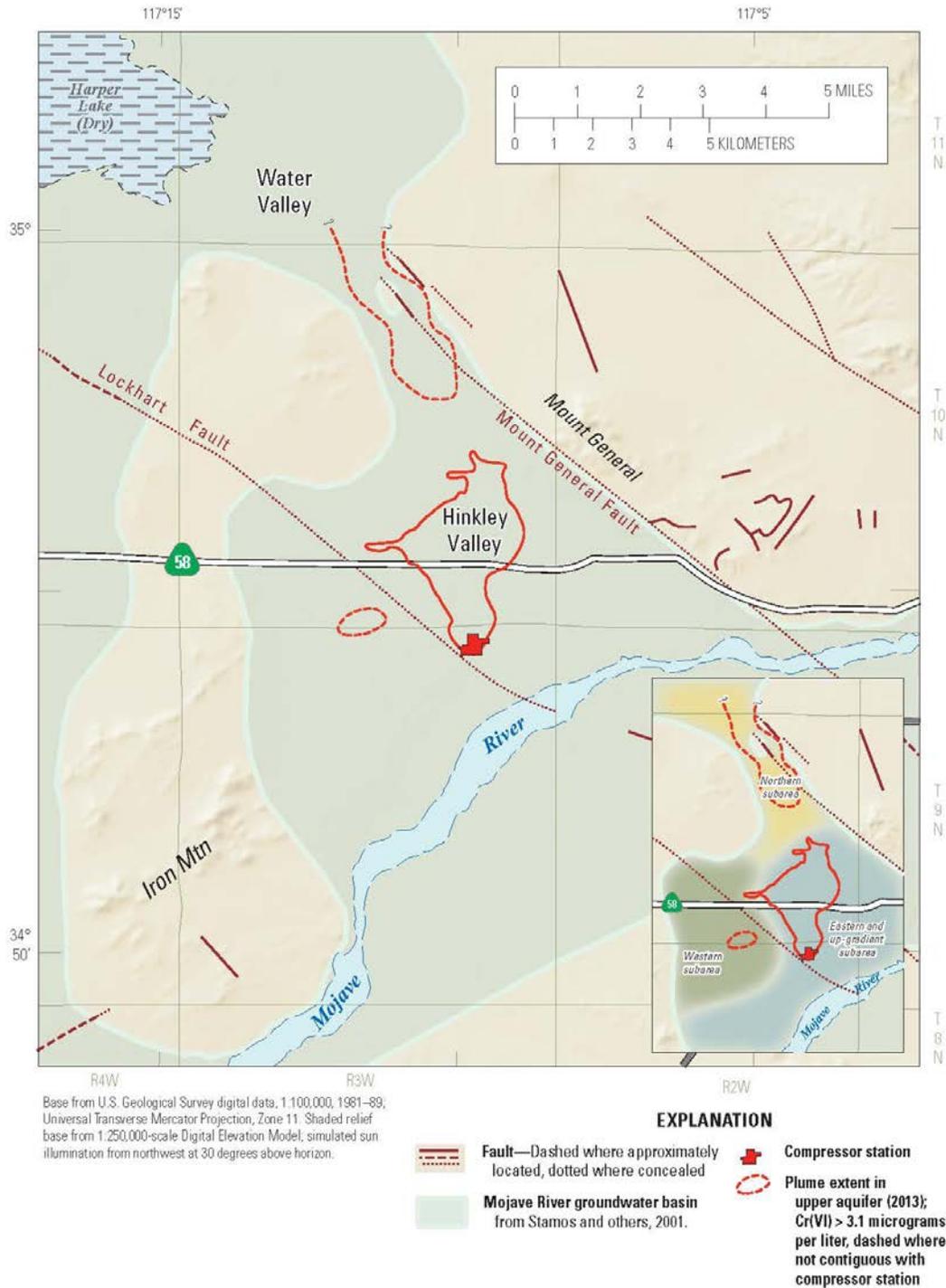


Figure 2.—Study area location.

Alluvial deposits within the valley consists of alluvial-fan deposits eroded from highlands along the valley margins, and alluvium from the Mojave River eroded largely from granitic rock in the San Bernardino Mountains 40 miles to the south. Alluvium within the valley is divided into an upper and lower aquifer by the “blue clay”. The upper aquifer is further divided by the “brown clay”. Alluvium is underlain by bedrock or weathered bedrock. Where the blue clay is not present the upper aquifer is in hydraulic communication with the surrounding bedrock. Detailed descriptions of alluvial aquifers and confining clay units within those aquifers are available in (CH2M-Hill, 2013a). Alluvium from the Mojave River composes the floodplain aquifer (Stamos and others, 2001) within the upper aquifer. The floodplain aquifer is present through the center of the valley and through the gap at the north end of Hinkley Valley into Water Valley.

The climate is arid, with hot summers and cool winters. Average annual precipitation is less than 110 millimeters per year (Barstow, CA, station 040519, 1903-1980 <http://www.wrcc.dri.edu/cgi-bin/cliMONtpre.pl?ca0519>, accessed July 16, 2003). In the Mojave Desert, little or no groundwater recharge occurs from infiltration of precipitation or from infiltration of intermittent runoff in small streams (Izbicki and others, 2007). Most groundwater recharge to the Hinkley Valley occurs as infiltration of streamflow from the Mojave River along the southern edge of valley (Thompson, 1929; Stamos and others, 2001; Izbicki, 2004). Streamflow in the Mojave River originates primarily as precipitation and runoff from near Cajon Pass and the San Bernardino Mountains (Izbicki, 2004). Large streamflows in the Mojave River that recharge the alluvial aquifer within Hinkley Valley occur infrequently, and many years may pass without significant flow along this reach of the river, and without groundwater recharge (Stamos and others, 2001).

Under predevelopment conditions, groundwater flow through Hinkley Valley was from intermittent recharge areas along the Mojave River, to the north through a gap at the northern end of the valley into Water Valley towards discharge areas near Harper (dry) Lake (Thompson, 1929; Stamos and others, 2001; Izbicki, 2004). Water levels in parts of Hinkley Valley were within 15 feet of land surface and flowing wells were present to the north in Water Valley (Thompson, 1929). On the basis of water level differences, the Lockhart Fault is an impediment to groundwater flow in the western part of Hinkley Valley (California Department of Water Resources, 1967). The Lockhart Fault does not impede groundwater flow in recent alluvial deposits along the Mojave River (Stamos and others, 2001). The extent to which groundwater flow is impeded by the Mount General Fault between Hinkley and Water valleys is not known.

Shallow depths to water enabled agricultural development by early settlers. Agricultural pumping peaked in this part of the Mojave River groundwater basin in the mid-1950's, and gradually declined in the following decades (Stamos and others, 2001). Water-level declines in some areas as a result of agricultural pumping were greater than 70 feet (California Department of Water Resources, 1967). In parts of the valley, formerly saturated alluvium was dry, and limited pumping by domestic wells was sustained by withdrawals from the underlying bedrock aquifer. The bedrock aquifer is hydraulically connected to the alluvial deposits. Regionally, water-level declines led to a series of lawsuits culminating in adjudication of the Mojave River groundwater basin in 1996. Reduction in agricultural pumping, natural recharge from the Mojave River, and artificial recharge of imported water along the river contributed to partial recovery of water levels in the area.

Under present-day conditions, groundwater flow is from recharge areas along the Mojave River toward a pumping depression underling land treatment units operated by PG&E to remove Cr VI through

reduction to Cr III by application to agricultural fields (CH2M-Hill, 2013a). Formerly saturated alluvium, especially in the western part of the valley, remains above the present-day water table.

Chromium releases beneath the compressor station began in 1952 and continued until 1964 (LRWQCB, 2012a). Although seasonal flows in the Mojave River occurred annually between 1940 and 1945, only a few small streamflows and consequently only small quantities of groundwater recharge occurred along this reach of the Mojave River during the time of chromium releases from the compressor station. Presumably during this time, chromium from the compressor station that reached the water table moved with existing groundwater towards pumping wells within the valley. In 1969 large flows in the Mojave River and subsequent large quantities of groundwater recharge increased water levels and changed groundwater flow within the system. The water table within Hinkley Valley, although mapped as part of regional investigations of groundwater conditions within the Mojave River basin (California Department of Water Resources, 1967), was not closely monitored during the period of chromium releases or during recharge associated with the 1969 streamflows. As a consequence, the movement of Cr VI, the dimensions of the plume, and the potential for mixing of native (uncontaminated) groundwater near the plume margin with small amounts of water containing Cr VI from the compressor station are not precisely known. Uncertainty concerning plume movement is increased as a result of water level changes occurring initially as a result of declining agricultural pumping and later as a result of management activities intended to control the plume.

The total mass of chromium released from the compressor station is not precisely known, but has been estimated to be about 10,000 pounds (LRWQCB, 2012a). More than 350 wells at more than 100 sites within the study area have been installed to monitor the plume. Historical Cr VI concentrations within the plume were as high as 5,000 mg/L (CH2M-Hill, 2007). The mass of chromium identifiable within the groundwater in the mapped plume in 2011 was about 4,200 pounds (ARCADIS US, Inc., written commun., 2013). Most of this mass is present within the core of the plume in areas having higher Cr VI concentrations. Some removal of chromium from groundwater occurred as a result of a combination of natural processes, management activities, and past agricultural use of contaminated water. However, Cr VI is highly soluble and mobile in alkaline, oxic groundwater; and Cr VI contamination in groundwater can migrate great distances with limited attenuation (Perlmutter et al., 1963; Blowes, 2002). In some areas, identifying the extent of Cr VI contamination near plume margins can be complicated by the presence of naturally-occurring Cr VI from weathering of rocks and minerals (Izbicki and others, 2008a), potential mobilization of Cr VI within the unsaturated zone by agricultural activities (Izbicki, 2008b and 2008c; Mills and others, 2011), and by reduction of Cr VI to Cr III with subsequent mixing of native and contaminated groundwater near the plume margin (Izbicki and others, 2012). In addition to Cr VI, other trace elements (including manganese, arsenic, and uranium) are present at concentrations of public health concern in parts of the valley. Concern has been expressed by local residents that management activities intended to control the Cr VI plume may contribute to high-concentrations of these elements. Specific concern has been raised about: 1) manganese and arsenic by-products resulting from the use of ethanol to reduce Cr VI to Cr III within the In situ Reactive Zone (IRZ), and 2) the fate of chromium on aquifer solids during decadal or longer time-scales as groundwater within the IRZ reoxygenates through natural processes.

To facilitate understanding of geology, hydrology, and the occurrence of natural and anthropogenic Cr VI, for the purposes of this study the site has been divided into the western, northern, and eastern subareas (CH2M-Hill, 2013b). In addition to areas east of the mapped plume, the eastern subarea also includes the mapped plume, and areas upgradient from the plume along the Mojave River. Each subarea has different geologic, hydrologic, geochemical, and land use histories that may affect naturally

occurring Cr VI concentrations and the potential for occurrence of Cr VI associated with the compressor station.

The western subarea contains alluvial fan deposits eroded from Iron Mountain and the surrounding hills, interfingering with Mojave River alluvium. The Lockhart Fault to the southwest has been recognized as an impediment to groundwater flow (California Department of Water Resources, 1967; Stamos and others, 2001). Alluvium north of the fault thins to the west as bedrock slopes upward to the surrounding hills, and to the north over a bedrock high. Much of the formerly saturated alluvium in the western subarea is unsaturated as a result of past pumping. Under present-day conditions the water table slopes to the east, and water-level gradients steepen near the Lockhart Fault consistent with an impediment to flow in that area (CH2M-Hill, 2013a). Present-day pumping for domestic and remaining agricultural use is sustained by wells often completed partly, or entirely, into underlying bedrock. Increasing Cr VI concentrations in part of the western subarea have called into question the effectiveness of injection wells installed near the mapped plume boundary to limit westward movement of Cr VI (Lahontan Regional Water Quality Control Board, 2013). Some other issues of concern in the western subarea include: 1) Has Cr VI associated with the plume entered the area in the past, and is this Cr VI still present to the west of injection wells installed to control plume movement?, 2) Does bedrock and alluvium eroded from local sources contain chromium that may weather and contribute Cr VI to groundwater under certain geochemical conditions?, 3) Does pumping from bedrock wells hydraulically connected to the overlying alluvial aquifer cause unforeseen movement of Cr VI associated with the plume?, and 4) Does oxidation of chromium containing minerals in formerly saturated alluvial deposits above the present-day water-table (Izbicki and others 2008), and does mobilization of soluble salts, including Cr VI, from the unsaturated zone by past agricultural activity (Izbicki and others, 2008; Mills and others, 2011) contribute Cr VI to the underlying groundwater?

The northern subarea includes parts of Hinkley and Water Valleys. The subarea contains Mojave River alluvium that composes the highly-permeable floodplain aquifer, surrounded by bedrock covered by alluvium and alluvial-fan deposits eroded from the surrounding hills. Saturated alluvium is within a bedrock channel extending from Hinkley Valley to the north through the gap in the surrounding hills into Water Valley. The thickness of alluvium within the gap and the influence of the Mount General Fault on groundwater flow through the gap are not known. Past agricultural pumping that lowered the water table reduced, or eliminated, groundwater flow through the gap; ultimately eliminating groundwater discharge from springs and flowing wells in Water Valley. Under present-day conditions, pumping as part of remediation and land-treatment of Cr VI maintains a depression in the water table, limiting groundwater flow to the north. An area of groundwater having Cr VI concentrations greater than the 3.1 µg/L background concentration is present in the northern subarea, and there is concern that the northern extent of the plume has not been defined (Lahontan Regional Water Quality Control Board, 2013). Some other issues of concern in the northern subarea include: 1) Has Cr VI associated with the plume entered part of the subarea in the past, 2) Does bedrock and alluvium eroded from local sources, especially volcanic rocks, contain Cr VI that may weather and contribute Cr VI to groundwater under certain geochemical conditions?, and 3) What is the depth of alluvium within the gap between Hinkley and Water Valleys and does the Mount General Fault impede groundwater flow through the gap?

The eastern subarea contains alluvial deposits from the Mojave River and alluvial fan deposits eroded from Mount General. The “blue clay” that separates the upper aquifer from the lower aquifer and the “brown clay” within the upper aquifer are present throughout much of the eastern subarea (CH2M-Hill, 2013a). In some areas near the margins of the eastern subarea (and adjacent parts of the western and northern subareas), the blue clay was deposited upon bedrock and the lower aquifer is absent. Although

some Cr VI contamination has been reported in the lower aquifer, at this time Cr VI contamination within the lower aquifer is a lesser concern to the TWG than Cr VI contamination in the upper aquifer and bedrock aquifer near the mapped plume margins. Water-level declines as a result of agricultural pumping were as great as 70 ft within the eastern subarea (California Department of Water Resources, 1967). Under present-day conditions, pumping for aquiculture continues in the eastern area, with additional pumping for land-treatment of Cr VI. Insitu reduction of Cr VI to Cr III through injection of ethanol occurs within the Insitu Reactive Zone (IRZ) within the eastern subarea. Manganese and other by-products of insitu reduction of Cr III to Cr VI and the permanence of insitu treatment as groundwater reoxygenates are a concern to residents and regulators. Recharge from irrigation return and dairy waste disposal has contributed to increased dissolved solids and nitrates in some areas. Some issues of concern in the eastern subarea include: 1) Does large-scale agricultural pumping of groundwater allow unexpected movement of Cr VI near production wells?, and 2) What are the chemical composition and Cr VI concentration of recently recharged water along the Mojave River upgradient from the compressor station?

**Objectives:** The purpose of this study is to evaluate the occurrence of natural and anthropogenic Cr VI, and estimate background Cr VI concentrations upgradient, near the plume margins, and downgradient from the mapped Cr VI contamination plume near Hinkley, CA.

In addition to data collected to evaluate Cr VI occurrence and estimate background Cr VI concentrations within the study area, there also is concern within the TWG about: 1) the occurrence of other trace elements in the study area including: manganese, arsenic, and uranium that are of public health concern, and 2) potential remobilization of Cr VI reduced to Cr within the IRZ on decadal, or longer, time-scales as groundwater reoxygenates by natural processes. Data collected as part of this study provide an opportunity to collect and interpret data that address these concerns.

**Relevance and Benefits:** Results of this study will be used to establish the extent of Cr VI contamination at the site, and naturally-occurring background Cr VI concentrations in the Hinkley Valley area. These data will be used to help establish clean-up goals for the Cr VI contamination plume near Hinkley, CA.

This proposal will contribute to the U.S. Geological Survey's ability to "ensure adequate quantity and quality of water to meet human and ecological needs in the face of growing competition among domestic, industrial-commercial, agricultural, and environmental uses" (National Research Council, 2004) as described in the U.S. Geological Survey Science Strategy (2007). The proposal is within U.S. Geological Survey Water Resources Mission Areas to "define and better protect the quality of the Nation's water resources". The project complies with the Federal role for the U.S. Geological Survey in that it provides services not readily available from the private sector (WRD Memorandum 04.01) and it:

1. advances knowledge of the regional hydrologic system
2. advances field methodology
3. advances understanding of hydrologic processes, and
4. provide data and results useful to multiple parties in potentially contentious conflicts over water resources.

**Science Plan:** The U.S. Geological Survey developed the scope of this study in collaboration with the Technical Working Group (TWG) composed of local stakeholders (the Hinkley Citizens Action Committee, CAC), community advisors (Project Navigator, Inc.), State regulatory agencies (Lahontan Regional Water Quality Control Board, LRWQCB), and Pacific Gas and Electric (PG&E) and their consultants. TWG

meetings beginning in January 2013 familiarized members with available data, and with issues of local, regulatory, and technical concern within the study area.

The scope of this study includes the following tasks: 1) evaluation of existing data, 2) sample collection and analyses of rock and alluvium, 3) sample collection and analysis for water chemistry and multiple tracers, 4) evaluation of local geologic, hydrologic, and geochemical conditions in western, northern, and eastern subareas within the study area, 5) evaluation of historic and present-day groundwater movement, 6) evaluation of the occurrence of natural and anthropogenic chromium, and 7) estimation of background Cr VI concentrations. Procedures for evaluation of laboratories, quality assurance, and data management are discussed in this section following discussion of the study tasks. Reports to be prepared for this study are discussed in a separate reports section.

Work plans and implementation of each of these tasks (including identification of specific wells to be sampled as part of this study) will be developed in collaboration with the TWG as the study moves forward. To assist with study design, in April, 2013 PG&E and their consultants in collaboration with the TWG evaluated existing water-chemistry data, and collected a “snapshot” of selected proposed tracers. These data in combination with other existing data are discussed within this proposal.

**Task 1: Evaluation of existing data.** Water-level and water-chemistry data are available from existing domestic wells and monitoring wells installed to monitor the plume. These data have been assembled and reviewed by PG&E and their consultants, and discussed during TWG meetings beginning in January 2013. Although this review familiarized TWG members with available data, opportunity to work directly with the data will give U.S. Geological Survey project staff greater familiarity with the data, and the spatial and temporal distribution of data, and data quality prior to the start of data collection. As a framework for the initial analysis, Principal Component Analyses (Kshirsagar, 1972; Gnanadesikan, 1974) will be used to evaluate water-level and water-quality data relative to the occurrence of Cr VI with respect to pH, specific conductance, major-ion chemistry, and temporal and spatial differences within the study area.

The Hinkley CAC has expressed concern over possible trends in Cr VI concentrations and the destruction of domestic wells having long-term Cr VI data as PG&E acquires property within and near the mapped plume. Although in many cases, domestic wells were replaced with monitoring wells (having short screened intervals, completed at different depths within the aquifer), there is concern from the CAC that the Cr VI concentration data from domestic and monitoring wells, and the spatial density of the data may not always be comparable.

Historic Cr VI data will be examined to determine if there are trends in total Cr and Cr VI concentrations in domestic wells, and if increasing trends are present in wells near the plume margins. Data will be analyzed using the nonparametric Mann–Kendall trend test (Mann, 1945; Helsel and Hirsch, 2002) to determine the significance of Kendall's  $\tau$  correlation between total Cr and Cr VI concentrations with time. The Sen slope estimator will be used to estimate trend magnitude (Sen, 1968; Hirsch et al., 1991). A minimum of four analyses for each well are necessary to attain a statistically significant result (p-value less than 0.1) for the Mann–Kendall test, although at least 8 points are recommended for statistical analysis of trends (Grath et al., 2001). To the extent possible data will be evaluated to determine if seasonality, well-construction data (where available), or other factors may influence the presence or absence of trends in wells (Kent and Landon, 2013).

**Task 2: sample collection and analyses of rock and alluvium.** Physical, mineralogic, and chemical analysis will be done on selected archived core material and cuttings from wells drilled by PG&E, and as part of previous work by the U.S. Geological Survey. Analyses also will be done on samples of alluvium and rock collected as part of this study by the U.S. Geological Survey within the study area and from other areas in the Mojave Desert known to have high naturally-occurring concentrations of chromium. Rock and alluvium will be evaluated using a hand-held X-Ray Fluorescence (XRF) instrument prior to collection, description, and analyses.

Physical, mineralogic, and chemical data collected as part of this task will be used to determine natural geologic occurrence of chromium in rock and alluvium in the study area. Results will be compared to: 1) average chromium abundances in continental crust and in specific rock types, 2) chromium abundances in areas known to have high chromium in groundwater, and 3) chromium abundances within the study area to determine if there are difference in chromium abundance that are related to local geology. Chemical data from sequential extractions for chromium, or other trace elements, are commonly normalized to the occurrence of more abundant elements, such as iron, or to physical properties, such as particle-size or surface area, prior to evaluation of abundance.

***Physical description of rock and alluvium:*** Core material and cuttings from selected wells drilled throughout the study area by PG&E and their consultants will be described and classified optically, using a petrographic microscope, with respect to texture (Folk, 1954), roundness (maturity) of sand grains (Folk, 1951), QAPF phaneritic mineralogy (Le Maitre, 2002), and the abundance and composition of lithic fragments. Archived core material and cuttings from USGS drilled wells along the Mojave River (Huff and others, 2002) will be used as reference material for alluvium from the Mojave River. Rock samples collected from outcrops and alluvium collected from streams draining upland areas adjacent to Hinkley Valley will be used as reference material for alluvium from those sources. Additional material from areas elsewhere in the Mojave Desert known to have high-chromium concentrations also will be collected and described. XRF data, physical descriptions, and optical analysis will be used to select approximately 100 samples for preparation of thin sections. Thin sections will be examined optically to provide semi-quantitative estimates of differences in mineral occurrence and abundance in different areas. Results will be used to select material for additional analyses of mineralogy and sequential extraction for selected trace element compositions.

Physical descriptions (including field and office XRF measurements) of rock, alluvium, core material and cuttings, and analysis of thin sections will be done in the San Diego USGS office in collaboration with Brett Cox and David Miller USGS, GD, Menlo Park, CA. Thin sections will be prepared by a contract laboratory.

***Mineralogy of cores and cuttings:*** Mineralogy of 30 previously described core material and cuttings, rock and alluvium from representative source areas (including material from other areas in the Mojave Desert known to have high chromium concentrations) will be determined by X-Ray diffraction. Mineral identification from X-Ray diffraction data will be made using pattern-fit routines within the computer programs MDI Jade, and Rockjock for clay-mineral bearing rocks. Selected samples will be sorted according to density in bromoform (specific gravity  $2.8 \text{ g/cm}^3$ ) (Peacock and others, 2000). Minerals containing Cr and other selected trace elements are associated with denser minerals. Minerals having a density greater than  $2.8 \text{ g/cm}^3$  will be sorted into highly magnetic (C1), weakly magnetic (C2), and nonmagnetic (C3) fractions using a Franz unit. Minerals in the nonmagnetic fraction will be identified optically, digested, and analyzed for chromium and other selected trace elements. Selected mineral grains from the bulk and C3 fractions will be examined using a Scanning Electron Microscope (SEM) to

determine the morphology, physical integrity (with respect to the extent of weathering,) and chemical composition of mineral grains.

X-Ray diffraction analyses, isolation description and analyses of the C3 mineral fraction, and Scanning Electron Microscope analyses will be done by the U.S. Geological Survey, Geologic Division, in Denver, Colo. in collaboration with Jean Morrison and William Benzel.

***Sequential extractions from cores and cuttings:*** Chromium and other selected trace elements (including iron, aluminum, manganese, arsenic, nickel, vanadium, and uranium) will be extracted from sorption sites, amorphous oxides, and crystalline oxides on the surfaces of mineral grains from 30 samples of alluvium collected during test drill for existing monitoring wells and from samples collected from representative source areas. The sequential extraction procedure to be used is modified from Wentzel and others (2001). Each step within the procedure is intended to extract trace elements from operationally-defined sorption sites on the surfaces of the mineral grains. These sorption sites include: 1) “non-specifically sorbed” trace elements dissolved in pore water and associated with water-soluble material 2) “Specifically-sorbed” trace elements potentially mobilized by changes in pH, or by exchange with more strongly sorbed oxyanions, 3) trace elements associated with poorly-crystallized (amorphous) iron, aluminum, and manganese oxides on the surfaces of mineral grains, and 4) trace elements associated with well-crystallized iron, aluminum, and manganese oxides on the surfaces of mineral grains. A fifth extraction step modified from Chao and Sanzolone (1989) will be done on a split of material obtained after the second extraction. This step is included to ensure all trace elements associated with well-crystallized iron, manganese, and aluminum oxides on mineral surfaces within the sample are measured. Results from the fifth step are comparable to strong-acid extraction data collected elsewhere in the Mojave Desert by Izbicki et al. (2008).

Extractions will be done at the U.S. Geological Survey Laboratory in San Diego, Calif., with chemical analyses done at the U.S. Geological Survey National Water Quality Laboratory (NWQL) in Denver, Colo.

**Task 3: Sample collection and analysis for water chemistry and for multiple chemical and isotopic tracers.** Water samples will be collected from 60 selected domestic, agricultural, and monitoring wells distributed throughout the study area within and near the mapped plume. Monitoring wells and other wells owned by PG&E will be pumped by PG&E’s consultants, with U.S. Geological Survey staff present to accept, preserve, and prepare samples for shipment to selected laboratories for analyses. Sample collection from monitoring wells will be done using protocols acceptable to the TWG that have been developed by PG&E and their consultants, and are consistent with U.S. Geological Survey (variously dated) field procedures for water-quality sample collection. These protocols will include decontamination of portable sample pumps, purging of wells with monitoring of field parameters to remove a minimum of three casing volumes from the well, and disposal of contaminated purge water. Samples from domestic, agricultural, and monitoring wells not owned by PG&E will be collected by U.S. Geological Survey personnel using U.S. Geological Survey sample collection protocols.

**Chemical data:** Water samples will be analyzed for field parameters, major ions, selected minor ions, and selected trace elements. Analyses for field parameters (including temperature, pH, alkalinity, and dissolved oxygen) and sample preservation will be done by U.S. Geological Survey personnel at the time of sample collection.

Analyses for major-ions will be done by PG&E contract laboratories to ensure consistency with data collected previously for regulatory purposes. Duplicates will be collected and analyzed on the first ten

samples by both PG&E contract laboratories and the U.S. Geological Survey National Water Quality Laboratory (NWQL) in Denver, Colo. If results are comparable, approximately one in ten of the remaining samples will be analyzed by both laboratories to assure continued comparability of data.

Analyses for selected minor ions (including strontium and bromide) will be done by the U.S. Geological Survey NWQL. These data are not routinely analyzed by PG&E, and comparison with previously collected data is a lesser concern than for major-ion data. Analyses of strontium by the NWQL will provide a consistent data set for interpretation of strontium isotopic data. Analysis of bromide by the NWQL using colorimetric techniques will provide for a lower detection limit (0.001 mg/L) and greater analytical precision than commonly available from commercial laboratories, facilitating use of bromide as a tracer in conjunction with chloride and isotopic data.

Analyses of selected trace elements (including iron, manganese, arsenic, and uranium) will be done by the NWQL and U.S. Geological Survey research laboratories in Denver, Colo. to address CAC concerns about the occurrence of these constituents within Hinkley Valley. Trace element data will be coupled to measurements of redox active couples including iron ( $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$ ) and arsenic ( $\text{As}^{+3}$  and  $\text{As}^{+5}$ ). Analyses for total chromium and chromium VI will be done by PG&E contract laboratories to ensure compliance with regulatory requirements and consistency with previously collected data, and by the U.S. Geological Survey research laboratory in Boulder, Colo. For both laboratories, Cr III will be calculated as the difference between Cr total and Cr VI. Redox determined from Cr III and Cr VI couple will be compared to redox estimated iron and arsenic couples.

Samples of filterable solids also will be collected from selected wells known to have “black water” associated with high total manganese concentrations. Filterable solids will be analyzed by SEM to determine the chemical composition and morphology of the solids. Filterable solids from wells within the IRZ also will be collected and analyzed. It is possible that the chemistry and morphology of material filtered from water samples near the IRZ where manganese associated with PG&E remediation activities is present may differ from other areas in the valley where filterable manganese is results from other processes.

Chemical data will be interpreted to determine the potential for occurrence of Cr VI in water with respect to measured pH, mineral solubility, and redox conditions. Major-ion data will be presented graphically using Trilinear (Piper) or Stiff diagrams as appropriate. Mineral solubility and the potential for weathering of minerals (identified as part of solid-phase analyses discussed previously) that may contain chromium will be assessed using the computer program WATEQ4F (Ball and Nordstrom, 1991). Thermodynamic and mineral databases within WATEQ4F are updated and maintained by the U.S. Geological Survey and contain thermodynamic data for chromium-bearing minerals (Ball, 1996) ([http://wwwbrr.cr.usgs.gov/projects/GWC\\_chemtherm/software.htm](http://wwwbrr.cr.usgs.gov/projects/GWC_chemtherm/software.htm)). Chemical data also will be used to determine net chemical reactions occurring along groundwater flowpaths groundwater using the computer program NETPATH (Plummer and others, 1994). Information on dissolution and precipitation of minerals will provide information on sources and sinks for chromium and can be used to help estimate groundwater ages and traveltimes discussed later in this Task.

Selected trace element and redox analyses will be done in collaboration with Kirk Nordstrom and Blaine McClesky, U.S. Geological Survey, National Research Program, Boulder, Colo. They also will provide assistance with thermodynamic interpretation of data relative to mineral solubility.

**Tracers of the source(s) and hydrologic history of water and chromium:** A multiple-tracer approach will be used to evaluate the source and hydrologic history of water and chromium, and the interaction of groundwater with aquifer materials within and near the mapped plume. Each tracer measures a slightly different aspect of the source, movement, and age (time since recharge) of groundwater and constituents dissolved within groundwater. The combination of chemical and multiple-tracer data with geologic and hydrologic data (Tasks 4 and 5) is intended to produce a more robust interpretation of hydrologic and chemical processes than can be obtained from individual tracers. This is important because of the focus of the study on low-concentrations of natural or anthropogenic chromium near the plume margin.

Tracers of the source and hydrologic history of water to be used in this study include the stable isotopes of oxygen and hydrogen in the water molecule ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively), and dissolved atmospheric gas (argon and nitrogen) concentrations. Tracers of groundwater age include tritium, tritium/helium-3, industrial gasses (chlorofluorocarbons and sulfur hexafluoride), and carbon-14. Tracers of the interaction between water and aquifer materials include chemical data (discussed previously) and strontium-87/86 isotopic ratios ( $^{87/86}\text{Sr}$ ). Tracers of the source and processes affecting Cr VI concentrations include the stable isotopes of chromium ( $\delta^{53}\text{Cr}$ ).

***delta Oxygen-18 and delta Deuterium:*** Most of the world's precipitation originates as evaporation of seawater. As a result, the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of precipitation throughout the world is linearly correlated and distributed along a line known as the global meteoric water line (Craig, 1961). Atmospheric and hydrologic processes combine to produce broad global and regional differences in the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of water. For example, water that condensed from precipitation in cooler environments at higher altitudes or higher latitudes is isotopically lighter, or more negative, than water that condensed in warmer environments or lower latitudes (IAEA, 1981a). Similarly, water that has been partly evaporated is shifted (by a process known as fractionation) to the right of the meteoric water line to isotopically heavier, or less negative, values along a line known as the evaporative trend line (IAEA, 1981a).

Streamflow in the Mojave River is the result of precipitation and subsequent runoff near Cajon Pass that entered the Mojave Desert without uplift over the higher altitudes of the San Bernardino and San Gabriel Mountains (Izbicki, 2004). The differences in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of water from different sources within the Mojave Desert provide a tool to evaluate the source and hydrologic history of water from wells in Hinkley Valley. For example, the volume-weighted average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of precipitation within Cajon Pass is -9.1 and -63 per mil (Izbicki, 2004), and the median  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of water from wells in the floodplain aquifer along the Mojave River is -8.8 and -62 per mil (Izbicki, 2004). Groundwater in the floodplain aquifer that has been partly evaporated as a result of agricultural use is commonly between -8.8 and -7.5 and -60 and -50 per mil, respectively (Izbicki, 2004). In contrast, volume-weighted average precipitation in higher altitudes of the San Gabriel and San Bernardino Mountains is -11.5 and -79 per mil. Winter precipitation in the Mojave Desert condensed over the higher altitudes of the mountains and has a  $\delta^{18}\text{O}$  and  $\delta\text{D}$  compositions of -10.9 and -77 per mil (Izbicki, 2004). The median  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of water from the regional aquifer is -10.5 and -78 per mil, respectively (Izbicki, 2004). The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of water collected by PG&E and their consultants from 30 wells as part of the April 2013 "snapshot" ranged from -7.7 to -9.0 and -58 to -67 per mil, respectively (CH2M-Hill, 2013c), and are within range of water recharged from the Mojave River and of water from the river that has been partly evaporated.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  will be collected to verify the

source (infiltration from streamflow in the Mojave River versus infiltration from local precipitation and runoff) and hydrologic history (with respect to evaporation) of water sampled.

$\delta^{18}\text{O}$  and  $\delta\text{D}$  data will be analyzed at the U.S. Geological Survey's stable isotope laboratory, in Reston, Va.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  analyses will be by mass spectrometry using standard operating procedures described in Revez and Copelan (2008a and 2008b, respectively). The one sigma precision of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  analyses is 0.1 and 1 per mil, respectively (<http://isotopes.usgs.gov/lab/methods.html>, accessed August 28, 2013).

**Dissolved gasses:** Dissolved argon and nitrogen gas concentrations will be measured as indicators of groundwater recharge history, and past reductive conditions within groundwater that may have affected Cr VI concentrations. Dissolved gas concentrations will be used to support interpretations on the source and hydrologic history of groundwater derived from  $\delta^{18}\text{O}$  and  $\delta\text{D}$  data, and to evaluate the representativeness of industrial gas (CFC and  $\text{SF}_6$ ) data discussed later in this task.

Argon is a noble gas and is not chemically reactive in water. The solubility of argon, and other noble gasses, is a function of temperature, pressure, and salinity according to Henry's Law (Stumm and Morgan, 1996). Argon concentrations, and other atmospheric gas concentrations, greater than expected according to Henry's Law may occur if infiltrating water traps bubbles of air, known as excess air, that later dissolve (Stute and Schlosser, 2000). If excess air is present, dissolved gas concentrations in groundwater increase with respect to the atmospheric concentration of the gas—rather than according to solubility from Henry's Law. If two or more non-reactive dissolved gases are measured (argon nitrogen, or neon for example), dissolved gas concentrations in groundwater from solubility and excess-air can be evaluated separately, and the history of the groundwater recharge process can be interpreted in terms of the source and timing (seasonality) of recharge.

In general, cooler groundwater recharge temperatures calculated from argon data and greater excess-air concentrations would be consistent with recharge from winter streamflow in the Mojave River that infiltrated rapidly through the unsaturated zone (entrapping air) prior to recharge. In contrast, warmer groundwater recharge temperatures and lower excess-air concentrations would be consistent with recharge that infiltrated slowly through the unsaturated zone prior to recharge. This includes areal recharge from precipitation and infiltration and recharge from sustained baseflow in small streams in the study area. The dissolved gas composition of irrigation return water also will be reset from its original composition to concentrations consistent with slower movement through the thick unsaturated zone in the area—consistent with evidence of evaporative fraction expected from  $\delta^{18}\text{O}$  and  $\delta\text{D}$  data. The complete suite of noble gasses (including krypton, and xenon) will not be measured as part of this proposal, although dissolved neon data will be available from tritium/helium-3 data discussed later in this section.

Nitrogen also is relatively non-reactive when dissolved in water. However, unlike argon, nitrogen may be produced in groundwater as a result of denitrification under reducing conditions. Differences in estimated recharge temperature and excess-air concentrations may reflect denitrification and reduced conditions within that occurred in the past within groundwater. Reduced conditions within the aquifer, if present, may have effected Cr VI concentrations, and  $\delta^{53}\text{Cr}$  isotopic compositions discussed later in this task.

Dissolved gas data will be measured at the U.S. Geological Survey dissolved-gas laboratory in Reston, Va. using a Hewlett Packard model 5890 gas chromatograph with a thermal conductivity detector

([http://water.usgs.gov/lab/dissolved-gas/lab/analytical\\_procedures/](http://water.usgs.gov/lab/dissolved-gas/lab/analytical_procedures/)). The minimum reporting levels for argon and nitrogen are 0.003 and 0.001 mg/L with precisions of 0.003 and 0.001, respectively.

**Tracers of the age of water:** Chromium releases at the compressor station occurred between 1952 and 1964. As a consequence, the age (time since recharge) of water in Hinkley Valley is important to understanding occurrence of anthropogenic Cr VI at the site. Younger groundwater will be evaluated using tritium, and its decay product helium-3, and industrial gasses (chlorofluorocarbons, and sulfur hexafluoride). Older groundwater will be evaluated on the basis of carbon-14 data. The multiple-tracer approach to determining groundwater age and groundwater contaminant history has found widespread hydrologic application in recent years. Multiple-tracer data will be interpreted with the aid of lumped-parameter models discussed in this section.

**Tritium:** Tritium ( $^3\text{H}$ ) is a naturally occurring radioactive isotope of hydrogen that has a half-life of 12.43 years. Tritium is measured as an activity in picoCuries per liter (pCi/L), with one picoCurie equal to 2.2 nuclear disintegrations per minute. (Tritium data also are expressed in tritium units (TU); one tritium unit is equal to 3.2 pCi/L, and is equivalent to one tritium atom in  $10^{18}$  atoms of hydrogen.) Tritium activities in precipitation in coastal southern California prior to 1952 and the onset of atmospheric testing of nuclear weapons were about 6 pCi/L (IAEA, 1981b; Michel, 1989). During 1952–62 about 800 kg of tritium was released to the atmosphere as a result of the atmospheric testing of nuclear weapons (Michel, 1976), and tritium activities in precipitation increased to about 2,200 pCi/L in coastal southern California (IAEA, 1981b). Tritium activities in precipitation at sites farther inland were higher (Michel, 1989). After the end of atmospheric testing of nuclear weapons in 1962, tritium activities in precipitation decreased and present-day tritium activities are near pre-1952 levels.

Tritium, part of the water molecule, is not affected by reactions other than radioactive decay, and can be used to identify the presence of groundwater recharged after the atmospheric testing of nuclear weapons beginning in 1952. Although the occurrence of tritium within groundwater in the Hinkley area also is controlled by the timing of streamflow and groundwater recharge from the Mojave River, tritium may provide information on the occurrence of Cr VI released from the compressor station. For example, tritium was present at concentrations greater than the detection limit of 0.3 pCi/L (0.09 TU) in water from 5 of 17 wells sampled in the western subarea, from 5 of 10 wells sampled in the northern subarea, and from 7 of 9 wells sampled in the eastern subarea as part of the April 2013 “snapshot”. Although wells in these subareas having detectable tritium were outside the mapped plume and had Cr VI concentrations less than 3.1  $\mu\text{g/L}$ , the presence of tritium is consistent with the presence of some fraction of groundwater recharged after the onset of atmospheric testing of nuclear weapons. In contrast, tritium was present at concentrations greater than the detection limit of 0.3 pCi/L (0.09 TU) in 5 of 9 wells sampled within the mapped plume as part of the April 2013 “snapshot”. For wells within the mapped plume having detectable tritium, Cr VI concentrations ranged from 1.1 to 952  $\mu\text{g/L}$ , and for wells where tritium was not detected Cr VI concentrations ranged from 1.3 to 3.8  $\mu\text{g/L}$ . The absence of detectable tritium and generally low Cr VI concentrations may be consistent with older groundwater having natural chromium present within the mapped plume, or may be consistent with the presence of Cr VI released from the compressor station into groundwater recharged prior to large streamflows in the Mojave River in 1969 that does not contain tritium. Additional tracer information provided from tritium’s decay product helium-3, carbon-14, and dissolved industrial gas data (especially CFC-11 and CFC-12 data) will be used to address this issue and refine groundwater age information developed from tritium data, especially with respect to the presence of mixtures of groundwater having different ages.

Tritium will be analyzed by liquid-scintillation using a Perkin-Elmer Quantulus tritium counter at the U.S. Geological Survey tritium laboratory in Menlo Park, Calif., in collaboration with Megan Young and Carol Kendall (U.S. Geological Survey National Research Program). To facilitate interpretation of tritium near the detection limit of 0.09 pCi/L, the one-sigma variability associated with the value for each sample will be provided. This estimate of analytical precision will be used to statistically evaluate the probability that tritium may be present in samples below the detection limit. This probability will be used with other age-dating information collected as part of this study to refine interpretation of mixed-age groundwater using lumped parameter models discussed later in this section.

***Tritium/Helium-3:*** The usefulness to tritium as a tracer of groundwater age is increased if the concentration of its decay product helium-3 ( $^3\text{He}$ ) also is known (Solomon and Cook, 2000). Helium-3 also occurs naturally in the atmosphere. Contributions of atmospheric helium-3 dissolved in water during recharge as a result of solubility at the temperature of groundwater recharge and excess-air entrapped during recharge must be known to calculate helium-3 from tritium decay. Atmospheric helium-3 is estimated from measurements of the helium-3 / helium-4 ratio ( $^3\text{He}/^4\text{He}$ ) and temperature at the time of recharge estimated from noble gas data. Dissolved neon gas data will be used for this purpose. Although the physical chemistry constants describing these processes are known with a high degree of certainty, use of the tritium / helium-3 method requires careful data collection, accurate estimation of the contributions of solubility and excess-air components within sample water, and estimates of the potential contribution of helium-3 from radioactive decay of uranium and thorium minerals within aquifer materials (estimated from helium-4 data and data from task 2).

Helium-3 data will be used to refine estimates of the age of recent groundwater containing tritium. These refined ages will be compared to the occurrence of streamflow and subsequent groundwater recharge from the Mojave River. Because the years when intermittent recharge from the Mojave River occurred is known, the tritium/helium-3 method is expected to be especially useful for interpretation of mixed-age groundwater using lumped parameter models discussed later in this section. Estimated ages developed from tritium/helium-3 data will be adjusted within reasonable ranges to refine model inputs as necessary.

Helium-3, helium-4, and neon data will be analyzed by the U.S. Geological Survey, Geologic Discipline, laboratory in Denver, Colo. Data from this laboratory will be used with tritium data discussed previously to estimate the age of groundwater.

***Industrial gasses:*** Certain gasses released to the atmosphere as a result of industrial activity since the 1940's can be used to estimate the age (time since recharge) of groundwater (Plummer and Busenberg, 2000). To be useful as a tracer of groundwater recharge, industrial gasses must be 1) soluble in water and measurable at the expected concentrations, 2) have low (or non-existent) natural background concentrations, and 3) be relatively stable (non-reactive) in groundwater. Gases commonly used for this purpose include chlorofluorocarbons (CFC-11, CFC-12, and CFC-113) and sulfur hexafluoride. Chlorofluorocarbons are stable in aerobic groundwater, although degradation of chlorofluorocarbons may occur in anerobic groundwater.

The timing of the release of these gases is different from the timing of tritium releases from the atmospheric testing of nuclear weapons. Concentrations of these gases in the atmosphere and in groundwater increased after the introduction of each gas with increasing industrial production and use. Decreases in the use of chlorofluorocarbons to protect the ozone layer beginning in 1987, as a result of the Montreal Protocol; and decreases in the use of sulfur hexafluoride, a potent greenhouse gas, have

resulted in decreasing atmospheric concentrations in recent years. CFC-12 is useful for dating post 1940's groundwater, CFC-11 for post 1945 groundwater, and CFC-113 for post 1953 groundwater, and sulfur hexafluoride for post 1970's groundwater. CFC-11 and CFC-12 data are expected to be especially useful for evaluation of water recharged in the early 1940's that was present within the aquifer prior to release of chromium from the compressor station and before introduction of large quantities of water recharge from the Mojave River that contained tritium in 1969. The combination of results for different gasses provides greater confidence in estimates of the time since recharge of younger groundwater, and the evaluation of mixtures of groundwater recharged at different times.

Chlorofluorocarbon and sulfur hexafluoride will be analyzed using a Shimadzu GC-8A gas chromatograph with an electron capture detector by the U.S. Geological Survey dissolved gas laboratory in Reston, Va. The detection limit for chlorofluorocarbons is 0.5 to 1 picograms ( $10^{-12}$ ) per liter, and for sulfur hexafluoride is 0.01 femtomoles ( $10^{-15}$ ) per liter. Multiple replicates are collected and analyzed for CFC's and sulfur hexafluoride. Analytical precision for CFC's is about 50 percent at the detection limit, improving to 3 percent at concentrations of 20 picograms and higher. Analytical precision for sulfur hexafluoride is about 20 percent at the detection limit, improving to 3 percent at higher concentrations.

**Carbon-14:** The age of older groundwater will be evaluated using the carbon-14 activity of dissolved inorganic carbon. Carbon-14 ( $^{14}\text{C}$ ) is produced naturally by interactions between cosmic rays and nitrogen gas in the earth's atmosphere and has a half-life of about 5,730 years (Mook, 1980). Carbon-14 data are expressed as percent modern carbon (pmc): 13.56 disintegrations per minute per gram of carbon in the year 1950 equals 100 pmc (Kalin, 2000). In addition to natural sources,  $^{14}\text{C}$  also was produced by the atmospheric testing of nuclear weapons (Mook, 1980), and  $^{14}\text{C}$  activities may exceed 100 pmc in areas where groundwater contains tritium from nuclear weapons tests. Because  $^{14}\text{C}$  is not part of the water molecule, its activity and interpreted groundwater ages may be affected by reactions between constituents dissolved in ground water and aquifer materials. Carbon-13 ( $^{13}\text{C}$ ), a naturally occurring stable isotope of carbon, is used in conjunction with chemical and mineralogic data to evaluate chemical reactions that effect interpreted carbon-14 ages.

$^{14}\text{C}$  data will be rank-ordered by activity. Higher activities will be compared to tritium, tritium/helium-3, and dissolved industrial gas data to establish the range of carbon-14 activities in recently-recharged (modern) groundwater, and the breakpoint between modern and older groundwater--commonly referred to as  $A_0$ . Older groundwater, having low  $^{14}\text{C}$  activity and no evidence of mixing with younger groundwater that may have been associated with releases from the compressor station, will be used as a starting point to evaluate potential natural occurrence of Cr VI. Groundwater chemistry and  $^{13}\text{C}$  data will be used to evaluate the nature, extent and rate of chemical reactions that have occurred in water from wells having lower  $^{14}\text{C}$  activities. It would not be reasonable to expect extensive weathering of chromium containing minerals that may be identified as part of this study, if more abundant, less-resistive minerals have not reacted with groundwater.

$^{14}\text{C}$  will be analyzed by accelerator mass spectrometry (AMS) under contract with the U.S. Geological Survey NWQL. Minimum reporting limits for  $^{14}\text{C}$  analysis in water are commonly near 0.5 pmc. This is much lower than activities expected for water in the Hinkley area, although very old groundwater beyond the range of  $^{14}\text{C}$  dating techniques is present in some parts of the Mojave Desert (Izbicki and Michel, 2004).  $^{13}\text{C}$  will be analyzed by mass spectrometry at the U.S. Geological Survey NWQL.

**Interpretation of age-tracer data:** The combination of tracers collected to evaluate groundwater age will be interpreted using lumped parameter models using the computer program TracerLPM (Jurgens

and others, 2012). Lumped parameter models mathematically evaluate simplified aquifer geometry and groundwater flow to account for effects of dispersion within the aquifer, mixing within the well bore, or converging groundwater flowpaths near discharge areas. The multiple tracer approach uses hydrogeologic conceptualization, visual examination of data and models, and best-fit parameter estimation to estimate a mean groundwater age from each tracer to determine which conceptual model best approximates the data. Mixtures of younger and older groundwater are likely to be present within the aquifer near the plume margins and will be evaluated as binary mixing models within TracerLPM to quantify the fraction of the water within a given sample that is in the age range of chromium releases at the compressor station. . Because the years when intermittent recharge from the Mojave River occurred are known, resolution of binary mixtures of even low fractions of younger groundwater with older groundwater may be highly effective using lumped parameter models.

Age-tracer results and the occurrence of mixtures of water having different ages will be compared to groundwater flow and particle-tracking results (Task 5). The approach will be similar to the approach used by Izbicki and others (2004) in a regional analysis of groundwater flow within the Mojave River groundwater basin, and is intended to ensure reasonable interpretation of geochemical data relative to hydrologic conditions within the study area.

**Tracers of rock-water interactions:** Strontium is an exchangeable, divalent cation; similar to calcium in chemistry. There are four naturally occurring stable isotopes of strontium having masses of 84, 86, 87, and 88. Strontium-87 ( $^{87}\text{Sr}$ ) is a naturally-occurring, stable, radiogenic isotope produced by the decay of rubidium-87 (part of the uranium/thorium decay series). The  $^{87}\text{Sr}$  isotopic composition differs in geologic materials as a result of the initial rubidium composition (related to the initial uranium and thorium composition) and the geologic age of the material (providing time for decay of uranium, and ultimately rubidium-87). The strontium-87/86 ( $^{87/86}\text{Sr}$ ) isotopic composition of dissolved strontium can be used to evaluate geologic material in contact with groundwater (Izbicki and others, 1994; McNutt, 2000).

Strontium isotopic data are not normalized to a standard and reported as per mil differences relative to the standard similar to many other isotopes; instead  $^{87}\text{Sr}$  abundances are normalized to non-radiogenic  $^{86}\text{Sr}$  abundances, and the ratio ( $^{87/86}\text{Sr}$ ) is typically reported to 5 significant digits. The overall crustal abundance of  $^{87}\text{Sr}$  is about 7 percent, and the abundance of  $^{86}\text{Sr}$  is about 9.8 percent, producing a ratio of 7.09939. Higher values containing more  $^{87}\text{Sr}$  and are more radiogenic; lower values containing less  $^{87}\text{Sr}$  are less radiogenic than the crustal abundance. Strontium isotopes do not fractionate in the environment, and differences in  $^{87/86}\text{Sr}$  isotopic ratios in the 4<sup>th</sup> and 5<sup>th</sup> significant digit are interpretable with respect to differences in geologic sources, and rock/water interactions in hydrologic settings.

As primary minerals weather, strontium from these minerals is incorporated into: secondary minerals, amorphous materials, and onto clay mineral exchange sites. Strontium on exchange sites exchanges rapidly and is generally in equilibrium with strontium in water. Consequently, the  $^{87/86}\text{Sr}$  ratio in water reflects the isotopic composition of strontium from rock weathering—providing information on the geologic source from which the aquifer material was eroded (Johnson and DePaolo, 1994; Izbicki and other, 1994). If different geologic source areas within the study area have higher or lower chromium abundances (on the basis of solid-phase analyses discussed in Task 2); then, depending on specific geochemical conditions, groundwater interacting with these materials may contain higher or lower Cr VI concentrations.

$^{87/86}\text{Sr}$  data collected as part of the April 2013 “snapshot” ranged from 0.7093 to 0.7106. Although variable, lower (less radiogenic) values were present in samples in the northern subarea—potentially

having greater abundance of alluvium eroded from local rocks. In contrast, higher (more radiogenic) values were present in samples in the eastern subarea—potentially having a higher abundance of alluvium derived from the Mojave River. The April 2013 snapshot data suggest a potential for interpretable results within the range of environmental  $^{87/86}\text{Sr}$  values in the study area.

$^{87/86}\text{Sr}$  analyses will be done by Thermal-Ionization Mass Spectrometry (TIMS) at the U.S. Geological Survey in Menlo Park, CA. Twenty selected samples of rock, alluvium, and strontium extracted from exchange sites also will be analyzed to evaluate the association between  $^{87/86}\text{Sr}$  ratios in water and ratios in geologic materials from different sources within the study area.

**Tracers of the source(s) of chromium:** There are four naturally-occurring isotopes of Cr, having masses of 50, 52, 53 and 54 (Coplen et al., 2002). The two most abundant isotopes,  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$ , compose about 83.8 and 9.5 percent of the chromium in the earth's crust, respectively. (Rosman and Taylor, 1998). The isotopic abundance of  $^{52}\text{Cr}$  and  $^{53}\text{Cr}$  isotopes is expressed in delta notation ( $\delta$ ) as part per thousand differences relative to standard hydrated chromium nitrate NIST SRM 979.

The average  $\delta^{53}\text{Cr}$  composition of the earth's crust is about 0 per mil (Ellis et al., 2002). This value is reasonably constant over a range of rock types. The  $\delta^{53}\text{Cr}$  composition of industrial compounds derived from crustal rock also is about 0 per mil. In contrast, the  $\delta^{53}\text{Cr}$  composition of native (uncontaminated) groundwater is commonly heavier than the composition of the earth's crust. Chromium isotopes have been suggested as a tool to determine the source of Cr in groundwater, and to more accurately define the extent of contamination in areas having high natural background Cr VI concentrations (Ellis et al., 2002; Izbicki et al., 2008).

In practice, there is overlap between natural and anthropogenic chromium  $\delta^{53}\text{Cr}$  compositions in groundwater. Some natural chromium, especially in areas where water is saline, may have near zero  $\delta^{53}\text{Cr}$  compositions, and anthropogenic Cr within plumes may have positive  $\delta^{53}\text{Cr}$  compositions as a result of fractionation during reduction of Cr VI to Cr III. As a consequence, Cr VI concentrations and  $\delta^{53}\text{Cr}$  isotopic compositions do not uniquely define natural and anthropogenic chromium in most settings. However, Cr VI and  $\delta^{53}\text{Cr}$  data contribute to understanding of the interaction between reductive and mixing processes that occur within and near the margins of Cr contamination plumes (Izbicki and others, 2012).

$\delta^{53}\text{Cr}$  data have been used to understand mixing and fractionation processes within Cr VI contamination plumes at several sites in the Mojave Desert, including Hinkley (Izbicki and others, 2012). Initial data interpretation will be done using a pattern-recognition approach (discussed in Task 6) that categorizes (bins) samples on the basis of data collected within the study area, and relates those categories to spatial occurrence and chemical, and expected isotopic differences associated with different sources, fractionation, or mixing (Izbicki and others, 2008 and 2012).

$\delta^{53}\text{Cr}$  compositions will be measured at the USGS laboratory in Menlo Park, CA. Sample processing to obtain approximately 500 ng of Cr VI for isotopic analysis includes purification of Cr VI to minimize interference from organic compounds and from anions such as sulfate (Bullen, 2007). Sample processing also includes addition of a mixed  $^{50}\text{Cr}$ – $^{54}\text{Cr}$  “double spike” solution as an internal standard during mass spectroscopy (Johnson and others, 2000; Bullen, 2007). The isotopic composition of chromium in samples and the double spike standard will be measured using thermal ionization mass spectrometry

(TIMS, Finnigan MAT 261). The analysis has a  $2\sigma$  precision of 0.11 per mil for analysis of chromium nitrate NIST SRM 979 standard, and a  $2\sigma$  precision of 0.29 per mil precision on duplicate analysis of water samples from a range of natural and contaminated sites in the Mojave Desert (Izbicki and others, 2008 and 2012).

**Task 4: Evaluation of local geologic, hydrologic, and geochemical conditions.** There are geologic, hydrologic, and geochemical differences between the western, northern, and eastern subareas of the Hinkley Valley. These differences create specific concerns from the TWG (discussed in the “Hydrologic setting” section) that can be addressed through site-specific data collection within each subarea. The discussion that follows outlines some of the potential concerns for each subarea and some of the data to be collected in addition to site-wide geologic and geochemical data previously discussed in Tasks 2 and 3. The timing and scope of work within each subarea will be defined in partnership with TWG to maximize collection of data for the background study with data that are being collected by PG&E and their consultants for management and regulatory purposes.

**Western subarea:** Under present-day conditions, the water table slopes to the east throughout much of the western subarea. In the past water levels were higher, although the configuration of the water table is not precisely known. Additional information on the bedrock altitude and thickness of alluvium, the hydraulic properties of the Lockhart Fault, the hydraulic connection between alluvium and bedrock, and geochemical reactions that may have occurred at the water-table interface may help address questions concerning groundwater movement and Cr VI occurrence in the western subarea.

Bedrock altitude and alluvial thickness in the western subarea will be estimated on the basis of gravity. Approximately 300 gravity measurements will be collected on a grid pattern using a LaCoste and Romberg Model D with ALIOD-100 gravity meter. The meter has a resolution of 0.01 milliGals, and repeatability under field conditions of 0.01 to 0.02 milliGals. Data density within the grid will be increased near the Lockhart Fault, and near areas of concern for Cr VI occurrence. Gravity data will be used with existing U.S. Geological Survey regional gravity data (Saltus and Jachens, 1995) to refine regional-scale residual gravity anomaly maps showing subsurface density variation, and refine existing regional-scale alluvial thickness maps. The initial alluvial thickness map developed from gravity data will be further refined on the basis of test-drilling data available from PG&E and their consultants. The alluvial thickness map will increase understanding of the location of the Lockhart Fault, the potential hydraulic connection between alluvium and underlying bedrock, and help identify the extent of saturated alluvium in the western subarea under historic and present-day conditions. These data also will support groundwater model updates described in Task 5.

Point velocity probes (PVP)(Labaky and others, 2009) will be used to measure groundwater flow direction and magnitude upgradient and downgradient the Lockhart Fault to address CAC concerns over Cr VI detections near the fault. (Although not specifically within the scope of this proposal, PVP data also may be useful to understand groundwater flow and Cr VI movement near injection wells near the plume margins in the western subarea.) PVP are typically installed within glass-bead packers deployed within the screened interval of existing monitoring wells. Monitoring wells installed by PG&E consultants near the Lockhart Fault are available for this purpose. Temperature based PVP can measure groundwater flow velocities as low as 0.5 feet per day in permeable materials to address the effects of aquifer heterogeneity on groundwater flow at centimeter scales. If lower-velocity measurements are required, use of salinity (or other tracer-based) PVP’s will be investigated. PVP data will be correlated with lithologic data collected during well installation (including physical descriptions developed as part of Task 1), and well-bore geophysical data PVP (including gamma and electromagnetic (EM) resistivity logs)

collected from wells to assess aquifer materials prior to installation of the PVP. Results will be correlated with water-level data to confirm direction of groundwater flow at depth within the aquifer interpreted from water level contour maps. PVP data will provide additional data on the magnitude of flow in heterogeneous alluvial deposits near the fault, and data on changes in flow under differing hydrologic conditions compared with estimates of aquifer hydraulic properties and heterogeneity produced from well-bore flow data collected in the western subarea and with data from paired upgradient and downgradient monitoring wells used to address groundwater movement from recharge areas along the Mojave River. Results will support model updates and calibration described in Task 5

Coupled well-bore flow and depth-dependent water quality data will be collected from three existing wells completed within alluvium and bedrock. The wells will be located: 1) in an area believed by the Lahontan RWQCB to have increasing Cr VI concentrations associated with the plume west of injection wells installed to control westward migration of the plume, 2) in areas to the west and north of the margin of present-day saturated alluvial deposits. Wells will be pumped at a rate appropriate for well construction and specific capacity. Pumped water will be treated and disposed according to standard operating procedures established by the Lahontan RWQCB for the site. Fluid temperature, fluid conductivity, and electromagnetic (EM) flow logs will be collected in the down direction at 5, 10, and 15 ft per minute from within the wells under unpumped and pumped conditions. Data at different trolling rates will be used to develop a field calibration for the EM flow tool. Additional logs to be collected include natural gamma and caliper logs (optical televiewer logs will be collected depending upon tool availability). Well discharge data will be collected during logging using a sonic flowmeter. The geophysical data are intended to show depths where water enters the wells. The depth-dependent water quality data will show the quality of the water entering the well between sample depths. In addition to chemistry and Cr VI data, isotopic data also will be collected from the wells to determine the source, hydrologic history and age of the water, history of rock-water interactions, and the source of Cr VI. Dissolved gas data (noble gas, chlorofluorocarbons, and sulfur hexafluoride) are not usually collected as part of these data sets, but can be collected using specialized sample collection techniques if needed.

Previous work elsewhere in the Mojave Desert showed oxidation of Cr III to Cr VI in formerly saturated alluvium resulted in Cr VI concentrations in the unsaturated zone above the water table as high as 28  $\mu\text{g/L}$  (Izbicki and others, 2008). This work was done in silty alluvium eroded partly from mafic rock having high-chromium concentrations, rather than in coarse-grained alluvium eroded from granitic rock or less mafic metamorphic rock typical of the study area. However, it is possible that this process may create a reservoir of Cr VI within the unsaturated zone that could enter groundwater if the water table should rise. The mass of Cr VI stored within the unsaturated zone would be a function of the thickness of the previously saturated alluvium, the Cr VI concentration in pore water within the unsaturated alluvium (related to the mineralogy of the alluvium and rate of oxidation of Cr III to Cr VI), and the residual water content within the unsaturated alluvium (related to the texture of the alluvium). To address this concern, Cr VI concentrations in alluvium above the water-table interface will be collected in the field using a hydraulic press to extract water from unsaturated alluvium, similar to methods described by Izbicki and others (2008). If alluvium in the study area is drier or coarser-textured than alluvium sampled by Izbicki and others (2008) and does not readily yield water pressure extraction may not work in unsaturated alluvial deposits in Hinkley Valley. If pressure extraction does not work, other alternatives such as water extraction can be used. The mass of Cr VI stored in the unsaturated zone will be compared to historic water levels and Cr VI concentrations in water from wells near the water table to determine the influence of mobilization of Cr VI from the unsaturated zone on Cr VI concentrations in the study area. It is likely that dedicated drilling, other than drilling done for regulatory purposes, at three sites will be required to collect data to address this issue.

**Northern subarea:** Under predevelopment conditions, groundwater flowed from recharger areas along the Mojave River through Hinkley Valley to the north into Water Valley and toward discharge areas near Harper (dry) Lake. Under present-day conditions, pumping for land treatment of Cr VI by PG&E has created a pumping depression that limits northward movement of groundwater containing Cr VI. However, the configuration of the water table in the past as agricultural pumping declined and pumping by PG&E to manage the plume is not precisely known. Additional information on the bedrock altitude and thickness of alluvium near the gap that separates Hinkley and Water Valleys and on groundwater flow near the Mount General Fault may help address questions concerning past groundwater movement and Cr VI transport in the northern subarea.

Gravity data will be collected to determine alluvial thickness in and near the gap between Hinkley and Water Valleys. The data will be collected and interpreted in a manner similar to gravity data collected in the western subarea. PVP data also will be collected in this subarea to address groundwater movement rates and effects of aquifer heterogeneity in a manner similar to PVP data collected in the western subarea. These data also will support model updates and calibration described in Task 5.

Low activities of tritium were present in water from 5 of 10 wells sampled in the northern subarea as part of 'snapshot' data collection has caused concern from PG&E and their consultants that nearby bedrock to the west of the sampled wells, having thin or absent alluvial cover, may contribute small amounts of locally derived recharge and potentially Cr VI to groundwater. This concern will be addressed through interpretation of the hydrologic history of the groundwater recharge process using dissolved atmospheric gas data (argon, nitrogen, and neon data collected as part of Task 3). Installation of wells in bedrock areas in the northern subarea is not recommended at this time. In addition to concerns about recharge from bedrock areas, low-activities of tritium caused concern that recharge from intermittent flows in local drainages also may contribute small amounts recharge that also may contribute Cr VI to groundwater. To address this concern, core material will be collected from two sites the unsaturated zone underlying selected streams. This core material will be analyzed for water content, water potential, soluble salts (including chloride, sulfate, nitrate, and bromide),  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , and tritium. The absence of soluble salts, especially chloride in unsaturated alluvium would be an indication of present-day recharge. In contrast accumulations of soluble salt in the unsaturated zone would be an indication that present-day recharge does not occur. Specialized sample collection, handling, and preservation methods described Izbicki and others (2000) will be used to ensure the representativeness of these samples. A water table well also will be installed at each location and sampled for chemical constituents and the entire suite of tracer data discussed in Task 2 (including  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , noble gases, age dating parameters,  $^{87/86}\text{Sr}$ , and  $\delta^{53}\text{Cr}$ ). Dedicated drilling, other than drilling done for regulatory purposes, will be required to install wells to address this issue.

In contrast to concerns expressed over the possibility of Cr VI associated with small amounts of locally derived recharge, areal recharge in the Mojave Desert is considered to be negligible under present-day climatic conditions (Izbicki and others, 2007). In the Mojave Desert soluble salts have accumulated in alluvial deposits near the base of the root zone since the climate dried near the end of the last ice age, about 10,000 years ago. The small amount of water (typically less than 5 percent volumetric moisture content) within the unsaturated zone at depths where soluble salts have accumulated is saline, highly alkaline ( $\text{pH} > 9.5$ ), and can be characterized as a saturated sodium bicarbonate solution (Izbicki, and others, 2000). In alluvium eroded from mafic rock, Cr VI is associated with this highly alkaline, saline water (Izbicki and others, 2008b; Mills and others, 2011). Movement of water through unsaturated mafic alluvium as a result of agricultural activity has been shown to mobilize Cr VI to the underlying

water table (Izbicki , 2008, Izbicki and others, 2008b). It is not known if saline, alkaline water within unsaturated alluvium eroded from granitic rock in the Mojave Desert also is associated with high Cr VI concentrations, or if Cr VI can be mobilized from the unsaturated zone by past agricultural activities or residential land use in Hinkley Valley. Selected unsaturated core material collected from the unsaturated zone during test drilling by PG&E and their consultants will be analyzed for soluble salts (including chloride, nitrate, sulfate, and bromide), water extractable Cr VI, and water content to determine the mass of Cr VI potentially stored within the unsaturated zone. Because of the high salinity, the  $\delta^{53}\text{Cr}$  isotopic composition of this water is likely near 0 per mil, and similar in composition to chromium released at the compressor station (Izbicki, 2008; Izbicki and others, 2012). If Cr VI is present analyses of  $\delta^{53}\text{Cr}$  will be attempted on water extracts from the unsaturated zone, although high-sulfate concentrations may interfere with those analyses. The total amount of Cr VI potentially released from the unsaturated zone by agricultural activity in Hinkley Valley will be estimated from borehole and land use data from areal photographs and compared to the mass of Cr VI released at the compressor station and its potential influence on Cr VI concentrations at the water table.

**Eastern subarea:** Some issues of concern in the east include: The eastern subarea contains groundwater in alluvial deposits to the east of the plume, within the mapped plume, and in areas upgradient from the mapped plume. Large-scale agricultural pumping which declined in much of the Hinkley Valley in recent decades remains in the eastern subarea.

The effect of large-scale agricultural pumping on groundwater movement near production wells, and potential movement of Cr VI contaminated groundwater through heterogeneous aquifer deposits will be addressed using coupled well-bore flow and depth-dependent water-quality data from two agricultural production wells. The wells sampled in the eastern subareas differ from wells sampled using this approach in the western subarea primarily in the magnitude of pumping from the well. Well-bore flow data will be analyzed using the computer program AnalyzeHOLE (Halford, 2009) to estimate aquifer hydraulic properties. Analyze-Hole is a MODFLOW based computer program equipped with a spreadsheet interface and a particle-tracker (Pollock, 1994) to aid in visualization of groundwater movement to wells. Depth-dependent water-quality data collected from the wells under pumping conditions will be used to determine differences in Cr VI concentrations (and isotopic compositions) with depth. If access into the wells is suitable, well-bore flow data will be collected using the tracer-pulse technique (Izbicki and others, 1996), and depth-dependent water-quality samples will be collected using a small-diameter, gas-displacement pump (Izbicki, 2004). If access to wells is not suitable, production pumps may need to be removed from the wells and temporary pumps installed to collect these data, potentially increasing costs. Aquifer property data will be used

Also of concern in the eastern subarea are the range of Cr VI concentrations in recently recharged water from the Mojave River upgradient of the mapped plume, and the rate of groundwater movement once recharged from the river towards the compressor station and the mapped plume (both in areas where the fault is present, and in areas where the fault is absent).

To determine the range of Cr VI concentrations in recently recharged groundwater samples will be collected and analyzed quarterly for field parameters, major ion, selected minor ions, and selected trace elements including Cr VI from eight wells near the Mojave River. These wells may include a combination of existing PG&E monitoring wells, USGS monitoring wells (installed as part of previous studies, Huff and others, 2002), and other existing wells having suitable construction information. The use of existing wells will permit collection of these data early in the study without having to wait for construction of new monitoring wells (additional monitoring wells installed as part of flowpath studies, next paragraph,

will provide data to evaluate initial Cr VI concentrations in water recharged from the Mojave River). Samples will be collected and analyzed twice during the study for tracer data described in Task 2 to determine how these constituents may vary with time near groundwater recharge areas along the river—especially if streamflow and recharge occurs along the river during the study. The potential influence of imported water recharged by Mojave Water Agency along the Mojave River will be considered if recharge using imported water occurs during this study.

To address the rate of groundwater movement from recharge areas along paired the river to the compressor station and the western subarea downgradient from the Lockhart Fault, multiple-well monitoring sites will be drilled at upgradient and downgradient positions along three flowpaths starting near the river. Data from the wells will be used to estimate the initial Cr VI concentration of water recharged from the Mojave River and rate of groundwater movement along the flowpaths. At each site, wells will be completed near the water table and at selected depths below the water table depending on site specific geologic conditions. Regional and local-scale water-level maps, and particle-tacking data from the USGS regional groundwater flow model (Stamos and others, 2000) will be used as a starting point to develop the flowpaths. The westernmost flowpath will extend from the Mojave River toward the Lockhart Fault and is intended to be within alluvial fan deposits that compose the regional aquifer. The other flowpaths will be located in areas alluvium upgradient and downgradient from the Lockhart Fault. Dedicated drilling, other than drilling done for regulatory purposes, will be required to install wells to address groundwater movement along the selected flowpaths. Once installed, wells will be sampled quarterly during the study for field parameters, major-ions, selected minor-ions, selected-trace elements, and  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . Wells will be sampled twice during the study for the entire suite of tracer data discussed in Task 2 (including  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , noble gasses, age dating parameters,  $^{87/86}\text{Sr}$ , and  $\delta^{53}\text{Cr}$ ). Data from the wells will be used to estimate the initial chemistry, Cr VI concentrations and isotopic composition of water recharge from the Mojave River. The potential influence of imported water recharged by Mojave Water Agency will be considered if recharge occurs during this study.

**Task 5: Evaluation of historic and present-day groundwater movement.** An existing MODFLOW groundwater flow model originally developed by Andrews and Neville (2003), and updated for estimation of management alternatives within the area (Arcadis/CH2M-Hill, 2011) will be used to evaluate historic and present-day groundwater movement in the study area. This task will be done by PG&E consultants in collaboration with U.S. Geological Survey hydrologists familiar with groundwater flow models, and with their use within the Mojave Desert of southern California. The modeling work will be divided into four steps: 1) review of groundwater flow model suitability for use for the purposes of this study, 2) update and recalibration of the model, 3) use of the model to estimate historical groundwater levels, and 4) use of the model with particle tracking to aid in the visualization of groundwater movement and interpretation of groundwater age data.

The U.S. Geological Survey in collaboration with PG&E and their consultants will review the existing groundwater flow-model to determine its suitability simulate groundwater flow in Hinkley Valley with respect to the model domain, boundary conditions, hydraulic properties (including the influence of aquifer heterogeneity on transport of Cr VI), and spatial and temporal discretization. On the basis of the initial evaluation the model will be updated, and the updated model will be recalibrated to available data. Depending on the results of the model evaluation, it may be necessary extend the model domain to appropriate hydrologic boundaries. In addition, the model may need to be refined to improve: 1) simulation of groundwater flow between the bedrock aquifer and the alluvial deposits, 2) simulation of drying and rewetting of alluvial deposits through time, 3) simulation of the effect of the Lockhart and Mount General Faults on groundwater flow, and 4) simulation of the effect of rapid, intermittent

infiltration and subsequent recharge of large quantities of streamflow from the Mojave River. Other refinements not specifically listed also may be required. Historic water-level and streamflow data (available digitally from U.S. Geological Survey, Mojave Water Agency, PG&E consultants, and Project Navigator data bases), test-drilling data collected by PG&E consultants during well installation (including texture data available digitally from Project Navigator), pumping data (available from the U.S. Geological Survey and the Mojave Watermaster), groundwater flow data collected during tracer tests done within the IRZ, geologic and hydrologic data from the western, northern and eastern subareas collected as part of this study, and other available data (including areal imagery) will be used to update aquifer property and other hydraulic data within the groundwater flow model prior to calibration.

The updated and calibrated groundwater flow model will be used to estimate historical groundwater levels and movement within the study during hydrologically important periods including: 1) prior to agricultural pumping, 2) after the onset of agricultural pumping during the time when Cr VI releases occurred from the compressor station, 3) as agricultural pumping declined but prior to pumping for land treatment of Cr VI by PG&E, and 4) present-day conditions, including the effect of ongoing management activities (such as pumping for land treatment, injection to control plume migration, and movement of groundwater within the IRZ) intended to control or remediate the plume.

A particle-tracker will be added to the model to aid in the visualization of water movement through the valley, the distribution of groundwater age data, and increase understanding of Cr VI movement from the compressor station. Reactive transport of Cr VI in groundwater will not be simulated. Special attention will be given to the influence of rapid, intermittent infiltration and subsequent recharge of large quantities of streamflow from the Mojave River on groundwater flow and movement. Particle-tracking results will be compared with tracer data collected as part of this study to evaluate the source, movement, and age of groundwater in a manner similar to a regional analysis of groundwater flow and movement in the Mojave River groundwater basin by Izbicki and others (2004). Model properties may need to be adjusted to improve calibration and simulation results where indicated on the basis of this comparison.

**Task 6: Evaluation of the occurrence of natural and anthropogenic chromium.** A wide range of geologic, geochemical, and isotopic data will be collected from the different subareas within the study area. No single type of data is expected to provide the complete answer to questions concerning background Cr VI concentrations. However, the combination of these data is expected to provide understanding to address this issue. It is likely that the data may show background Cr VI concentrations differ in different subareas.

Initial data analyses will be done using a pattern-recognition approach developed using a summative scale. Most people are familiar with a type of summative scale commonly used to assess public opinion known as a Linkert scale (Linkert, 1932). To analyses results from a Linkert opinion survey, ordinal values are assigned to responses to questions within the survey (known as items) such as: strongly agree, agree, no opinion, disagree, strongly disagree (in a typical Linkert survey scores could range from 1 through 5, respectively). The ordinal values are then summed to determine the overall opinion of the participant. Summative scales have application in the physical sciences as an initial data-analysis tool for problems where multiple processes may affect the measured data, and there is not a strong consensus or understanding of the importance of the individual processes. Their use in this study is intended to provide a transparent process that facilitates input from TWG members during data interpretation.

For the purposes of initial data analysis, binary-ordinate (nominal) values will be assigned to items developed on the basis of metrics measured during this study that compose the scale. The items that

compose the scale, analogous to questions in a Linkert opinion survey, will be relevant to the occurrence of natural (value = 0) or anthropogenic (value = 1) Cr VI. For example: 1) Is tritium absent (value = 0)? , Is tritium present (value = 1)? , or 2) Is chromium less abundant than average in local geologic material (value = 1)? , Is chromium more abundant than average in local geologic material (value = 0)? Summed values will be used to categorize (bin) data to assist with pattern-recognition on graphics developed as part of this study. These graphics will include maps for spatial analyses, and representations of geochemical processes, such fractionation or mixing trends on plots of  $\delta^{53}\text{Cr}$  as a function of Cr VI concentrations.

After the initial analysis, geologic, hydrologic, and geochemical knowledge coupled with traditional parametric and non-parametric statistical analyses will be used refine results to 1) identify items within the scale that contribute most to interpretable patterns, 2) identify items within the scale that covary and may be eliminated from the scale without loss of interpretative power (Principal Component Analysis may be especially suited for this), 3) refine items within the scale from data oriented responses to process oriented hydrologically based responses, 4) if appropriate, values other than binary-ordinate (nominal) values will be assigned to refined items within the scale 5) if appropriate, weights will be assigned to selected items within the refined scale. Graphics will be revised to improve pattern recognition and interpretation of the data as the scale is modified. It is likely that in at least some wells mixtures of natural and anthropogenic Cr VI may be present, and in some areas it may not be possible to identify with certainty the source of low concentrations of Cr VI.

Although the use of a summative scale is intended to reduce complex data to easily understandable visual graphics that facilitate input from TWG members during data interpretation, final interpretation of the data will be scientifically based and process oriented; and preparation of the final report remains the responsibility of the U.S. Geological Survey.

**Task 7: Estimation of background Cr VI concentrations.** Results from this study and interpretation of data as part of Task 6 will form the basis for identifying where background Cr VI concentrations are present within the different subareas within Hinkley Valley. After identification of areas containing natural and anthropogenic Cr VI (and mixtures of end-members from sources identified as part of this study) it may be possible to estimate background Cr VI concentration in areas not affected by discharges from the compressor station using existing data and data collected as part of this study.

However given criticism of the 2007 background study, the TWG may determine that it is necessary to produce a statistically-defensible background Cr VI concentration for one or more of the subareas within the study area. If a statistically-defensible approach is needed, it may be necessary for PG&E to install additional monitoring wells in areas identified as having naturally-occurring Cr VI similar to the approach proposed in response to criticism of the 2007 study (Stantec, 2012). The approach and specific details associated with this task will be outlined in the preliminary report to be prepared in Federal Fiscal Year 2014.

Regardless of the scope of this task, wells selected for inclusion in background Cr VI calculations will need verifiable construction data, and representative spatial distribution within the study area. Scope of work for this task includes quarterly sample collection and analyses of total dissolved chromium, and Cr VI from 30 wells and associated data analyses. The wells will be identified on the basis of data collected as part of this study in consultation with the TWG. Selected wells will be sampled and analyzed quarterly for a period of one year (4 samples) to obtain a data to assess variability in naturally-occurring Cr VI concentrations in different parts of the study area. Cr VI data will be collected by PG&E consultants and

U.S. Geological Survey staff. Samples will be split and analyzed by both groups. The average of the two samples will be used for estimation of background. In cases where Cr VI data differ by more than 10 percent, the sample the best fits data from other quarters will be used for estimation of background.

**Task 8: Fate of chromium during insitu reduction.** PG&E is injecting a carbon source (ethanol) into the alluvial aquifer downgradient from the compressor stations to create reducing conditions within the mapped plume that reduce soluble Cr VI to insoluble Cr III; and thereby, remove Cr VI from solution. As previously discussed, there is concern from the CAC over manganese and arsenic by products that enter groundwater within the reduced zone (known as the insitu reactive zone, or IRZ) produced by this process. There also is concern that chromium removed from solution within the IRZ may be remobilized over decadal time-scales through reoxygenation of treated aquifer material as oxic groundwater recharged from the Mojave River flows through the aquifer.

Consider a  $1,000 \text{ cm}^3$  volume of aquifer material having a porosity of  $0.3 \text{ cm}^3/\text{cm}^3$ . Assuming a mineral grain density of  $2.65 \text{ g/cm}^3$  (density of quartz), this  $1,000 \text{ cm}^3$  of aquifer material would contain about 1.8 kg of alluvium and  $300 \text{ cm}^3$  (0.3 liters) of groundwater. Given a Cr VI concentration in groundwater within the plume of  $1,000 \text{ }\mu\text{g/L}$ , 300  $\mu\text{g}$  of chromium would be added to a  $1000 \text{ cm}^3$  volume of aquifer material as a result of insitu reduction of Cr VI to Cr III. In this example, the chromium concentration of the aquifer material would increase by  $170 \text{ }\mu\text{g/kg}$  as a result of insitu reduction.

Chromium concentrations on aquifer material extracted using a citrate bicarbonate dithionite (CBD) extraction (Mehra, and Jackson, 1960) to completely digest iron, manganese, and aluminum oxide surface coatings from alluvium within the IRZ in Hinkley Valley ranged from 0.5 to 6 mg/kg (ARCADIS, Inc., 2011). This value is similar to the range of chromium extracted using the strong acid digestion proposed for this study (Chao and Sanzalone, 1989) from oxide surface coatings on alluvium eroded from granitic rock elsewhere in Mojave Desert ranged from 0.3 to 3 mg/kg (Izbicki and others, in review). Both data sets indicate an order of magnitude variation in total extractable chromium on aquifer material, and show the chromium added to aquifer material through insitu reduction is small compared to the mass of naturally occurring chromium obtained through a complete digestion of crystalline iron, manganese, and aluminum oxides commonly occurring on the surfaces of mineral grains.

Consistent with these data, ARCADIS, Inc. (2011) did not find a significant difference in chromium concentrations in CBD extracts from iron, manganese, and aluminum oxide surface coatings on alluvium collected within the in Hinkley IRZ before and after insitu reduction (ARCADIS, Inc., 2011). On the basis of X-ray spectrographic data chromium in post IRZ alluvial material was associated with iron oxide minerals on the surfaces of mineral grains (ARCADIS, Inc., 2011). As a consequence, reduced Cr III produced as a result of insitu reduction was believed to be relatively immobile. However, the experimental design at Hinkley, and similar work at the PG&E compressor station at Topock, CA (ARCADIS, Inc. 2009), did not distinguish between comparatively abundant naturally-occurring chromium associated with crystalline oxide mineral surface coatings measured using the CDB extraction, and the smaller mass of chromium potentially added to the more reactive “non-specifically sorbed” and “specifically sorbed” operational fractions (measured as part of Task 2) (Wentzel and others, 2001).

In contrast to previous interpretations (ARCADIS, Inc., 2009, 2011), it is possible that reduced chromium added as a result of insitu reduction may initially be sorbed to aquifer material through cation exchange, rather than directly incorporated into crystalline oxide mineral structures on the surfaces of mineral grains. Chromium extracted from “non-specifically sorbed” and “specifically-sorbed” operational fractions (Wentzel and others, 2001) within alluvium eroded from granitic rock in Antelope Valley was

less than 6 and 4.5 µg/kg. These data suggest the mass of chromium added to aquifer material by insitu reduction (170 µg/L in the example above) may be several orders of magnitude greater than chromium sorbed in the more reactive fractions under natural conditions, and chromium may be potentially more reactive than indicated in previous interpretations (ARCADIS, Inc., 2009, 2011).

In contrast to field sample collection and analyses of different material collected pre and post insitu reduction, this study proposes controlled laboratory experiments to measure the fate of chromium within the IRZ. As part of these experiments, 6 sets of paired microcosms will be prepared from each of six homogenized samples of aquifer material selected to be representative of aquifer material within the IRZ (72 microcosms total). Selected materials will be described physically and characterized chemically using sequential extraction procedures (discussed in Task 2) to determine the range of naturally occurring chromium within the operational fractions defined by Wentzel and others (1991) and Chao and Sanzalone (1989). Extraction procedures will be modified to include an additional step to quantify Cr III sorbed through cation exchange.

Cr VI added to the experimental microcosms will be isotopically labeled chromium. In three sets of microcosms, the Cr VI will contain chromium-51 ( $^{51}\text{Cr}$ ).  $^{51}\text{Cr}$  is a man-made, radioactive isotope of chromium having a half-life of approximately 27.8 days. Initial  $^{51}\text{Cr}$  activities in the microcosms will be large enough to ensure sufficient radiation to trace the distribution of chromium on operationally-defined surface sorption sites within the microcosms for up to 6 months.  $^{51}\text{Cr}$  cannot be used for time periods longer 6 months because of radiation safety concerns associated with  $^{51}\text{Cr}$  activities needed for the longer time periods. In the three other sets of microcosms, the isotopically labeled Cr VI will be composed of chromium-50 ( $^{50}\text{Cr}$ ) and chromium-54 ( $^{54}\text{Cr}$ ).  $^{50}\text{Cr}$  and  $^{54}\text{Cr}$  are naturally occurring stable isotopes of chromium having low crustal abundances of 4.3 and 2.3 percent, respectively. The Labeled  $^{50}\text{Cr}/^{54}\text{Cr}$  stable isotope ratios will be different from the natural ration and used to trace the distribution of chromium on surface sorption sites within the microcosms for time periods longer than 6 months.

Once prepared, labeled Cr VI within the microcosms will be reduced to Cr III to simulate removal of chromium from solution within the IRZ. After reduction, the samples will be placed on a shaker table and incubated at room temperature. One microcosm from each set will be fully capped to exclude atmospheric oxygen and maintain reduced conditions. The other microcosm will be loosely capped to permit entry of atmospheric oxygen and maintain oxic conditions. Both microcosms from each set will be harvested at selected intervals during a two-year incubation (times = 0, 3, 6, 12, and 24 months. The sixth set of microcosms will be held in reserved and analyzed if a longer incubation time is needed). The isotopically labeled chromium in various operational fractions will be sequentially extracted using procedures described previously in Task 2 (Wentzel and others, 1991; Chao and Sanzalone, 1989) and analyzed in duplicate either using gamma spectroscopy (for  $^{51}\text{Cr}$ ), or thermal-ionization mass spectroscopy (for  $^{50}\text{Cr}$  and  $^{54}\text{Cr}$ ). Similar results are expected for the different isotopes and analytical techniques and experimental design will provide for overlap of the prepared microcosms and analyses using both approaches.

Data will be evaluated to determine if chromium reduced within the microcosms is: 1) initially sorbed as Cr III, or directly incorporated into crystalline mineral oxides, and 2) to determine if the operational fraction of chromium on aquifer solids changes with time and becomes increasingly mineralized and potentially less mobile with time. Similar experiments on arsenic sorption to alluvium eroded from granitic rock in the Antelope Valley (Izbicki and others, 2012) showed that some arsenic, initially sorbed to exchange sites on the surfaces on mineral grains, was incorporation into less reactive amorphous and crystalline oxide minerals within one year. Precision of replicate analyses and recovery of labeled arsenic for that experiment ranged from 91 to 96 percent with a median recovery of labeled arsenic of 94

percent (Izbicki and others, 2012). Similar precision and recovery of labeled chromium is expected for this experiment.

Included for analyses within each time step will be five additional sets of two microcosms containing iron and manganese oxides precipitated on to an artificial substrate (either glass beads or glass slides). The oxide precipitates will consist of: 1) iron oxide, 2) three iron and manganese oxide mixtures bracketing the range of known proportions of these elements in natural oxide coatings, and 3) manganese oxide. The prepared artificial substrates will be incubated at room temperature on the shaker table with the other microcosms (one under reduced condition, one under oxic conditions) to serve as a control for aquifer materials. The artificial substrates will enable examination of isotopically labeled chromium reduced from Cr VI to Cr III and sorbed on to the oxide precipitate without the presence of naturally occurring chromium; thereby, permitting examination of potential reoxidation of Cr III to Cr VI through time.

The presence of Cr VI from reoxidation within the microcosms and on the artificial substrates will be measured using XANES spectroscopy. Detection of Cr VI using XANES would indicate reoxidation of chromium within the microcosms. Reoxidation is more likely to occur in the oxic microcosm and the reduced microcosm will serve as a control for the experiment. Previous work showed detection of Cr VI in alluvial material 9 months after insitu reduction was not possible using XANES (ARCADIS, Inc., 2011). The use of material from controlled laboratory microcosms, including: 1) initial examination of materials, 2) use of artificial substrate that do not contain natural chromium, and 3) examination of materials at various time steps (including time steps longer than 9 months), is intended to improve XANES resolution and detection of Cr VI. If necessary the sixth microcosm will be held for a longer time period to ensure sufficient time to measure reoxidation of Cr III to Cr VI.

Microcosms will be prepared, incubated, and analyzed in a U.S. Geological Survey laboratory in Menlo Park, CA that is licensed and equipped for handling radioactive material under the direction of John Izbicki and Thomas Bullen. <sup>51</sup>Cr analyses will be made using a Wallac Wizard 1480 gamma counter (Perkin Elmer Inc., Waltham, MA), and <sup>50</sup>Cr and <sup>54</sup>Cr analyses will be made using thermal ionization mass spectrometry (TIMS, Finnigan MAT 261) with sample processing and purification procedures discussed in Task 3.

Potentially reactive sorbed chromium and reoxidation of Cr III to Cr VI, if present within the microcosm experiments does not necessarily mean that insitu reduction of Cr VI to Cr III within the aquifer is not a viable option or appropriate remediation technique for the site; however, reoxidation would suggest that insitu reduction is not a permanent solution; and PG&E, regulators responsible for the site, and the community should be prepared to retreat the site in the future.

**Procedures for laboratory evaluation, quality assurance, data management, and project management.**

Data for this study will be analyzed by a number of different highly specialized U.S. Geological Survey and contract laboratories. In accordance with U.S. Geological Survey Policy (2006), performance data from laboratories used to analyze data as part of this study will be evaluated according to their ability to meet specific project needs as defined in this proposal. The laboratory evaluation is subject to approval by the Water Science Center Director and regular review to show the laboratory meets performance criteria throughout the study.

Approximately 10 percent of the analytical budget from tasks within this proposal has been reserved for quality assurance samples. Quality assurance will consist of a combination of replicate/duplicate analyses, blank samples of various types, and spike samples as appropriate. Higher frequency of data

will be collected for analytes of higher importance to the project goals, and for analytes known to have high analytical variability on the basis of laboratory evaluation data. Lower frequency of quality assurance data will be collected for analytes of lesser importance to project goals, and for analytes known to have less analytical variability on the basis of laboratory evaluation data.

All data collected as part of this study will be publically available after internal project review. All water chemistry and isotopic data collected as part of this study will be transferred to the U.S. Geological Survey on-line data base NWIS-Web after review and approval. Geophysical data including gravity data and geophysical log data will be archived according to U.S. Geological Survey policies and publically available. After review and approval data also will be transferred to the TWG to update project data maintained by the TWG in support of this study. Details for transfer to TWG and will be developed as the project moves forward: however, NWIS-Web and other U.S. Geological Survey databases are to remain the primary mechanism for public release of data when available.

**Reports:** A fact-sheet style Open-File report will be prepared early in Federal Fiscal Year 2014 to describe the study purpose and approach. A report will be prepared in FFY 2016 to describe selected preliminary results and how those results contribute to understanding of the movement of water and the occurrence of chromium in Hinkley Valley near the contamination plume. A final report will be prepared in FFY-2017 for review, and publication in FFY-2018. Due to the complexity of the study multiple reports describing important results may be required. The final report(s) will be accompanied by a fact-sheet style Open-File report describing the results of the study. Updates on study design, progress, and data interpretation will be provided periodically to the TWG, interested stakeholders within the community, and the Lahontan RWQCB as appropriate.

**Budget:** The cooperator for this study is the Lahontan RWQCB. The total cost of the proposed work is \$4,549,067 (NOTE: Costs are estimated costs for FFY-13. After approval of the proposal scope by the TWG, cost will be distributed between fiscal years according to the project timeline, and burdened at a rate of 5 percent per year to account for inflation). For studies done with local agencies, the U.S. Geological Survey has Federal Matching Fund (FMF) to share costs for certain expenses, such as labor and travel, to a maximum of 30 percent of the cost for that expense. The maximum potential contribution from the U.S. Geological Survey by Federal Fiscal Year (FFY) is summarized in the following table:

	FFY-14	FFY-15	FFY-16	FFY-17	FFY-18	Total (FY-13 costs)
<b>Maximum Potential</b>						
<b>USGS FMF contribution</b>						997,500
<b>Cooperator contribution</b>						3,551,567
<b>Total</b>						4,549,067

Assuming the maximum USGS FMF contribution, total cost to the cooperator for the proposed work is 3,551,567 (NOTE: FFY-13 costs not burdened for inflation in FFYs 14-18). Costs by Task, Budget Category, and Federal Fiscal Year are in Table 1.

**Personnel:** The study will require the near fulltime services of two Research Hydrologists (GS-14 and GS-12) familiar with trace element geochemistry in desert aquifers. In addition the study will require part-time services of 1) a Research Hydrologist and a Hydrologist familiar with groundwater flow modeling in desert aquifers (GS-13, and GS-12, respectively), and 2) part-time services of several Hydrologic Technicians familiar with groundwater-quality data collection, geophysical log collection, gravity data collection, description of geologic material, and data management (various GS levels ranging from GS-11 to GS-7). The project also will require part-time services of geospatial, reports, and fiscal support staff. These personnel are on staff within the San Diego Office of the California Water Science Center. The project also requires specialized services of U.S. Geological Survey research personnel within the Water and Geologic Disciplines. These personnel have been identified within the proposal and they have agreed to provide the project services described within the proposal.

**Work Plan:** The project will be done during Federal Fiscal Years 2014 through 2018. Data collection and interpretation will occur during Federal Fiscal Years 2014 through 2017. Interim reports will be prepared for release in 2014, and 2016. Preparation of a final report will begin in Federal Fiscal Year 2016 for release in 2018. The work plan is in Table 2.

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### **Job Hazard Analysis For New Projects**

- Check the numbered box(s) for all significant safety concerns this project should address. Significant safety concerns are commonly those that require training, purchase of safety equipment, or specialized preparation to address potentially hazardous conditions.
- Identify any unlisted safety concerns at bottom of the page.
- Provide details on the back of this page.

Proposal Number: CA-14X

Project Title (Short): Hinkley Chromium

Project Chief or Proposal Author: Izbicki

√	Safety Concerns
1.	Wading, bridge, boat, or cableway measurements or sampling
2.	Working on ice covered rivers or lakes
3.	Measuring or sampling during floods
4. x	Well drilling; borehole logging
5. x	Electrical hazards in the work area
6.	Construction
7. x	Working in remote areas, communication, office call in procedures
8. x	Ergonomics, carpal tunnel syndrome
9. x	Field Vehicles appropriate for task?- Safety screens, equipment restraints.
10.	All terrain vehicles, snowmobiles
11.	Helicopter or fixed wing aircraft usage
12.	Site access
13. x	Hypothermia or heat stroke
14.	Hantavirus, Lyme Disease, Histoplasmosis, Pfiesteria, West Nile Virus, Others?
15. x	Contaminated water with sanitary, biological, or chemical concerns
16.	Immunizations
17.	Laboratory or mobile laboratory. Chemical hygiene plan.
18.	Hazardous waste disposal
19.	Hazardous waste site operations
20.	Confined space
21.	Radioactivity
22.	Respiratory protection
23.	Scuba Diving
24.	Electrofishing
25.	

Box no.	<p>For each numbered box checked on the previous page, briefly:</p> <p>A. Describe the safety concern as it relates to this project.</p> <p>B. Describe how this safety concern will be addressed. Include training, safety equipment and other actions that will be required.</p> <p>C. Estimate costs.</p>
4.	<p>The work will be done with the California WSC geophysical logging equipment and staff trained using established methods and field procedures. Standard safety precautions including morning safety updates for logging and sample collection crew, and personal protective gear will be in place. Some lifting is required to use this equipment in the field. The drawworks operator will be accompanied by additional personal to assist with tasks that require lifting of heavy objects.</p>
5.	<p>Geophysical and sample collection equipment commonly require use of field generators for power. All personnel will be informed of the DOI Learn course titled, "Safety: Electrical Safety Design" and encouraged to complete this course if they are not familiar with electrical hazards. No additional costs are expected.</p>
7.	<p>Although not especially remote, office call-in procedures will be in effect to ensure daily reporting of field staff during sample collection. A satellite phone (available for check out from the IT Section) or SPOT transmitter is required in areas that do not have cell phone coverage.</p>
8.	<p>Ergonomic assessments of employee workstations are available upon request to the CAWSC safety coordinator, Stephen Schmitt. The CAWSC has developed an SOP for procuring approved ergonomic equipment. Employees should contact the CAWSC safety coordinator for additional information.</p> <p>Performing work duties requiring moving or lifting heavy objects, long periods of sampling operation, or other repetitive activities, could result in injury. Employees will team lift if a load appears too heavy or awkward for one person to handle. When lifting employees will bend at the knees (not stoop), keep their backs straight, and lift with strong leg muscles (not weaker back muscles). When possible, mechanical equipment will be used to move heavy items.</p>
9.	<p>California Water Science Center field vehicles will be used to collect data for this project. Responsibility for vehicle maintenance resides with the person primarily responsible for upkeep of that vehicle. That person is to complete the USGS Motor Vehicle Safety Inspection Checklist (<a href="http://water.wr.usgs.gov/safety/vehicle_safety_check.shtml">http://water.wr.usgs.gov/safety/vehicle_safety_check.shtml</a>) annually and send it to Stephen Schmitt, CAWSC safety coordinator, who reviews it and then sends it on to Dawn Nahhas, the Center's vehicle coordinator. This checklist can be accessed from the 'Forms' section of the Center's Safety and Environmental webpage. Vehicles shall contain appropriate safety barriers to protect occupants from potential cargo projectiles. All project employees will be current with their driver safety training. The 4-hour DOI Learn training compliance module is called "NSC Defensive Driving 2" and must be completed every 3 years. Supplemental driver safety training will be provided to employees who may be driving utility trucks. No additional costs to the project are expected.</p>

13.	<p>Field conditions may range from extremely cold to extremely hot. Field staff will be adequately equipped for the range of environmental conditions to be encountered. Heat stress, from exertion or hot environments, places workers at risk for illnesses such as heat stroke, heat exhaustion, or heat cramps. Symptoms include rapid pulse, heavy sweating, fatigue, dizziness, nausea, irritability, and muscle cramps. First Aid includes stopping work activities, moving to cool, shaded area, removing excess clothes, applying cool water to body, increasing fluid intake (water or Sports drink), and seeking medical attention (if symptoms are severe or do not improve). Prevention includes monitoring the physical condition of yourself and coworkers, wearing light-colored, loose-fitting, breathable clothing (like cotton, not synthetics), scheduling heavy work for coolest parts of day, taking frequent breaks in shaded areas, and frequent water intake. Field personnel will be provided with First Aid training, adequate water, Sports drinks, shade, sunscreen (for body and lips), and shade (umbrella or canopy cover). To guard against hypothermia resulting from cold exposure, employees are instructed to minimize heat loss by any or all of the following: wear proper clothing, dress in layers including appropriate outerwear/survival suits, eat high energy foods, seek shelter from wind/waves, stay as dry as possible, and know the signs of hypothermia. In the case of hypothermia, take appropriate action/seek medical attention immediately. There is no cost associated with this requirement.</p>
15.	<p>Field staff are familiar with hygienic procedures to ensure safe collection and handling of environmental water samples. Groundwater in the study area may have low to high levels of contamination from Cr VI. Although contaminant concentrations are likely to be not so high as to pose an immediate danger to workers on-site, USGS activities will conform to site access and hygiene requirements at those sites. Field personnel will be advised of the contamination risk and will be provided onsite with protective equipment and supplies (e.g. impermeable gloves, splash resistant safety glasses, clean water supply, and antibacterial soap). Appropriate dust masks will be supplied if needed.</p>

**Discussed job hazard analysis (JHA) with District**

**Collateral Duty Safety Officer**

**Yes**\_\_\_\_ **No**\_\_\_\_

**and/or copy of JHA given to**

**Yes**\_\_\_\_ **No**\_\_\_\_

**Collateral Duty Safety Officer**

**Center Director**\_\_\_\_\_ **Date** \_\_\_\_\_

**Regional Program Officer** \_\_\_\_\_ **Date** \_\_\_\_\_

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# **ENCLOSURE 2**

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**Pacific Gas and  
Electric  
Company**

**Kevin M. Sullivan**  
Principal Remediation  
Specialist  
Hinkley Remediation  
Project

3401 Crow Canyon Rd  
San Ramon, CA 94583  
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November 6, 2013

Dr. John A. Izbicki  
United States Geological Survey  
4165 Spruance Rd  
San Diego, CA 92106

Re: Preliminary Comments on United States Geological Survey Draft Proposal titled:  
“*Occurrence of Natural and Anthropogenic Cr VI near a Mapped Plume, Hinkley, CA*”

Dear Dr. Izbicki:

On October 22, 2013 representatives of the United States Geological Survey (USGS), Project Navigator (IRP Manager for the Hinkley Community Advisory Committee – CAC), and Pacific Gas and Electric Company (PG&E) met at your office in San Diego to discuss the above-referenced draft proposal. First and foremost, PG&E supports the USGS proposal and looks forward to working with you and your staff to see the project to completion.

The draft proposal is well written; it identifies and details the myriad of tasks required to evaluate multiple lines of evidence for a thorough understanding of background chromium conditions in the groundwater of the Hinkley Valley. This letter provides preliminary comments on the draft proposal. As we discussed, one or more technical meetings are needed in the near future to further our discussions on key items. We will provide additional technical comments to you as appropriate following those discussions.

#### **Interim Deliverables to Answer Key Questions**

The draft proposal includes an interim report in USGS fiscal year 2016 (beginning Oct 2015) that would “*present selected preliminary results and how those results contribute to understanding of the movement of water and the occurrence of chromium in the Hinkley Valley near the contamination plume.*” A critical path for the study will be to provide timely answers to key questions as soon as technically feasible. Two specific examples we discussed on October 22<sup>nd</sup> were: “*What is the probability that chromium present north of Sonoma Road is associated with the PG&E plume?*” and “*What is the probability that chromium west of the current freshwater injection wells in the west is associated with the PG&E plume?*”

PG&E is recommending that the draft proposal be amended to identify the key questions that will be answered by the individual tasks in the study and associated work scope(s) that will be used to develop the multiple lines of evidence needed to answer these questions. Once work begins, PG&E suggests several of the key questions can potentially be answered at a relatively high level of certainty through the presentation of results in technical interim documents that are prepared by the USGS within a 12 to 18 month period.

It will be important that the TWG work collectively up front in the review of the draft proposal to ensure the interim deliverables, study objectives and schedule reflect realistic expectations. We need to clarify the questions that can likely be answered relatively quickly at a relatively high level of certainty while other questions may take a considerably longer time to address. We look forward to working with the USGS and the other TWG members to work through this process in a timely manner.

### **Task 1**

PG&E supports the scope of work presented in Task 1, consisting of data review and statistical evaluation of existing data for domestic and monitoring wells. As we discussed, it is important that the TWG fully understand the purpose of the work scope and what questions will and will not be answered by each task. In this case, the draft proposal should clarify that the Task 1 statistical evaluation will identify statistical trends and not by itself draw conclusions regarding the extent of the chromium plume or the potential for plume migration. The data will simply identify those areas with decreasing, stable, and increasing chromium concentrations and these results may then help guide additional data collection as described in other tasks to better understand the information.

### **Tasks 2 and 3**

The majority of the work scopes in Task 2 (Mineralogy) and Task 3 (Groundwater Geochemistry) appear relatively straight forward and are largely consistent with the technical discussions between PG&E and the USGS over the last several months. PG&E supports prompt implementation of both tasks, and understands that the data collection and evaluation can likely be completed within 12 to 18 months of starting work. We recognize that some of the details are still to be determined, such as what soil cores will be used as part of Task 2 and what wells will be sampled as part of Task 3. To the extent the work is focused on understanding background chromium concentrations, PG&E is supportive of the work. To do this, an overall understanding of geochemical conditions at the site is required, and hence some sampling and analysis of other trace elements is appropriate and justified. Sampling and analysis that is related to questions related to IRZ byproducts should be broken out and included as a separate work scope, to be completed as part of the IRZ review and permitting process. We look forward to working with the USGS to solidify these details.

### **Tasks 4 and 5**

Much of the data collection proposed in Task 4 (Evaluation of Local Conditions) will be integrated into Task 5 (Evaluation of Groundwater Movement). Task 5 basically consists of evaluation, update (as needed), and use of the existing numerical groundwater flow model. Several of the Task 4 work scopes are related to a better understanding of the groundwater flow across the Lockhart Fault (west), Mt. General Fault (east and north), and in areas where groundwater flow may be present in alluvium, weathered rock, and rock (primarily the west but also to the north at Red Hill).

PG&E recommends that additional discussions should be had on the existing flow model and the overall objectives of Task 5 before the specific work scopes for Task 4 are finalized and begun. The model will be an important tool to simulate groundwater flow in the present and provide a better understanding of historic groundwater flow conditions in the Hinkley Valley. We concur that the appropriate level of hydrogeologic data must be available to support the modeling effort. Based on discussions from October 22<sup>nd</sup>, PG&E understands that the USGS supports near term technical discussions to explore in more detail what data may be needed to support the model and that Task 4 can be modified as necessary to be fully aligned with the objectives of Task 5. We look forward to these discussions, and PG&E will likely provide more detailed comments on both Tasks 4 and 5 as follow-up to the dialogue.

### **Refine Objectives and Work Scope in the Near Term for Task 7**

Much of the studies outlined in Tasks 1 to 6 are intended to provide data to understand the occurrence of naturally occurring chromium in groundwater in the Hinkley Valley and to a lesser extent, where the PG&E chromium plume is present and is not present. Task 7 provides for an estimation of background chromium concentrations; in essence, something to replace the current incorrect calculated background levels for hexavalent chromium (Cr6) and total dissolved chromium (CrT).

The text of Task 7 acknowledges that at this time there is no clear path to meet the stated objective, and that the scope will be refined following completion of the first six tasks. PG&E concurs that, to date, discussion on this topic among the TWG members has been somewhat elusive. It is likely that replacing the 3.1 and 3.2 values will be a critical path forward for many stakeholders that are part of this process, and the first six tasks will likely not be complete for several years. PG&E recommends that discussions be held in the near future to discuss the goals and objectives of Task 7, and identify a series of options. The scope and nature of Task 7 can then be promptly re-evaluated to facilitate a timely implementation schedule.

### **Move Task 8 outside the Background Studies**

PG&E understands that Task 8 (Fate of Chromium during In-Situ Remediation) is an important item for the remediation elements of the project, and significant work on this question has already been undertaken. As we discussed, the work scope proposed is more appropriate outside the context of the background studies as part of the IRZ review and permitting process. PG&E is

November 6, 2013  
Page 4

requesting that Task 8 be removed from the draft proposal. We look forward to further discussions with the USGS on the appropriate work scope, timing, and funding vehicle.

We look forward to additional discussions with the USGS in the near future on the technical details of the draft proposal. If you have any questions in the meantime regarding this letter, please feel free to contact me.

Best Regards,



Kevin Sullivan

# **ENCLOSURE 3**

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October 22, 2013

John Izbicki, Ph.D.  
United States Geological Survey (USGS)  
4165 Spruance Road  
San Diego, CA 92106

**RE: The Hinkley CAC and IRP Manager Comments Regarding USGS Project Proposal on “*Occurrence of Natural and Anthropogenic Cr VI near a Mapped Plume, Hinkley, California*”, September 16, 2013**

Dear John:

The CAC and the IRP Manager have reviewed the United States Geological Survey (USGS) proposed scope of work (SOW) regarding the new Cr6 Background Study (BGS) for the Hinkley Valley. We thank you for providing us the opportunity to review the SOW. As you well know, the CAC and Community are very interested in your proposed program and understanding the role it will have in determining what the final Cr6 clean up goals are for the PG&E Cr6 discharge.

The new Cr6 background study is a key component of the Hinkley Groundwater Remediation Program. It will seemingly play a significant role in determining the final Cr6 groundwater cleanup number(s) in Hinkley, which will eventually be established<sup>1</sup> by the Lahontan Regional Water Quality Control Board. In our

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<sup>1</sup> The language for the cleanup of contaminated water can be found in State Water Resources Control Board Resolution No. 92-49 under section III. G. which states:

III. The Regional Water Board shall implement the following procedures to ensure that dischargers shall have the opportunity to select cost-effective methods for detecting discharges or threatened discharges and methods for cleaning up or abating the effects thereof. The Regional Water Board shall:

G. Ensure that dischargers are required to clean up and abate the effects of discharges in a manner that promotes attainment of either background water quality, or the best water quality which is reasonable if background levels of water quality cannot be restored, considering all demands being made and to be made on those waters and the total values involved, beneficial and detrimental, economic and social, tangible and intangible; in approving any alternative cleanup levels less stringent than background, apply Section 2550.4 of Chapter 15, or, for cleanup and abatement associated with underground storage tanks, apply Section 2725 of Chapter 16, provided that the Regional Water Board considers the conditions set forth in Section 2550.4 of Chapter 15 in setting alternative cleanup levels pursuant to Section 2725 of Chapter 16; any such alternative cleanup level shall:

1. Be consistent with maximum benefit to the people of the state;
2. Not unreasonably affect present and anticipated beneficial use of such water; and

opinion, the USGS Project Proposal is scientifically sound and it will address many of the concerns that the CAC and Hinkley Community have expressed during the monthly Community meetings.

An important feature of the USGS Project Proposal is that it is independent, but at the same time complementary, of proposed, parallel PG&E work on the same topic. For example, independently, USGS will be performing specialized groundwater analysis (tracer and isotopic analysis), under your own sample chain of custody. Those results will be interpreted by USGS and discussed with the BGS Technical Working Group (TWG). This recognition of the need for data quality and transparency, which will hopefully result in USGSs' conclusions being widely accepted by the Community stakeholders, is an important study component which the CAC and the Hinkley Community have long been advocating.

This said, below are the CAC and IRP Manager's questions and further clarifications regarding the USGS proposed work.

### **Task 1: Evaluation of Existing Data**

Will the evaluation of "existing data" include the review of all MWA and USGS historical data and field study reports? Does this task include the review and use of USGS and MWA historical databases, along with PG&E's database(s) which will be ultimately used for statistical calculations of Cr6 trends in the Hinkley Valley? What is the plan to integrate all data into one main database? Please discuss in greater detail how data from different sources (e.g. MWA and PG&E) will be integrated, evaluated and managed. As you know, data integrity and its blue-chip management have been pin-pointed by the IRP Manager and the CAC's independent facilitator<sup>2</sup> as key facets of the success of the program.

At the completion of the USGS evaluation of PG&E's existing data (or USGS, MWA and PG&E databases), the IRP Manager suggests that USGS prepares a report/memo summarizing key data trends, and makes interim recommendations regarding the installation of any additional monitoring wells required to fill data gaps for the background study.

### **Task 2: Sample Collection and Analysis of Rock and Alluvium**

How many readings per rock sample will be taken with the handheld XRF unit? Discuss how the surface concentrations of each XRF measurement be further "averaged" to arrive at a useable measurement? Does the handheld XRF unit require any special standards before calibration?

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3. Not result in water quality less than that prescribed in the Water Quality Control Plans and Policies adopted by the State and Regional Water Boards

<sup>2</sup> Mindy Meyer from The Center of Collaborative Policy at Sacramento State University, Sacramento, CA

Will the planned thirty (30) core materials and cuttings to be subjected to analysis be from the saturated zone? Are any core materials and cuttings from the unsaturated zone planned to be analyzed?

Historical agricultural pumping and water rights adjudication has fluctuated the height of water table over the years. Therefore does this require to be considered when collecting samples at the interface between the saturated and non saturated zones?

### **Task 3: Sample Collection and Analysis for Water Chemistry, and for Multiple Chemical and Isotopic Tracers:**

How is the 60-field samples number estimated for the background study? Please provide some perspectives; perhaps from other programs you have been involved. Are the 60 field samples the minimum number of samples required to conduct the study? Will all the samples be collected in the same quarter, or will the sample be collected in different quarters?

Do you plan to measure the vertical age profiles at a few selected locations? How will these locations be selected?

Because of water injection, extraction and possibly remedy driven recharging could there be difficulties identifying what water comes from where? How do you see mixing affecting the outcome locally measured Cr6 from either the natural or anthropogenic sources?

We recommend that a comprehensive summary table, outlining all the analysis USGS plans to conduct along with the number of samples, individual/lab that will be performing the analysis, etc., should be included in the SOW.

### **Task 4: Evaluation of Local Geologic, Hydrologic, and Geochemical Conditions:**

Is the cost of reviewing and insuring that PG&E Work Plans are in alignment with the USGS SOW included in this Task?

### **Task 5: Evaluation of Historic and Present-Day Groundwater Movement:**

Will any updated forecasting via the MODFLOW model (with the current boundary conditions) be applied to the Northwest Freshwater Injection System area? After learning about the general concepts of groundwater modeling, the CAC has suggested that the computational grid for the MODFLOW model in the area of the Northwest Freshwater Injection System could be refined to evaluate the four Cr6 transport hypotheses for the area.

**Task 6: Evaluation of Occurrence of Natural and Anthropogenic Chromium:**

Will a decision tree (or related decision management approach) be employed to determine the location of the new monitoring wells planned specifically for the BGS? Can you discuss in the SOW the approximate minimum number of data points required to run the data pattern recognition and Principle Component Analysis software?

**Task 7: Estimation of Background Cr6 Concentrations:**

No comments.

**Task 8: Fate of Chromium During *In-Situ* Reduction:**

Does this Task include a literature review of any similar studies, or evaluation of information on Cr6 conversion kinetics as they could affect the long-term permanence of the Hinkley remedy?

**General Comments:**

Is one interim report going to be produced or will there be several interim reports?

Does the budget incorporate the cost of attending all BGS TEMs? Is the cost of producing presentations to the TWG and the Community included in the budget?

What is the USGS “change process” to manage and incorporate data from MWA, PG&E consultants, and early generated “new data” into subsequent program modifications?

Should you have any questions or comments, please feel free to contact either of the undersigned at [rsanchez@projectnavigator.com](mailto:rsanchez@projectnavigator.com) or [iwebster@projectnavigator.com](mailto:iwebster@projectnavigator.com) (714-388-1800 (PNL main number) or 714-388-1821 (RS) or 714-863-0483 (IAW mobile)).

Sincerely yours,



Raudel Sanchez, Ph.D.  
Project Manager



Ian A. Webster, Sc.D.  
IRP Manager

CC:

CAC Members

PNL Staff

Kevin Sullivan, PG&E

Devin Hassett, Keadjian and Associates

Lisa Dernbach, Lahontan Regional Water Quality Control Board

Anne Holden, Lahontan Regional Water Quality Control Board

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# **ENCLOSURE 4**

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## Lahontan Regional Water Quality Control Board

October 30, 2013

Dr. John Izbicki  
U. S. Geological Survey  
4165 Spruance Road  
San Diego, CA 92106

### Comments on Proposal to Study the Occurrence of Natural and Anthropogenic Cr(VI), Hinkley, California

Water Board staff is providing comments on your September 16, 2013 proposal to study hexavalent chromium near the mapped plume in Hinkley. Overall, we believe the proposed study to be thorough and comprehensive in tasks recommended for evaluating natural versus anthropogenic chromium in the Hinkley Valley and estimating background chromium concentrations in different locations. We also support tasks that will evaluate the potential for oxidizing Cr(III) to Cr(VI) in the unsaturated zone, as this is not only a community concern but also a Water Board concern due to potential future implications on water quality.

The comments that follow are divided into Contract, Comments/Questions, and Suggested Edits.

#### Contract

The contract scope of work, task 4, requires:

Preparation of background study proposal and workplan(s). The draft background study proposal and workplan(s) will include, but not be limited to:

- i. A discussion of the scientific and management questions to be addressed by the proposal; specifically a discussion of whether or not the study will be able to determine the source(s) of hexavalent chromium in groundwater (i.e., from PG&E's waste discharge from the Compressor Station or from geologic materials in the Mojave Hydrologic Unit).
- ii. An assessment of the confidence level of the proposal to successfully address the scientific and management questions.

**Comment:** Please add a section or appendix to specifically address tasks 4.i and ii. The Water Board has stated that it is important for the public and the Board to clearly see what questions will be addressed (and what won't) along with the confidence level (which could be as simple as a high-medium-low ranking).

PETER C. PUMPHREY, CHAIR | PATTY Z. KOUYOUMDJIAN, EXECUTIVE OFFICER

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**Comments/Questions**

1. The document focuses solely on Cr(VI). Consider adding total chromium to the study since the Water Board believes that PG&E's remedial actions (agricultural units and in-situ remediation) over time have added Cr(T) concentrations in groundwater above natural background by converting Cr(VI) to Cr(III), the latter which can be found in the soluble form.
2. Pages 2 and 3: the document states that cooling tower water was treated with a compound containing chromium to inhibit corrosion. Recommend listing or citing the compound if known.
3. Pages 2, 3 and 9: the document states that the results of the study will be used to set cleanup goals for the Cr(VI) contamination plume in groundwater. The statement should be revised to state that the study results will evaluate the variations in background Cr(VI), which may be used by regulators in the future to determine cleanup goals.
4. On page 6, fourth paragraph: the second sentence states that water level declines in some areas were greater than 70 feet. In the section on historical groundwater pumping in the Hinkley Valley, the Water Board's July 2013 Final EIR discusses in Appendix A that water level declines were as much as 90 feet. Suggest comparing the references in the Final EIR to verify the amount of decline.
5. Page 7, first paragraph: not sure what is meant by the term "formerly saturated alluvium." Is this historically saturated alluvium prior to agricultural pumping in the 1950s and 1960s?
6. Page 7, second paragraph: recommend revising the first sentence and adding the following sentences:

"Chromium-containing waste water was applied to unlined ponds on the compressor station property beginning in 1952 and continued until 1964. Impacts to groundwater likely began in 1959, based upon an estimate 7-year percolation rate. In 1965, the chromium waste water was treated prior to disposal to land. In 1966, phosphorus was substituted for chromium in cooling tower water. Disposal to the unlined ponds ceased in 1973 when eight lined ponds were constructed under a permit by the Lahontan Water Board. Downward percolation to groundwater may have continued to 1980.

Water for the cooling towers comes from supply wells located on the southern portion of the compressor station property. The original supply wells were screened across the upper and lower aquifers until replaced in the mid-2000s with supply wells screened across just the lower aquifer. Originally, 50,000 gallons per day annual average (gpd) of groundwater was pumped for supplying water to the cooling towers. This amount was reduced to 30,000 gpd starting about 1997."

7. Page 8, third paragraph, last sentence, change to read: ...through the gap, and 4) what is the hydraulic connection between Hinkley Valley and Water Valley potentially affecting plume migration.

8. Page 12: Do the sequential extractions from cores and cuttings help understand the stability of Cr3 (operationally defined sorption sites on the surfaces of the mineral grains?) Or something else?
9. Suggest mentioning that the isolated chromium detections exceeding background levels in the west at Community Boulevard and Hinkley Road will be investigated to determine whether the source is natural or anthropogenic, such as from the waste pit on PG&E-owned land.
10. Page 19: Strontium (Sr) ratio of crustal abundance of 7.09939 doesn't seem right; should be less than 1?

### **Suggested Edits**

*Consider adding underlined text, and removing strikethrough text where noted.*

Throughout: Check usage of CAC - Community Advisory Committee – not Citizens Action Committee.

Pages 2 and 3: Average Cr6 background value is 1.2 ppb.

Page 3: The normal 95 percent upper tolerance level of 3.1 µg/L was determined from the 2007 background study and adopted by the Board as maximum background concentrations. ~~– was adopted as the cleanup level for remediation activities at the site.~~ (Note: the Water Board has not adopted cleanup levels yet for the site).

Page 6, third paragraph: suggest adding the word “artesian” when discussing flowing wells since that term is common to some people.

Page 7, third paragraph, third sentence: The chromium concentration high should be changed to 9,000 µg/L Cr(VI) (CH2MHill, August 2010).

Page 9, first paragraph: Recharge from irrigation return and dairy waste has contributed to increased dissolved solids and nitrates at very high concentrations in some areas.

Page 9, fourth paragraph: “These data will be used by regulators to establish cleanup goals...”

Page 23: ~~Installed~~ Installation of wells in ~~in~~ bedrock areas in the northern subarea is not recommended at this time.

Page 23: To address this concern, core material will be collected from two sites in the unsaturated zone underlying selected streams.

Page 25: To address the rate of groundwater movement from recharge areas along ~~paired~~ the river to the compressor station and the western subarea downgradient from the Lockhart Fault . . .

Page 25: Regional and local-scale water-level maps, and particle-tracking ~~tacking~~ tracking data

Page 26, fifth paragraph: To analyses analyze results from a Linkert opinion survey...  
Also, is it Likert Scale instead of Linkert Scale? Is this part of task 4?

We appreciate the opportunity to provide comments on your proposal and look forward to working with the U. S. Geological Survey in the future.

Should you have any questions, please contact Anne Holden at (530) 542-5450 or [aholden@waterboards.ca.gov](mailto:aholden@waterboards.ca.gov) or Lisa Dernbach at (530) 542-5424 or [ldernbach@waterboards.ca.gov](mailto:ldernbach@waterboards.ca.gov).



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