

**California Regional Water Quality Control Board
Lahontan Region**

STAFF REPORT

**BACKGROUND CHROMIUM STUDY
PACIFIC GAS AND ELECTRIC COMPANY
COMPRESSOR STATION
35863 FAIRVIEW ROAD
HINKLEY**

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Lisa Dernbach, P.G., C.Hg., C.E.G.
Senior Engineering Geologist (Specialist)

Reviewed by: Chuck Curtis, P.E.
Cleanup and Enforcement Division Manager

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FOREWARD

In February 2007, the Pacific Gas and Electric Company (PG&E) submitted to the California Regional Water Quality Control Board, Lahontan Region (Water Board), the document, "Groundwater Background Study Report" (Report) (CH2M Hill, 2007a). The purpose for the background study was to estimate the concentration of naturally-occurring total chromium [Cr(T)] and hexavalent chromium [Cr(VI)] in groundwater near the PG&E natural gas compressor station in Hinkley, California (Figure 1).

The background study was completed based on the September 2004 "Revised Background Chromium Study Work Plan (Work Plan)." The Work Plan incorporated comments from three University of California professors who peer-reviewed the original 2002 work plan. As a result of the peer review, the criteria for selecting wells for the study was refined, depth-discrete sampling was added, and the statistical analysis method used to evaluate the data was selected. The Work Plan was accepted by the Water Board in November 2004.

EXECUTIVE SUMMARY

Forty-eight wells in the Hinkley Valley were sampled during 2006 for the background study. About 90 percent of the wells sampled were domestic wells and the remainder were agricultural wells. The number of sampling events for each well ranged from one to four during the year. Besides chromium, the water samples results were analyzed for hydrogeochemical similarities, temporal trends, mathematical outliers, and data set balance to check that each sample was representative of the background study area. The background study also included analysis of stable chromium isotopes by the United States Geological Survey.

The maximum detected Cr(T) value during the background study was 3.15 micrograms per liter ($\mu\text{g/L}$). The maximum detected Cr(VI) value was 2.69 $\mu\text{g/L}$. The individual Cr(T) and Cr(VI) results at each well were averaged to determine a representative concentration for each well. These averages were used in the statistical evaluation of the background study data set.

The maximum likelihood estimate approach was used to determine the mean and standard deviation for the Cr(T) and Cr(VI) data sets. Using this approach, the means were 1.52 $\mu\text{g/L}$ for Cr(T) and 1.19 $\mu\text{g/L}$ for Cr(VI). The maximum likely background concentrations in the Hinkley area were calculated based on the 95th percent upper tolerance limits (UTLs). The UTLs are 3.23 $\mu\text{g/L}$ for Cr(T) and 3.09 $\mu\text{g/L}$ for Cr(VI). These values are shown in the table below, along with the means and maximum values detected.

Table 1.
Summary of Chromium Values from Background Study

	Cr(T) (µg/L)	Cr(VI) (µg/L)
Mean	1.52	1.19
Maximum detected	3.15	2.69
UTL	3.23	3.09

Water Board staff finds the background study was conducted in a reasonable manner, and the study results are generally acceptable.

SITE HISTORY

The PG&E compressor station (Facility) is located at 35863 Fairview Road, east of the community of Hinkley in San Bernardino County. PG&E owns the land on which the compressor station is located. While not discussed in the Report, it is essential to understand how the discharge of chromium came to be in the Hinkley Valley, prompting the need for the background study.

The Facility began operating in 1952 and added hexavalent chromium to cooling tower water to prevent corrosion. The untreated cooling tower water was discharged to unlined ponds until 1964. In 1965, phosphate replaced hexavalent chromium as the corrosion inhibitor. The ponds were taken out of service in 1966 and replaced with lined ponds. Chromium contaminated soil has since been excavated from shallow depths in the area of the former unlined ponds, pipelines, and beneath tanks.

In 1987, PG&E reported to the Water Board that off-site monitoring wells, located to the north of the Facility, showed chromium concentrations in groundwater exceeding the California drinking water standard of 50 µg/L. As of February 2008, the chromium plume in groundwater extends 2 miles long and 1.3 miles wide. The highest levels, up to 5,000 µg/L Cr(T), are detected at and just north of the compressor station. Remediation is underway to contain plume migration and clean up chromium in groundwater.

HYDROGEOLOGY

The Facility is located in the Harper Valley Subarea of the Mojave Hydrologic Unit. The Mojave River contributes more than 80 percent of the natural groundwater recharge to the Hinkley Valley. The groundwater flows to the north into the Harper Lake Playa. Groundwater at the Facility generally flows to the north and then to the northwest starting at about Frontier Road. Sediments in the Hinkley Valley originate from floodplain deposits from the Mojave River that overlay regional deposits from erosion of the surrounding mountains.

The evaluation of water budget was based on a numerical groundwater flow model that was developed for the Hinkley site. On average, about 7,000 acre-feet of groundwater enters the modeled area from the south each year. About 20 percent of this subsurface flow continues eastward towards Barstow, and about 2 percent flows out of the modeled boundary to the north toward Harper Lake Playa. The bulk of the groundwater inflow is pumped for irrigation, industrial, or domestic/municipal supply. Concentrations of total dissolved solids (TDS) generally increase to the north with distance from the Mojave River (Figure 2). This is typical of a freshwater recharge system in which low-TDS river water migrates away from the recharge source, accumulating salts and dissolved solids as it passes through the aquifer. The source of salts and dissolved solids can originate naturally from alluvial sediments and anthropogenically from activities on the ground surface, such as agriculture.

The majority of the Hinkley Valley is underlain by two distinct aquifer units separated by a clay unit, referred to as the Blue Clay (Figure 3). The Upper Aquifer consists of interbedded gravels, sands, silts, and minor amounts of clay. The thickness of this unconfined aquifer is about 180 feet beneath the compressor station with groundwater typically at 80 feet below the surface. The Upper Aquifer gets thinner towards the north and the west.

The Blue Clay is a low-permeability aquitard, likely of lacustrine (lake) origin. The thickness of the Blue Clay ranges from 40 feet beneath the compressor station to being absent north of Highway 58 and within a few hundred feet of the Mojave River to the south.

Below the Blue Clay is the deeper, semi-confined water-bearing zone referred to as the Lower Aquifer. The sediments that comprise the Lower Aquifer include calcareous sedimentary rock and highly weathered, decomposed, and fractured bedrock. The Lower Aquifer is thickest beneath the compressor station at about 40 feet. As with the Blue Clay, the Lower Aquifer pinches out to the north of Highway 58 and west of Mountain View Road. Below the Lower Aquifer is a granitic bedrock unit that is encountered at depths of 100 feet in the northwest portion of the chromium plume and as deep as 300 feet below the compressor station.

The chromium plume is detected only in the Upper Aquifer. Multi-depth sampling has shown that the chromium plume exists in the saturated zone from about 80 to 135 feet below ground surface in the vicinity of the Facility. As the Upper Aquifer becomes shallower towards the north, the plume becomes less thick. Sampling at the Desert View Dairy indicates the plume's thickness to only be half that at the Facility or about 25 feet. Past investigations of the Lower Aquifer detected Cr(T) up to 8 µg/L.

Sources of Natural Chromium in Groundwater

Even though not a topic in the background study, it is important to note the sources of natural chromium in groundwater when reviewing water quality data presented in

the following sections. The following explanations for natural chromium sources were taken from references cited in the background study.

In general, chromium is a relatively common element, naturally occurring in rocks, soil, plants, animals, and in volcanic dust and gases. Chromium typically occurs in the trivalent oxidation state when a solid and in the hexavalent oxidation state when dissolved. Chromium occurs naturally in many aquifers throughout the world, including in the western Mojave Desert. Aquifers consisting of alluvium weathered from granitic, metamorphic, and volcanic rock may contain hexavalent chromium from chromate or dichromate. Groundwater near the Mojave River in the Hinkley area generally contains little or no detectable chromium.

BACKGROUND CONCENTRATION CALCULATIONS

This section provides the methodology used to estimate background values for Cr(T) and Cr(VI) in groundwater in the study area.

Water samples were collected from background wells during four quarters in 2006. Fourteen wells were sampled during all four consecutive events, two wells were sampled during three events, 23 wells were sampled during two events, and nine wells were sampled during one event. The wells range in distance from 750 to 16,000 feet from the chromium plume boundaries. The data set comprises geographically distinct samples collected from geologically variable materials, representative of the Hinkley Valley.

The maximum detected Cr(T) value in background wells was 3.15 µg/L (Figure 4). The maximum detected Cr(VI) value was 2.69 µg/L. Five of the wells sampled did not contain Cr(T) or Cr(VI) above the 1.0 µg/L and 0.2 µg/L reporting limits, respectively, during any of the sampling events.

The individual Cr(T) and Cr(VI) results at each well were averaged to determine a representative concentration. These averages were used in the statistical evaluation of the background study set and to restrict bias from wells that were sampled fewer than all four quarterly events. The maximum likelihood estimate approach was used to determine the mean and standard deviation for the data sets (USEPA, 2006).

The mean Cr(T) of background wells was 1.52 µg/L, and the mean Cr(VI) of background wells was 1.19 µg/L. This represents the average total and hexavalent chromium concentrations in the area groundwater not affected by chromium contamination.

One goal of this effort was to determine the maximum likely background concentrations in the Hinkley area, called the background threshold values. These values can be larger than the maximum detected concentrations during the sampling because the sampling represents a subset of all potential background chromium concentrations in the area. The study Report calculated these thresholds as the sum

of the upper tolerance limits (UTLs) and the laboratory method accuracy limits. The background UTLs were calculated as the upper bound (with 95 percent confidence) of the 95th percentile of the background total and hexavalent chromium concentrations. The UTLs are 3.23 µg/L for Cr(T) and 3.09 µg/L for Cr(VI). The analytical methods used for Cr(T) have an accuracy of +/-25 percent, and the analytical method used for Cr(VI) has a accuracy of +/-15 percent. The background threshold values presented in the Report are 4.04 µg/L for Cr(T) and 3.55 µg/L for Cr(VI). Water Board staff does not agree that adding the laboratory accuracy limits to the UTLs is appropriate. Water Board staff have not found any documentation that supports inclusion of laboratory method accuracy limits in determining background concentrations.

The values described in this section are summarized in Table 2.

Table 2.
Summary Statistics for Cr(T) and Cr(VI) Using Well Averages

Parameter	No. of Samples	No. of Detects	Percent Detects	Min. Detect*	Max. Detect*	Mean*	Std. Dev.*	95% UTL*	Threshold Value*
Cr(T)	48	36	75	0.683	2.8	1.52	0.824	3.23	4.04
Cr(VI)	48	41	85	0.181	2.57	1.19	0.915	3.09	3.55

* Concentrations in micrograms per liter.

COMPARISON TO OTHER CHROMIUM STUDIES

The chromium background results from Hinkley are compared to the results of previous studies of naturally occurring chromium concentrations that have been performed in the Mojave Desert and adjacent areas. The studies that were considered include:

- Topock compressor station background study recommendations (CH2M Hill, 2007b).
- California Department of Health Services sampling results, as of April 2004, for Cr(VI) in public supply wells in California (CDHS, 2004).
- Evaluation of Cr(VI) in the southwestern portion of the Mojave Desert, which includes the Hinkley area (USGS, 2004).

The Cr(VI) results of these studies are shown in Table 3.

Table 3.
Summary Statistics for Cr(T) and Cr(VI) Using Well Averages of Other Studies
(micrograms per liter)

Parameter	Hinkley Background Mean	Hinkley Background UTL	Topock Background Mean	Topock Background UTL	CDHS Mean	USGS Mojave UTL
Cr(T)	1.52	3.23	9.37	34.1	NA	Not calculated
Cr(VI)	1.19	3.09	7.8	31.8	5.8*	27

*San Bernardino County public water systems

Overall, mean chromium concentrations and calculated UTLs in the Hinkley groundwater background study are lower than chromium concentrations found in other site-specific studies.

OTHER FINDINGS

The following additional findings are noted in the Report.

1. An evaluation was completed to determine each well's suitability for inclusion in the final data set. The evaluation concluded that all 48 wells were properly located within the target study area based on hydrochemistry and lithologic analyses.
2. Total chromium and hexavalent chromium concentrations in groundwater are typically at low or non-detectable levels in the area of the Mojave River. Detectable chromium concentrations increase with distance away from the river up to a maximum detection of 3.15 µg/L for Cr(T).
3. Seasonal variation of Cr(T) and Cr(VI) concentrations among the 14 wells that were sampled during all four sampling event was minimal. Only one of the 14 wells indicated a potential trend, that being a decreasing one. The lack of significant evidence for a temporal trend was supported by the major ions plot showing similar locations in the Trilinear diagrams during each quarter.
4. Discrete-depth water samples were collected at only two well locations, and all showed non-detectable levels for Cr(T) and Cr(VI), or less than 0.2 µg/L and 1.0 µg/L, respectively. Therefore, the results of depth-discrete sampling within the Upper Aquifer are inconclusive for evaluating potential variations of chromium background concentrations with depth in the upper aquifer.
5. No conclusions were drawn about background chromium concentrations in the Upper Aquifer versus Lower Aquifer, as only 17 of the 48 wells had boring logs and the logs indicated wells were often screened across both the upper and lower aquifers.

6. The Lockhart Fault, a northwest trending, right-lateral, strike-slip fault that crosses the southwest corner of the Facility, is considered to impede groundwater flow somewhat but has no affect upon background chromium concentrations.
7. Besides the Facility, no other anthropogenic sources of chromium were identified in the Hinkley Valley.
8. In addition to the well sampling and analyses described above, the U.S. Geological Survey evaluated the chromium isotope ratios in samples collected from 15 wells inside and outside of the chromium plume over three sampling events. The goal of this testing was to investigate whether isotope results: (1) might indicate a site-specific reduction pattern of Cr(VI) along flow paths within the mapped groundwater plume and (2) might be used to differentiate anthropogenic Cr(VI) from non-anthropogenic Cr(VI). The results indicate that chromium isotope ratios were not useful to delineate the specific chromium degradation pattern within the plume, or to differentiate anthropogenic versus non-anthropogenic concentrations of Cr(VI).

COMMENTS

The background study followed the September 2004 Work Plan accepted by Water Board staff, with the exceptions discussed below. The Report included the following expected Work Plan topics:

- Evaluation of existing wells in the background target area and review of boring logs and well construction details.
- Evaluation of past pumping in the Hinkley area.
- A numerical groundwater flow model to evaluate the water budget of the Hinkley Valley.
- Creation of wind rose diagrams to assess potential wind deposition of airborne chromium.
- Evaluation of groundwater geochemistry to determine each background well's suitability for inclusion in the final data set.
- Chromium stable isotope analysis.
- Evaluation of seasonal trends of sample data.
- Statistical analysis of Cr(T) and Cr(VI) analytical data.

Work Plan topics that were either changed or were incomplete in the Report include the addition of wells, depth-discrete well sampling, and calculation of the background threshold concentrations. Each of these topics is discussed in more detail in the following sections.

Wells Added During Study

The Work Plan states that water samples would be collected quarterly (every three months) at approximately 20 locations. Background wells would be selected with emphasis on being located along the flow path of the Mojave River, or cross gradient from the chromium plume at the Hinkley site. A groundwater flow model created for the Hinkley site was used to estimate the groundwater flow paths and verify well locations in the upgradient and cross gradient location direction. The Work Plan also states that wells would also be located in a hydrogeologic setting representative of plume conditions.

The first and second sampling event consisted of 17 well locations. Of the 48 wells included in the background study, 31 wells were added after the Work Plan was accepted by the Water Board and after two sampling events had already occurred. The background study explains that wells were added to compensate for the three wells not available for depth discrete sampling. The new wells were also added to create a larger data set, thereby providing more information on the natural variation in Cr(T) and Cr(VI) concentrations in the study area.

Of some concern are added wells located in areas not fitting the criteria cited in the Work Plan. The added wells are located: (1) in the apparent down and cross gradient flow direction of the chromium plume (BGS-46, 47, 48, 51); (2) up to 3.2 miles cross gradient from the plume boundary (04E-01); and (3) outside the regional and floodplain aquifers (BGS-18 & 19). It can be argued that these specific wells are not truly background locations because they do not represent background conditions in the area of the chromium plume. The Cr(T) and Cr(VI) concentrations in these wells vary from less than 1.0 µg/L to 2.94 µg/L in 15 samples. The average values for this limited data set is 1.38 µg/L Cr(T) and 1.33 µg/L Cr(VI). When the limited data set is subtracted from the total data set for the background study, the results show a 5 percent change or less of the original means calculated for Cr(T) and Cr(VI) discussed earlier in this document; 1.58 µg/L instead of 1.52 µg/L for Cr(T) and 1.13 µg/L instead of 1.19 µg/L for Cr(VI). Because the change is so small, it is considered insignificant. Deleting the data from these seven wells will not significantly alter the UTLs or threshold values from the background study.

Depth-Discrete Samples

The Work Plan states that five wells would be selected for collection of depth-discrete samples to determine if variations in background chromium concentrations existed within the Upper Aquifer. The Report states that discrete depth samples from the Upper Aquifer were collected at only two well locations and the sample results were all at non-detectable concentrations. It is explained that additional discrete-depth samples could not be collected due to well access limitations. The Work Plan assumed large-diameter agricultural wells would be available for discrete-depth sampling, but the vast majority of these wells contained submerged debris or had been filled in and abandoned entirely.

The concern is whether naturally-occurring chromium concentrations vary with depth. Boring logs were only available for 17 of the 48 background study wells, or 35 percent. The depth of background study wells ranged from 55 to 115 feet. All 17 wells with boring logs are screened in either the Upper Aquifer or both the Upper and Lower Aquifers, including a few wells with notations of bedrock. This information indicates that water samples from these wells likely represent a variety of depths within the aquifers.

Analysis of Maximum Likely Background Concentrations

The Report calculated background threshold values as the sum of the UTLs and the laboratory analytical method accuracy limits. UTLs are an accepted method of determining the maximum likely background values, and this was the method identified in the Work Plan for determining the Hinkley chromium background threshold values. Adding the laboratory method accuracy limits of 15 percent for hexavalent chromium and 25 percent for total chromium increases the estimate of the maximum likely background concentrations from the UTL of 3.23 µg/L to 4.04 µg/L for Cr(T) and from the UTL of 3.09 µg/L to 3.55 µg/L for Cr(VI). Water Board staff have found no documentation that supports inclusion of laboratory method accuracy limits in determining background concentrations.

CONCLUSION

In general, the background study followed the September 2004 Work Plan accepted by Water Board staff. The final calculated mean background values are 1.52 µg/L for Cr(T) and 1.19 µg/L for Cr(VI), and the background threshold values based on the UTLs are 3.23 µg/L for Cr(T) and 3.09 µg/L for Cr(VI). These threshold values are considered the maximum likely concentrations of naturally occurring chromium in groundwater. Water Board staff does not accept the addition of laboratory method accuracy limits to the UTLs to calculate background threshold values. And while the background study added well locations that were outside the criteria established in the Work Plan, the change in calculated UTLs from deleting data from those locations is insignificant. Water Board staff finds the background study was conducted in a reasonable manner, and the study results are acceptable, except as noted above regarding using laboratory method accuracy limits in the background threshold concentrations calculations.

Water Board staff recommend that the Water Board establish background threshold levels at a maximum of 3.23 µg/L with a mean of 1.52 µg/L for total chromium and a maximum of 3.09 µg/L with a mean of 1.19 µg/L for hexavalent chromium. If cleanup is required to background levels, the resultant average chromium concentrations in the cleanup area should be equal or less than these mean background values. The calculated background threshold values may be used to assess whether a given sample represents background conditions or the effect of the release; values above

the background thresholds may indicate the groundwater has been affected by the release.

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