Appendices

Appendix A
Groundwater and Remediation Supporting Documentation

Appendix A.1

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A.1 Introduction

The purpose of this appendix is to supplement the EIR Section 3.1, *Water Resources and Water Quality* and provide readers a more detailed and technical understanding of groundwater in the Hinkley Valley, groundwater modeling efforts, characteristics of the chromium plume, and the existing and proposed remediation efforts to treat the chromium plume. The focus of this appendix is on the dynamics of the chromium plume in the Hinkley Valley Groundwater Aquifer, which is the primary aquifer that would be affected by remedial activities, and on the groundwater remediation activities being proposed to address the plume. As discussed in Section 3.1, *Water Resources and Water Quality*, the project area also includes a portion of the Harper Valley groundwater basin north of Red Hill, which may also be affected by remedial activities. Discussion in this appendix about issues related to remediation would also apply to activities that may occur in the groundwater basin north of Red Hill.

A.2 Hinkley Valley Groundwater Aquifer

The Hinkley Valley Groundwater basin is located north of the Mojave River between Hodge and Barstow. Based on the topography of the surrounding mountains, the Hinkley Valley groundwater basin is estimated to cover about 40 square miles (35,600 acres). **Figure A-1** shows a conceptual diagram of the hydrogeology and groundwater in the Hinkley Valley.

The basin is located in an alluvial valley filled with about 100 to 200 feet of unconsolidated sands and clays from watershed erosion from the surrounding mountains and sediment transported into the valley by the Mojave River flood events. There is evidence of a blue clay layer below portions of the Hinkley chromium plume that is likely the remnant of a playa lake deposit that separates the alluvial deposits into an upper and a lower layer. The blue clay does not extend below the Mojave River fluvial deposits, so water enters both the upper and lower aquifers from the river (fluvial) deposits. Historically, the Mojave River may have periodically flowed towards the north into Harper Valley, which is indicated by alluvial deposits connecting these two valleys. The best indication of the alluvial materials that form the Hinkley groundwater basin (i.e., clay, silt, sand, and gravel sizes) comes from well drilling logs. ~~The alluvial deposits are similar to the soil material that is evident at the surface in the Hinkley Valley; finer silt and clay materials are found along the mountain boundaries, with more sand and gravel material along the Mojave River and in the valley leading north to Harper Lake.~~ The project area is primarily made up of different types of alluvium, but is mostly composed of recent floodplain deposits closer to the Mojave River and older fan, lake deposits, and dune sand in the northern portion of the project area. Soils are described in more detail in Section 3.4, *Geology and Soils*, and shown in **Figure 5** of Appendix C, *Biological Resources Report*.

The project area also includes the northeastern portion of the Harper Lake Valley (defined as north and west of Red Hill including the areas around the eastern side of the lake). However, only the Hinkley Valley aquifer has been considered in the groundwater modeling analyses to date as it is the primary aquifer affected by the project.

A.2.1 Groundwater Movement

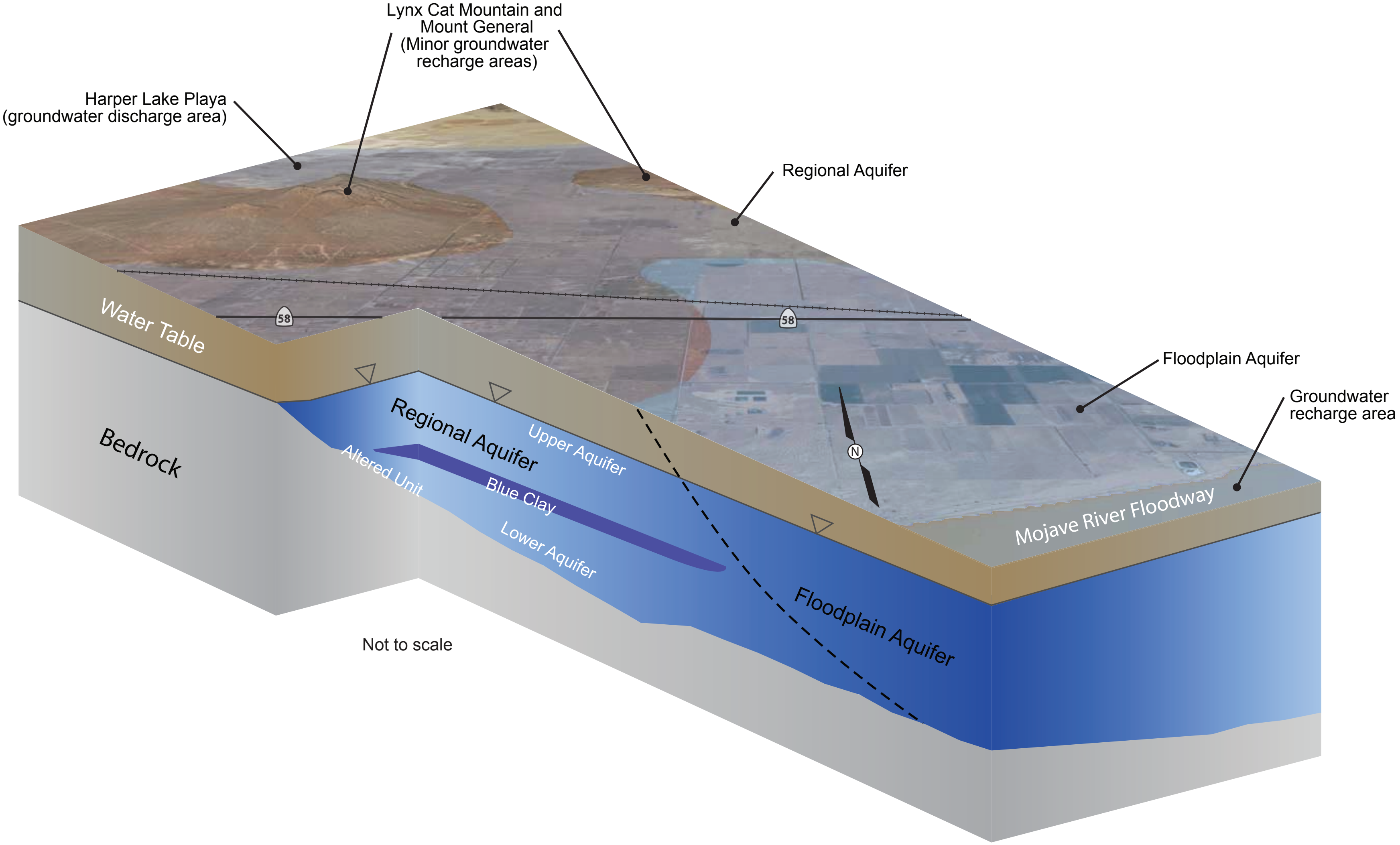
The movement of groundwater normally occurs as slow seepage through the pore spaces between loose (unconsolidated) rocks or through networks of fractures and openings in consolidated rocks. Groundwater movement through the Hinkley Valley alluvial channel is controlled by the aquifer geology, hydraulic conductivity and changes in groundwater elevations (groundwater inflows and outflows). If there were no sources of water (i.e., recharge) into the Hinkley Valley groundwater basin, and no outflows from the basin, the groundwater elevation would be uniform across the basin and there would be no movement of groundwater.

Groundwater in the Hinkley Valley groundwater basin generally flows in a north-northwesterly direction, ~~from the Compressor Station to the northern end of the valley.~~toward Harper Lake Valley. This is because the Mojave River is located along the southern end of the Hinkley Valley, and provides a majority of this recharge water that flows to the north toward the Harper Dry Lake which is at a lower elevation. As recharge water moves through the Hinkley Valley, it raised groundwater elevations. The alluvial channel at the north end of the Hinkley Valley is the other basin feature that is important for groundwater movement as it acts like a narrow funnel that increases flow movement to Water Valley (Harper Dry Lake).

Localized groundwater flow varies throughout the basin. For example, in the immediate vicinity of the Compressor Station, groundwater flow moves to the north or northwest but in other areas, such as near the Desert View Dairy, can be to northeast. **Figures 3.1-4b** and **3.1-4c** in Section 3.1, *Water Resources and Water Quality*, show groundwater elevations and flow directions in shallow and deep zones of upper aquifer from PG&E Fourth Quarter 2012 data in portions of the project study area.

A.2.2 Groundwater Elevations

Groundwater ~~elevations are raised during~~ recharge occurs due to large runoff events from the Mojave River and groundwater levels are subsequently raised. ~~;G~~ groundwater levels are lowered when overall pumping rates exceed groundwater recharge rates in the Hinkley Valley. It may take several years or more for a river recharge event to ~~raise groundwater levels~~reach ~~throughout~~ the Hinkley Valley. The Mojave River alluvial channel is periodically recharged (every 5 to 10 years) during major runoff or storm events. The water levels along the Mojave River channel may be recharged by as much as 20 to 40 feet during these surface flow events (Stamos et al 2001). The effects of storm or flood flows on groundwater levels are observed in monitoring wells in and near the river's floodplain, but are much less immediately apparent in wells further away from the river. For example, water table maps prepared by the US Geological Survey (USGS) for the winter of 1993 (the largest runoff year from the headwaters area since 1931 as of 1996) show that, between November 1992 and March 1993, water table rises in the project study area were roughly 16 feet to over 48 feet beneath and immediately adjacent to the Mojave River, 8 feet to 16 feet up to 0.75 mile north of the river, 4 feet to 8 feet up to 1.25 miles north of the river, and 1 foot to 4 feet up to



Source: Pacific Gas and Electric 2007a.

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Figure A-1
Generalized Conceptual Diagram of Local Geology and Groundwater in the Hinkley Valley

1.75 miles north of the river (Lines 1996)[1]. Recent years with some recharge in the Hinkley Valley portion of the Mojave River aquifer are 1983, 1993, 1998, 2005, and 2010.

Water elevations near the Compressor S~~s~~tation have been generally stable between 2,100 feet and 2,130 feet above mean sea level (msl). **Figures 3.1-4a** through **3.1-4c** in Section 3.1 show groundwater elevations based on data from PG&E Fourth Quarter 2011 and 2012 monitoring results.

A.2.3 Groundwater Pumping in the Hinkley Valley

Because the Mojave River alluvial channel is the only major source of recharge water, pumping in the Hinkley Valley will generally move groundwater in a northly direction, from the Mojave River towards the pumping. When pumping near the center of the valley occurs during periods between river recharge events, groundwater likely moves away from the mountain boundaries. The opposite is also likely true. When pumping near the center of the valley occurs following river recharge events, groundwater likely moves towards the mountain boundaries due to groundwater elevation increases. The groundwater elevations of the surrounding area will control the amount of the groundwater pumping that will be drawn from each direction around the well.

There is not a complete record of the locations and volumes of historical pumping for irrigation for the Hinkley Valley. However, the location and magnitude of existing groundwater pumping rates are used to approximate the expected future movement of the chromium plume. An additional complication is that there is an outcrop of bedrock between the town of Hinkley and the Desert View Dairy (DVD). Northward groundwater flow in the valley occurs both to the east and west of the bedrock outcrop on Mountain View Road. Pumping can modify (increase) the regional groundwater movement in the Hinkley Valley and change the groundwater elevation patterns.

Groundwater pumping in the Hinkley Valley is primarily used for domestic and agricultural supply. These wells vary in size and associated pumping capacity. Groundwater pumping volumes increase with well diameter at a constant pumping velocity. For example, an agricultural well typically has a much larger well diameter than a typical domestic well and, therefore, can pump greater volumes of water than a domestic well while applying the same pumping rate. **Table A-1** gives some typical well diameters with corresponding estimated pumping capacities.

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[1] Estimates of water table changes and distances from the Mojave River should not be considered exact as they were very roughly scaled by hand from a figure in Lines (1996) showing water-table rises along the Mojave River.

Table A-1. Well Size and Pumping Capacity Estimates

Well Diameter (inches)	Pumping Capacity (gpm)	Notes
2	4	
4	16	Typical case for domestic wells
6	36	
8	64	
10	100	
12	144	Typical case for agricultural wells
18	324	
24	576	

Notes:
Well pumping velocity of 5 ft/sec (300 ft/min) assumed
1 cubic foot of water = 7.48 gallons
Gpm = gallons per minute

Many of the wells in the Hinkley Valley are for individual domestic supply. Domestic wells are generally small, with diameters of 4 to 6 inches, and pump small amounts of water (usually less than 1 gpm). The domestic well capacity is usually greater than the needed water supply except possibly during the heat of summer. So during most of the year, domestic wells therefore pump only as needed each day to fill a small tank.

Agricultural supply wells are larger, with diameters of 12 to 24 inches. Well pumping capacities used for irrigation can be used to demonstrate drawdown levels. As shown in **Figure 3.1-12** of Section 3.1, *Water Resources and Water Quality*, a typical agricultural well supplying a 40-acre parcel with a pivot irrigation system (irrigating about 30 acres) would generally pump a maximum of about 250 gpm to supply a maximum of 1.10 acre-~~foot~~feet of water per day onto the 30-acre irrigated ~~field~~area. This would be approximately 0.45 inches of applied water per day across the field. On an annual basis, the well would deliver an average of about 150 gpm or 240 acre-feet of water per year. This would provide about 8 feet of applied water per year for the 30-acre irrigated area, but would withdraw about 6 feet of groundwater from below the 40-acre parcel. However, some of the applied water will infiltrate through the soil and the unsaturated zone back to the groundwater. About 5 feet of water will be used for evaporation and plant transpiration, known as evapotranspiration (ET). The remainder of the applied water will ultimately infiltrate and recharge the aquifer below the irrigation field. If the 6 feet of water for the 40-acre parcel came exclusively from the aquifer beneath the 40-acre parcel, the reduction in the groundwater level (drawdown) under the 40-acre parcel would be about 30 feet per year. The calculation is as follows:

$$\frac{6\ \frac{\text{ft applied water}}{\text{yr}}}{0.20\ [\text{soil porosity}]} = 30\ \frac{\text{ft}\cancel{.}\text{drawdown}}{\text{yr}}$$

Historically, there was more agricultural activity~~ was larger~~ than today, and pumping for irrigated agriculture could not be sustained across the entire Hinkley Valley because the average aquifer saturated thickness is less than 100 feet. Saturated thickness is the vertical thickness of an aquifer in which the pore spaces are filled (saturated) with water. But if only one 40-acre parcel were irrigated within each square mile (640 acres), the groundwater level would decline by about 1.88 feet per year (i.e., 30/16). The calculation is as follows:

$$\frac{30\,\dfrac{\text{ft drawdown}}{\text{yr}}}{\dfrac{640\text{ acres}}{40\text{ acres}}} = 1.88\,\frac{\text{ft drawdown}}{\text{yr}}$$

The total pumping in the Hinkley Valley for irrigation was estimated from irrigated acreage to be about 5,000 af/yr in 1940, about 15,000 af/yr in 1950 and about 15,000 af/yr in 1960 (DWR 1967). Assuming 8~~.00~~ feet of applied water per acre, this would represent an irrigated area of about 1,875 acres (about 7% of the Hinkley Valley). Some of the estimated pumping would return to the aquifer as recharge. About 5 to 6 feet of applied water would be lost to ET. Therefore, the 15,000 af/yr maximum estimated pumping would represent about 9,500 af/yr to 11,250 af/yr of water ultimately removed from the groundwater. This reduction in groundwater volume can ultimately affect groundwater movement. Pumping for irrigation would cause the groundwater elevation below the wells to decline and this would cause groundwater from adjoining parcels to move towards the wells. Distributed groundwater pumping will therefore cause a rate of groundwater movement equal to the pumping flow lost to ET (about 60% to 75% of the total pumping).

There is also considerable pumping for irrigation north of the Mojave River to the east of the PG&E Compressor Station. As shown in **Figure 3.2-2**, Section 3.2, *Land Use, Agriculture, Population and Housing,* there are numerous pivot irrigation fields located east of Summerset Road and south of Community Boulevard (estimated at 450 acres), east of Summerset Road and north of Community Boulevard (~~est.~~estimated at 150 acres), and east of Dixie Road and south of Community Boulevard (~~est.~~estimated at 350 acres). Pumping in these areas will have a large effect on the groundwater flow from the Mojave River alluvial sands towards these irrigation wells located just 1~~-~~ to 2 miles north of the river. Since each acre of irrigation will require about 5 feet of water per year, the pumping in the area east of Summerset Road and north of Community Boulevard would be approximately 750 af/yr, and the pumping in the area east of Summerset Road and south of Community Boulevard could be approximately 1,750 af/yr.

Besides the areas of pumping mentioned above, a large area of declining water levels (or cone of depression) is present in the upper aquifer in the area of the DVD land treatment unit (LTU) (Pacific Gas and Electric 2011a). **Figure 3.1-4** in Section 3.1, *Water Resources and Water Quality*, shows the measured groundwater elevation contours for the contaminated Cr[VI] plume. The extraction wells for the DVD ~~land treatment~~LTU are shown north of Santa Fe Avenue. There are four extraction wells for the DVD ~~land treatment~~LTU (EX-01 to EX-04). According to the PG&E Fourth Quarter 2010 DVD Monitoring Report, pumping from EX-01 averaged about 185 gpm, pumping from EX-02 averaged 125 gpm, pumping from EX-03 averaged 45 gpm, and pumping from EX-04 averaged about 5 gpm during 2010, for a combined total average rate of 360 gpm. However, the extraction pumping varied from periods of shutdown in the winter to 600 gpm in the summer. Groundwater levels~~drawdown resulting from pumping at~~ measured daily at several monitoring wells indicate the aquifer response (localized drawdown) to the increases in pumping. The local drawdown was~~these well locations is~~ most evident at downgradient wells, as opposed to upgradient wells, which were~~are~~ less affected by pumping rates; and groundwater drawdown increased~~s~~ as pumping rates increased.

~~As shown in~~ **Table A-2** gives~~,~~ ~~daily~~the~~annual~~ responses of water elevations, or drawdown, at several monitoring wells near extraction wells EX-01 and EX-02 to ~~increased~~different ~~increases in daily~~

pumping rates~~–~~. For the monitoring well located 300 feet east (MW # 21B), the drawdown was about 4 feet when pumping was 300 gpm, and increased to about 10 feet when pumping was 600 gpm.~~are highest at the closest well~~ The measured drawdown at the monitoring well located 1,600 feet down-gradient (MW #62A) was similar~~. to the east of the EX-01 and EX-02 and downgradient of EX-01 and EX-02~~. Whereas, the~~an~~ drawdown at the up-gradient monitoring well (MW #28B) ~~up-gradient~~upgradient ~~well, further away from EX-01 and EX-02 only~~ had a small decline of about 3 feet over the year with no noticeable responses to ~~the~~various changes in extraction pumping during the year.

Table A-2: ~~Daily~~ Annual Drawdown Response for Increases in Daily Pumping Rates at Monitoring Wells nearby DVD Extraction Wells EX-01 and EX-02

Monitoring Well	~~Increase in~~Daily Pumping Rate of nearby Extraction wells (EX-01/EX-02) (gpm)	~~Daily~~Annual Drawdown Response in Monitoring Wells (feet) During this Pumping Rate ~~in 2010 (ft/yr)~~
~~The~~ U~~u~~p-gradient monitoring well (MW # ~~(~~28B) (~~-located~~ 3,000 feet southwest from EX-01 and EX-02)	Various	3
~~The~~ C~~c~~losest well (MW # 21B)~~-~~ ~~located~~ (300 feet east of EX-02 and 700 feet east of EX-01)	300 450 600	4 7 10
D~~The d~~own-gradient well (MW # 62A)~~-~~ ~~located~~ (1,600 feet from EX-02 and 2,000 feet from EX-01)	300 450 600	3 5 10

A.3 Groundwater Modeling

Groundwater modeling is conducted by PG&E to determine potential movement of the chromium plume. This section discusses general conceptual approaches to groundwater modeling and the specific groundwater modeling that has been done to support development of the PG&E remediation project to date.

A.3.1 General methods for Groundwater Modeling

This subsection discusses general conceptual approaches to groundwater modeling of groundwater movement and drawdown.

A.3.1.1 Methods for Estimating Groundwater Movement

Groundwater movement in the Hinkley Valley can be estimated using three methods: differences in groundwater elevations~~,~~ throughout an area and the distribution of chromium plume concentrations, and groundwater pumping. These methods are described below.

Groundwater Elevations Method

The measured groundwater elevations in the existing wells (i.e., water elevation contours) are used for the primary method in determining the direction and the magnitude (volume/day) of groundwater movement in the Hinkley Valley. Groundwater elevations from PG&E's 4~~th~~Fourth Quarter 2011 and 2012 ~~M~~monitoring reports are shown in **Figure 3.1-44a through 3.1-4c** of Section 3.1, *Water Resources, and Water Quality.* Groundwater will move along pathways of the least resistance (highest conductivity), and will flow preferentially along gravel and/or sand deposits. Silt and clay layers or lenses within the sand and gravel will retard or reduce groundwater movement. ~~Based on the available~~Available groundwater elevation measurements ~~(i.e., water elevations)~~ and well boring logs (showing aquifer materials) are used to describe the depth and thickness of the Hinkley Valley groundwater basin ~~(i.e., aquifers)~~ and the corresponding groundwater movement. However, the ~~magnitude~~patterns of ~~the~~ groundwater elevation contours are also ~~an~~ important factors when considering groundwater movement; For example, steeper water elevation gradients ~~(i.e.,~~indicated by closer contour lines~~)~~ may indicate either greater volumes/day of groundwater movement in an area with larger pore spaces and greater hydraulic conductivity, or more resistance to water movement ~~(i.e.,~~in an area with smaller size material ~~with~~and lower hydraulic conductivity~~)~~.

Groundwater movement (volume/day) can be calculated by the hydraulic gradient (i.e., water elevation slope), the hydraulic conductivity, and the ~~thickness of the aquifer (i.e.,~~ saturated thickness of the aquifer). Groundwater movement (i.e., volume/day) is described by Darcy's Law and can be calculated for a given width of an aquifer as shown in equation [1].

[1]

$$\text{GW Movement}\left[\frac{\text{af}}{\text{day}}\right]=\left(\frac{(\text{aquifer thickness [ft]})(\text{width [mi]})}{\left(43{,}560\left[\frac{\text{ft}^2}{\text{acre}}\right]\right)}\right)\text{x}\left(\left(\text{water elevation gradient }\left[\frac{\text{ft}}{\text{mi}}\right]\right)\text{ x }\left(\text{hydraulic conductivity }\left[\frac{\text{ft}}{\text{day}}\right]\right)\right)$$

As shown in equation [1], groundwater movement (volume/day) will increase with a greater saturated thickness, a greater hydraulic conductivity, or a greater elevation gradient. As an example, for an aquifer width of 1 mile with a saturated thickness of 75 feet, a water elevation gradient of about 20 ft/mile and a hydraulic conductivity of 50 ft/day, the groundwater movement across a mile of the aquifer (flowing north) would be 1.72 af/day, equivalent to 0.567 million gallons of water per day (mgd) or about 395 gallons per minute (gpm). This calculation is shown as follows:

$$\left(\frac{(75ft)(1\,mi)}{\left(43{,}560\,\frac{ft^2}{acre}\right)}\right)\text{x}\left(\left(20\ \frac{\text{ft}}{\text{mi}}\right)\text{x}\left(50\ \frac{ft}{day}\right)\right)=1.72\ \frac{\text{af}}{\text{day}}=\ 0.567\text{ mgd}=\ 395\text{ gpm}$$

Table A-3 provides some conversion factors for these different groundwater units of measure for a saturated thickness at different soil porosities. The porosity of soil or geologic materials is the ratio of the volume of pore space, or voids, in a unit of material to the total volume of material within the aquifer. The voids are the areas where groundwater can flow. For example, 20% porosity means that groundwater can flow through 20% of the aquifer material. ~~Table A-4 provides estimated water movement values for a range of hydraulic conductivities and groundwater gradients.~~

Table A-3. Groundwater Volume and Flow Unit Conversions

Volume of Water in Aquifer below 1 acre (acre-foot):

	Porosity			
Saturated Thickness (feet)	10%	20%	30%	40%
25	2.5	5.0	7.5	10.0
50	5.0	10.0	15.0	20.0
75[a]	**7.5**	**15.0**	**22.5**	**30.0**
100	10.0	20.0	30.0	40.0

Conversions:

1 mile = 5,280 feet
1 cubic foot = 7.48 gallons
1 acre-foot (af) = 43,560 ft^3
1 million gallons (MG) = 3.06 acre-feet (af)
1 gallon per minute (gpm) = 1,440 gallon per day (gpd) = 192.5 ft^3/day

[a] The saturated thickness for the Hinkley groundwater model is assumed to be 75 feet and is shown in **Bold.**

Table A-4 provides estimated groundwater flow rate values for a range of hydraulic conductivities and groundwater gradients within a 1-acre parcel. Flow rates are a function of hydraulic conductivity and gradient. Hydraulic conductivity is the ease with which water moves through the aquifer. It should be noted that average groundwater flow usually changes as areas get larger because of greater variations in the type of aquifer materials; therefore, hydraulic conductivities become more variable.

Table A-4. Groundwater Movement Estimates

Groundwater flow beneath 1 acre (210 feet wide) cell (gpm):

	Groundwater Gradient (ft/mile)			
Hydraulic Conductivity (ft/day)	5	10	15	20
20	1.5	3.1	4.6	6.2
40[a]	3.1	6.2	9.2	12.3
60[a]	4.6	9.2	12.3	18.5
80	6.2	12.3	18.5	24.6
100	7.7	15.4	23.1	30.8

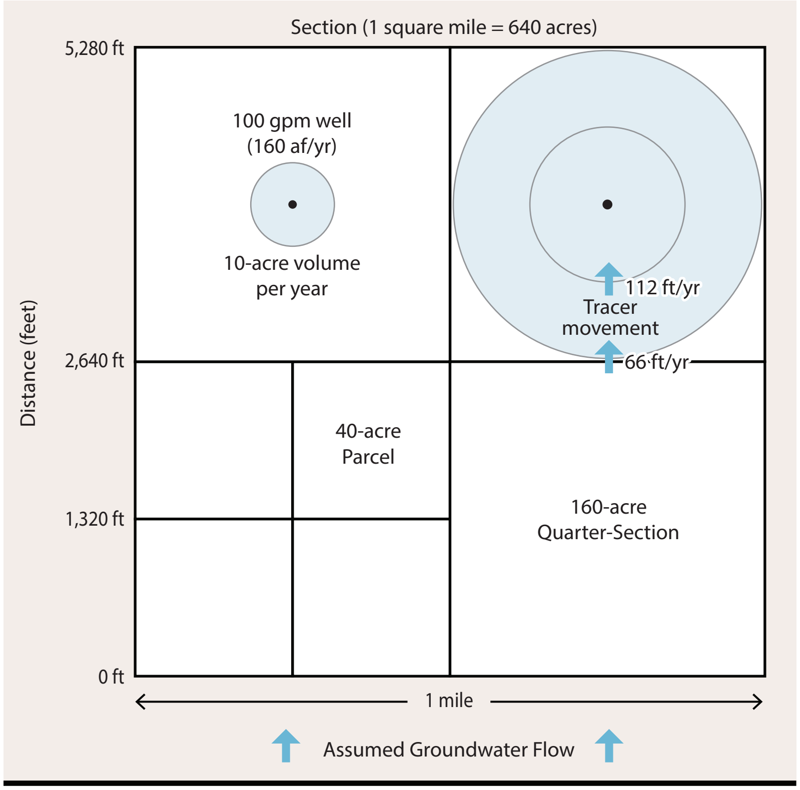
Notes:

Saturated thickness of 75 feet assumed. The hydraulic conductivity within the 1-acre parcel is assumed to be homogenous.

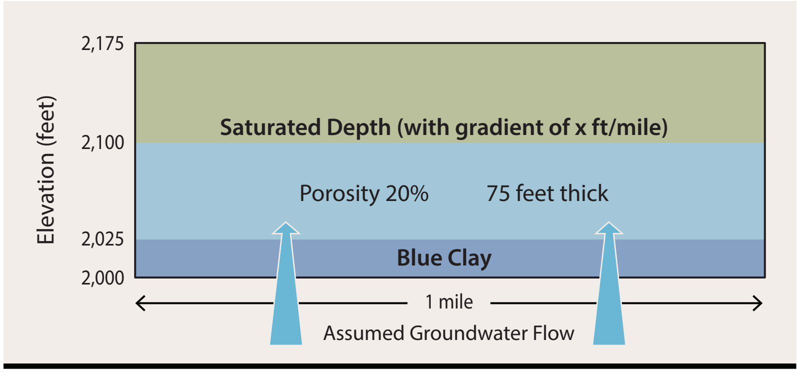
~~Key:~~

[a] Hydraulic conductivity for the Hinkley groundwater model is assumed to be 50 ft/day within a 1-acre parcel, which would be between these two values of 40 and 60 ft/day~~as shown in **bold** above~~.

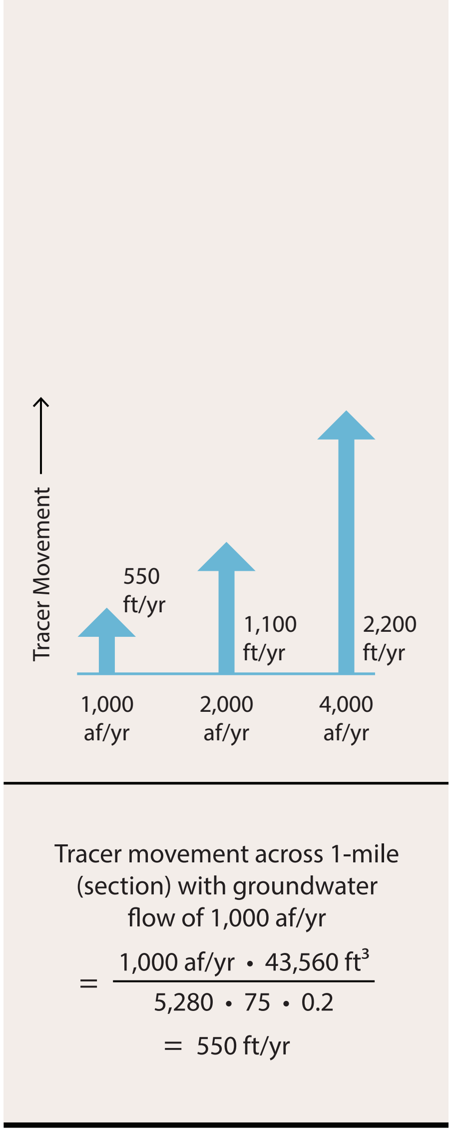
Tracer studies can also help determine groundwater movement along an aquifer. A tracer study involves the injection of a safe and non-toxic chemical or compound which movement can be followed with groundwater flow. Common types of tracers are dyes, salts, and fluorescent



A. Aerial View



B. Side View



C. Tracer Movement (feet) for Various Assumed Groundwater Flows (af/yr)

D. Annual Groundwater Flow (af/yr) Across 1-Mile Width for Selected Water Elevation Gradients and Hydraulic Conductivities

Groundwater Elevation Gradient	Hydraulic Conductivity (ft/day)			
	10	25	50	100
5 ft/mile	31	79	157	314
10 ft/mile	63	157	314	628
15ft/mile	94	236	471	943
20 ft/mile	126	314	628	1257

Source: Based on information from Pacific Gas and Electric 2010.

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Figure A-2
Effect on Groundwater Elevation Gradient on Groundwater Flow

compounds. **Figure A-2** provides a schematic on how tracer studies can be used to describe groundwater movement. The physical movement of water (i.e., tracer velocity) through the aquifer pore spaces (sometimes called Darcy's velocity) can be estimated from the water movement and assumed porosity with Equation [2]:

[2]

$$\text{Groundwater tracer velocity}\left[\frac{\text{ft}}{\text{day}}\right]=\left(\frac{\left(\left(\text{Groundwater movement}\left[\frac{\text{af}}{\text{day}}\right]\right)\right)\text{x}\left(43{,}560\ \left[\frac{\text{ft}^2}{\text{acre}}\right]\right)}{\left(\text{saturated thickness [ft]x(width [ft])x(mobile porosity (fraction))}\right)}\right)$$

For the average porosity of 0.2 (20 percent) estimated for the Hinkley Valley aquifer (Stamos et al. 2001), with the groundwater movement estimated for the previous example, the tracer velocity would be about 0.95 ft/day, or about 345 ft/year. This calculation is shown as follows:

$$\left(\frac{\left(1.72\,\frac{\text{af}}{\text{day}}\right)\left(43{,}560\ \frac{\text{ft}^2}{\text{acre}}\right)}{(75\text{ ft})\text{x}(5{,}280\text{ ft})\text{x }(.2)}\right)=0.95\text{ ft./day}=345\text{ ft/year}$$

A similar calculation is provided in box C of **Figure A-2**, which provides a calculation for groundwater flow of 1,000 af/yr, which results in a tracer movement flow of 550 af/yr. If some of the total porosity is in pockets of silt and clay that is not involved in groundwater movement, this porosity value would be reduced and the tracer movement velocity would be increased. **Table A-5** gives the estimated groundwater tracer movement (in ft/year) for a range of porosities and hydraulic conductivities.

Table A-5. Tracer Movement Estimates

Tracer Movement beneath 1 acre cell (ft/year):				
	Mobile Porosity			
Hydraulic Conductivity (ft/day)	5%	10%	15%	20%
20	~~35~~560	~~70~~280	~~105~~185	140
40	~~70~~1120	~~140~~560	~~210~~370	280
60	~~105~~1680	~~210~~840	~~315~~555	420
80	~~140~~2240	~~280~~1320	~~420~~740	560
100	~~175~~2800	~~350~~1400	~~525~~925	700

Notes:
Saturated thickness of 75 feet with hydraulic gradient of 20 ft/mile assumed

~~If~~Assuming the chromium plume ~~was dissolved and moving with~~moves at the same velocity as the groundwater, ~~this would~~the amounts in Table A-5 would be the distance that the edge of the plume would move downgradient (in the direction of decreasing water elevation) each year. This would be the expected velocity of the chromium plume within the upper aquifer. The measured groundwater elevations in the Hinkley Valley indicate that this flow would generally be northward, away from the Mojave River and towards the Harper Valley divide (i.e., underflow). Using ~~the calculations~~Equation

[2] above, tracer dye injected into the groundwater below the Compressor Station in 1961 would have moved approximately 3.27 miles to the north under natural conditions by 2011 (50 years) if these estimated ~~groundwater~~aquifer conditions (i.e~~.g.,~~ ., 20 ft/mile gradient with hydraulic conductivity of 50 ft/day with a thickness of 75 feet and a ~~mobile porosity~~20% of 20%) had remained the same. However, due to pumping influences by agricultural wells at the three dairies to the north of the Compressor Station and other agricultural fields, the chromium plume ~~likely~~may have moved in those areas at a greater rate in groundwater than under ~~normal~~assumed conditions. This may explain current chromium detections above maximum background levels at the far north end of the Hinkley Valley. At present, the plume is thought to be at least ~~5~~6.5 miles north of the Compressor Station~~,~~ (based on Q4 2012 monitoring report mapping), but the northern boundary is still being defined.[1]

Chromium Concentrations Method

A second method for determining groundwater movement near Hinkley is to interpret the historical chromium concentrations which record ~~(i.e., track)~~ the~~ slow~~ movement and spreading of the chromium plume that originated below the PG&E Hinkley Compressor station. This method may be useful for evaluating the likely future movement and spreading of the existing chromium plume. Because the only places where the chromium concentrations can be measured are in existing water supply wells (agricultural or domestic) or in monitoring wells, the plume concentration contours are sometimes inexact, and the ~~slow~~ movement of the chromium plume can be difficult to detect at times. Each well has a screen that extends some distance along the well casing within the aquifer saturated interval. Monitoring wells are usually screened with a short screen to measure water from about 10-40 feet of the saturated interval, while agricultural or domestic wells are often screened over the entire saturated interval which averages 75-100 feet in the Hinkley Valley. This concentration tracking method will be more thoroughly discussed in the following sections to explain the potential response of the chromium plume to injection and extraction (or pumping) in wells that are proposed for various treatment alternatives.

Groundwater Pumping Method

The third method for estimating groundwater movement is based on pumping records from the major agricultural and industrial (e.g., PG&E) supply wells and remedial wells located in the Hinkley Valley. Groundwater will move towards the wells to supply the water being pumped. Water will generally come from all directions, unless the well is near a basin boundary, the well is screened in a different aquifer, or there is a regional water elevation gradient away from the well. All of the pumping in the basin will tend to lower the ground water elevations, but the lowering will be greatest near the wells. This method is useful in looking at localized flow movement around areas of heavy pumping, particularly for agriculture/land treatment unit pumping and extraction for~~pumping for LTU and~~ IRZ remediation~~n areas~~, -as heavy pumping can alter groundwater movement patterns by creating localized cones of depression.

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[1] As described in Chapter 2, *Project Description*, the Q4 2012 monitoring report did not include areas north of Holstead Road in the delineated plume. However, the EIR project study area includes areas north of Holstead Road where there were detections of Cr[VI] in domestic wells higher than the maximum background level of 3.1 ppb. This northern area may also be part of the PG&E plume. With this addition, the plume would be approximately 9 miles north of the Compressor Station.

A.3.1.2 Approaches to Modeling Groundwater Elevations (Drawdown)

Groundwater pumping will cause a localized drawdown of water elevations around the well because a pressure gradient (i.e., water slope) is needed for the groundwater to move through the aquifer material to the well. This phenomenon is also known as a cone of depression. The aerial view is not truly a circle or cone but more like a comet with a long tail in the upgradient groundwater flow direction. But for modeling purposes, a circle is used to represent the shape of a cone of depression. The shape (i.e., depth) of the drawdown cone can be described based on Equation [1]. For example, an irrigation well pumping 150 gpm would draw approximately 0.65 af of water from the surrounding aquifer each day. A cylinder surrounding a well with a radius of 50 feet would have a circumference of 314 feet (i.e., (2π) x (radius)). For an assumed saturated thickness of 75 feet, with an assumed hydraulic conductivity of 50 ft/day, equation [1] can be rearranged to estimate the water elevation gradient (ft/mile) at a distance of 50 feet that would produce a flow (pumping rate) of 0.65 af/day. The necessary water elevation gradient would be about 128 feet/mile (slope of 0.025).

$$\frac{\left(\left(0.65\ \frac{\text{af}}{\text{day}}\right) \text{x} \left(43{,}560\ \frac{\text{ft}^2}{\text{acre}}\right)\right)}{\left(\left((75\ \text{ft})\text{x}\left(314\ \text{ft}^*\frac{1\ \text{mi}}{5280\ \text{ft}}\right)\right)\text{x}\left(50\ \frac{\text{ft}}{\text{day}}\right)\right)} = 128\ \frac{\text{ft}}{\text{mi}}$$

Figure A-3 provides a diagram of the effects of pumping for land treatment on groundwater movement**. Table A-6** shows calculated water elevation gradients with a varying cone of depression radius using Re-arranged Equation [1].

Table A-6: Estimated Water Elevation Gradients with Varying Size of Cones of Depression

Radius of Cone of Depression	Estimated Water Elevation Gradient (ft/mile)
50 feet	128
100 feet	64
200 feet	32
400 feet	16
0.125 mile (660 feet)	10
0.25 mile	5
0.5 mile	2.5

Notes:
A pumping rate of 150 gpm (0.65 af/day) with a thickness of 75 feet and a hydraulic conductivity of 50 ft/day assumed

The depth of the cone of depression below the saturated elevation can be calculated by integrating the required water slope from a large radius to near the well. A reasonable estimate of the shape of the drawdown can be calculated using the Thiem equation (Equation 3), assuming the drawdown at 2 miles (10,560 feet) would be small:

[3]

$$\text{Drawdown (feet) at distance from well} = \frac{\left(\left(\text{flow }[\frac{\text{ft}^3}{\text{day}}]\right) \text{x} \left(\ln \left(\frac{10{,}560\text{ ft}}{\text{distance [ft]}}\right)\right)\right)}{\left((2\pi)\text{x(thickness [ft])x}\left(\text{hydraulic conductivity }[\frac{\text{ft}}{\text{day}}]\right)\right)}$$

Calculated drawdown levels with a varying cone of depression radius using Equation [3] are shown in **Table A-7**. The drawdown cone would be deeper for a smaller groundwater thickness, a smaller hydraulic conductivity, and for greater pumping.

Table A-7: Calculated Drawdown Estimates

Radius of Cone of Depression	Estimated Drawdown (feet)
1 mile	0.9
0.5 mile	1.7
0.25 mile	2.5
1/8 mile (660 feet)	3.4
50 feet	6.5

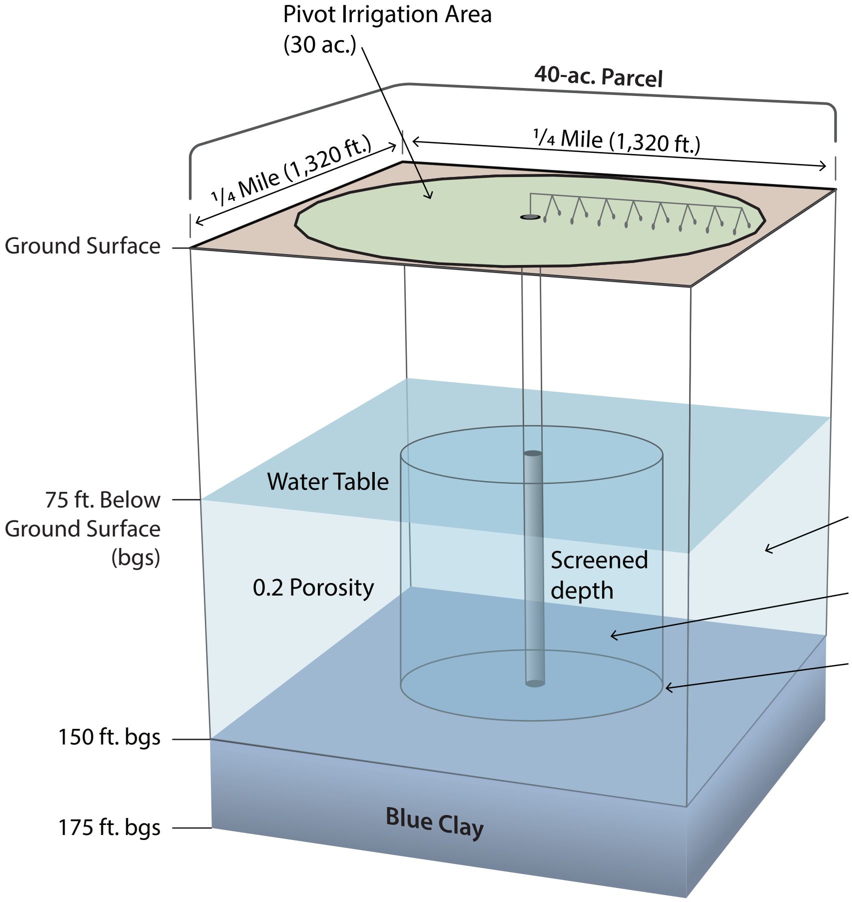
Notes:
A pumping rate of 150 gpm with a thickness of 75 feet and a hydraulic conductivity of 50 ft/day assumed.

When there is a regional groundwater gradient, the well will intercept water ~~only~~primarily from the sides and from up-gradient of the well. The radius of capture can be approximated as the distance from the well where the drawdown gradient equals the regional gradient. For the pumping example given above (150 gpm) assuming a regional gradient of about 20 ft/mile, the capture zone radius would be about 330 feet. The zone of capture would extend about 330 feet on each side of the well, but most of the water would move from up-gradient because the overall gradient would be stronger in this direction. These groundwater elevation gradients, drawdown depths, and capture zones will increase with the pumping rate. The effects of injection wells on the surrounding groundwater elevations, flows, and zone of influence will be the same magnitude but opposite in direction than with the extraction (pumping) wells. With this information, the effects of pumping and injection wells can be used in a localized groundwater movement and plume movement accounting framework.

A.3.2 Hinkley Remediation Project Groundwater Modeling

The Lahontan RWQCB asked PG&E to develop a groundwater model for tracking Hinkley Valley groundwater elevations and ~~the~~ Cr[VI] concentrations in ~~the contaminated plume~~groundwater. The model would be used to track plume containment and clean-up efforts. Three versions of a groundwater flow and chemical transport model have been developed: (1) SS. Papadopulos Model (Pacific Gas and Electric 1998); (2) CH2MHill Model (Pacific Gas and Electric 2007); and ~~the~~ (3) Arcadis Model (Pacific Gas and Electric ~~Company~~ 2010). The Arcadis model is the current model being used for the Project.

Groundwater modeling was conducted by PG&E to characterize the Hinkley aquifer system, forecast groundwater drawdown as a result of remedial pumping activities, and to simulate future Cr[VI]



For a saturated depth of 75 feet:

- Aquifer volume below parcel = 3,000 af
  Water volume below parcel = 600 af
- Aquifer volume pumped per year = 1,200 af (240 af / 0.2 porosity)
- Pumping radius = 470 feet (16 acres) for a year of pumping

Assuming 8 feet of water (depth) is applied to 30 acres (240 af/yr) with a 150 gpm pumping rate, 6 feet of water would be pumped from the 40-acre parcel.

The water level would drop by 30 feet during the year (6 feet /0.2 porosity) if ground water did not move from adjoining parcels.

If the groundwater came from the surrounding square-mile section, the water level would drop by about 2 feet because each 40-acre parcel would contribute 15 af/yr (30 ft /16 parcels).

The water movement from the four sides of the 40-acre parcel with the well would be 60 af/yr. Tracer from the edges of the 40-acre parcel would move about 132 ft/yr.

Tracer movement at the four sides of a quarter-section (160 acres) would be about 76 ft/yr. Tracer movement at the four sides of a section (640acres) would be about 38 ft/yr.

Source: Based on information from Pacific Gas and Electric 2010.

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Figure A-3
Diagram of Pumping Effects on Groundwater Movement

concentrations (i.e., chromium plume) for each remediation alternative evaluated in the EIR. This section describes the model parameter values, assumptions, and specified pumping and injection patterns that were used to simulate future groundwater conditions for each remediation alternative. It also provides an overview of the historical measurements and observations that were included in the development and calibration of the groundwater models. The documents used to describe groundwater modeling in this section include:

- Groundwater Flow and Chemical transport Modeling Report Prepared by SS Papadopolus at the Alisto Engineering Group (Pacific Gas and Electric 1998).
- Simulation of Ground-Water Flow in the Mojave River Basin, California. (Stamos et al. 2001).
- Groundwater Background Study Report, Hinkley Compressor Station, Hinkley California. Appendix B. Groundwater Flow Model. Prepared by CH2MHill (Pacific Gas and Electric 2007).
- PG&E 2011 Feasibility Study Addendum #3, Appendix G - Development of a Groundwater Flow and Solute Transport Model, Prepared by Arcadis (Pacific Gas and Electric ~~Company~~ 2011a).

The ~~base~~ model used for all modeling efforts to characterize groundwater flow in the Hinkley aquifer is a USGS ~~3-D~~ groundwater flow model, MODFLOW. MODFLOW was used to describe hydrological characteristics of the aquifer, such as groundwater volume, movement (i.e., flow rate, velocity, direction) and water elevation (i.e., depth to water)~~, with a time-step of one year~~. A 3-D chemical mass-transport model (MT3D) was also applied with~~to~~ MODFLOW to characterize chromium concentrations in the aquifer. MT3D uses the MODFLOW results for the water volumes and water movement ~~was used~~ to simulate changes in the concentration of Cr[VI] and dissolved carbon (i.e., ethanol). These computer models are general tools that can be used to study any groundwater basin.

MODFLOW simulates transient or steady-state, saturated groundwater flow in three dimensions. MODFLOW simulates groundwater flow in aquifer systems using the finite-difference method. Using this method, the model domain is divided into rows, columns, and layers that form cells. When overlain on a map of the study area, each cell represents a small part of the region. Each cell is assigned a series of parameters that relate to the average aquifer properties and stresses for that particular region. As the cell size increases, the parameter values describing the actual aquifer properties, which vary over the cell area, become more generalized. The three modeling efforts have used different representations of the aquifers (different size grids) to describe the Hinkley Valley groundwater conditions. ~~The finite-difference grid used in this model consists of 386 rows, 384 columns, and six layers, totaling 763,185 cells. Both rows and columns have variable spacing and vary between 1,000 feet wide in the outer portions of the model and 25 feet wide in the central portion of the model. The model used a one-year timestep.~~

A.3.2.1 S.S. Papadopulos Model

The initial model, developed by PG&E consultants, S.S. Papadopulos (SSP), was used to evaluate potential impacts from the proposed project and alternative treatment approaches. Because it was the first model that characterized the chromium plume, it is described here as the basic tool for understanding the historical plume movement and spreading, as well as the basic remediation options. This computer model was applied to the chromium plume based on previous measurements of groundwater elevations and chromium concentrations, as well as the measured aquifer thickness and well bore materials (sand, silt, and clay). A conceptual model was initially developed to define the site specific conditions and geologic characteristics that affect groundwater flow and chemical transport mechanisms and provide the basis for the computer simulation (Pacific Gas and Electric 1998).

Data on monitoring wells installed during previous site investigations and on existing irrigation wells were reviewed to estimate the hydraulic parameters for the aquifer material. The vertical variations in hydraulic parameters were incorporated into the model domain as structural layers. The upper aquifer system was subdivided into two distinct units: a coarse grained unit overlying a fine grained unit. The vertical layers together with the lateral area of the aquifer comprise the three-dimensional finite difference grid system used for the computer model. The thickness of each vertical layer varies within the model domain based on interpolation of strata elevation data from available boring logs for the existing water supply and groundwater monitoring wells.

It was assumed that chromium within the aquifer is a conservative constituent and that naturally occurring attenuation processes have no effect on the fate and transport of chromium in the subsurface. The rate of chromium transport or attenuation in the porous media is dictated by several processes: advection, dispersion, partitioning, and geochemical reactions. Advection represents the transport of dissolved contaminant caused by groundwater movement (tracer velocity). Dispersion in porous media refers to the migration or spreading of contaminants within the ~~small scales~~ areas of aquifer materials. It is dominated by the spatial structure of an area with homogenous hydraulic conductivity, which typically occurs on a small scale.

The geochemical processes of adsorption/desorption or the slow dispersion between clay and sand layers or lenses can be described empirically as a partitioning process. For the groundwater model, this partitioning was described as the fraction of the total contaminant mass that will be transported by advection. A partition factor of 1 indicates no partitioning, so that all the contaminant is dissolved and moves with the water. A partition factor of 2 would indicate that ½ of the contaminant mass will move with the water, and half will remain associated with the aquifer material (i.e., adsorbed or in clay lenses that are not moving). A partition factor of 4 indicates that only ¼ of the mass would move with the water. Because the highest concentrations of chromium remain below the PG&E Compressor Station after more than 50 years ~~of movement~~ indicates that much of the chromium mass remains in the sediments. Therefore, a very high partition factor of 8 or 16 was used for the lower fine-grain layer to simulate the chromium plume. This indicates that only 1/8 (12.5%) or 1/16 (6.25%) of the estimated Cr[VI] mass will move with the groundwater velocity. The remaining mass will remain in the aquifer matrix (saturated sediment particles).

Most of the Cr[VI] was simulated to remain below the PG&E Compressor Station. The measured chromium concentration being extracted for the East LTU, which had operated from 1992 to 1998 was about 200 to 300 parts per billion (ppb), and had removed a total of about 1,000 pounds (lbs) of Cr[VI] while pumping about 500 million gallons (1,500 acre-feet [af]). However, the assumed partition factor of 8 suggests that the remaining mass was 7 times the mass estimated from the well concentrations. The calibration of the model to match the measured plume concentrations in 1994 suggested that the original Cr[VI] mass was about 10,000 lbs. Using these calculations, T~~t~~he East LTU ~~had therefore removed~~would be estimated to have converted about 10% of the initial mass of Cr[VI] to Cr[III] by 1998.

~~A journal article describing this initial groundwater modeling (Andrews and Neville 2003) suggests that the initial movement of the Cr[VI] plume was influenced by the regional drawdown of the aquifer between 1950 and 1970. Because the irrigation pumping was reduced, the groundwater movement and corresponding plume movement has also been reduced in the last 40 years. They~~

~~suggest that most (80%) of the Cr[VI] mass was partitioned in the clay deposits near the bottom of the upper aquifer and that some might be trapped in the pore water remaining in the unsaturated zone as the groundwater elevations were reduced from about 2,140 feet in 1950 to about 2,110 feet in 1970.~~

A.3.2.2 CH2MHill Model

The second groundwater flow model was developed by CH2MHill. This model ~~is based in part on a combination the MODLFLOW model and~~incorporated elements of the previous SSP groundwater flow model developed for the Hinkley project area (Pacific Gas and Electric 1998). The 2007 Background Study Report refers to the CH2MHill groundwater model. Water table contours from the Mojave River to the northern portion of the site were developed from groundwater-level data collected in 2006 from project monitoring wells to indicate the direction of groundwater movement. The depth to groundwater ranged from approximately 75 to 102 feet below ~~the~~ ground surface (bgs). The saturated ~~U~~upper ~~A~~aquifer thickness ranged from approximately 25 feet (northwest area along Mountain View Road) to approximately 100 feet (eastern areas north of Highway 58). Lateral gradients range from 10 ft/mile to 20 ft/mile across the study area, generally flowing in a north-northwesterly direction from the compressor station to the northern end of the study area. The water budget described as part of the Arcadis model below was initially developed as part of this model.

The model was recalibrated after the 2006 drilling program ~~(~~using new well logs~~)~~. The assumed properties of the regional groundwater flow model were adjusted locally such that simulated hydraulic heads matched measured groundwater elevations for the simulated period. During model calibration the assumed aquifer properties (e.g., hydraulic conductivity and storage coefficients) were further adjusted within reasonable bounds to match simulated drawdown with drawdown observed in numerous aquifer tests performed at the site.

A.3.2.3 Arcadis Model (Current Model)

The third groundwater model was a revised and updated groundwater model developed and utilized by Arcadis for the chromium transport modeling conducted for the 2010 Feasibility Study and subsequent Addenda. The model used three layers to represent the upper aquifer. Model layers are further described below under the discussion of layer thicknesses. The boundary conditions for the flow model (i.e., groundwater elevations and inflows and outflow at the model boundary as well as internal pumping rates) were specified, and the solute transport model simulated likely plume concentrations over the next 100 years.

Each alternative was simulated with different well locations and flow rates at various time periods to optimize the effectiveness of the remedy in meeting project objectives. All types of remediation measures were simulated; extraction for agricultural land treatment, extraction and injection of ethanol for in-situ remediation zone, extraction for surface treatment and extraction of water from outside the plume for injection to provide plume containment along the sides of the plume.

The Arcadis transport model (MT3DMS) uses the flow terms and velocities computed by MODFLOW in its transport calculations. MT3DMS also uses the same finite-difference grid structure and boundary conditions as the groundwater flow model. MT3DMS has a comprehensive set of options and capabilities for simulating advection, dispersion/diffusion, and chemical reactions of contaminants in groundwater flow systems under general hydrogeologic conditions. Solute transport was simulated using the dual-domain formulation. In a dual-domain model, mobile porosity represents the fraction of the aquifer through which most groundwater flows (advection), while the immobile porosity represents the less mobile portions of the formation where diffusion is the dominant transport mechanism. Mass transfer (of Cr[VI] and ethanol) into and out of the less mobile zone is generally slow, since the process is controlled by diffusion. In the dual-domain model, ~~M~~mobile porosity was assumed to be 7% of the aquifer volume and immobile porosity was assumed to be 28% of the aquifer volume in all regions and layers (Pacific Gas and Electric 2011a).

~~In this formulation, water tracer movement is much faster than would be expected if all of the aquifer porosity were used.~~ This is a convenient way to model the~~a~~ Hinkley chromium plume; low concentrations have~~ that has~~ moved several miles (5-6 miles~~in~~ length), while the high concentration Cr[VI] has moved a much shorter distance (most is “trapped” in the immobile porosity volume). The mass transfer coefficient between the two zones and the porosity values were calibrated using detailed performance data from the Central Area In-situ Remediation Zone, and adjusted based on the historical plume measurements.

The initial plume concentrations used to develop the model were based on the contours that were developed from February 2010 data. For the mobile phase, the measured concentrations were used. But for the immobile phase, much higher Cr[VI] concentrations were assumed, and the slow exchange rate was adjusted to simulate a steady-state initial mobile phase plume concentration pattern.

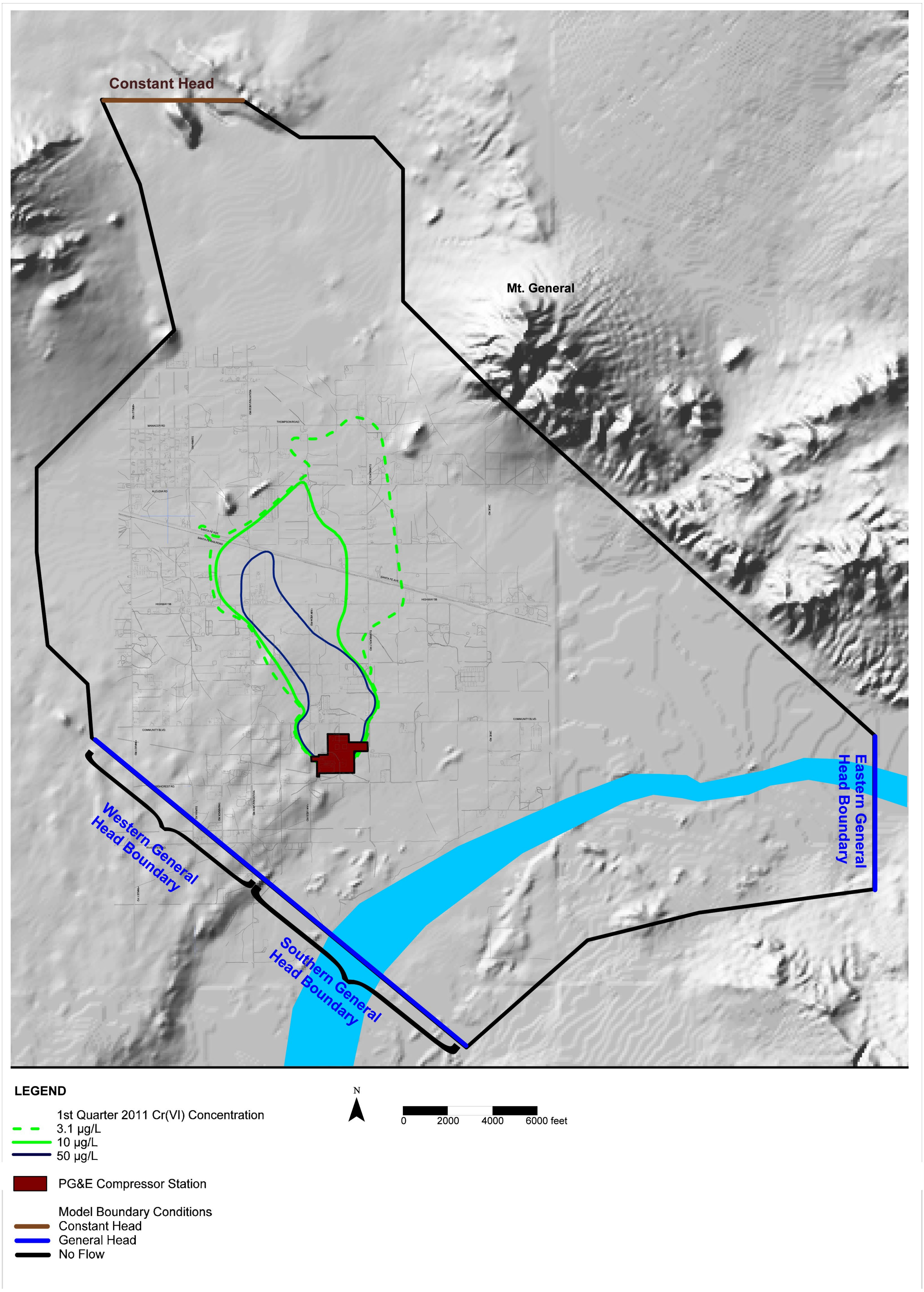
Model Parameters

In developing a model, the boundary and initial conditions need to be established first. Basic boundary conditions are shown in **Figure A-4**. These conditions are used to characterize the Hinkley Valley aquifer system. Boundary conditions include (1) aquifer aerial and vertical extent (model domain); (2) hydraulic properties of the aquifer (i.e., flow conditions, hydraulic conductivity, porosity and volume, groundwater elevations); (3) aquifer water budget (natural groundwater recharge and discharge zones and anthropogenic influence on groundwater). The initial conditions refer to initial values of elements that may increase or decrease in the course of the time inside the model domain and they cover largely the same phenomena as the boundary conditions.

Model Domain

The model was designed to represent groundwater conditions over approximately 25 square miles of Hinkley Valley. The main Hinkley valley is approximately 7 miles long and 3 miles wide extending northwest from the river toward Harper Valley (Pacific Gas and Electric 2011a), extending northwest from the Mojave River toward Harper Valley. The model extends from south of the PG&E compressor station to north of Red Rock Canyon. **Figure A-5** shows the model domain.

The boundary conditions, which describe the exchange of flow between the model and the external system, are located at the edges of the model domain. General head boundaries typically represent heads in a model that are influenced by a surface water body, such as a river, outside the model domain and require a record of water levels at a known distance from the model boundary. Based on this conceptual model, groundwater enters the southwest model domain along the Mojave River channel (Southern GHB) and from the alluvial fan or ancestral channel deposits west and southwest from the compressor station (Western GHB) (Pacific Gas and Electric 2011a). Likewise, groundwater exits the model domain along the Mojave River channel toward Barstow (Eastern



Source: Pacific Gas and Electric 2011a.

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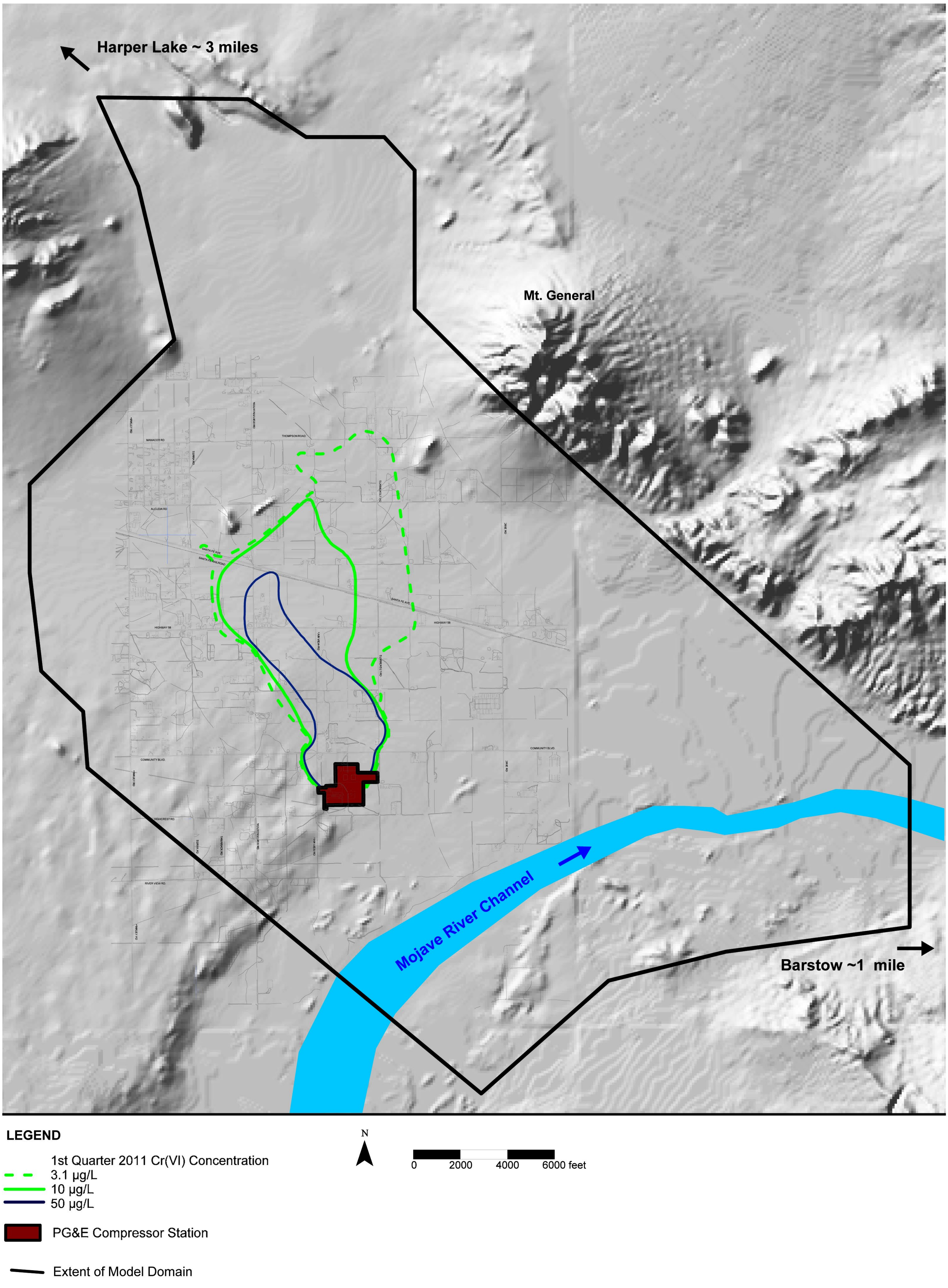
Figure A-4
Hinkley Groundwater Model Boundary Conditions



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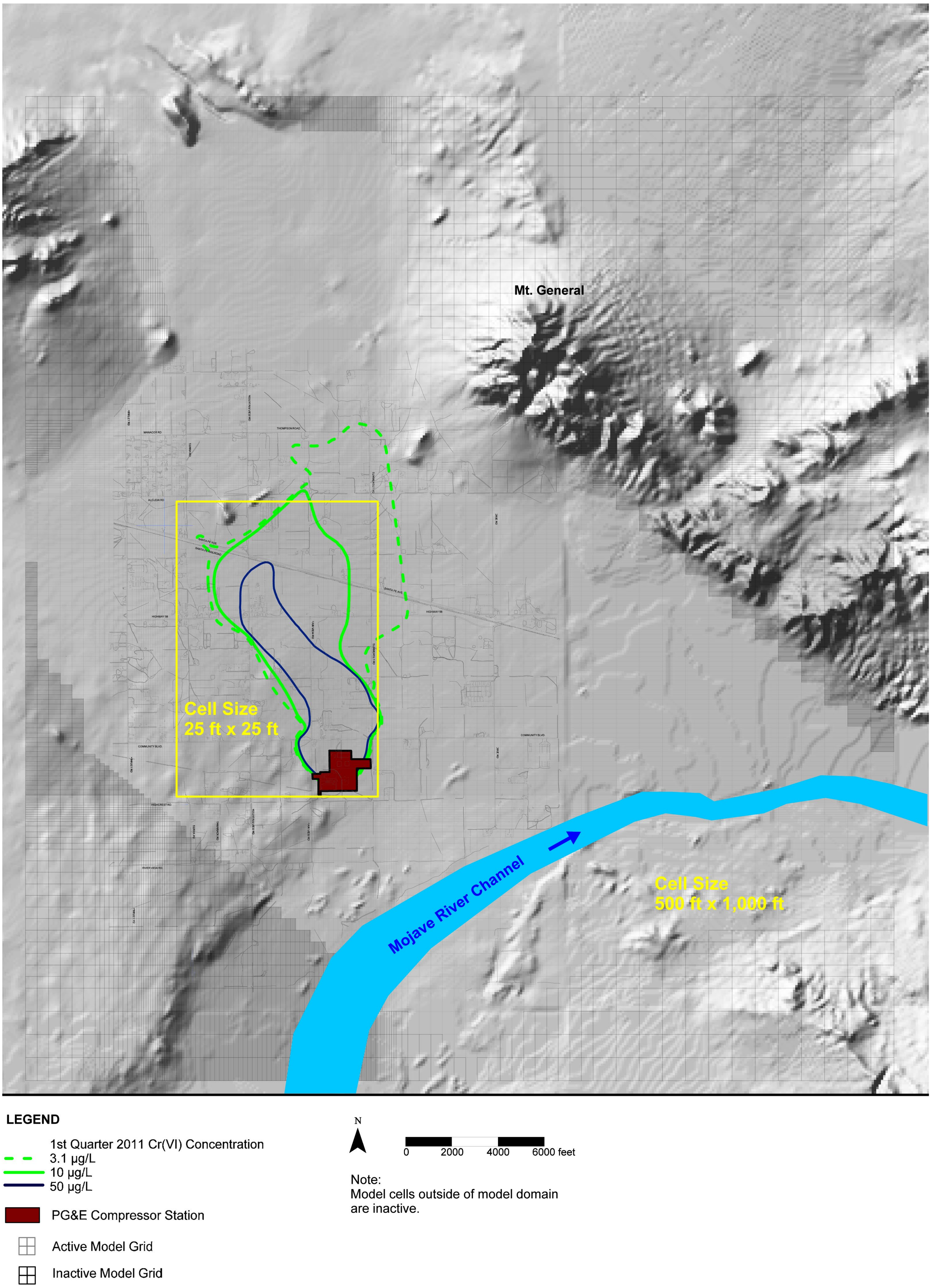
Source: Pacific Gas and Electric 2011a.

Figure A-5
Hinkley Groundwater Model Domain



Note:
Model cells outside of model domain are inactive.

Source: Pacific Gas and Electric 2011a.

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Figure A-6
Hinkley Groundwater Model Grid Structure

GHB) (Pacific Gas and Electric 2011a). Constant head boundaries are used to fix the head value in the system that does not consider the influence of surrounding conditions, thus acting as an infinite source of water entering the system, or as an infinite sink for water leaving the system. A constant head boundary was used for the groundwater that exits the model domain in the north toward Harper Lake, as a lack of water level records in this area prevented the use of a general head boundary in this area (Pacific Gas and Electric 2011a). The remaining edges of the model domain were assumed to be no-flow boundaries (Pacific Gas and Electric 2011a). These generally represent the contact between alluvium and bedrock (Pacific Gas and Electric 2011a).

The full extent of the Hinkley Valley aquifer is included in the model, although the area of focus is on the simulated groundwater movement and chromium concentrations. MODFLOW allows for a finer grid in areas of interest where greater accuracy is required and a coarser grid in areas requiring less detail, as shown in **Figure A-6**. The majority of grid cells are aligned with the direction of groundwater flow. The boundaries of the model grid are based on natural hydrogeologic boundaries, where possible. The aquifer model boundaries were identified from the areal (surface) patterns of bedrock mountains surrounding the Hinkley Valley, as well as the outcropping ridges and hills within the valley (i.e., from topographic maps). As described in Section 3.4*, Geology and Soils*, the Mojave River groundwater basin consists primarily of unconsolidated alluvial deposits. The limits of the basin are defined by nonwater-bearing consolidated rocks (i.e., bedrock) that underlie the alluvial deposits of the basin and outcrop in the surrounding mountains and hills. In some places, the confining rocks at the limits of the basin are buried by unsaturated alluvial deposits. The southern model boundary is the relatively deep alluvial materials below the Mojave River channel.

There are two major fault lines, the Lockhart fault and the Mount General Fault, that suggest vertical discontinuities in the aquifer materials which may impede and affect groundwater flow and thus provide internal boundaries with reduced water movement. In the model, the Lockhart fault is assumed to provide significant resistance to flow, but not to entirely prevent flow, and is simulated in models as a zone of low hydraulic conductivity (Pacific Gas and Electric 2011a). The Mount General fault also extends northwest-to-southeast along the northeast model boundary. There is no evidence of this fault extending into the north Hinkley Valley. Fault lines in the project vicinity are shown in **Figure 3.4-1** in Section 3.4, *Geology and Soils*.

Aquifer Stratigraphy

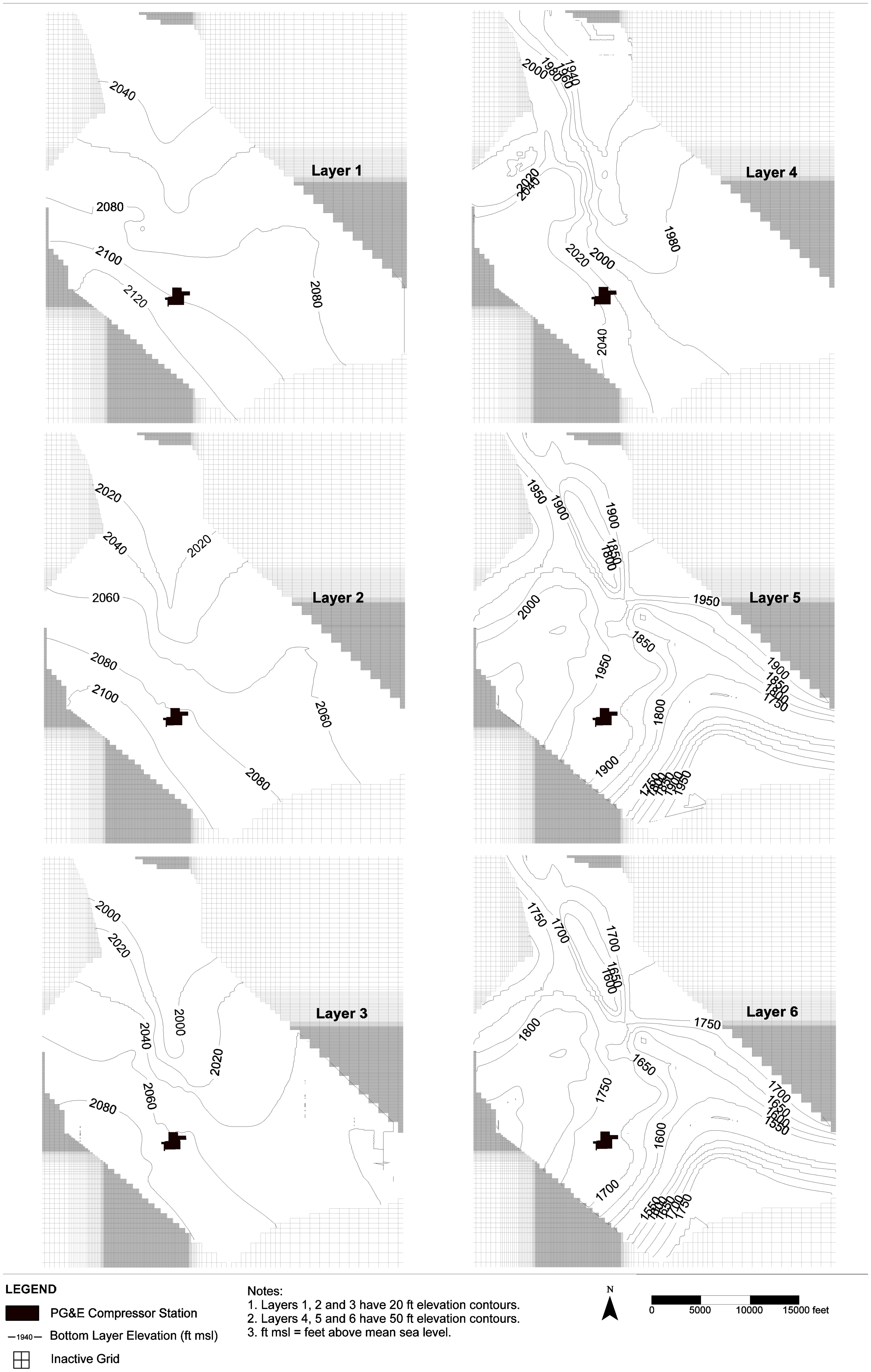
The historical distribution of wells within the Hinkley Valley indicates the general extent of the aquifer stratigraphy, or layers. Drilled wells that did not provide sufficient water yield indicate the aquifer did not extend to the well location. Because there was extensive historical drilling and considerable domestic and agricultural pumping in the Hinkley Valley, the areal extent of the upper aquifer is well understood. The areal extent of the lower aquifer (i.e.~~g.~~, below the blue clay) is less well known than the upper aquifer because only a few wells have been drilled into the lower aquifer. The information from the monitoring wells that have been installed by PG&E as part of the remedial investigation and monitoring effort gives the most complete set of data on vertical sediment sequences. Because these wells are located throughout and surrounding the existing chromium plume, the vertical definition of the aquifer(s) are most accurate in this central portion of the Hinkley Valley.

Determining the areal extent of the “blue clay” layer that is assumed to separate the upper and lower aquifers, and the “brown clay” layer that may separate the upper zone from the lower zone of the upper aquifer is more difficult. The aquifer is assumed to be filled with many clay "pockets" or "lenses" with limited extent; but these localized clay features do not limit water movement. The computer model (layers of boxes) can be easily shown on a map of the Hinkley Valley; but the internal boundaries that are assumed to limit the aquifer or reduce water movement are the most important groundwater model features.

The general geological boundaries in the model were validated with the available well-drilling data, including the sequence of vertical layers of materials (rock and sediment materials) and some general characteristics of these sediments. The depth to bedrock is generally confirmed from a few isolated deep wells. The sediment layers are assumed to be generally horizontal, although alluvial materials will often trend with the land surface, and can be lifted or shifted geologically.

Each box in the model grid system is divided into six layers consisting of three active layers, the upper and lower zones of the upper aquifer and the lower aquifer, interlain with two dividing clay layers. The upper aquifer has been separated into two layers because many of the PG&E monitoring wells with (multiple) sampling depths in the shallow (well A) and deep (well B) portions of the upper aquifer have shown different chromium concentrations. **Figure A-7** shows groundwater elevations and **Figure A-8** shows layer thickness for each groundwater model layer (Pacific Gas and Electric 2011a). The layers are described as follows:

- **Layer 1 (shallow zone of the upper aquifer):** The thickness the shallow zone of the upper aquifer (Layer 1) is controlled by the groundwater elevation and the top of the brown clay. The modeled thickness of layer 1 is about 20 feet in the vicinity of the compressor station, and increases to about 40 feet toward the north.
- **Layer 2 (brown clay layer):** The top of the brown clay (Layer 2) is shown to slope downward to the north, from an elevation of 2,100 feet above mean sea level (amsl) at the compressor station to 2,040 feet msl about 3 miles to the north, with a slope of about 20 ft/mile. The groundwater elevation also slopes at about 10 ft/mile toward the north, so the saturated thickness of model layer 1 increases by about 10 ft/mile toward the north. The brown clay separating the shallow and deep portion of the upper aquifer is shown to have a thickness of about 20 feet at the station and about 30 feet at the north end of the plume.
- **Layer 3 (lower zone of the upper aquifer):** The lower zone of the upper aquifer (Layer 3) is shown to have the same thickness contours as Layer 2. The thickness of these layers was~~were~~ equally divided, using the top of the brown clay and the top of the blue clay elevation contours, based on multiple well logs.
- **Layer 4 (blue clay):** The blue clay (layer 4) is shown to be continuous, fully separating the upper and lower aquifers in the Hinkley Valley north of the river. The Blue Clay is about 20 to 50 feet thick in most of the Hinkley Valley, but pinches out within the distal end of the plume and is not present to the west, and is not present within a few to several hundred feet of the current Mojave River channel. The blue clay thickness is indicated to be about 30 feet at the station, but to be reduced to 10 feet in the vicinity of Hinkley and to the north. The thickness of the blue clay is shown to be 40 feet in the vicinity of the Mojave River and to extend to the southern boundary of the aquifer. This, however, would isolate the lower aquifer from the river alluvial deposits and prevent Mojave River flood flows from recharging (filling) the lower aquifer. The blue clay does not likely extend across the Mojave River channel but the model structure requires the layers to extend to the boundaries.



Notes:
1. Layers 1, 2 and 3 have 20 ft elevation contours.
2. Layers 4, 5 and 6 have 50 ft elevation contours.
3. ft msl = feet above mean sea level.

Source: Pacific Gas and Electric 2011a.

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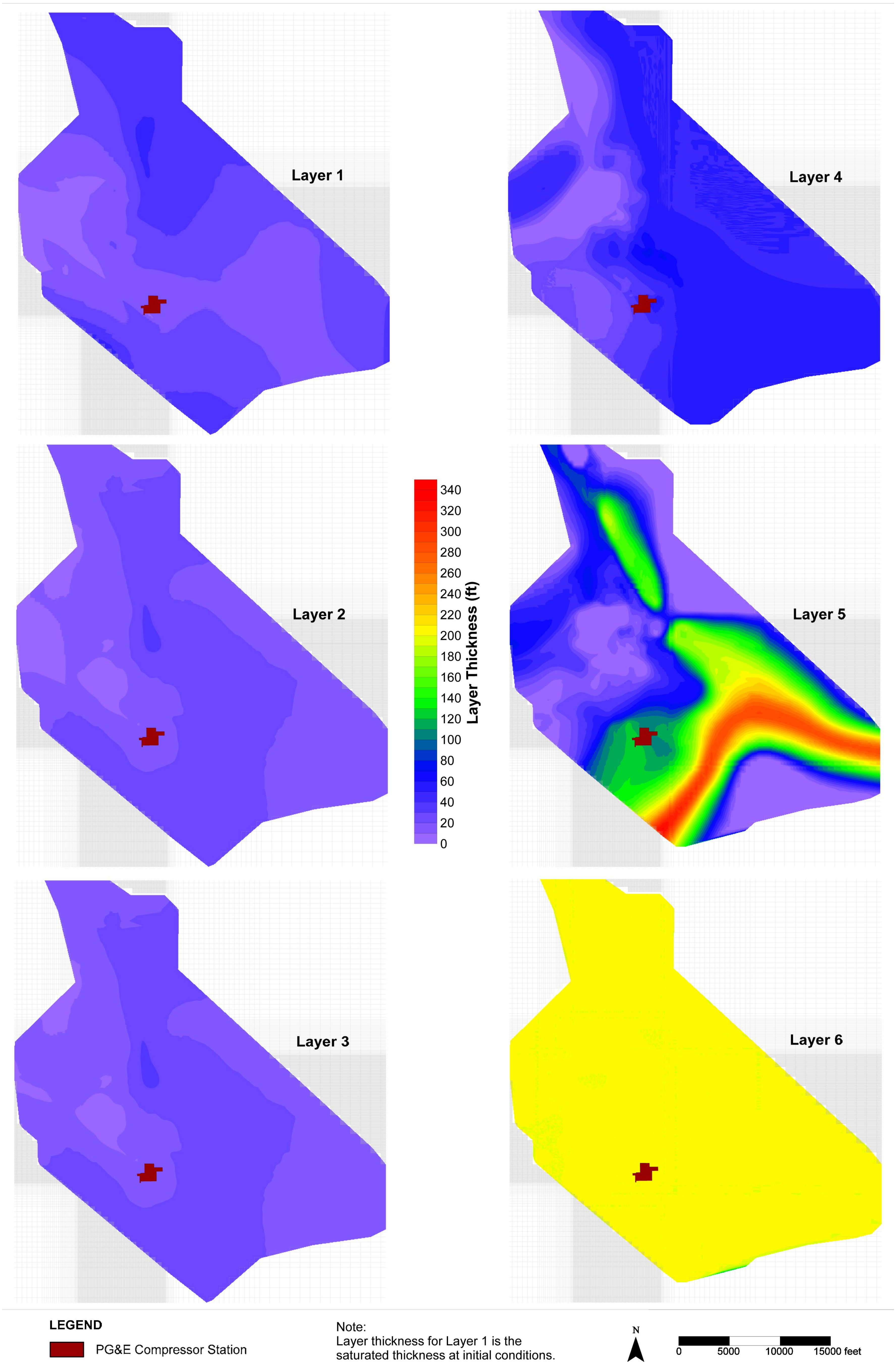
Figure A-7
Hinkley Groundwater Model Layer Elevations



Note:
Layer thickness for Layer 1 is the saturated thickness at initial conditions.

Source: Pacific Gas and Electric 2011a.

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Figure A-8
Hinkley Groundwater Model Layer Thicknesses

- **Layer 5 (lower aquifer):** The lower aquifer (layer 5) is shown to have a thickness of 100 feet at the compressor station, and to increase to over 250 feet below the Mojave River channel. The thickness of the lower aquifer is shown to reduce to about 20 feet below Hinkley. The specified thickness of the lower aquifer may not be as important as determining the internal boundaries (faults and outcroppings) and the connections with the upper aquifer.
- **Layer 6 (bedrock):** This layer consists of consolidated bedrock which constricts flow and defines the deepest boundary, or limit, of the aquifer.

Groundwater Elevations

~~The n~~Numerous well logs from across the Hinkley Valley reveal that the saturated thickness of the upper aquifer ranges from less than 25 feet to more than 100 feet. The average saturated thickness for ~~existing conditions (2011)~~the analysis is assumed to be about 75 feet.

Short-term and long-term changes in groundwater levels were also accounted for in the model. Pump tests involve monitoring the response of nearby wells to changed pumping from the target well. PG&E operates several continuous water elevation monitoring wells in the DVD Land Treatment Unit. The MODFLOW model results can be compared to the response in the various monitoring wells to confirm the hydraulic conductivity values (and aquifer thickness) in the vicinity of these wells. Similar analysis of the long-term water elevation response to recent flood flows (i.e., 1997, 2005, 2010 recharge events) at several wells located at various distances from the Mojave River can be used to confirm the aquifer thickness and hydraulic conductivity for the Hinkley Valley aquifers.

Aquifer Hydraulic Properties

For groundwater analysis and modeling purposes, the size of the alluvial material is important for two reasons; (1) the porosity (i.e., water storage capacity) and (2) the hydraulic conductivity (i.e., water movement capacity) of the aquifer. **Table A-8** describes assumptions for the hydraulic properties (porosity and specific yield, defined in text below) typically used for groundwater model development.

Table A-8: Assumed Porosity and Specific Yield for Groundwater Model Development

Porosity	
Average porosity (mobile porosity)	20%
Bulk porosity (sand, silt and clay)	30% to 40%
Bulk porosity assumed for Hinkley Valley aquifer layers	35%
Mobile porosity assumed for Hinkley Valley aquifer	7%
Immobile porosity assumed for Hinkley Valley aquifer	28%
Specific Yield (water storage capacity)	
gravels and sands	20-25%
silt	10%
clay	5%

USGS modeling of the Mojave River groundwater basin (Stamos et al. 2001) has estimated an average porosity of about 0.2 (20%) for the Hinkley Valley basin. The water in the saturated portion of the aquifer layers can be estimated from the thickness of the layer and the assumed sediment porosity (percentage of saturated volume filled with water). Sediment porosity (bulk porosity) is often about 30% to 40% for a wide variety of sand, silt and clay, but the effective porosity (mobile porosity) that is available for water movement may be considerably less than the bulk porosity.

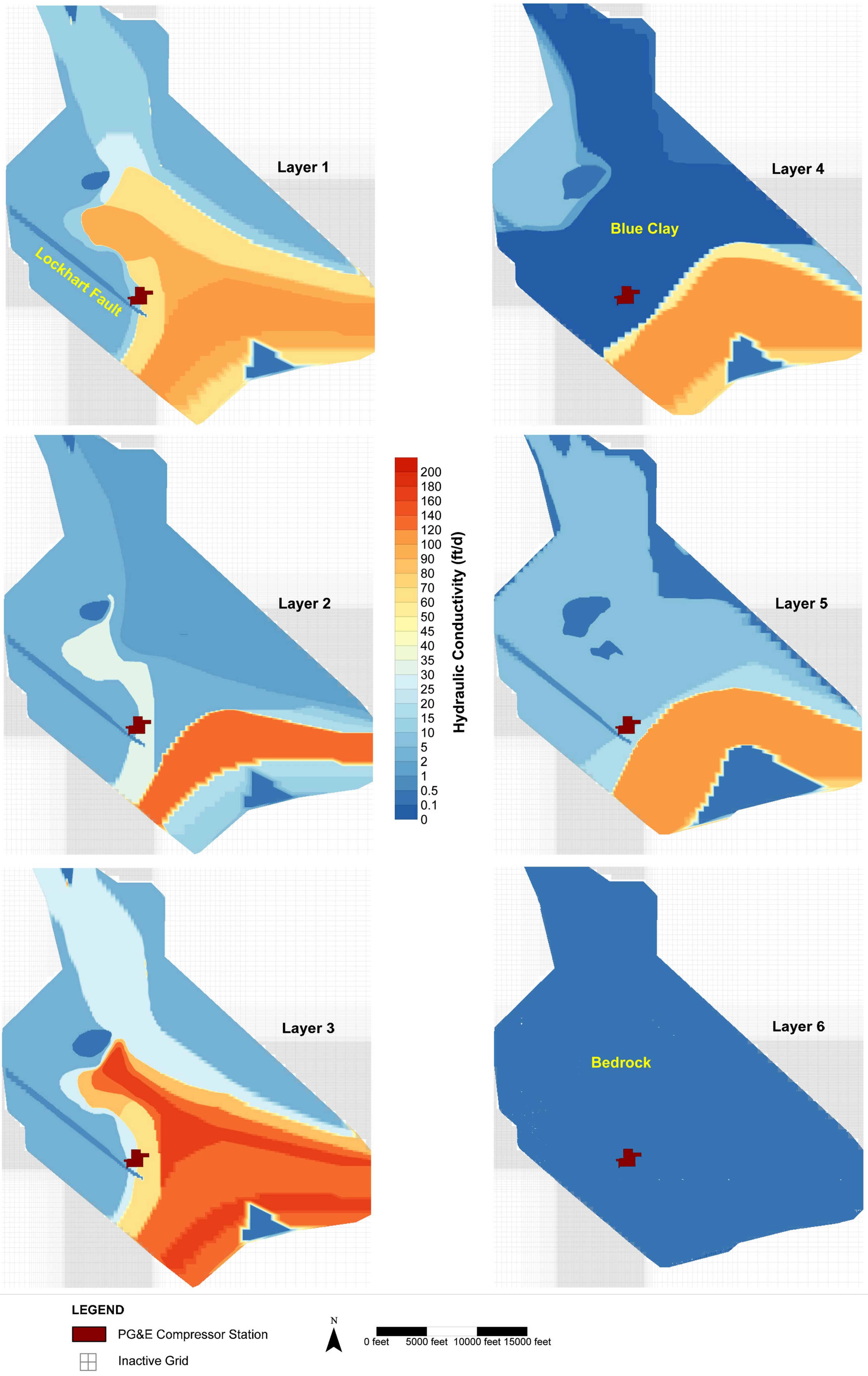
The specific yield is the portion of the aquifer pore water that will drain from the material under gravity. The specific yield is about 20-25% for gravels and sands, but is less than 10% for silt and may be less than 5% for clay. An aquifer layer with a thickness of 20 feet and bulk porosity of 40% would contain about 8 feet of water. If all of the water could be removed, a well would lower the water level by 2.5 feet (i.e., 1/0.4) for every acre-foot of pumping (from an acre) of the aquifer. However, pumping from a sand aquifer would remove 25% (specific yield) of the aquifer volume as water (15% would remain in the pores), and the water level would decline by 4 feet for every foot of water removed. Most of the pore water would remain within the sediments (bound by surface tension) for silts and clays. The water level would decline faster than the bulk porosity would indicate. For example, if half of the pore water (20% of volume) remained bound to the sediment particles, the water level would decline by twice the anticipated amount (5 feet for each foot of water extracted).

The groundwater model assumes that the total (bulk) porosity for each of the aquifer layers is 35%. The model documentation does not state the assumed specific yield; this parameter is needed to compare the water level decline with the historical or existing pumping. The MT3D model assumes that the majority (80%) of this porosity is water that is trapped within clay lenses and other features that are separated from the moving portion of the groundwater. ~~A movement~~The mobile porosity ~~of~~ is assumed be 7% of the aquifer volume with ~~an~~the immobile porosity ~~of~~ assumed to be 28% ~~is assumed~~ of the aquifer volume for the chromium transport model. ~~This 7% mobile porosity might also be the specific yield, corresponding to silt or clay.~~ These ~~specific yield and~~ mobile/immobile porosity parameters have several important effects on simulated groundwater movement and plume behavior.

Hydraulic Conductivity

Hydraulic conductivity (K) describes the ease with which water can move through pore spaces or fractures. It is typically described as the volume of water flowing through a 1 foot by 1 foot cross-sectional area of an aquifer under a hydraulic gradient (the change in groundwater level per unit distance) of 1 foot/1 foot in a given amount of time (typically one day). Hydraulic conductivity values can range approximately 12 orders of magnitude depending upon differing water transmitting characteristics of aquifer materials. Although the units are the same (length per time), hydraulic conductivity differs from groundwater velocity, which is equal to hydraulic conductivity multiplied by the hydraulic gradient. The hydraulic conductivity is generally estimated for the USGS modeling (Stamos et al. 2001) to range from about 10 to 100 ft/day.

Hydraulic conductivity varies by aquifer layer. Because the hydraulic conductivity of Layer 2 (brown clay) is much less than Layers 1 and 3, most of the groundwater flow will move towards the north in Layers 1 and 3, in proportion to the layer thickness. The greater thickness shown to the east of the PG&E Compressor Station, along the center or Hinkley Valley, indicate that more groundwater will move in this portion of the aquifer (for a given water surface slope), unless there are variations in the hydraulic conductivity. The greater thickness also suggests that water movement (velocity) will decrease. **Figure A-9** shows assumed hydraulic conductivity zones for each model layer. The highest hydraulic conductivity values in each layer originate from near the Mojave River. Layers 1 and 3



Source: Pacific Gas and Electric 2011a.

Graphics...00122.11 (3-6-2013)

Figure A-9
Hinkley Groundwater Model Hydraulic Conductivity Zones for Model Layers 1-6

show the highest general hydraulic conductivity zones, whereas the brown and blue clay layers (model layers 2 and 4), as well as the bedrock (layer 6) show little to no hydraulic conductivity values.

The drawdown response of monitoring wells to extraction pumping from nearby wells shown in **Table A-7** can be used to estimate the hydraulic conductivity, by matching the estimates of expected drawdown to the measured drawdown. The observed responses to the DVD LTU pumping were comparable to the expected drawdown for the example calculations given above for pumping of 150 gpm (28,879 ft^3/day) with a thickness of 75 feet and a hydraulic conductivity of 50 ft/day. An example calculation is as follows:

$$\frac{\left(\left(28{,}879\ [\frac{\text{ft}^3}{\text{day}}]\right)\text{x}\left(\ln\left(\frac{10{,}560\text{ ft}}{\text{distance [ft]}}\right)\right)\right)-(\text{Drawdown})\text{x}((2\pi)\text{x}(75\text{ [ft]}))}{\text{Drawdown}}=\text{Hydraulic Conductivity }[\frac{\text{ft}}{\text{day}}]$$

The Lockhart fault zone is shown with a very low hydraulic conductivity (0.1 ft/day) that trends to the northwest from the Compressor Station~~.~~, ~~This model feature will block any groundwater flow from the south, and force all movement from the Compressor Station along this northwest trend.~~ but the fault zone also shows large elevation gradients as one proceeds from southwest to northeast and thus does not appear to be impeding flow from south to north. The outcropping hills to the west of DVD LTU will force any groundwater movement to turn northeast towards the center of the Hinkley Valley. These structural boundaries are confirmed by the water elevation gradients; a large drop across the Lockhart fault, and low gradient (indicating no flow) towards the outcropping hills. **Figure 3.1-4a** in Section 3.1, *Water Resources and Water Quality*, presents the groundwater elevation contours from Fourth Quarter 2011 data for the upper aquifer, discussed below, in the aquifer surrounding the plume. **Figures 3.1-4b** and **3.1-4c** in Section 3.1 show groundwater elevations and general groundwater flow directions in shallow and deep zones of upper aquifer, based on Fourth Quarter 2012 data for portions of the study area.

Aquifer Water Budget

Modeling inputs and outputs within the aquifer system consist of sources of natural recharge and discharge and ~~anthropocentric~~ anthropogenic influences (i.e., groundwater withdrawals from pumping).

The water budget for the Hinkley Valley provides a basis for understanding the sources and uses of groundwater in the Hinkley Valley and provides an overall view of the water movement within the groundwater system. The groundwater model domain is shown in **Figure A-5**. To quantify water budget components, the groundwater flow model was run for water-years 1997 through 2005. Groundwater pumping rates for this period were obtained from the Mojave Watermaster. Domestic pumping for some residential areas was estimated based on published values for typical single-family household domestic water use. Water budget values were calculated as the yearly average for the period. On average, about 7,000 acre-feet of groundwater entered the modeled area from the south each year. About 20 percent of this subsurface flow continued eastward toward Barstow, and about 2 percent flowed out of the model boundary to the north toward Harper Valley. The bulk of the groundwater inflow was pumped for irrigation or domestic use.

Natural Recharge and Discharge

Natural sources of recharge and discharge in the Hinkley Valley aquifer include the flow from Mojave River and precipitation. Accurate representation of the Valley's natural boundaries in the numerical model is required to accurately simulate the basin-wide groundwater flow patterns.

Mojave River

Based on this conceptual model, groundwater enters the southwest model domain along the Mojave River channel and from the alluvial fan or ancestral channel deposits west and southwest from the compressor station. Although the Mojave River is an intermittent stream, when it does flow, it can deliver substantial amounts of water to the subsurface. These boundaries and the eastern portion of the Mojave floodplain aquifer, where flow is directed towards Barstow, are represented as general head boundaries. Indeed, the sharp water level rises in the general head boundary well records occur in years of large discharge events on the Mojave River. The Mojave River periodically flows within the model domain, and recharge from the river is simulated using injection wells. A series of 45 injection wells along the Mojave River channel was used to simulate this recharge from the riverbed~~.~~ (Pacific Gas and Electric 2011a).

Groundwater exits the model domain along the Mojave River channel toward Barstow. Groundwater also exits the model domain in the north toward Harper Lake via a constant head boundary, representing subsurface outflow to the Harper Valley. A constant head boundary was used here, as a lack of water level records in this area prevented the use of a general head boundary in this area. Based on extrapolation of water level gradients to the north, a steady-state value of 2,050 ft was used at the northern boundary. The remaining edges of the model domain were assumed to be no-flow boundaries. These generally represent the contact between alluvium and bedrock.

Precipitation

The average annual precipitation at Barstow from 1889 to 2000 was 4.3 inches with a maximum annual precipitation of less than 10 inches. Because these rates are low, and evapotranspiration rates far exceed precipitation rates on an annual basis, recharge into the model from infiltrating precipitation was not included in the model.

~~Anthropocentric~~Anthropogenic Influences

The MODFLOW model considers the effects of groundwater elevations and pumping on groundwater movement in the Hinkley Valley. The primary types of pumping in the valley are for agricultural, domestic uses, and PG&E remedial purposes. The Hinkley Basin is agricultural in nature, with several dairies and farms. Alfalfa and grass are the primary crops. Water is supplied to irrigated fields from wells with the Hinkley Basin, including within the model domain. Quarterly pumping rates from 1993 to 2004 provided by Mojave Watermaster reports were used as inputs to the model for the relevant years, and the average quarterly distribution from 1993 to 2004 was used to extrapolate pumping rates beyond 2004. Deep percolation and groundwater recharge from agricultural irrigation was estimated at 20% of applied water based on climatic conditions and an alfalfa crop under standard agricultural management practices.

The Mojave Watermaster typically does not collect or record use rates from domestic wells. Therefore, domestic groundwater withdrawals were estimated using a population of about 1,000 residents by assuming a use rate of 100 gallons per day per person. The total estimated average domestic demand over the model domain is thus 70 gallons per minute (gpm), and 10 domestic surrogate wells pumping 7 gpm were used to simulate domestic withdrawals. Return flow from septic systems was not included in the model.

PG&E operates supply wells for the compressor station and for various site remedial actions. These flow rates were incorporated into the model.

Groundwater Flow Modeling

The MODFLOW model calculates groundwater flow using Equation [1], the basic groundwater equation (Darcy's law). The movement of tracer (Darcy's velocity) will be faster than the water flow divided by the aquifer cross-section would indicate. For a bulk porosity of 40%, the rate of movement would be 2.5 times faster. However, only the mobile porosity (specific yield) is involved in water movement. The water that remains immobile (bound to sediment particles) will increase the water (or tracer) velocity. The groundwater model documentation indicates that a total porosity of 35% was specified for each of the Hinkley Valley aquifer layers. Therefore the effective water thickness is 35% of the overall layer thickness.

Total water volume equals water thickness times the surface area of the aquifer (or portion of the layer).However, the mobile porosity was just 7%~~,~~ of the aquifer volume, so the tracer movement will be confined to just 7% of the aquifer volume and will be 5 times the water movement calculated from the bulk porosity. Most of the water (28% of aquifer volume) will remain within the soil matrix (immobile porosity). The precise rate of transfer (exchange) of Cr[VI] and carbon between the mobile volume and the immobile volume remains somewhat uncertain as it cannot be directly measured.

Aquifer flow conditions are characterized to predict the movement of chromium plume within the Hinkley aquifer. Two separate models are used for simulating the future distribution of Cr[VI] within the aquifer. The groundwater volume, movement (i.e., flow rate, velocity, direction) and water elevation (i.e., depth to water) are simulated using MODFLOW. The concentration of Cr[VI] and dissolved carbon (i.e., ethanol) are simulated with MT3D that uses the MODFLOW results for the aquifer volumes and water movement patterns.

As previously described, Hinkley Valley groundwater flow conditions are characterized in grid cells. The original model (Pacific Gas and Electric 1998) used a rectangular grid of MODFLOW cells that were 264 feet on a side (1.6 acres). There were 17,500 cells in an area of 47.5 square miles. Many of the cells were inactive (i.e., outside the aquifer). The current model has much smaller cells in the region of the chromium plume (25 feet on a side, 0.015 acres) and the number of MODFLOW cells is increased to about 250,000 in an area of about 55 square miles, with about half of the cells inactive (outside the aquifer boundary).

Groundwater Movement Modeling

The MODFLOW model is calibrated by matching the measured groundwater water surface ~~(saturated)~~ elevations with the available well measurements for a sufficient period of time to include changes in pumping, recharge, and corresponding water elevations. The responses of the groundwater elevations to recharge events and to changes in major pumping activities provide the best opportunity for calibrating the basin parameters and confirming the movement of groundwater (hydraulic conductivity) and the drawdown (specific yield) caused by pumping. As shown in **~~Table~~Figure A-9**, the highest conductivity values were assumed to be along the existing plume in

Layers 1 and 3 (upper aquifer). These assumed values will cause the majority of the groundwater flow to be directed along this "conductivity channel". The fact that this "conductivity channel" ends abruptly near the DVD (rock outcropping) will force the plume to spread east/west, as has been observed in the last decade.

Recent particle tracking results provide an excellent visualization of the modeled water (tracer) movement (mobile porosity). A series of comparative tracking diagrams are given in Appendix B of the PG&E Feasibility Study Addendum No. 3 (Pacific Gas and Electric 2011a). Tracer studies were conducted in the capture zone along Summerset Rd., which is more complex than other areas within the aquifer. Movement from the south (Highway 58) is quite rapid, but movement from the north (Thompson Rd~~)~~.) is very slow. There is a strong interplay between the pumping rates and the hydraulic conductivity and the layer thicknesses needed to calculate the tracer movement. For example, the velocity of the groundwater tracer movement will increase as the inverse of the mobile porosity. It is relatively fast for the currently assumed ~~7%~~ mobile porosity (7% of aquifer volume), but would be half as fast (with a smaller capture zone) if the mobile porosity were actually 14%~~.~~ of the aquifer volume. It is likely that the assumed zones of hydraulic conductivity (**Figure A-9**~~**, Table A-9**~~) are the major factor controlling the particle movement patterns.

Pumping from an aquifer layer is the typical source of groundwater movement in a closed alluvial basin. If there were no pumping, the groundwater volume would remain constant and there would be no movement and no change in the water elevations. The amount (af/yr) and areal distribution of pumping from each aquifer layer is therefore the most important required input for the GW flow model (MODFLOW). Because pumping is from specific wells, the pumping rates for the known wells are the required input.

Modeling of Groundwater Drawdown

The MODFLOW groundwater model was used by PG&E to forecast groundwater drawdown within the project area for each Alternative based on various pumping rates. To evaluate the relative amounts of drawdown beyond 5 years of pumping remedial activities, groundwater contour maps were prepared from groundwater model outputs. These maps were provided in PG&E's Feasibility Study No. 3 (Pacific Gas and Electric 2011a), and are shown in **Figures 3.1-14 to 3.1-18** in Section 3.1, *Water Resources and Water Quality*.

A.4 Modeling of Chromium Plume Concentrations

A.4.1 Existing Chromium Plume Concentrations

This section provides a summary of the existing (Fourth Quarter ~~2011~~2012) Cr[VI] concentrations within the chromium plume boundary.

A.4.1.1 Plume Extent and Scale

As of the ~~4th quarter 2011~~Fourth Quarter 2012, the existing 3.1 ppb Cr[VI] plume is thought to be at least ~~5~~6.5 miles north of the Compressor Station and cover approximately 3,122 acres, but the northern boundary is not fully delineated yet (**Figure 3.1-5**). The chromium plume ~~of concentrations 3.1 ppb of Cr[VI] or greater currently~~ covered approximately 2,950 acres in late 2011 and extended 5.5 miles north of the Compressor Station. The highest concentrations of Cr[VI] are ~~greater than 1,000 ppb and are~~ measured almost directly below the previous Compressor Station settling ponds, although it has been nearly 50 years since the contaminated Cr[VI] discharge (infiltration from ponds) was stopped. This may indicate that Cr[VI] is trapped in pockets (called immobile porosity) within the aquifer material and that only a portion of the ~~aquifer water (called mobile porosity) is moving down-gradient towards the north~~chromium-contaminated groundwater (called mobile porosity) is moving down-gradient towards the north. The highest Cr[VI] concentrations in the Source Area are decreasing through time. The highest Cr[VI] level detected in the upper aquifer in Fourth Quarter (October-December) 2012 monitoring period at Well SA-MW-05D was 3,100 ppb, as shown in **Figure 3.1-5**. At this same monitoring well (SA-MW-05D), prior detections were 9,030 ppb Cr[VI] in August 2010 and 5,400 ppb Cr[VI] in June 2011. This may indicate that remediation activities have been effective in reducing concentrations in the Source Area.

The volume of groundwater (measured as acre-feet) in the contaminated plume can be estimated from these plume areas by assuming that there is about 15 feet of water in the upper aquifer (saturated thickness of about 75-feet with a total porosity of about 20%). Therefore, the water volume in acre-feet (af) is simply 15 times the acreage of the plume. Because the plume covered about ~~2,950~~ 3,112 acres in late ~~2011~~2012, with an assumed effective water thickness of 15 feet, the total plume volume can be estimated at about ~~44,250~~47,000 acre-feet. The mass of Cr[VI] in the existing plume can be calculated from the concentration contours, but there is uncertainty in this calculation if most of the Cr[VI] remains trapped in pockets within the aquifer, in concentrations that are considerably higher than the water pumped from the monitoring wells.

The ~~ARCADIS~~Arcadis/PG&E mass estimate (PG&E Feasibility Study Addendum No. 1, January 2011) of 4,700 lbs of Cr[VI] ~~was calculated based on~~in the ~~current plume concentrations of Cr[VI] and~~plume accounts for the mobile portion and immobile portion of the Cr[VI] mass. It is true that monitoring wells sample only the mobile portion of groundwater because that is all that flows to the well borehole. Evaluation of the data indicates there is a shallow and deep plume in the Upper Aquifer, so separate plumes were delineated to account for the variability in Cr[VI] concentrations in these two units of the upper aquifer. Although the plume footprints reflect only the Cr[VI] concentrations in the mobile portion, equivalent plume footprints are also initialized in the immobile portion. It was assumed there is equilibrium between the mobile and immobile portions. Persistent source areas below the water table in the vicinity of the Compressor Station were also accounted for in the model. Initial modeling showed that the high concentration areas near the Compressor Station were flushing out too quickly. Historic concentration trends in these areas indicate prolonged elevated concentrations which support the existence of an immobile and mobile porosity within the aquifer. To account for these persistent source areas, enhanced immobile portion concentrations were initialized that exceeded the maximum observed Cr[VI] concentration. Specifically, in locations where the initialized mobile portion plume exceeded 500 ppb Cr[VI], the immobile portion Cr[VI] concentrations were initialized at 2,000 ppb. These concentrations were determined during calibration of the solute transport model to historic plume distributions. This conceptual model of the upper aquifer is sensitive to the assumed porosity values and the exchange of water between these two aquifer unit volumes.

The greatest uncertainties in the Cr[VI] plume distribution are the concentrations present in the clay lenses (immobile porosity) of the ~~U~~upper ~~A~~aquifer. The majority of monitoring wells were screened in the more permeable upper and lower portions of the ~~U~~upper ~~A~~aquifer (Layers 1 and 3). The intermediate portion of the ~~U~~upper ~~A~~aquifer is the predominantly less permeable "Brown Clay" and, therefore, likely contains less Cr[VI] than would have actively migrated into this unit. The few monitoring wells that were screened in the Brown Clay indicated lower Cr[VI] concentrations, but there were insufficient data points to delineate a specific plume distribution for the Brown Clay. The Cr[VI] distribution from the deep portion of the ~~U~~upper ~~A~~aquifer (Model Layer 3) was assumed for Model Layer 2. The Cr[VI] plume modeling results are therefore dependent on these important assumptions about the initial Cr[VI] concentrations in each model layer, and the assumed porosity for the mobile and immobile portions of each layer (Pacific Gas and Electric 2011b).

A.4.1.2 Existing Cr[VI] Plume Distribution by Layer

The main purpose for the groundwater models is to show the future plume concentrations using various containment and remediation options presented by each a~~A~~lternative. The existing Cr[VI] plume distribution is determined with Geographic Information System (GIS) tools from recent monitoring well data. Many of the PG&E monitoring wells have multiple openings in the upper and/or lower aquifer layers. The water samples provide good concentrations for the mobile porosity water, but may not reflect (higher or lower) concentrations in the immobile porosity water (which is assumed to be 80% of the pore water). The model uses initial concentrations for each aquifer layer ~~(5)~~ that are specified with a GIS application on the 250,000 active cells. The movement (spreading) of these initial Cr[VI] concentrations depends on the layer thicknesses (pore water volumes) and the simulated movement of water between cells, as simulated with the MODFLOW portion of the GW transport model. The assumed transfer between the mobile porosity fraction (7%) and the immobile porosity fraction (28%) ~~water~~ and exchange of water between the clay layers and the active aquifer layers is also important. The simulation of the plume boundary depends on the water movement and exchange between the mobile and immobile porosity. Cr[VI] mass is assumed to remain constant unless remediation measures are incorporated into the model simulations (e.g., pumping for LTU or pumping/injection for In-situ Remediation Zone).

A.4.1.3 Sampling Wells and Vertical Concentration Patterns

PG&E has conducted extensive investigations to attempt to define the lateral and vertical limits of Cr[VI] in the Hinkley Valley groundwater. These i~~I~~nvestigations ~~has~~ have been completed primarily through the installation and sampling of monitoring wells. Numerous groundwater monitoring wells have been installed in the ~~U~~upper ~~A~~aquifer and are sampled periodically, not including in-situ treatment monitoring wells which have generally been installed as pairs with a shallow and deep well at the same location. Results from these wells are reported quarterly. PG&E has prepared Cr[VI] plume maps, using data from the quarterly sampling of the shallow and deep wells in the upper aquifer. However, because only a portion of monitoring wells are sampled each quarter, the number of wells with data for each quarterly plume contour map is variable. Separate maps for the shallow and deep portion of the upper aquifer should be compared because the source of Cr[VI] and subsequent plume movement and spreading has been different in these two portions of the upper aquifer.

Results from existing supply wells and monitoring wells help characterize the nature and extent of the chromium plume in the aquifer. There about numerous locations with two monitoring wells (i.e., pairs) that have been screened in the shallow and deep portion of the upper aquifer in the vicinity of the chromium plume. The vertical distribution of Cr[VI] within the contaminated plume can vary considerably. For example, the Cr[VI] concentrations tend to be higher in the deeper portion of the upper aquifer in the core section of the plume. The shape of the plume concentrations in the shallow and deep units appears to be somewhat different near the source of the Cr[VI] contamination. However, at the north end of the plume, the Cr[VI] concentrations tend to be higher in the shallow portion of the aquifer.

The blue clay has apparently been effective in separating the majority of the chromium plume from the lower aquifer layer. Chromium migration from the upper aquifer into the lower aquifer appears to have occurred where the regional blue clay layer is thin or not present. However, as shown in **Figure 3.1-6** in Section 3.1, *Water Resources*, recent data shows chromium levels exceeding 10 ppb in the lower aquifer in a small area extending from the southern portion of the DVD agricultural treatment unit to near SR 58. The maximum detected Cr[VI] concentration in the lower aquifer in recent sampling was ~~41.6~~20.9 ppb (PG&E 4th ~~quarter monitoring report). For now~~Quarter 2012 Monitoring Report). At present it appears that the area of contamination in the lower aquifer is limited in extent.

A.5 Plume Treatment Methods

This section describes each treatment methods proposed as part of project alternatives for clean-up of the chromium plume. A relatively simple accounting procedure (mass-balance) for the groundwater movement and chemical processes within the plume is also provided to allow a clear understanding of the basic results of agricultural land treatment, In-situ Remediation Zone treatment and treatment.

A.5.1 Agricultural Land Treatment

A.5.1.1 Treatment Activities

Agricultural activities for chromium treatment involve groundwater extraction and irrigation of crops in agricultural treatment units (also called land treatment units). **Figure 3.1-12** in *Section 3.1, Water Resources and Water Quality,* shows a diagram of an agricultural treatment unit. The Cr[VI] in the groundwater is treated as it passes through the soil and root zone, through the following mechanisms:

- **Cr[VI] in water interacts with electron donors in soil and organic matter and is reduced to solid Cr[III].** The metabolic process used by bacteria to produce energy requires a "terminal electron acceptor" to metabolize the carbon source to carbon dioxide (or methane). Microbes are classified by the carbon and electron acceptor they use to carry out metabolic processes. Bacteria that use oxygen as their electron acceptor are aerobic; those that use a compound other than oxygen, (e.g., nitrate, sulfate), are anaerobic; and those that can utilize both oxygen and other compounds as electron acceptors are facultative (USEPA 2000). More about the different anaerobic electron acceptor compounds will be described in the next section on reduction by-products (Fe, Mn, As).
- **Cr[VI] in water is taken up by plant roots and reduced to Cr[III].** Natural soil bacteria (anaerobic) in the root zone will result in the reduction of Cr[VI] in the extracted ground water by reducing the Cr[VI]to trivalent chromium (Cr[III]). Based on ground water and unsaturated zone monitoring data from the East LTU that operated for about 9 years (1992 to 2001), the estimated Cr[VI] reduction is expected to be approximately 95 percent.

- **Cr[VI] adheres (or "adsorbs") onto organic matter in the root zone, and subsequent reactions involving soil microbes results in reduction to Cr[III].** Cr[III] will likely precipitate and will predominantly remain in the soil column. The slightly alkaline pH and low natural oxidants (manganese oxides) and presence of organics in the soil will assure that the Cr[III] will not be ~~re-oxidized~~substantially reconverted to Cr[VI] at the agricultural treatment units (refer to the technical memo on reconversion in Appendix A.3 for additional discussion of this topic). Reduced Cr[VI] concentrations would result in a minor loading of Cr[T] to the soil by the reduction process based on soil data from the East and Ranch LTUs. ~~According to the baseline soil data obtained at the DVDLTU in April 2004, the average Cr[T] concentration is 12 mg/kg (Cr[T] ranges from 5 mg/kg to 20 mg/kg).~~ Results from measurements below the irrigated fields of the East, Ranch, and Desert View Dairy agricultural treatment units demonstrate the performance of the agricultural treatment units in converting Cr[VI] to Cr[III], and the results are summarized in Table A-9 below. PG&E also characterized soils at the former East and Ranch land treatment units and continues to collect soil samples at the DVD land treatment unit. Sampling at the East and Ranch Land Treatment showed levels of total chromium from 1994 through 1997 of up to 24 ppm and levels of total chromium from 1997 to 2001 of up to 34 ppm with the data not indicating a distinct pattern or trend of chromium (PG&E 2003). Soil s~~S~~ampling at the DVD in the third quarter of 2005 indicated soil total chromium levels ranging between 3 and 19 ppm with no detections of Cr~~R~~[VI] (detection limit of < 0.5 ppm) (PG&E 2005). Soil Sampling at the DVD in the third quarter of 2012 indicated soil total chromium between 3 and 13 ppm with no detections of Cr~~R~~[VI] (detection limit of < 0.5 ppm) (PG&E 2012), indicating no substantial change from 2005 to 2012 in soil chromium levels.
- **Cr[VI] forms compounds with organic elements and compounds involved in the reduction**. A comprehensive monitoring program was established for the DVD LTU. Concentrations of Cr[T] and Cr[VI] detected during the Fourth Quarter ~~2011~~2012 (Pacific Gas and Electric ~~2011b~~2012b)are shown in **Figures 3.1-5** and **3.1-6,** *Section 3.1 Water Resources and Water Quality,* and concentrations of nitrate as N and TDS, are shown in **Figures 3.1-7** and **3.1-8,** *Section 3.1 Water Resources and Water Quality*. Concentrations in each extraction well have been stable once the pumping was initiated, but depend on where in the plume the extraction well is located. The average Cr[VI] concentration in the extracted ground water is about 20 ppb (blend of the major extraction wells). Sixteen lysimeters are located at 5 feet below ground surface (bgs), and 16 lysimeters are located at 20 feet bgs. Samples collected from the 5-foot-deep lysimeters were analyzed for Cr[T] and Cr[VI], and samples collected from the 20-foot-deep lysimeters were analyzed for TDS and nitrate (as N). Because the upper confidence limits of the median Cr[VI] concentrations from these 5-feet depth (pore water) data were 0.73 ppb for Cr[VI] and 1.40 ppb for Cr[T], about 95% the Cr[VI] is removed with the land treatment method. Groundwater monitoring data indicate that Cr[VI] and Cr[T] concentrations in most of the 44 performance monitoring wells have shown a stable or decreasing trend since the startup of the DVD LTU in 2004.

Table A-9: Performance Summary for Cr[VI] to Cr[III] Conversion for the East, Ranch and Desert View Dairy Agricultural Treatment Units

Agricultural Treatment Units Summary Data	East Agricultural Treatment Units	Ranch Agricultural Treatment Units	Desert View Dairy Agricultural Treatment Units
Area (acres)	30	52	80
Period of Operation	1991–2001	1998–2001	2005–ongoing
Amount of extracted groundwater	2,400	1,050	550

over life of treatment (af)			
Average Cr[VI] concentration [a] in extracted water (ppb) after treatment (concentrations before treatment were higher)	130	13	20
Reduction of Cr[VI] (lbs.) in extracted water to Cr[III] in soil	850	40	174
Cr[VI] Reduction Efficiencies[a]	95%	95%	>95%

Source: 2002 Feasibility Study (Pacific Gas and Electric 2002), 2010 Feasibility Study (Pacific Gas and Electric Company 2010a).

Notes:

[a] Efficiencies were calculated by PG&E based on sampling of water from lysimeters beneath the agricultural treatment units.

Water from extraction wells sent to agricultural treatment units provide for plume containment (hydraulic control) as well as treatment of the Cr[VI] in the root zone of irrigated crops. In general, the large volume of pumping causes large cones of depression and thus large zones of hydraulic control. Because summer pumping rates are greater than winter pumping rates, summer cones of depression are larger than those in the winter. In unconfined alluvial systems, steady-state water level conditions may take considerable time to develop, on the order of months or even years. Cones of depression and capture zones in these areas change in response to variations in seasonal and intra-seasonal pumping rates, including changes in agricultural operations (Pacific Gas and Electric 2010).

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, and protozoa. Of these organisms, bacteria are the most numerous and biochemically active group, particularly at low oxygen levels. Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. Bacteria also require nitrogen and phosphorus for cell growth. Although sufficient types and quantities of microorganisms are usually present in the soil, blending the soil with cultured microorganisms or animal manure serves to both augment the microbial population and provide additional nutrients. Manure was applied at the DVD by the dairy owner prior to starting agricultural treatment unit operations, but it has not been added since then. The East LTU and Ranch LTU, the original agricultural land treatment units, were both operated by farmers, and it is likely that manure was applied. At new agricultural treatment units, application of manure and dairy hay prior to operation is likely to be recommended to establish and build the soil organic material.

A.5.1.2 Model Simulation of Agricultural Land Treatment

General model assumptions for the simulation of agricultural land treatment include a constant pumping rate during 3-month increments. ~~All of the Cr[VI] mass was assumed to be converted into Cr[III] in the root zone. The~~ Although this model did ~~not~~ assume ~~any~~ residual water was infiltrating back to the aquifer (Layer 1) during the summer period, ~~but~~it did not describe the Cr[VI] removal efficiencies for the winter period when the ET rate would be reduced and allow some water to percolate back to the aquifer. This assumption reduces model certainty in determining the potential for water to return to the aquifer after land treatment of winter crops, which can occur in greater volumes than during the summer period due to decreased ET rates.

A.5.2 In-situ Reduction Zone Treatment

~~Project in~~In-situ treatment involves the injection of carbon-containing compounds (i.e., ethanol) to stimulate microbial and chemical processes which convert Cr[VI] to Cr[III] through a biological (microbial) and chemical reduction process.

A.5.2.1 Carbon Injection Process

The initial dosing concentration of ethanol measured as total organic carbon (TOC) was estimated based on the amount required for the reduction of the aerobic electron acceptors (O_2 and NO_3) and to distribute organic carbon laterally from injection locations. Based on initial pilot testing, TOC injection concentrations in the Central Area were targeted between 100 and 150 mg/L TOC. Adjustments to carbon dosing can be made to take into account the changing Cr[VI] concentrations around the wells, travel times, and the concentration of reduction byproducts (i.e., Fe, Mn, As). The ethanol or other carbon source can be injected continuously or periodically. Periodic dosing is used at the Hinkley Site because during the time that injection is not occurring, the continued recirculation of groundwater reduces the potential for biofouling within the well screen and filter pack (Pacific Gas and Electric 2010).

Because degradable organic carbon is the driver for the in-situ remediation zone treatment process, the key factors for treatment are the adequate delivery and distribution of the ethanol to achieve full treatment and carbon persistence within the mobile and immobile porosity. Distribution of the injected carbon solution is dependent on the groundwater movement within the aquifer and the decay of the organic carbon (rate that the organic carbon is consumed by biological processes). The decay of the organic carbon and the groundwater flow within the aquifer (mobile and immobile porosity) determine the travel time for the carbon and the predicted extent of the in-situ remediation zone. The treatment zone will increase with ethanol concentration because the persistence above the effective reduction concentration will be longer for higher initial concentrations. The treatment zone will increase with higher injection rates (gpm).

A.5.2.2 Reduction of Cr[VI] to Cr[III]

Biological reduction of Cr[VI] to Cr[III] can occur under anaerobic reducing conditions (negative oxidation-reduction potential). Soluble organic carbon (i.e., ethanol) can be injected into the groundwater to stimulate microorganisms to create the reducing conditions to convert Cr[VI] to Cr[III]. The soluble organic carbon is used by natural anaerobic microorganisms in the subsurface as an electron donor for energy production. The carbon substrates ~~are~~may be supplied to the subsurface using active injection wells or passive infiltration galleries (infiltration galleries are not used to date at Hinkley). Mixing in the subsurface can occur from the natural hydraulic gradient (passive) or using a recirculation system consisting of pairs of injection and extraction wells (recirculation). Extracted water is amended with the carbon substrates and injected and drawn through the target treatment zone using extraction wells. **Figure 3.1-13**, in Section 3.1, *Water Resources and Water Quality*, shows a diagram with the two basic methods for in-situ remediation zone treatment (passive and recirculation). Recirculation anaerobic (reducing) treatment systems have been used for a number of years for the in-situ treatment of chlorinated solvents at other remediation sites.

An evaluation of the geochemistry using bench-scale microcosm testing is very useful to select the most effective carbon substrate and estimate the carbon dose required. Microcosm testing is used to evaluate carbon substrate efficiency and to generate transformation rate data, which is the time required to reduce Cr[VI] to Cr[III] with each electron donor. Following laboratory testing, pilot testing is often used to evaluate performance at the field level and to establish final design parameters (e.g., carbon dose and the number of injection and extraction wells [if required]). In--situ treatment technologies ~~(e.g., biological treatment)~~ generally do not produce solid waste products that require ~~management~~landfill or hazardous waste disposal.

Microorganisms can support the reduction of Cr[VI] to Cr[III] by a variety of mechanisms. While direct microbial reduction is one potential mechanism, the primary mechanism may be through the reduction of ~~naturally-occurring~~ iron and sulfate (by microbial respiration) to produce ferrous iron (Fe[II]) and sulfides (H_2S, HS-) that can react chemically with Cr[VI], reducing it to Cr[III]. The Cr[III] will form precipitates with other elements in the soil matrix, thus removing the mass of Cr[VI] from the groundwater. Analysis of post-operation soil samples collected in the Central Area in-situ remediation zone confirmed that the removal mechanism of Cr[VI] from groundwater was reduction and subsequent precipitation. The analyses indicated that reduced iron and sulfide minerals were formed which can provide extended capacity for reducing Cr[VI] beyond the period of operation of the in-situ remediation zones (Pacific Gas and Electric 2010).

The rate of microbial growth and the reduction conditions (biodegradation) are controlled by the type of bacterial population present, which generally use different electron acceptor molecules. Site-specific differences in biodegradation rates are due to the presence of microbial communities defined by the dominant electron acceptor present at that location and time. Microbial electron-accepting processes include oxygen reduction (aerobic respiration), nitrate reduction, Mn(IV) reduction, Fe(III) reduction, sulfate reduction, and methanogenesis; each process is believed to be facilitated by a different set of microbes. Dissolved oxygen is usually the preferred electron acceptor for the degradation of organic compounds by microbes as it often provides the greatest energy yield. Often, aerobic conditions are initially found in aquifer systems. However, many spills result in a plume of contamination where dissolved oxygen is rapidly depleted due to aerobic respiration; once the dissolved oxygen concentration has dropped sufficiently (to 0.5-1 mg/L), anaerobic bacteria are able to function. Nitrate is often found in aquifers impacted by anthropogenic sources and is the next most preferred electron acceptor. Once nitrate is depleted, manganese(IV), iron(III), and sulfate are often sequentially used; these are generally ~~naturally~~ abundant in many aquifers. CO_2 becomes the terminal acceptor in the most reducing environments, producing methane during the process of methanogenesis. It should be emphasized that within an aquifer, even along a single flow path in an aquifer, the terminal electron-accepting process can vary with time and location resulting in several different redox conditions for a single field study (Cozzarelli et al. 2000).

Biodegradation in aquifers is often evaluated by measuring dissolved chemical species that are characteristic of particular microbial processes; these include the concentration of dissolved electron acceptors, mainly O_2, NO_3, and SO_4, or the reduced products of electron acceptor utilization, such as NH_4, HS, Fe, Mn, and CH_4. The reduction of iron and manganese oxides in sediments by microbial processes can result in the accumulation of high concentrations of dissolved Fe and Mn in groundwater. (Cozzarelli et al. 2000).

More information on the process of chromium reduction is provided in Section 3.1, *Water Resources and Water Quality*, and in Appendix A.3.

A.5.2.3 PG&E Pilot Testing of In-Situ Remediation Zone Treatment

Two small in-situ remediation zone cells were pilot tested in December 2004 through May 2005: (1) Cell 1 was located just north of the PG&E Compressor Station industrial ponds (source area) and (2) Cell 2 was 1,000 feet north of Community Boulevard. In recirculation mode, each test cell pumped about 10 gpm from an extraction well and injected about 10 gpm (in two wells) located about 50 feet upgradient from the extraction wells. Cell 1 tested lactate additions and Cell 2 tested emulsified vegetable oil (EVO). Six monitoring wells were located about 10-40 feet downgradient. The cells were operated for about 3 months in passive mode and 3 months in active recirculation mode. The Cr[VI] concentrations in nearby monitoring wells (10-20 feet away) were reduced during the passive mode, and the Cr[VI] at the monitoring wells located 25-50 feet away were reduced during the active recirculation mode (Pacific Gas and Electric 2005). Although these cells were very small (0.05 acre), monitoring for the Cr[VI] reduction to Cr[III] and for anaerobic byproducts allowed the potential for in-situ treatment to be evaluated.

After depletion of dissolved oxygen, anaerobic microbes use nitrate as an electron acceptor, followed by iron (III) and manganese (IV), sulfate and, finally, carbon dioxide. Monitoring of these parameters in the pilot testing helped to understand the fate of the Cr[VI], because the reduction of nitrate, sulfate, manganese, iron, and arsenic with lower oxidation-reduction potential (ORP) values are correlated with the reduction of Cr[VI] to Cr[III]. The following results were noted:

- Nitrate reduction (to nitrogen gas) was found to be a beneficial result of the in-situ remediation zone. ~~Baseline~~Prior to IRZ pilot testing, nitrate-N concentrations ranged from 2.88 to 4.30 mg/L at Cell 1. In order for Cr[VI] reduction to occur, nitrate must also be reduced. Comparison of Cr[VI] and nitrate data showed a direct correlation between the reduction of nitrate and Cr[VI].
- ~~Baseline d~~Dissolved iron concentrations were below the reporting limit of 0.3 mg/L, indicating that ~~background~~ iron is in relatively low concentrations in the aquifer at the site. Iron is typically present as ferric iron oxides or hydroxides under aerobic conditions. During the pilot study, dissolved iron was detected only at the Cell 1 injection wells at concentrations up to 5 ppm, a likely result of the reduction of solid-phase ferric iron to dissolved ferrous iron. The detection of dissolved reduced iron in these wells correlated with the lowest ORP levels observed during the pilot study.
- ~~Baseline~~Prior to IRZ pilot testing, dissolved manganese concentrations ranged from less than 1 to about ~~30~~34 ppb at Cell 1~~.~~ and up to 55 ppb at Cell 2. Manganese is present as manganese (IV) oxides or hydroxides under aerobic conditions. During the pilot study, dissolve manganese concentrations increased to a maximum of 10 mg/L, a result of the reduction of manganese (IV) to soluble manganese (II). The increase of dissolved reduced manganese also correlated well with decreases in Cr[VI].
- Production of methane (final stage of anaerobic reduction) was observed primarily at wells near the injection zone, where excess biological substrate was present and ORP levels were the lowest.

A.5.2.4 Existing In-Situ Remediation Zone Treatment Areas

The current combined IRZ project comprises three IRZ treatment areas: (1) Central Area In Situ Remediation Zone; (2) South Central Reinjection Area; and the (3) Source Area In-Situ Remediation Zone. Most of the wells in the In-situ Remediation Zone have shallow and deep screened wells in the upper aquifer.

Central Area In-Situ Remediation Zone

Remedial activities in the Central Area in-situ remediation zone include groundwater extraction, amendment with organic carbon (that is, ethanol), and injection using 12 remediation wells to create an in-situ remediation zone along 1,500 feet of Frontier Road, both east and west (500 feet) of Fairview Road. From December 2007 to September 2009, the system was operated in a dipole configuration, with recirculation completed by extracting groundwater from the even numbered well in each pair and injecting the groundwater amended with organic carbon into the odd-numbered well in each pair. In October 2008, the substrate was changed from sodium lactate to ethanol. In September 2009 the Central Area in-situ remediation zone system was modified to fill-in treatment gaps observed downgradient of some in-situ remediation zone wells. The system changes allowed injection into former extraction wells. The current full-scale operations plan consists of monitoring Cr[VI] concentrations in 10 performance monitoring wells and modifying the injection and pumping scheme to optimize carbon distribution and chromium reduction. Water is currently extracted from 2 wells and injected into 5 wells within the Central Area in-situ remediation zone. A total of 87 million gallons (MG) has been extracted and injected with carbon into the 12 injection wells. Therefore a total of about 265 AF of aquifer water may have been treated with the in-situ remediation zone injection from these wells.

The Central in-situ remediation zone wells are screened in the shallow portion of the upper aquifer (above 120 feet bgs). If the injected water has moved just in the shallow portion of the aquifer, the equivalent water thickness would be about 7.5 feet (50% of the entire aquifer effective water thickness). The treatment area might therefore include about 35 acres (of the shallow upper aquifer). The treatment zone has been observed by reduced Cr[VI] and reduced nitrate, as well as increased iron and manganese at monitoring wells located 400 feet downgradient and at most of the monitoring wells located 800 feet downgradient. This would suggest the treatment area is about 1,500 X 1,000 feet (35 acres).

South Central Reinjection Area

Remedial activities in the SCRIA include groundwater extraction from up to six wells within the northwest portion of the chromium plume, amendment with ethanol, and injection using 12 injection wells located within the plume area south of the Central Area in-situ remediation zone. The Northwest Area extraction wells EX-15, EX-16, EX-20, EX-21, and EX-22 are used to enhance plume containment and provide water for the SCRIA. The 2008 CAO allows 110 gpm to be extracted, amended with carbon, and injected into the South-Central in-situ remediation zone area. Full-scale operations began in November 2009. The average concentration of Cr[VI] from the extraction wells was about 40 ppb. The system is currently configured so that amended groundwater can be injected into the shallow (approximately 80 to 110 feet bgs and/or deep (approximately 120 to 145 feet bgs) intervals of the upper aquifer. Ethanol was added to give an initial ethanol concentration of 225-250 ppm (carbon concentration of about 115-125 ppm). These are relatively small injection wells, with a total of about 50 million gallons (MG) of carbon-amended water injected during 2010. This is equivalent to about 150 af, and would potentially have treated the Cr[VI] in about 10 acres of the plume (assuming the aquifer was 75 feet deep with 20% porosity). If the water was injected into just the shallow or deep upper aquifer, the treated area might be twice as large. The overall injection rate into the SCRIA is often maintained at a reduced rate to minimize potential lateral migration of the plume boundary (Pacific Gas ~~&~~and Electric 2012).

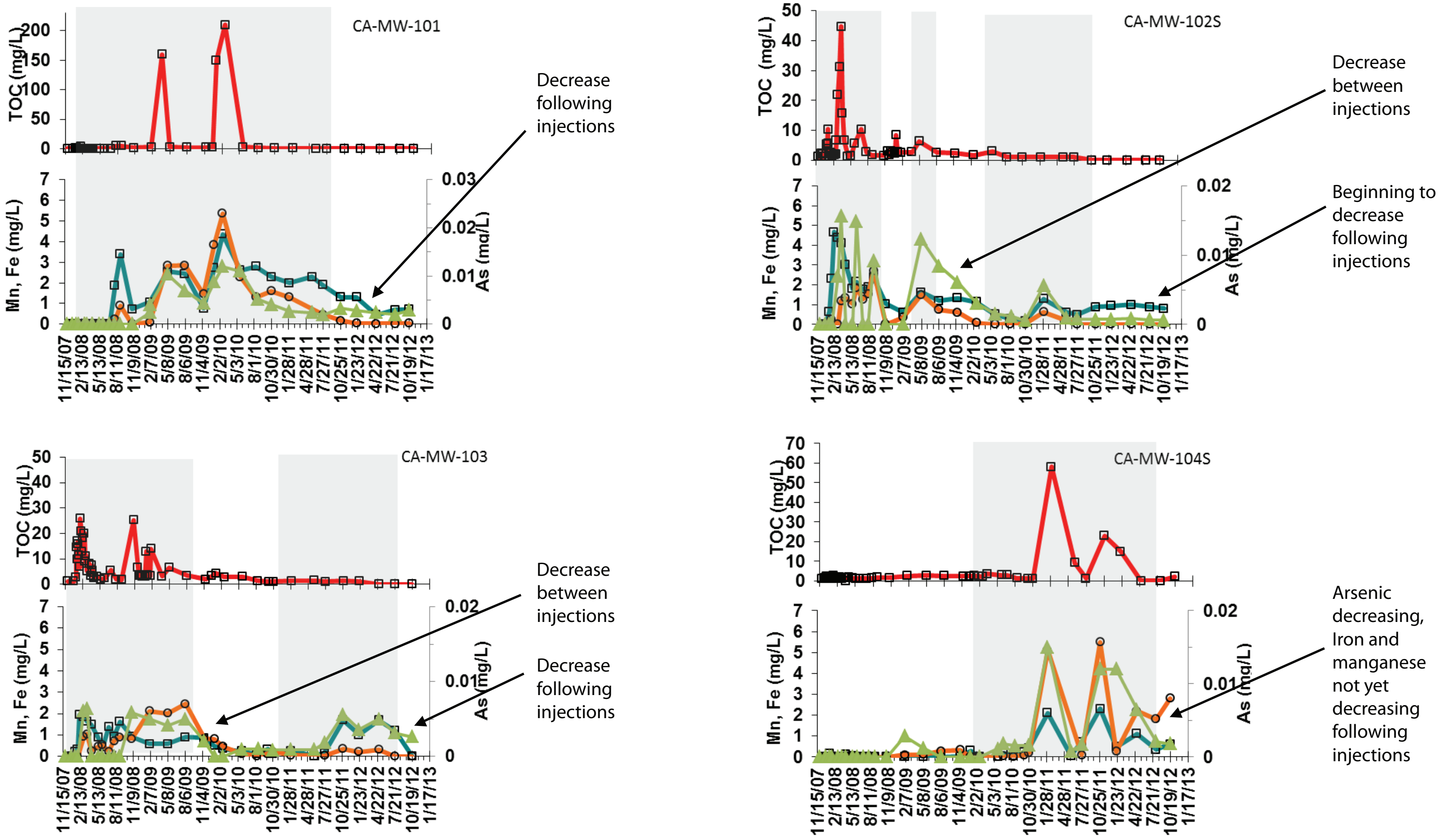
Source Area In-Situ Remediation Zone

Remedial activities in the Source Area in-situ remediation zone include groundwater extraction, amendment with ethanol, and injection using up to 21 remediation wells. Full-scale operation of the Source Area in-situ remediation zone system began in May 2008. Injection and extraction locations have been rotated, in response to decreased flow rates and/or increasing water levels in injection wells. A total of about 52 MG has been pumped from the four wells and injected into the 12 injection wells between May 2008 and December 2010. Therefore, during this time, the area potentially treated an aquifer volume of 150 af, depending on the effective spreading of the injected carbon into the immobile porosity of the aquifer. Because this is a recirculation in-situ remediation zone, the area between the extraction wells (located along 750 feet) and the injection wells (located 400 to 1200 feet upgradient from the injection wells) has shown the greatest reduction of Cr[VI] concentrations. The Source Area in-situ remediation zone system was ~~underwent full expansion~~ expanded up to the current permit limitations on May 22, 2011. Expanded wells to the northwest, north, and northeast of the existing line of extraction wells (SA-RW-01 to SA-RW-04) to treat the areas with some of the highest remaining Cr[VI] concentrations. Four new extraction wells were constructed in a 1,500 feet east-west line about 400 feet north of Community Blvd. The expanded system includes conversion of the four existing extraction wells to injection wells, and installation of five new dual-screened recirculation wells to the east and west of the current extraction wells. The injection wells are located along a 2,000 feet east-west line. The goal of the expanded Source Area in-situ remediation zone is to reduce the Cr[VI] concentrations in the shallow and deep portion of the upper aquifer and eliminate the source of high Cr[VI] that is moving north with the regional groundwater movement past the south-central and Central in-situ remediation zone.

A.5.2.5 Effectiveness of In-Situ Remediation Zone Treatment

The area of treated groundwater (i.e., area in which nitrate and Cr[VI] concentrations are reduced) can be larger than the extent of the carbon distribution. In the Central Area in-situ remediation zone, the carbon was distributed and utilized within the first few hundred feet, creating reducing conditions near the first two rows of monitoring wells and reducing Cr[VI] concentrations to less than 3.1 ppb. During initial operation of injection wells, when the microbial community was not yet fully established, organic carbon traveled as far as 400 feet down gradient. As the microbial community became established, the organic carbon was consumed closer to the injection wells and was no longer detected in the monitoring wells 400 feet down gradient. Based on sampling results, the treatment areas around the Central Area in-situ remediation zone injection wells range from 40 to 150 feet wide and extend 1,000 to 1,600 feet down gradient. This movement of the treated water from the in-situ remediation zone to down gradient locations was caused by the regional groundwater gradient (no recirculation). However, it is difficult to determine how much treatment of the Cr[VI] in the down gradient immobile porosity will occur if the reducing conditions do not persist (Pacific Gas and Electric 2010).

TOC was consistently distributed throughout the Source Area in-situ remediation zone 400 feet down gradient of the injection wells (because this is a recirculation in-situ remediation zone). Greater TOC distribution was a result of higher injected concentrations of ethanol, initially between 200 and 400 mg/L. In the case of the Source Area in-situ remediation zone, the treatment area is approximately the same as the area of carbon distribution. It is difficult to determine how far the in-situ remediation zone will extend beyond the immediate vicinity of the injection-extraction wells. Adjustments in the extraction and injection wells (location and pumping rates) and adjustments in



Decrease following injections

Decrease between injections

Beginning to decrease following injections

Decrease between injections

Decrease following injections

Arsenic decreasing, Iron and manganese not yet decreasing following injections

■ Dissolved Manganese (Mn)

▲ Dissolved Arsenic (As)

● Dissolved Iron (Fe)

▨ Grey shading indicates periods of TOC injection)

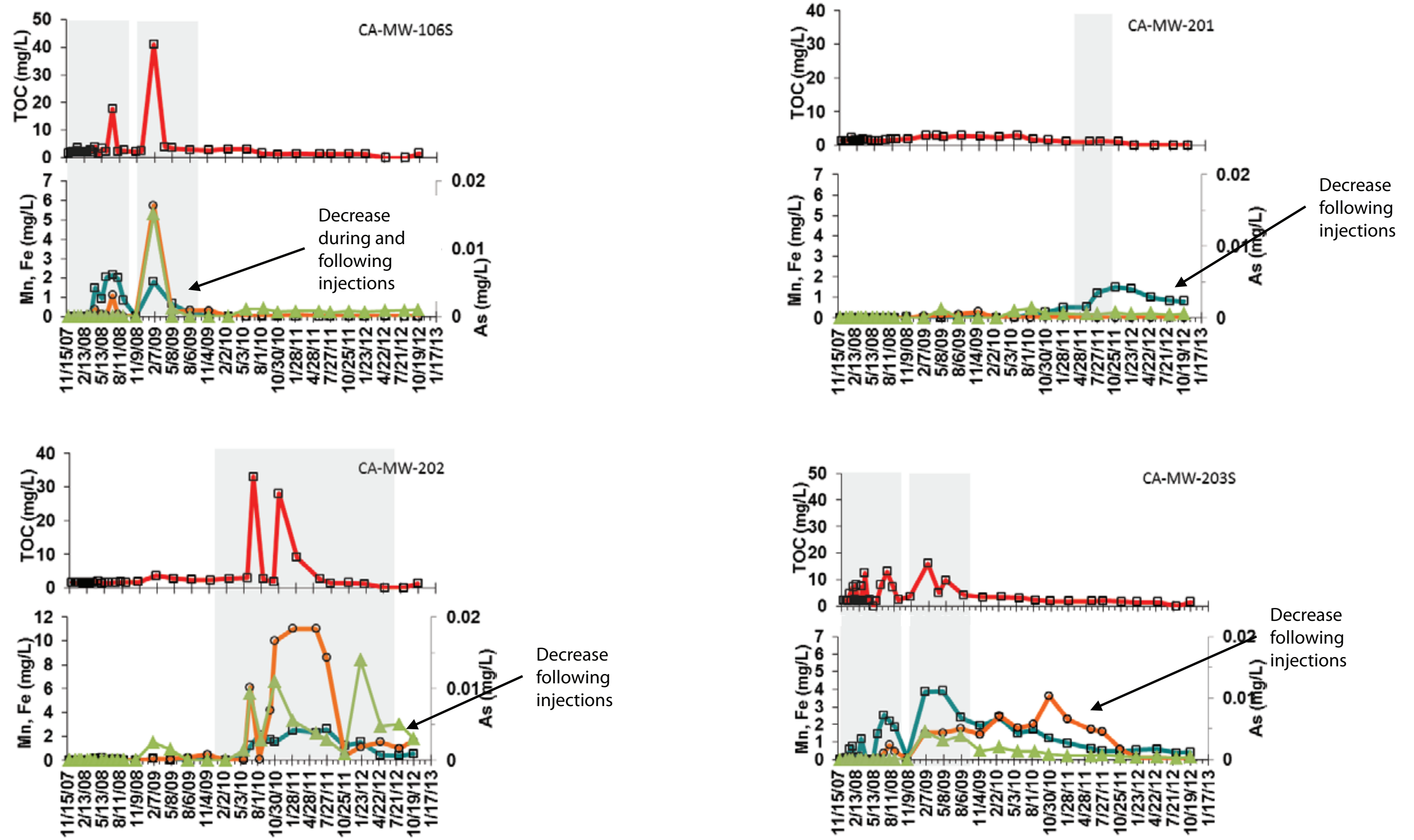
TOC	Total organic carbon
Mn	manganese
Fe	iron
CA-MW-#	PG&E monitoring well Identification
Mg/L	milligrams per liter (1 mg/l = 1 parts per million [ppm])

Note: This figure shows changes in concentrations of byproducts (iron, manganese, and arsenic) over time in relation to total organic carbon injections for In-Situ Treatment at PG&E monitoring wells in the Central Area (near injection locations).

Graphics/Projects/00122.11 Hinkley (Mar-2013) SS

Source: PG&E 2010

Figure A-10a
Changes in Byproduct Concentrations



- Dissolved Manganese (Mn)
- Dissolved Arsenic (As)
- Dissolved Iron (Fe)
- Grey shading indicates periods of TOC injection)

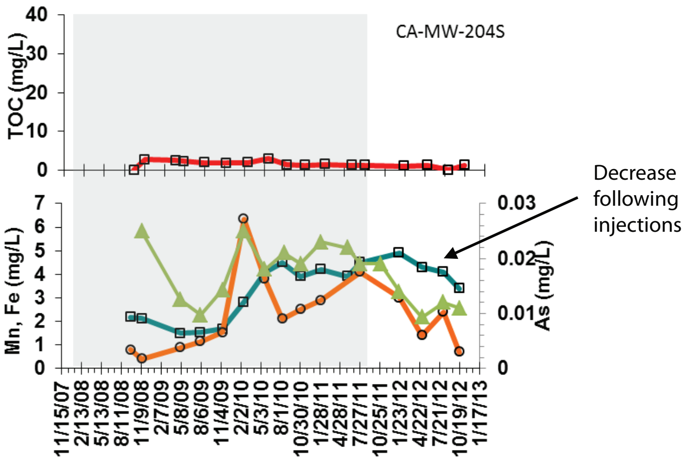
TOC	Total organic carbon
Mn	manganese
Fe	iron
CA-MW-#	PG&E monitoring well Identification
Mg/L	milligrams per liter (1 mg/l = 1 parts per million [ppm])

Note: This figure shows changes in concentrations of byproducts (iron, manganese, and arsenic) over time in relation to total organic carbon injections for In-Situ Treatment at PG&E monitoring wells in the Central Area (near injection locations).

Graphics/Projects/00122.11 Hinkley (Mar-2013) SS

Source: PG&E 2010

Figure A-10b
Changes in Byproduct Concentrations



Decrease following injections

-□- Dissolved Manganese (Mn)

-▲- Dissolved Arsenic (As)

-○- Dissolved Iron (Fe)

▭ Grey shading indicates periods of TOC injection)

TOC	Total organic carbon
Mn	manganese
Fe	iron
CA-MW-#	PG&E monitoring well Identification
Mg/L	milligrams per liter (1 mg/l = 1 parts per million [ppm])

Note: This figure shows changes in concentrations of byproducts (iron, manganese, and arsenic) over time in relation to total organic carbon injections for In-Situ Treatment at PG&E monitoring wells in the Central Area (near injection locations).

Graphics/Projects/00122.11 Hinkley (Mar-2013) SS

Source: PG&E 2010

Figure A-10c
Changes in Byproduct Concentrations

the ethanol concentrations have been made based on monitoring results for the Central in-situ remediation zone and the Source Area in-situ remediation zone. Similar monitoring with adjustments will be needed throughout the operation of all of the in-situ remediation zone areas for the complete clean-up operations.

In-situ Remediation Byproducts

Temporary mobilization of reduced metals (arsenic, manganese, and iron) as well as sulfide and methane (i.e., reduced byproducts) may occur as a result anaerobic groundwater conditions caused by injecting organic carbon (ethanol) into the aquifer. ~~While the duration of mobilization is unknown, mobilized metals are expected to precipitate once the ethanol has been depleted and the metals are exposed to background aerobic groundwater conditions. Although the distance that byproducts may migrate from the treatment zone is unknown, byproducts should precipitate before reaching receptors, such as domestic and agricultural wells.~~ Although carbon injection can mobilize the levels of byproducts in the aquifer, this mobilization is temporary and levels dissipate on the order of several months to several years. When organic carbon is injected for remediation and then consumed by microbial action, the concentrations of byproducts (iron, manganese, and arsenic) begin to return to pre-dosing concentrations through a number of processes including dilution, sorption, precipitation and coprecipitation. The return of aerobic conditions in the treatment area (due to mixing of groundwater with dissolved oxygen content) further decreases byproduct concentrations as dissolved iron and manganese are oxidized, reforming oxide minerals. **Figure A-10** shows that when total organic carbon (TOC) levels decline, byproduct concentrations also subsequently decline within a period of several months to several years. Sampling results to date have indicated that byproducts stay within or in the vicinity of in-situ remediation zone and within the chromium plume area. Once carbon increases are consumed by microorganisms, they are expected to eventually reduce in concentration and return to pre-injection levels when constituents reach oxygenated groundwater outside of the immediate remediation area. As described in Section 3.1, *Water Resources and Water Quality*, sampling results from several sources indicate that current evidence does not indicate a connection between summer/fall 2012 manganese detections in domestic wells west of the chromium plume and in-situ operations. Detections outside of the in-situ remediation areas may be attributed to naturally-occurring conditions or other man-made pollutant sources. Additional investigations are ongoing to evaluate patterns of manganese detections near the IRZ areas. The existing in-situ remediation zone contingency plan includes monitoring with mitigation measures to be performed if threshold concentrations of remediation byproducts (ethanol and reduced metals) are exceeded at designated sentry monitoring wells within the project recovery zone. Mitigation measures will be initiated to prevent remediation byproducts above the threshold concentrations from migrating beyond the IRZ area~~recovery zone~~, and to protect the water quality at nearby private wells. ~~Ethanol injection will be scaled back or shut off.~~ If groundwater monitoring indicates that remediation byproducts are not attenuating within the IRZ area ~~project boundaries~~, additional extraction wells for recirculation back to the in-situ remediation zone or air sparging (i.e., surface oxidation) and reinjection will be initiated to prevent migration to the contingency zone (Pacific Gas and Electric 2011a).

More information on the effects of in-situ remediation on byproduct levels is provided in Section 3.1, *Water Resources and Water Quality.*

A.5.2.6 Stability of Reduced and Precipitated Chromium (Cr[III])

~~The stability of Cr[III] (relative to re-oxidation) that has been reduced and precipitated from agricultural land treatment or in-situ reduction treatment is expected to be similar or greater than naturally occurring Cr[III]. While the kinetics of Cr[VI] reduction are fairly rapid (days) in reduced groundwater environments, the re-oxidation of Cr[III] is relatively slow. There are only a few oxidants present in natural systems that are known to be capable of oxidizing Cr[III] to Cr[VI]. These include oxygen and manganese oxide (Pacific Gas and Electric 2011a).~~

~~Dissolved oxygen can oxidize Cr[III] to Cr[VI], but the kinetics are very slow at the neutral to slightly acidic groundwater pH typical of most aquifer systems, such as Hinkley. As a result, dissolved oxygen is more likely to react with other materials in the subsurface before reacting with aqueous Cr[III]. This is particularly true in a former anaerobic reactive zone, where reduced minerals (such as iron sulfides) are formed and stored in the aquifer. In addition, Cr[III] will have sufficient time to be sequestered through precipitation and sorption reactions before oxygen can react with it. As a result, the available literature concludes that the oxidation of Cr[III] by dissolved oxygen is not likely in typical groundwater systems.~~

~~Manganese oxides are more effective in oxidizing Cr[III] than dissolved oxygen, and occur in the subsurface primarily as coatings on soil grains. The rate at which they react with dissolved Cr[III] is affected by both the reactive surface area of the manganese oxides, and the dissolved concentrations of Cr[III]. For the oxidation reactions to proceed, Cr[III] must adsorb directly to the surface of the manganese oxide minerals. Because aqueous Cr[III] concentrations will be effectively controlled by low solubility Cr[III] hydroxides and mixed iron-Cr[III] hydroxides formed through treatment, the amount of aqueous Cr[III] available for adsorption onto manganese oxide surfaces and subsequent oxidation will be limited. A portion of the manganese liberated in the in-situ remediation zone will precipitate as carbonate minerals. In addition, reaction of manganese with Cr[III] will be inhibited by reduced iron minerals such as iron sulfide (FeS) that will be formed within the in-situ remediation zone s in the same area where chromium is precipitated (Pacific Gas and Electric 2011a).~~

<u>One of the ways that remedial activities could alter chromium concentrations is via potential reconversion of Cr[III] to the Cr[VI] within the aquifer post remedial treatment. Increased stability of Cr[III] reduces the potential for reconversion.</u>

<u>More information on the general conditions in the Hinkley Valley and how conditions may affect the ability for chromium reconversion is provided in Appendix A.3.</u>

A.5.2.7 Model Simulation of In-Situ Remediation Zone Treatment Areas

Figure 3.1-13 <u>in</u> Section 3.1, *Water Resources and Water Quality,* shows a diagram of the two different types of In-situ Remediation Zones that can be used to help understand the in-situ remediation zone monitoring results from the <u>2004-</u>2005 pilot testing and full-scale in-situ remediation zone areas (Central, Source, and SCRIA) within the Hinkley chromium plume. This conceptual model was used to better understand information, such as what the 3D groundwater flow (MODFLOW) and chemical transport model (MT3DMS) would calculate within a representative model cell. The size of the conceptual model example cell was an acre with a time-step of a month for a year. This allowed the change in groundwater flow and Cr[VI] concentrations within the example cell to be tracked for a year, to understand the likely effects of different in-situ remediation zone designs with various assumed aquifer properties.

As described previously, model assumptions for the Hinkley Valley groundwater flow in the upper aquifer include a saturated thickness of about 75 feet, with a porosity of about 20% and a hydraulic conductivity of about 50 ft/day. There is a regional groundwater elevation gradient of 20 ft/mile, which indicates a northward water tracer movement of about 1 ft/day through the aquifer thickness. This regional water movement through the one acre example cell (about 210 feet wide) can be specified as a regional flow rate (15 gpm based on model assumptions). The in-situ remediation zone cell would include some injection of carbon-amended water into the cell, which is specified as an injection rate (gpm). These flow parameters will provide the basic aquifer movement and pumping rate required for in-situ remediation zone treatment within the cell. A higher regional flow will move the plume faster, but will require increased carbon injection pumping to create the necessary chemical conditions to cause the Cr[VI] to be reduced and precipitate as Cr[III].

The highest concentrations of Cr[VI] remain below the Compressor Station evaporation ponds, suggesting that not all of the water in the aquifer is moving north with the groundwater elevation gradient (regional flow). Some portion of the aquifer porosity is trapped behind clay layers or lenses that prevent movement in this portion of the aquifer. For the conceptual model, half of the porosity (10%) will be assumed to be mobile (water moving with the groundwater gradient) and half will be assumed to be immobile (trapped within the aquifer matrix). The water between these two porosity units will exchange (mix) at a specified rate (% of the mobile volume mixing with the immobile volume each month). The conceptual model will track the Cr[VI] concentration and the injected carbon concentration, which will can be used to indicate reduced chemical conditions within the one-acre example cell. The Cr[VI] in the mobile porosity will be transported by the regional groundwater flow. The injection flow will replace some of the regional flow from the south. The Cr[VI] in the immobile porosity will slowly exchange with the mobile porosity, and will cause the concentrations of Cr[VI] in the cell to remain higher than if the entire cell porosity was mobile and being moved and diluted by the regional groundwater flow.

The MT3D model tracks the average Cr[VI] and carbon concentrations in the mobile and immobile pore water within each model cell (25 feet by 25 feet). The exchange rate is apparently about 2% in a month. But the carbon decay rate was assumed to be 0.05 per day (half the concentration in 14 days). The reduction of Cr[VI] and precipitation of Cr[III] in the aquifer was simulated in the presence of injected carbon whenever it exceeds a concentration of 0.1 ppm. A carbon half-life of 14 days (0.05 per day) was estimated, to account for the degradation of the injected carbon over time. For an injection of 100 ppm, the concentration would be 50 ppm in 14 days and would be 0.1 ppm in about 150 days. The effective zone for the in-situ remediation zone would be the mobile volume filled by the ethanol within 150 days of injection pumping. But the carbon would then be expected to spread into the immobile porosity, diluting the carbon by a factor of 5, because total porosity of 35% with mobile porosity fraction of 7% was assumed. So the treatment zone would extend as far as 0.5 ppm in the mobile porosity zone, which would be about 100 days of movement if the initial injection was 100 ppm.

No byproduct formation or persistence is included in the MT3D model at the present time. Only Cr[VI] and carbon (ethanol) concentrations have been simulated with the chemical groundwater model, MT3D. ~~Nitrate and sulfate concentrations would be much lower within the chemical reduced conditions that are expected in the in-situ remediation zone. With the lack of other chemicals, such as nitrate and sulfate, incorporated into the model, the anaerobic processes and development of lower redox conditions are only indirectly estimated with the injected carbon concentrations.~~

A.5.3 Above-ground Treatment

Above ground (ex-situ) treatment includes various physical-chemical and biological treatment processes that can be used to treat extracted groundwater containing chromium. The treatment process options include liquid-phase treatment to reduce toxicity, mobility, or mass of chromium in groundwater prior to reuse/injection. The physical-chemical methods that can be used to remove chromium from groundwater include chemical reduction/precipitation, electrochemical precipitation, coagulation/microfiltration, ion exchange, ~~and~~ reverse osmosis, and electrocoagulation. A separate memo discussing electrocoagulation is provided in Appendix A.2.

In general, chemical reduction/precipitation treatment is implemented by mixing treatment chemicals with the water stream to promote a reduction/oxidation (redox) reaction. Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). For the case of Cr[VI] treatment, the chromate ion would gain electrons and be reduced to Cr[III], and iron would lose electrons and be converted from ~~Fe_2~~Fe(II) to ~~Fe_3.~~Fe(III). Reducing agents most commonly used for treatment of Cr[VI] are ferrous sulfate, ferrous chloride, sodium bisulfite, and sodium hydrosulfite. Redox chemicals must be added in quantities greater than the stoichiometric ratio because the chemicals will be consumed by other oxidized chemicals. Unit processes for chemical reduction/precipitation systems for chromium removal typically include a reactant feed system, reaction (reduction) vessel, aeration tank for oxidation of excess iron, filtration system, and solids handling equipment for dewatering and disposal of precipitated materials. The technology has been proven effective for chromium removal in both bench and full-scale applications, has been implemented at a number of similar sites for groundwater treatment, and could be implemented at the Hinkley site. The process does generate a chemical waste sludge that will require disposal, possibly as a hazardous waste (Pacific Gas and Electric 2010).

Reduction and precipitation of Cr[VI] from extracted groundwater involves at least two reactors. The ferrous iron reduction process is typically carried out with two reactors in series, the first for Cr[VI] reduction and the second, an aerated reactor to oxidize residual ferrous iron to the insoluble ferric state. Flocculants to aid settling of the Cr[III] and Fe_3 are added. The precipitated solids containing Cr[III] and Fe_3 hydroxides are removed by media filtration. Filter backwash is collected in a large tank where solids are settled, and clear liquid decanted for reuse/disposal.

There are generally two major limitations for ~~surface~~aboveground treatment of Cr[VI] pumped from groundwater. The treatment capacity needed to treat the Hinkley plume within a reasonable time would be relatively large. Because there is an estimated volume of about 7,500 af with concentrations of greater than 50 ppb, a facility with a capacity of 250 gpm would pump and treat about 400 af per year, requiring 20 years to pump and treat the plume core (>50 ppb). A facility with a capacity of 1,000 gpm would still require five years to pump the existing plume core (>50 ppb) volume. The second limitation is that it is difficult to pump all of the contaminant from the groundwater, because of immobile porosity zones within the aquifer material. The Hinkley Source Area monitoring wells suggest that this is a characteristic of the chromium plume. Therefore, pumping several times the existing plume volume may be required to remove the majority of the Cr[VI] from the plume core. Pumping several times the core plume volume would require many more years. The sludge will likely be considered a toxic waste and would need to be disposed of in an appropriate landfill facility. However, unlike agricultural land treatment and in situ operations, above-ground treatment will remove the Cr[VI] from the aquifer material, rather than leaving the

Cr[III] precipitated in the aquifer material. ~~Also refer to~~ Appendix A.2 includes a discussion of similar limitations for the electrocoagulation~~for a discussion on the limitations of this~~ technology.

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Appendix A.2

Elecrocoagulation

Appendix A.2

Review of Electrocoagulation

Date:	April 22, 2013
To:	Kim Niemeyer, Lahontan Regional Water Quality Control Board
Cc:	Anne Holden, Lahontan Regional Water Quality Control Board Kate Giberson, ICF International
From:	Rich Walter, Alexa La Plante and Erin Healy, ICF International
Subject:	**Data Review Summary and Response to Water Board Questions regarding the use of Electrocoagulation for the Hinkley Groundwater Remediation Project**

Introduction

This memorandum provides a general overview of electrocoagulation (EC) technology, its current uses, and an evaluation of its potential for remediation of Cr[VI] in groundwater at Hinkley. The purpose of this memo is to assist the Lahontan Regional Water Quality Control Board (Water Board) in evaluating comments on the Hinkley Groundwater Remediation Project (Project) Draft Environmental Impact Report (EIR) urging the Water Board to consider EC technology for application at the Hinkley site.

Background

Libre Energy, Inc. ("Libre") has suggested electrocoagulation (EC) as a viable remedial alternative that should be considered to remove hexavalent chromium (Cr[VI]) from the Hinkley groundwater aquifer as part of the Project (Libre Energy, Inc. 2012). In addition, the Water Board received several comments from the public on the Draft EIR for the Project about incorporating an impact analysis of the EC method as an ex-situ treatment method.

Electrocoagulation Technology

The process of EC involves applying an electrical current through an anode-cathode system to destabilize dissolved ionic or suspended contaminants. The anode and cathodes are composed of metal plates and different types of plates may be used (e.g., iron, aluminum). In the EC system proposed by Libre (Powell Water Electrocoagulation), the metal plates are composed of iron. During treatment, the system pumps water into a chamber containing multiple sets of anode and cathode pairs and applies an electrical charge. The electric charge causes the anode metal to dissolve and release ferrous iron (in the case of iron anode/cathodes), into the water. The ferrous iron reduces the Cr[VI] to its trivalent state(CrIII), which forms an oxide or hydroxide solid. The solid is separated and disposed of as a sludge, and the remaining effluent is re-injected into the aquifer.

An EC unit consists of at least four main parts:

- Reaction chamber(s) – pairs of anode and cathodes that are uniformly spaced.
- Electric system – the electronic controls and power supply for the unit.
- Clarifier – allows material to settle out.
- Dewatering system – removes excess water from the sludge.

Additional system components may include influent and/or effluent storage tanks and transfer pumps and potentially additional influent (pre-treatment) and/or effluent (post-treatment) modules (e.g., pH adjustment tanks). The chromium oxide sludge produced during EC of Cr[VI] typically will pass the Toxicity Characteristic Leaching Procedure (TCLP) as the chromium produced is not readily leachable (DOE 2012); however, any sludge would need to be adequately tested for all contaminants of concern before proper disposal could be determined. Additionally, due to the effectiveness of EC on removing dissolved and suspended material and inorganic contaminants, the sludge produced will likely contain other inorganic contaminants that are present in the influent groundwater in addition to chromium. Based on existing groundwater quality conditions at Hinkley, this may include TDS, arsenic and radionuclides. Nitrate, which is also in study area groundwater, has also been successfully removed using EC in bench-scale studies using aluminum anode/cathode pairs, but has not been proven with iron anode/cathode pairs.

Proven Uses

Proven applications for EC include treatment of fairly consistent influents from wastewater and industrial processes. These include treatment of municipal wastewater and effluents and/or process waters from paper mills, textile mills, tanneries, petroleum refineries, and slaughterhouses.

EC has not been used as a primary treatment for groundwater contamination. It has been studied in several pilot tests, most notably a study that used EC to treat Cr[VI] at the Hanford Site in Richland, Washington.

Evaluation of Potential Use for Groundwater Remediation at Hinkley

Small bench-scale studies in laboratory settings of aqueous matrices demonstrate that EC can effectively reduce concentrations of Cr[VI]. However, the technology has never been fully implemented for groundwater environmental remediation at the capacity suggested by Libre, 600 gallons per minute (GPM) per unit. Researchers conducted a single pilot study of a 50 GPM system to remove Cr[VI] from groundwater in Richland, WA at the Hanford site in 2007. The results of the pilot study demonstrate some of the potential advantages and disadvantages of the technology.

Hanford Pilot Study

The Hanford pilot study demonstrated that Cr[VI] concentrations could be successfully reduced in groundwater to concentrations less than 20 μg/L (parts per billion) from initial concentrations ranging from 200 to 250 μg/L; when the system was operating optimally some effluent samples had concentration down to 8 μg/L. Comparatively at Hinkley, the cleanup goal for Hinkley is 3.1 μg/L.

Hanford researchers encountered several operational problems resulting in significant down time for maintenance and repair of the system. These included the build-up of calcium carbonate, or scaling of the cathode, and coating of the anode with iron oxide in the form of magnetite. This resulted in reduced efficiency of the system (reduction in Cr[VI] removal over time) and required extended down periods so that the materials could be physically removed. Additionally, the magnetite on the anode had a tendency to periodically become dislodged and nodules of the material, which is conductive, created bridges between the electrodes causing short circuits in the system. Researchers attempted to remove the calcium carbonate and magnetite coatings by reversing the polarity of the anode/cathode regularly and cleaning the electrodes chemical with hydrochloric acid both of which were unsuccessful.

Researchers made some additional recommendations from the study including:

- Carefully planned fundamental investigations into the EC process are needed to provide a firm technical basis for design and predictable performance.
- Pilot testing should be performed with equipment from the manufacturer who will provide the full-scale system.

Other Considerations

In addition to the difficulties and limitations of EC exemplified at Hanford, one needs to consider several issues identified in past research of EC in evaluating this technology for use at Hinkley that were not evaluated in the Hanford study. These include the following:

1. **System Efficiency.** A number of site-specific and system specific factors may affect the ability of the system to remove contaminants.
    - Properties of the water to be treated including pH, conductivity, chemical concentrations, and particle size affect the efficiency of EC.
    - Numerous operation factors need to be adjusted on a site-specific basis for EC systems to run efficiently including electrode materials and design, electrode spacing, using consistent or alternating polarity and the time intervals for switching polarities if using the later, flow configuration, and current density or the electric current the area.
    - EC systems are most efficient when concentrations are low.
2. **Side Reactions.** Multiple electrochemical reactions occur during EC operation that may introduce complications to the treatment process.
    - Hydrogen gas is generated at the cathode during operation and may be released in sufficient quantity to potentially cause explosive conditions. Hydrogen monitoring removal process need to be incorporated into system design.
    - During treatment, the pH of the groundwater may increase due to an excess of hydroxyl ions produced at the cathode. If pH increase is pronounced, effluent may need to be treated before re-injection into the aquifer.

3. **Process Byproduct.** The treatment sludge requires proper testing and disposal.
    - The sludge produced will contain the reduced trivalent chromium and other materials present in the groundwater that are capable of being treated with EC.

  - The chromium oxide formed during the process has passed Toxicity Characteristic Leaching Procedure (TCLP) analysis as it is not readily leachable. General leachability of other potential components of the sludge at Hinkley, such as arsenic and radionuclides, are not known.
  - Any sludge will require testing before disposal methods may be determined.

Libre Claims for Timeframe of Groundwater Cleanup with Electrocoagulation

Libre has claimed that Cr[VI] concentration in groundwater at Hinkley will be reduced to required clean-up levels in different areas of the site in approximately one to four years. These estimates are based on factors including pumping and treatment capacity that have not been demonstrated, which are further discussed below.

Libre Claim: EC system will operate at 830,000 gallons per day (GPD) or roughly 600 gallons per minute (GPM).

- Alternative 4C-5 has a pumping rate of 200 gpm. Typically, well placement and pumping rates are optimized to minimize cleanup times. The pumping rates that the aquifer can tolerate are the limiting factor, not the volume the treatment method can handle. Thus, pumping from four units at 600 gpm would have to be modeled to show that it is feasible.
- Pumping rates would need to be determined in a pilot study. Low flow rates through the treatment cellls would be required for high-concentration influent to allow time to apply sufficient current to reduce all Cr[VI] and avoid fouling. The treatment time would be determined during the pilot study.

Libre Claim: EC system will reduce Cr[VI] concentrations to clean-up levels in each volume of water in 60 seconds.

- Research demonstrates that removal rates for chromium are much less efficient than for other metals like copper and zinc. Treatment times will be affected by complex site-specific factors including initial Cr[VI] concentration and other chemicals present in the groundwater.

Libre Claim: EC system electrodes will need to be changed out every four months.

- Based on scaling issues in the Hanford pilot study and the number of complex site-specific factors that may contribute to such scaling, the timeframe proposed may be optimistic.

Libre Claim: EC system will consume 480 volts direct current (VDC).

- Much of the energy consumed by the EC system will rely on the current density required to effectively reduce Cr[VI] concentrations to clean-up goals and the retention time (needed treatment time in the EC unit). This could be verified in a pilot study.

Libre Question: Why EC did not pass the initial screen in the FS and chemical ex-situ treatment did pass?

- Chemical treatment has been used effectively at groundwater cleanup sites; EC has not been used on a full scale groundwater treatment system. Pilot testing for groundwater treatment has been limited, has indicated certain technical issues (rapid loss of treatment efficiency), and would have to be tested for any given site.

ICF Response to Water Board Staff Questions on EC

1. Are the effectiveness claims for high concentration plume area reasonable (96% removal rate for Cr6)? How many passes through system are needed to to get 3500 ppb Cr6 down to 1.2 ppb?

The removal rates would have to be determined based on a pilot study. Results for a pilot study at Hanford demonstrated that Cr[VI] concentrations could be successfully reduced in groundwater to concentrations less than 20 μg/L (parts per billion) from initial concentrations ranging from 200 to 250 μg/L (which would indicated a 90 to 92% removal rate); when the system was operating optimally with some effluent samples showing concentration reductions down to 8 μg/L (which would indicate a 96 to 97% removal rate). Clean up to 3.1 or 1.2 ug/L Cr[VI] has not been demonstrated for environmental remediation (although reduction to these levels has apparently been achieved in industrial applications). Also, the Hanford pilot test had considerable problems with maintaining efficiencies due to fouling of the electrode. Given these results, a 96% removal rate may or may not be achievable, and multiple units with low flows may be required to treat high concentrations of 3500 ppb.

2. Are the remediation times feasible? What are the assumptions? Are they reasonable?

The underlying assumptions are not backed up by a specific pilot or proven case study for environmental cleanup. They may or may not be reasonable, but would have to be proven in a pilot study at the site.

3. Are the pumping rates viable?

Alt 4C-5 has a pumping rate of 200 gpm. Typically, well placement and pumping rates are optimized to minimize cleanup times. The pumping rates that the aquifer can tolerate are the limiting factor, not the volume the treatment method can handle. Thus, pumping from four units at 600 gpm would have to be modeled to show that it is feasible; but given that higher pumping rates are proposed for agricultural treatment units, pumping up to 2,400 gpm is theoretically possible.

Pumping rates would need to be determined in a pilot study. Low flow rates through the treatment cellls would be required for high-concentration influent to allow time to apply sufficient current to reduce all Cr [VI] and avoid fouling. The treatment time would be determined during the pilot study.

4. One 600 GPM unit = 864,000 GPD; Four units = 3.5 million gallons per day. Libre asserts that waste is ~0.02% by volume, so 0.02% of 3.5 million gallons would be 700 gallons of waste per day. What is the waste residue for 4C-3 (ex-situ treatment of 1,222 gpm)? Can’t find any estimates from PGE in their feasibility study or addenda.

Again, waste would be determined based on a pilot study. The sludge may also contain other reduced components of the influent (possibly arsenic, manganese and radionuclides).

5. Is sludge removed with 2 hour clarifier treatment? Comments indicate no clarifier required (water/solids pumped into injection well). How does this work without extensive well maintenance to prevent fouling? What are the solids? What is the clarifying treatment?

The amount of produced solids would be determined on a site pilot test. The probability that water and solids could be re-injected is low without settling/clarifying to reduce solids. Sludge would then need to be disposed of, and the chemical characteristics of the sludge would need to be determined based on a pilot test.

6. Libre says that sludge can be discharged to dumpsters and hauled to landfill (or they claim on-site disposal is feasible).

Unknown. The sludge may pass a TCLP test, although that would need to be proven through the pilot study. However, concentrations of heavy metals may or may not preclude on-site application.

7. Waste/sludge disposal: On-site disposal not likely feasible from regulatory standpoint.

See above.

8. Electrodes 30,380 lbs? Where do you get those?

We were unable to identify a source. May need to be custom built.

9. Treatment table showing cumulative years, treatment times (59 sec, 58 sec, etc) plume dilution, corrected treatment volumes – do these numbers make sense? What are practical limitations, oversimplifications, fatal flaws?

See answers to questions above for limitations and oversimplifications.

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Appendix A.3

Potential for Reconversion of Trivalent Chromium to Hexavalent Chromium at the PG&E Hinkley Groundwater Remediation Project

Appendix A.3

Potential for Reconversion of Trivalent Chromium to Hexavalent Chromium at the PG&E Hinkley Groundwater Remediation Project

Prepared by ICF for the Lahontan Regional Water Quality Control Board.
April 22, 2013

Background

The cleanup of chromium contamination in groundwater in Hinkley, California (Hinkley site) involves the use of both agricultural and in-situ treatment with carbon amendment to reduce hexavalent chromium (Cr[VI]) to the less toxic trivalent chromium (Cr[III]). Recently, concern has been expressed that the reduced Cr[III] could convert back (or be "reconverted") to Cr[VI] after the remediation is complete. The different chromium species, chromium oxidation and reduction reactions, and the potential for oxidation of Cr[III] to reform Cr[VI] at the Hinkley site are discussed below.

Chromium Chemistry

Chromium Species

Chromium (Cr) is a naturally-occurring element found in rock, soil, plants, and organisms in combination with other elements to form different compounds. Chromium can be found in its elemental form as well as in various compounds and minerals by combining in varying ratios with other elements. Depending on the other elements in the compounds and the ratios, chromium can be categorized in different forms or oxidation states. Oxidation states describe the electron charge contribution of chromium to the compound, are constant for elements in specific compounds, and can fundamentally affect the nature of the compound.

The four main forms or species of chromium are:

- Cr[0] or elemental chromium,
- Cr[II] or divalent chromium,
- Cr[III] or trivalent chromium , and
- Cr[VI] or hexavalent chromium.

Elemental chromium, Cr[0], is relatively unstable and only derived through industrial processes (Kotas and Stasicka 2000). Cr[II] is not usually detected in the environment, because it is generally unstable and readily oxidized to Cr[III]. Cr[III] is stable under a wide range of conditions and is naturally occurring in the environment. The Cr[VI] species is naturally occurring in some areas (including in the Mojave Desert), but is often encountered from anthropogenic sources and is stable under a more limited set of conditions (Petchova and Pavlata 2007).

With chromium, toxicity differs widely depending on the oxidation state or species. In particular among the two most common forms, Cr[III] and Cr[VI] species have very different toxicities. Cr[III] has been shown to be essential to normal carbohydrate, lipid and protein metabolism in humans at very low levels and is less toxic than all other essential elements (e.g., Cu, I, Mn, Se, Zn) (Petchova and Pavlata 2007). Cr[VI] is classified as a known human carcinogen and has a toxicity far greater than Cr[III]. Due to the high toxicity of Cr[VI], remediation of contaminated sites often focuses on reduction of Cr[VI] to the stable and less toxic Cr[III].

Chromium Reduction and Oxidation Pathways

Chromium can be converted from one species to another through oxidation or reduction reactions. Reactions of Cr[VI] to Cr[III] are termed reduction while the reverse (i.e. transformation of Cr[III] to CR[VI]) is known as oxidation. In the environment, particularly in aqueous systems (i.e., groundwater or surface water), chromium compounds undergo constant reactions, causing conversions between the oxidation states. Like all chemical reactions, the equilibrium between reduction-oxidation (redox) reactions is governed by stability of the reaction products (thermodynamics) and relative speed of these reactions (kinetics). The background concentrations of Cr[III] and Cr[VI] species in a given location (independent of any man-made contamination sources) are dependent on the natural geochemistry of the particular area (Palmer and Puls 1994) reflecting the equilibrium of the redox reactions under those environmental conditions.

There are many pathways or mechanisms for the reduction of Cr[Vl] in the environment to the less toxic Cr[III]. These pathways are influenced by dissolved oxygen, pH and oxidation-reduction potential (ORP). Chromium reduction occurs readily in the environment through exposure to electron donors. Some natural electron donors include dissolved ferrous iron, ferrous iron minerals, reduced sulfur, and soil organic matter (Palmer and Puls 1994). Chromium may also be reduced through plant uptake and through reactions with soil microbes (Hawley et al 2004), with microbial reduction occurring in both aerobic and anaerobic environments, although the latter is more common (Palmer and Puls 1994).

Mechanisms for the oxidation of Cr[lll] to Cr[VI] are less prevalent than for the reduction process. The only constituents that occur naturally in the environment that oxidize Cr[III] to Cr[VI] are dissolved oxygen and manganese oxides (Stanin and Pirnie 2004). Although dissolved oxygen could potentially act as a chromium oxidizer, studies have shown the potential for chromium oxidation from dissolved oxygen alone to be extremely minimal or non-existent (Palmer and Puls 1994) and negligible (Stanin and Pirnie 2004). Dissolved oxygen will preferentially react with other materials in the subsurface before reacting with Cr[III] particularly where reduced minerals (such as iron sulfides) can act as a buffer to the oxidation of Cr[III]. As a result, the available literature concludes that the oxidation of Cr[III] by dissolved oxygen is not a meaningful pathway in typical groundwater systems (Schroeder & Lee, 1975; Eary & Rai, 1987; Rai et al, 1989; Hwang et al, 2002; Guertin et al, 2005). For dissolved oxygen to oxidize Cr[III], other chemical conditions are required, such as an alkaline pH. For example, some areas in the western Mojave Desert (i.e., Surprise Spring and Sheep Creek) have high naturally occurring Cr[VI] concentrations due to high dissolved oxygen levels and very alkaline pH values (greater than 8.0 and occasionally greater than 9.0), as well as significant amounts of mafic rock (Izbicki et al 2008) due to the close proximity to the San Gabriel and San Bernardino Mountains (PG&E 2011). Dissolved oxygen and related environmental parameters, such as pH, in the Hinkley Valley are discussed further in the *Effects of DO, pH, and ORP on Chromium Speciation* section below.

Chromium Oxidation by Manganese Oxides

Manganese oxides can oxidize chromium in the environment under certain conditions (Stanin and Pirnie 2004). Manganese oxides present in the environment are most commonly found as mixed valence states of Mn(III) and Mn(IV) species from minerals such as pyrolusite, birnessite, and hausmannite. Chromium oxidation by manganese oxides follows three basic steps:

1. Cr[III] must adsorb (adhere) onto manganese oxide surface sites,
2. Cr[III] must be oxidized by Mn[III/IV] on the surface sites, and
3. Cr[VI] needs to desorb (Stanin and Pirnie 2004).

For the oxidation reactions to proceed, Cr[III] must sorb directly to the surface of the manganese oxide mineral (Schroeder & Lee, 1975; Rai et al, 1986; Eary & Rai, 1987; Richard & Bourg, 1991;Hwang et al, 2002; Guertin et al, 2005). However this requires that the Cr[III] must be mobile and in the aqueous (or dissolved) phase. Solubility of the chromium compounds depends on their specific compounds and associated environmental conditions, such as pH and redox potential. Under wide ranging environmental conditions, most common Cr[III] hydroxides are insoluble. Cr[III] hydroxides generally precipitate as a solid and can remain stable in groundwater exhibiting a pH greater than 5 and a redox potential of less than 600 mV (Deutsch 1997). ~~Groundwater with pH values from 5 to 12 can be expected to have aqueous Cr[III] concentrations of less than 50 ug/L (Fendorf 1995). At pH values ranging from 7 to 10, this concentration has been estimated at less than 20 ug/L (McNeill and McLean 2012).~~ Another important factor limiting mobility of Cr[III] is the tendency for it to adsorb (or attach) to materials in the subsurface, which has been measured as 90% chromium sorption to clay minerals and iron oxides within 24-hours (Hawley et al 2004). Because of this high likelihood for Cr[III] to readily sorb to soil particles, it limits its mobility and ability to sorb onto manganese oxides (Palmer and Puls 1994; Fendorf 1995).

In addition, factors that limit the availability of reactive manganese oxide surfaces will limit oxidation of Cr[III]. During remediation of Cr[VI], liberated manganese can precipitate in the form of a Mn(II) carbonate (i.e., manganese carbonate). During and after Cr[VI] remediation processes, other minerals form along with manganese precipitates (e.g., calcite, ferrous and ferric iron minerals) that can obscure the surfaces of manganese oxides. Chromium hydroxide precipitates also have been shown to coat the reactive surfaces of manganese oxides preventing binding of the Cr[III] (Fendorf et al., 1992; Fendorf, 1995). In addition, the reaction of manganese with Cr[III] is inhibited by the presence of reduced iron minerals such as iron sulfide (Deng and Wu, 2006), a mineral that will be formed where chromium is precipitated. The presence of iron sulfide essentially deactivates manganese oxides, and prevents them from reacting with Cr[III].

Effects of Dissolved Oxygen, pH, and Reduction Potential on Chromium Chemistry

Water quality parameters that may affect chromium solubility, mobility, and rates of chromium reducing and oxidizing reactions include presence of oxidizers (such as dissolved oxygen and manganese oxides), pH, and reduction potential (Eh) (Ore et al 2007). Other factors that may affect the likelihood of oxidation include the capacity of soils to bind chromium and microbial activity; however, these are generally less critical. For Cr[VI] oxidation, manganese oxides have been demonstrated to be the most effective oxidizers generally available in the environment. Dissolved oxygen can also act as an oxidizer but only in alkaline environments, generally indicated by pH values greater than 8. Oxidation by manganese oxides requires dissolution of the chromium species and mobility to allow for adhesion to surface reaction sites of the manganese oxides.

The pH of the aqueous environment is a key factor in mobility of chromium species. Reduction potential (Eh) is a measure of the ability of a chemical species to acquire electrons (i.e., be reduced). In the presence of oxidizers and without barriers to reaction (such as from an impermeable layer), Eh and pH can be used to predict the predominant species of chromium. The Eh-pH diagram in **Figure 1** describes theoretical predominant species within a broad range of conditions. Eh is measured in volts (V) According to the figure, trivalent chromium species (Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_3$ and $Cr(OH)_4^-$ ions) predominate in a wide range of pH values and Eh values. Hexavalent species (hydrogen chromate ($HCrO_4^-$) and chromate (CrO_4^{2-}) ions) are predominant in a more limited range as shown on the figure. The dotted lines represent the threshold between solid and aqueous phases, indicating that the trivalent species are in solid phase and hexavalent species are in the aqueous phase.

Review of Water Quality Measurements at Hinkley and Potential for Reconversion of Cr[III] to Cr[VI]

Water quality measurements including dissolved oxygen, pH, Eh, and dissolved manganese are regularly monitored at Hinkley within the in-situ remediation zones (IRZs) and at residential and monitoring wells within and downgradient of the chromium plume. These data at the Hinkley site reflect a long and ongoing influence of irrigated agriculture and other activities and therefore any influence of these activities on groundwater conditions are already represented in the data results.

2001 – 2013 Data Review

To further assess the potential of oxidation of Cr[III] to Cr[VI] in and around the Hinkley groundwater remediation area, ICF reviewed a wide data set of more than 6,000 data points from more than 300 PG&E groundwater sampling locations collected from 2001 to 2013 for parameters that indicate chromium speciation including pH, Eh, manganese, and dissolved oxygen. Groundwater measurement data was provided by PG&E for review and in presented in **Figures 2, 3 and 4** and summarized in **Table 1**. Although dissolved oxygen can act as an oxidizer, the generally slightly acidic to slightly alkaline pH conditions at the Hinkley site (only 2% of all pH measurements reviewed were above pH 8.0) limit the effectiveness of this mechanism. The concentrations of dissolved manganese suggest that manganese oxides may be present to act as an oxidizer although the specific manganese compounds have not been determined. Specifically, reformation of Cr[VI] requires Mn[III/IV] species and reactive surfaces. Manganese liberated in the IRZs precipitates at least partially as a manganese carbonate Mn[II] species. In addition, minerals that form along with manganese precipitates including calcite, ferrous and ferric iron minerals can block reactive surface sites and reduce the potential for oxidation of Cr[III]. Chromium hydroxide precipitates themselves have been shown to deactivate reactive surfaces of MnO_2 through the same mechanisms (Fendorf et al., 1992; Fendorf, 1995). In addition, reaction of manganese with Cr[III] is inhibited by the presence of reduced iron minerals, such as iron sulfide (Deng and Wu, 2006) which also will be formed within the IRZs. The presence of iron sulfide further inactivates manganese oxides to limit availability to bind Cr[III].

PG&E groundwater measurement data demonstrate conditions of predominance of the Cr[III] species at Hinkley. According to the Eh-pH diagram (**Figure 1**), Cr[III] predominates in the range of conditions of 1) Eh between -0.3 and +0.3 V and 2) pH of less than 8. Less than 2% of the data provided (119 of 6265 data points) are outside this Eh-pH range (see **Figure 4**), where Cr[III] is still prevalent but Cr[VI] may be formed and may be significant. These parameters of +/- 0.3 V Eh and pH of <8 were selected based on the Eh-pH diagram and literature values (Palmer and Wittbrodt, 1991) to provide a worst case estimate of environmental conditions where Cr[VI] formation could possibly be significant relative to competing mechanisms causing reduction to Cr[III]. However based on this data, the conditions at the Hinkley site appear to highly favor formation of trivalent species and minimize the likelihood for Cr[III] oxidation to Cr[VI]. Minimal oxidation is also supported by the 2007 Background Study (PG&E 2007). Since the PG&E Compressor Station is the only known anthropogenic source of Cr[VI] in Hinkley (CRWQCB 2008), the relatively low concentrations of hexavalent chromium outside the plume (compared to some other locations in the Mojave Desert with higher naturally occurring hexavalent chromium) are indicative of conditions representing a low predominance of hexavalent chromium species as part of non-PG&E discharge groundwater conditions in the Hinkley Valley.

2012 Data Review

Review of the water quality data collected by PG&E in July and August 2012 shows that the groundwater within the plume as well as outside the plume is ~~t~~oxic (high dissolved oxygen levels), neutral pH groundwater with low potential to promote oxidation (low Eh). 2012 water quality data is summarized for the IRZ and Northwest Freshwater Injection areas versus through the chromium plume and surrounding area below.

<u>Within the IRZ and Northwest Freshwater Injection Areas</u>

- Oxygenated with dissolved oxygen values greater than 0.5 mg/L with most wells having high dissolved oxygen values of 4 to 8 mg/L at 20 to 25°C
- Neutral with pH values ranging from 6.5 to 7.5
- Low ORP values from -0.2 V to +0.2 V (Eh values of 0 to 0.4V) and not indicative of conditions under which Cr[III] would likely be oxidized

Throughout the Plume and Surrounding Area outside the Plume

- Oxygenated with dissolved oxygen values greater than 0.5 mg/L with most wells having high dissolved oxygen values of 4 to 8 mg/L at 20 to 25°C
- Generally neutral pH values ranging from 6.5 to 8.0
- Low ORP values from -0.2 V to +0.2 V (Eh values of 0 to 0.4V) and not indicative of strongly oxidizing conditions

Dissolved oxygen, pH, and Eh values in the aquifer, particularly for groundwater outside the plume, is indicative of groundwater conditions beyond the area of influence of the treatment technologies, and is helpful in evaluating the potential for oxidation of Cr[III] to Cr[VI] at the Hinkley site after groundwater remediation is complete. Although the groundwater in this area is oxygenated and in some cases highly oxygenated, it is neither acidic nor alkaline, and so is not indicative of oxidizing conditions. Therefore, the following conclusions are generally true.

- Although the dissolved oxygen content of groundwater is high at the Hinkley sampling locations, high dissolved oxygen alone does not result in chromium oxidation (Palmer and Puls 1994; Stanin and Pirnie 2004) without additional factors like high (or alkaline) pH (Izbicki et al 2008). Although groundwater dissolved oxygen is high, pH values are relatively neutral.[1]
- Cr[III] hydroxides will be the predominant form of chromium in the area as groundwater pH and Eh values fall comfortably within the ranges in which Cr[III] hydroxides dominate (see Figure 1).
- Natural reducing processes (e.g., aqueous Fe(II), organic matter) are active at pH values from 5 to 9 but may be inhibited at values outside this range (Hawley et al 2004). Area groundwater pH values fall comfortably within the range where natural reducing processes are known to occur.

Potential Effect of Increased Chromium and Dissolved Manganese Due to Remediation Activities

While the review above indicates that existing geochemical conditions are not favorable for substantial chromium oxidation, remediation activities will change the amount of total Cr[III] in soil and may result in temporary increases in the amount of dissolved manganese in the area. To fully evaluate the potential for chromium reformation, these two additional factors are addressed below.

While additional Cr[III] in the environment will not change the natural oxidation and reduction processes or the rates at which these occur, it may result in increased Cr[VI] simply by providing additional Cr[III] for oxidation. Chromium occurs naturally in soils and occurs at levels of 0.5 to 6.0 mg/kg in the Hinkley area (PG&E 2011). The potential contribution of in-situ remediation to Cr[III] concentrations from Cr[III] hydroxides has been estimated to be approximately 0.01 to 0.8 mg/kg, which is minimal compared to existing naturally-occurring levels (PG&E 2011). The

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[1] Current conditions reflect a long history of agricultural activity in the Hinkley Valley and thus the general influence of irrigated agricultural on pH should be similar over time with the use of agricultural treatment units for remediation.

greatest mass of chromium will be in the IRZs, at and just north of the Hinkley Compressor Station, at the depth of the water table and deeper, or 75 to 105 feet below ground surface (bgs). To a lesser extent Cr[III] will also increase at lower concentrations within the top 5 feet of the soil in the agricultural treatment units (PG&E 2011) due to the formation of Cr[III] at the root zones of crops. As previously discussed, chromium hydroxides are highly insoluble and readily sorb to the soil greatly limiting their mobility. That, along with neutral pH groundwater values, limit the ability of Cr[III] compounds to sorb to manganese oxides that could act as oxidizers. Therefore the slight increases in Cr[III] are unlikely to increase Cr[VI] concentrations.

Dissolved manganese concentrations are expected to increase from in-situ reduction as native manganese in the soil and groundwater is reduced to Mn[II] compounds, such as manganese carbonate. However this increase is expected to be short-term and not provide any additional manganese that could support oxidation of Cr[III]. While manganese oxides as Mn[III/IV] species under certain conditions may act as chromium oxidizers, Mn(II) species do not effectively oxidize Cr[III]. In-situ remediation has shown that concentrations of remedial byproducts like Mn(II) return to background levels as the injected carbon is consumed by microbial processes and is diluted with downgradient migration. Manganese concentrations are expected to return to pre-IRZ levels following the end of the carbon injection (see further discussion in Section 3.1 *Water Resources and Water Quality*, and discussion and Figure A-10 in Appendix A.1). Outside the reducing environment of the IRZ, Mn[II] compounds can reform into Mn[III/IV] oxides however the concentrations will return to the pre-IRZ levels. Therefore it will not result in a net increase of Mn[III/IV] oxide concentrations capable of supporting Cr[III] oxidation. While conditions such as alkaline pH and the presence of mafic rock and high Eh values are more likely to promote Cr[III] oxidation via Mn[III/IV] oxides, these conditions are largely absent at Hinkley. The lack of net increase in Mn[III/IV] oxides due to remediation should not further impact potential for chromium oxidation.

Conclusions and Limitations

Overall conditions for area groundwater at the Hinkley site are not supportive of chromium oxidation. Since the Hinkley Compressor Station is considered to be the only anthropogenic source of Cr[VI] in Hinkley (CRWQCB 2008), the background chromium concentrations outside the plume are indicative of the net effect of all the competing chromium oxidation and reduction reactions without the influence of the PG &E's remediation activities to date, and are relatively low, indicated by the maximum background value of 3.1 ug/L Cr[VI] (CRWQCB 2008). Once treatment of the chromium plume is complete, the competing chromium oxidation and reduction mechanisms inherent in the area will continue and the net effect of these reactions should maintain the stability of CR[III] and maintain Cr[VI] at the achieved background concentrations mandated for remediation.

Despite these overall conclusions, data limitations indicate that there are still some unknowns that have not been evaluated in this memorandum. Significant oxidation to Cr[VI] at the Hinkley site is unlikely to occur based on existing data and the current understanding of remedial effects. However, other chemical constituents and biological processes may also affect the ability for reconversion to occur. For example, the presence of other oxidizers, competing reactants, binding surface and material types may enhance or inhibit reconversion. Some chemical species that might promote or restrict oxidation are arsenic, organic acids, chlorine, chromium citrate, and sulfur. Some of these species (i.e., low molecular weight organic acid complexes, such as chromium citrate) would enhance oxidation while others (i.e., organic acids) would inhibit it. Although likelihood of reduction and oxidation may be predicted under a set of conditions, the process may be negligible in cases where the reaction rate is slow. Therefore, further sampling and analysis may be conducted to fill in these data gaps.

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Figure 1: Eh-pH Diagram for Chromium Speciation
(Palmer and Wittbrodt, 1991)

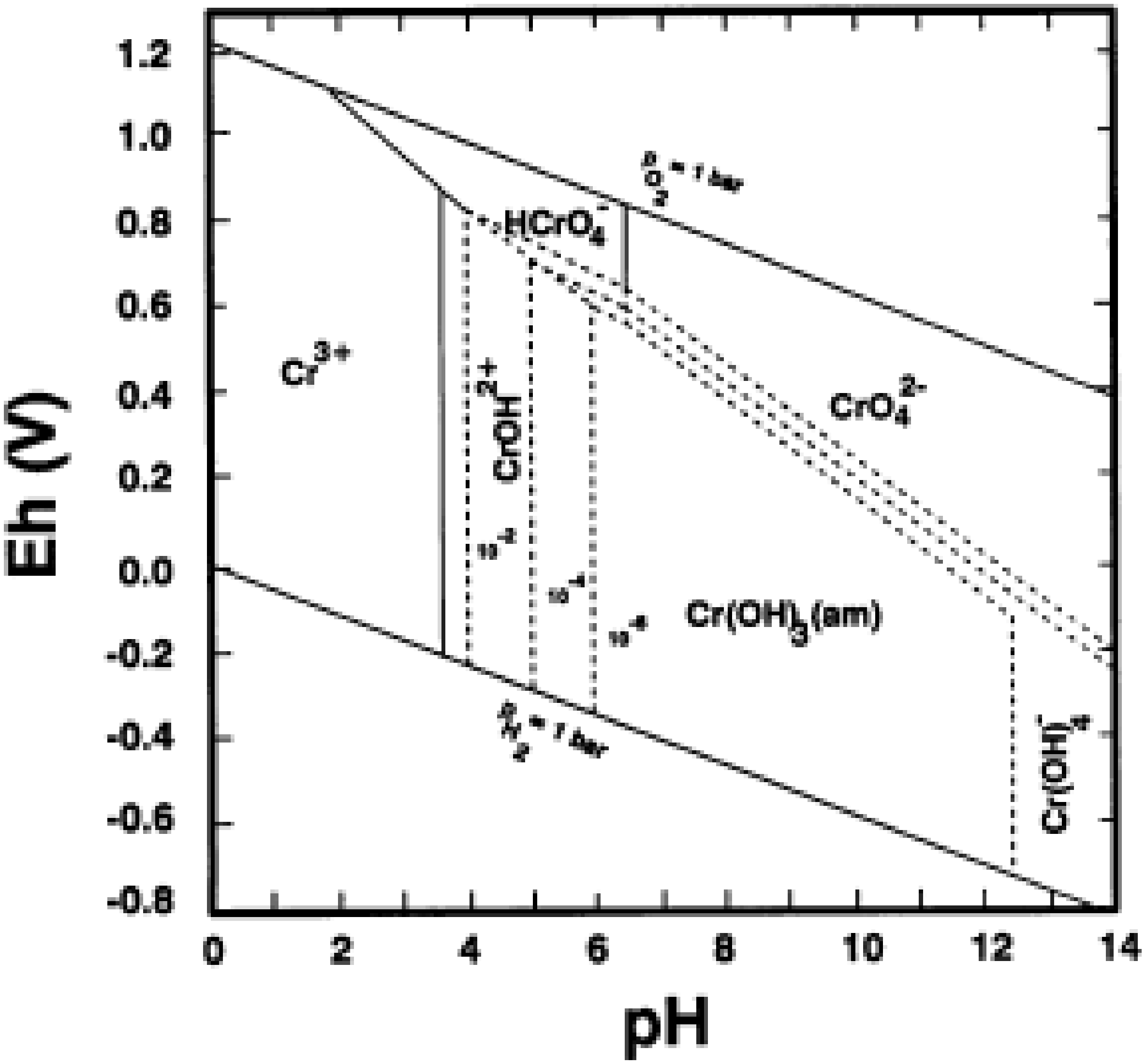


Figure 2: Range of pH Hinkley Groundwater Measurements

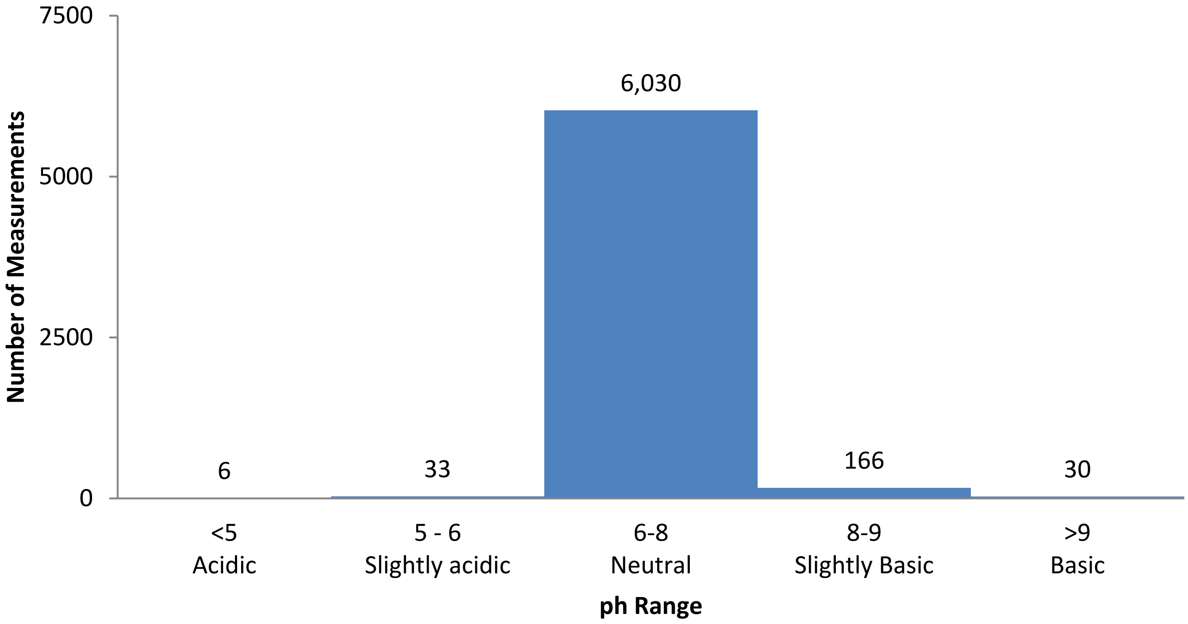
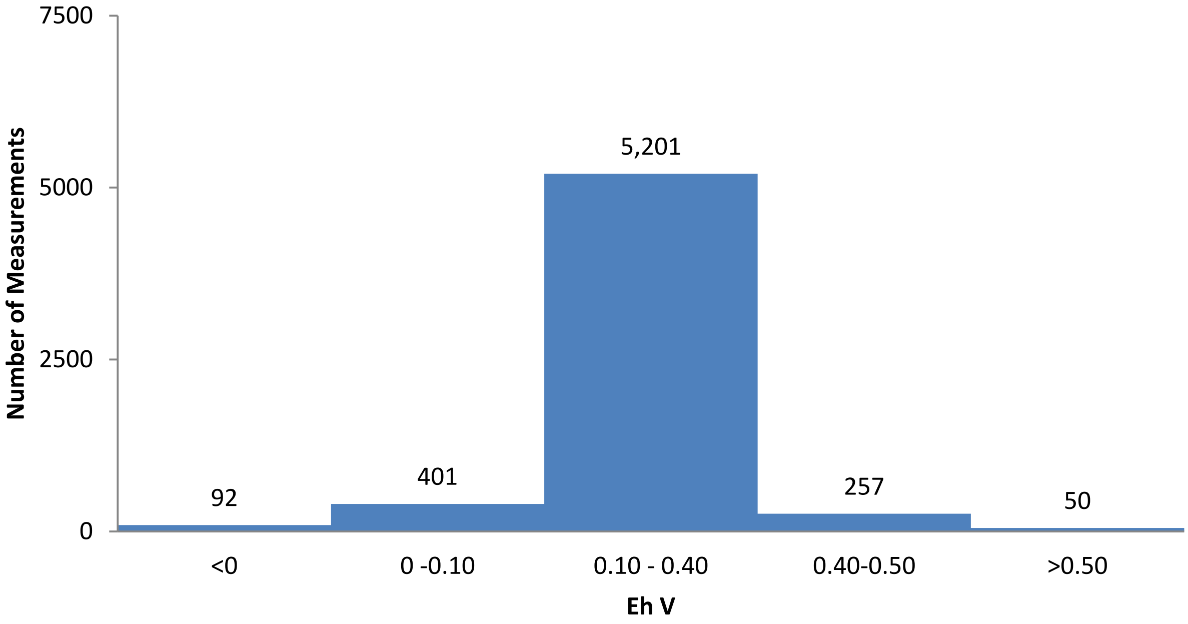
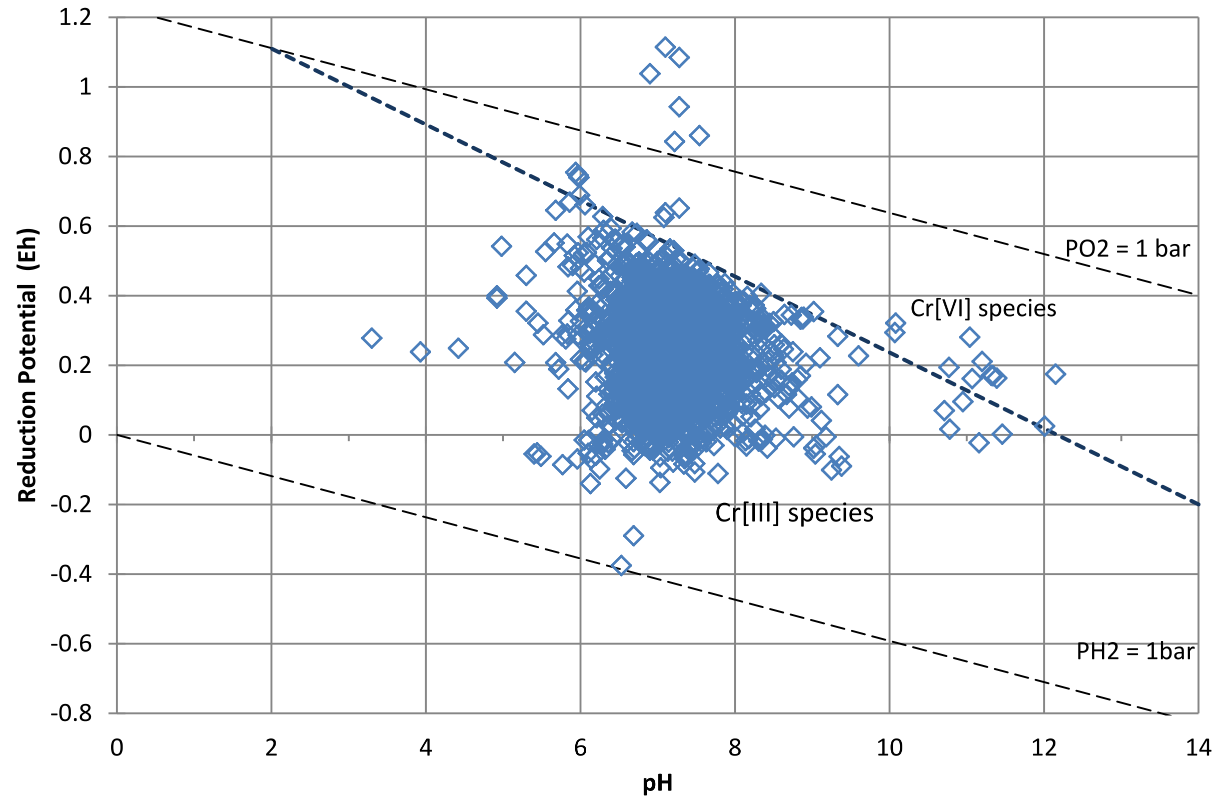


Figure 3: Range of Eh Hinkley Groundwater Measurements



Data Source for Figures 2 and 3: PG&E, 2001 - 2013 Groundwater sampling data.

Figure 4: Hinkley Site Groundwater Eh-pH Measurements



Data Source: PG&E, 2001 - 2013 Groundwater sampling data.

Figure 4 notes:

1. This is a scattergram of the Eh-pH data using the Eh-pH framework from Figure 1 and applying the data from Hinkley groundwater sampling data. The figure does show a number of individual points that could represent conditions favorable to Cr[VI] oxidation but these are quite minor compared to bulk of the data.
2. A review of the data within the Cr[VI] zone indicates that all of these data points reflect single quarterly sampling events wherein conditions more favorable to CR[III] dominate in prior and subsequent sampling events. The data does not indicate any locations with persistently favorable conditions for Cr[VI] species.
3. The 6 points above the pO2 = 1 bar line may be indicators of bad data measurements or indicators of error bar in assumptions because that is the theoretical stability line of water at standard temperature and pressure (STP). Possible sources of error could include different reference electrode used for Eh or faulty Eh probe. It is not unusual to occasionally get such high readings, but these are high enough to suggest bad data for those few points not just normal measurement uncertainty.

Table 1: Range of Hinkley Site Data (2001 – 2013 Data)

	Dissolved oxygen	Eh	pH	Dissolved Manganese
	mg/l	V	pH units	mg/L
Min	0.05	-0.376	3.3	0.0002
Max	1051	1.110	12.1	14
Average	5.14	0.235	7.2	0.66
95% confidence limit	+/-40.3	+/-0.242	+/-0.88	+/-3