A1-1: James Jacobs, Clearwater Group

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October 7, 2011

Ms. Lauri Kemper, P.E.
California Regional Water Quality Control Board
Lahontan Region
2501 Lake Tahoe Blvd.
South Lake Tahoe, CA 96150

Transmittal via email to: Lkemper@waterboards.ca.gov

Re: Task Order: PEER REVIEW OF CH2MHILL'S FEBRUARY 2007 *GROUNDWATER BACKGROUND STUDY REPORT, HINKLEY COMPRESSOR STATION, HINKLEY, CALIFORNIA* PREPARED FOR PACIFIC GAS AND ELECTRIC COMPANY (PG&E)

Dear Ms. Kemper:

This memorandum summarizes my review of CH2MHILL's February 2007 *Groundwater Background Study Report, Hinkley Compressor Station, Hinkley, California* (BSP3) prepared for PG&E. In addition to the 7 documents initially furnished by your office, and the 2002 Workplan which you furnished upon request, you also furnished the link to the Lahontan Water Board webpage (to access additional information, including maps since August 2006), so the complete list of reports besides the review report is as follows:

> Workplans
> *Scope of the Background Chromium Study at the PG&E Compressor Station, Hinkley California*, CH2MHILL, 2002 (BSP1)
>
> *Revised Background Chromium Study at the PG&E Compressor Station, Hinkley, California*, CH2MHILL, 2004 (BSP2)
>
> Regulatory Correspondence
> *Comments on Revised Background Chromium Study at the PG&E Compressor Station, Hinkley, San Bernadino County*, 2004 Workplan Review and Conditional Acceptance
>
> Regulatory Staff Report
> Dernbach, L., 2008, *Background Chromium Study, Pacific Gas and Electric Company, Compressor Station, 35863 Fairview Road, Hinkley*, CRWQCB, Lahontan Region.

Peer Reviews

February 2004 reviews on 2002 BSP: 3 reviews

Letters of February 2004, on 2002 BSP1:

- Thomas C. Harmon, University of California, Merced
- James R. Hunt, University of California, Berkeley
- Timothy R. Ginn, University of California, Davis

Groundwater Monitoring Reports

Groundwater Monitoring Report; October 2007 Sampling Event; Site-wide Groundwater Monitoring Program, PG&E Hinkley Compressor Station, Hinkley, California, CH2MHILL, 2007

Second Quarter 2010, Groundwater Monitoring Report, *Site-wide Groundwater Monitoring Program, PG&E Hinkley Compressor Station, Hinkley, California,* CH2MHILL, 2010

Review Subject: *Groundwater Background Study Report, Hinkley Compressor Station, Hinkley, California* (BSP3) CH2MHILL, February 2007.

Report Date: February 2007

Report Author: CH2MHILL, Oakland, California

Site of Release: Pacific Gas & Electric Company
Hinkley Natural Gas Compressor Station Site
35863 Fairview Road
Hinkley, California

Responsible Party: Pacific Gas & Electric Company (PG&E)

Requesting Agency: RWQCB, Lahontan Region (LRWQCB), Region 6
Review Program
Sponsor: US EPA

Representative: Ms. Anne Holden, aholden@waterboards.ca.gov, 530-542-5450
Representative: Ms. Lisa Dernbach, ldernbach@waterboards.ca.gov, 530-542-5424
Review sent to: Ms. Lauri Kemper, Lkemper@waterboards.ca.gov, 530-542-5400

Agency providing Reviewers:	Cal/EPA Scientific Peer Review Program, Office of Research, Planning and Performance, State Water Resources Control Board
Due Date:	October 7, 2011
Reviewer:	James A. Jacobs, PG, CHG, is a Fulbright Scholar and has practiced geology for 30 years, teaches Sustainable Remediation Methods for Soils and Water at the UC Berkeley Extension and co-authored The Chromium (VI) Handbook, 2005, CRC Press.

Project Background

Per the LRWQCB staff letter of May 19, 2011 to Dr. Gerald Bowes, Manager of the Cal/EPA Scientific Peer Review Program, Office of Research, Planning and Performance, State Water Resources Control Board, the purpose of reviewing the 2007 report (BSP3) is as follows: "...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. The data contained in the 2007 Background Study Report are intended to assist the Lahontan Water Board in setting cleanup goals for chromium pollution in groundwater in the Hinkley area... At issue is whether the deviations in carrying out the Background Study from the conditionally approved background Study Workplan were appropriate or whether the deviations resulted in biased estimates of background chromium levels."

Project Report Setting

The method described in the 2007 report (BSP3) is premised on previous work. The purpose of the 2002 Background Study Plan (BSP1) was to determine background conditions as a cleanup goal for groundwater remediation. The BSP1 proposal to sample 12 wells over 4 quarters in the upper aquifer was amended in 2004 (BSP2) and resulted in the 2006 sampling and the 2007 reporting (BSP3).

According to Attachment 1 of the May 19, 2011 Lahontan RWQCB document, two aquifers are identified in the valley fill: the upper unconfined aquifer (referred to in this review as the Upper Aquifer) and the lower confined aquifer (referred to in this review as the Lower Aquifer). The aquifers are separated by an aquitard composed of fine-grained clay and silts, laid down as a lacustrine deposit, called the Blue Clay. As noted in previous studies, the Blue Clay and the Lower Aquifer pinch out to the north of Highway 58 and west of Mountain View Road (Dernbach, 2008).

Current Status

The overall objective of the Background Study Plan is to provide a background threshold contaminant level so that a cleanup goal can be established. After 10 years with three background study workplans and reports, the background condition (the remediation or cleanup goal) has not yet been established. Recent reports (Stantec, 2011) document that vertical migration and lateral expansion of the Cr(T) and Cr(VI) plume appear to be occurring.

Sampling from Existing Domestic and Agricultural Wells

Groundwater samples were obtained from the domestic and agricultural wells chosen for the background well study because the wells were already installed and available for sampling. Many of the wells which were sampled for the background study were not intended to provide the highest quality groundwater samples due to construction design. Of the wells that were used in the background study, the agricultural wells (about 10 percent of the wells sampled) and domestic wells (about 90% of the wells sampled) were designed for irrigation and home water supply purposes, respectively. Given the age of most of the wells, the well construction likely predated the current California well standards. Most of these wells are many decades old, and the well construction details, such as perforation or screen depth information and geologic boring logs, are not available.

NOTE: For the purposes of this review, although it is likely that some of the wells installed have perforated well openings in the steel well casings rather than slotted screens, I will refer to the zones where groundwater enters the well bore as the “screened” interval.

As would be expected in a heavily agricultural area, many of the wells, especially wells used for irrigation, were designed for maximum groundwater flow, and the screened zones in the well may include both the unconfined Upper Aquifer and confined Lower Aquifer. Screening across two or more aquifers, thus commingling the aquifers, is common in wells where groundwater production is the objective. Of the wells used for the background study, most of them (44 out of 48 or 92%) were either screened over more than one aquifer zone, or the screen depths were unknown and well construction information is currently unavailable. Although specific wells may vary in well diameter, domestic wells can be about 6-inches in diameter, and agricultural wells can be about 14 to 18-inches in diameter.

As opposed to wells designed for groundwater production, monitoring wells are designed and installed for geochemical sampling and background studies. Monitoring wells require a fundamentally different well design. Many monitoring wells are a minimum of 2-inches in diameter which reflects the design purpose of high-quality groundwater sampling and not water production. Detailed geochemical studies including background studies provide geologic information about the subsurface conditions by isolating specific aquifer units from other groundwater bearing units. This isolation is a key concept in the design of the monitoring well so that a specific groundwater bearing zone in a specific geologic unit can be sampled and analyzed in the laboratory for Cr(T) and Cr(VI) and other chemicals of concern.

Sampling Data

Sampling of agricultural or domestic wells containing commingled groundwater aquifers provides useful information as to overall groundwater quality of that particular well and specific exposure and toxicity data related to Cr(T) and Cr(VI) to human health if the water is ingested, or the environment, if the water is applied to the land through irrigation.

For the purposes of a detailed geochemical background study, however, no useful geologic information on background concentrations can be obtained from mixed well waters that are available in a well which is screened over two aquifer zones. The laboratory sample results from wells containing 'mixed aquifer' waters cannot be considered reflective of any specific aquifer and, therefore, they should not be used in a scientifically based background study of Cr(T) and Cr(VI). All of the wells used in the CH2MHILL background study are either domestic or agricultural wells. The majority of these wells (92%) have well screens covering more than one aquifer zone (i.e. both the Upper Aquifer and the Lower Aquifer), or the screen intervals are unknown.

According to the United States Geological Survey (USGS) Water Supply Paper 2220 (Heath, 1983), groundwater occurs in aquifers under two different conditions. Where groundwater only partly fills an aquifer, the upper surface of the saturated zone is free to rise and decline. The water head in a well installed in an unconfined aquifer reflects the elevation differences between the water source and the elevation of the groundwater in the well. The groundwater in such aquifers is said to be unconfined, and the aquifers are referred to as unconfined aquifers. Unconfined aquifers are also widely referred to as water-table aquifers. The Upper Aquifer is an unconfined aquifer.

Where groundwater completely fills an aquifer that is overlain by a confining bed such as the Blue Clay in the Hinkley, California area, the groundwater in the aquifer is said to be confined. Such aquifers are referred to as confined aquifers or as artesian aquifers. In some cases, the confined aquifers come to the surface as artesian springs. The Lower Aquifer is a confined aquifer, and as such, the water will rise due to the elevation differences as noted above, as well as the pressure in the aquifer.

Depending on the water pressures associated with each aquifer, the Upper Aquifer Cr(T) and Cr(VI) concentrations in 'mixed aquifer' wells will likely be diluted by the cleaner Lower Aquifer. If the Lower Aquifer has significantly higher pressure than the Upper Aquifer, the overall concentrations of Cr(T) and Cr(VI) will be more diluted.

In wells where the groundwater is sourced from two aquifer zones at the same time, such as is found in the Hinkley area, laboratory analyses of those groundwater samples to define specific background levels of Cr(T), Cr(VI) or other chemicals is not scientifically valid as no vertical definition or aquifer specific continuity is possible. Comparing sample results from 'mixed aquifer' wells allows for evaluation of human or environment exposure, but the laboratory data are devoid of any specific geologic or aquifer significance. Statistics based on 'mixed aquifer' laboratory data are not valid or relevant as to the aquifer-specific levels for Cr(T), Cr(VI), or other chemicals.

Focused Groundwater Sampling

For the purpose of groundwater sampling and geochemical characterization, wells with proper screens covering only one aquifer zone are needed so aquifer-discrete samples can be collected and analyzed. This is necessary and important if the vertical and lateral migration of the Cr(T) and Cr(VI) in the subsurface is to be understood and properly documented. The isolation of these two aquifers (Upper Aquifer and Lower Aquifer) has not occurred in most of the wells used in the background study, and as such, these domestic and agricultural wells are useful in showing concentrations of Cr(T) and Cr(VI) in groundwater in wells with commingled aquifers. These concentrations of the well water reflect the overall water quality from the individual wells and the overall Cr(T) and Cr(VI) exposure potential to humans or the environment. However, these wells have almost no value in showing background levels of Cr(T), Cr(VI), or other chemicals. As such, detailed statistical evaluation of laboratory data from wells that are screened in more than one aquifer, or in wells where the screen and filter packs (if present) are unknown, do not and cannot accurately reflect true background concentration levels. Statistical methods applied to these types of well sample results, for the purpose of trying to identify a background Cr(T) and Cr(VI) concentration, provide mixed-well aquifer statistics, not background levels.

Format of Peer Review Tasks

As part of the overall Scientific Peer Review process, the reviewers were asked to address Specific Requested Comments (**Task I**), to make General Comments on (BSP3) to address any additional scientific issues (**Task II**), and to comment on whether the scientific portion of (BSP3) is based upon sound scientific knowledge, methods, and practices (**Task III**). All the Tasks and my responses are provided below:

Task I - Specific Requested Comments on BSP3

Background: Are the deviations in carrying out the Background Study, BSP3, (from the conditionally approved Background Study Workplan, BSP2) appropriate or did they result in biased estimates of background Cr levels? Make a determination of each of the following four (as expertise allows):

1. Quality of spatial sampling of background chromium in 21 square miles (sq. mi.)
   Sampling Dataset: Total of 48 wells of which 14 were sampled all four quarters (see Table 3-1; CH2MHILL 2007 Study).

- Event 1 - 17 well locations
- Event 2 - 18 well locations
- Event 3 - 45 well locations (original 17 wells, plus 8 wells, plus 23 new wells which are near chromium impacted well BGS-04 in <1 sq. mi.)
- Event 4 – 38 well locations

Comments: The wells used for the background study reported in the CH2MHILL (2007) report show an inconsistent pattern of well sampling as shown above. The Hinkley Valley in the background study area can be divided into five main areas (see attached **Figure 1**; based on the Figure 4-1; CH2MHILL 2007 Study). The five main areas are as follows: Core Area, South Upgradient Area, East Cross Gradient Area, West Cross Gradient, and North Downgradient Area. Across these there is an Upper and a Lower Aquifer. These aquifers are separated in most areas by a confining clay aquitard, called the Blue Clay, except as noted below.

A. Core Area

This is the area of the Cr(VI) plume (Core Area) in 2006 (Figure 4-1; CH2MHILL, 2007), showing a Cr(VI) concentration of 4 micrograms per liter (µg/L). The Core Area has both Floodplain and Regional Aquifers as mapped on Figure 4-1. The Upper and Lower Aquifers are separated by a confining clay.

B. South Upgradient Area

This is the area south of the Core Area (shown on Figure 4-1; CH2MHILL, 2007), south of the hatched black line, reflecting an "upgradient boundary including buffer zone." According to Figure 4-1, the Regional Aquifer lies below the South Upgradient Area. The Upper and Lower Aquifers are separated by a confining clay.

C. East Cross Gradient Area

This is the area east of the Core Area (shown on Figure 4-1; CH2MHILL, 2007) which is shown as having the Floodplain Aquifer. In the northern portion of the area, the Upper and Lower Aquifers are separated by a confining clay. A small area to the northeast contains the Regional Aquifer.

D.	West Cross Gradient Area

This is the area west of the Core Area (shown on Figure 4-1; CH2MHILL, 2007) containing the Regional Aquifer. A small portion of this area (to the southeast) contains Floodplain Aquifer. The Upper and Lower Aquifers are separated by a confining clay.

E.	North Downgradient Area

This is the area north of the Core Area (shown on Figure 4-1; CH2MHILL, 2007), having both the Floodplain and Regional Aquifers as mapped on Figure 4-1. As with the confining clay layer called the Blue Clay, the Lower Aquifer also pinches out to the north of Highway 58 and west of Mountain View Road (Dernbach, 2008).

Table 1 summarizes the 48 background study wells within the five different areas based on the known, discrete aquifer differentiation. Of these wells, four wells are screened only in the Upper Aquifer. The remaining background study wells either have well screens over both the Upper and Lower Aquifer or there is no information available as to the screened zone. A monitoring well can be designed for sampling a specific aquifer or zone, but production wells, both irrigation and domestic, tend to be designed for maximum groundwater production and sometimes contain more than one aquifer or producing zone within their screened intervals. Consequently, the mixing of groundwater from the different aquifer zones in the production wells, where screen and filter pack information is either unknown or the wells are screened over both the Upper and Lower Aquifers, will provide a mixed well concentration for Cr(T) and Cr(VI); it will not accurately reflect the conditions of the specific aquifer zone. **Table 1** shows the background study wells based on the CH2MHILL (2007) report, Table 4-1.

Table 1 – Summary of Background Wells in Hinkley Area

Area	**Primary** Aquifers (as shown on Figure 4-1; CH2MHILL, 2007)	Specific Upper Aquifer Data (# of Wells)	Specific Lower Aquifer Data (# of Wells)	Background wells without specific aquifer screen information	Total # of Background Wells in CH2MHILL (2007) Study
Core Area	Regional and Floodplain	Not Evaluated	Not Evaluated	Not Applicable	Not Applicable
South Upgradient Area	Floodplain	**1 well**: 01-06	0	3	4
East Cross Gradient Area	Floodplain primarily with minor Regional Aquifer in northeast corner	0	0	14	14
West Cross	Regional and small	**3 wells**: BGS-01,	0	27	30

Gradient Area	portion in the southeast of Floodplain Aquifer	BGS-04, and BGS-15			
North Downgradient Area	Regional and Floodplain	0	0	0	0
Totals		4 wells	0 wells	44 wells	48 wells

Of the areas shown in **Figure 1**, the South Upgradient Area is the most likely to provide natural or background levels of Cr(T) and Cr(VI). Samples from the Mojave River, although more than one mile from the PG&E facilities, may show less anthropogenic influences for background samples of Cr(T) and Cr(VI) for the region.

The Upper Aquifer has levels of Cr(T) and Cr(VI) as shown in Figure 4-1 (CH2MHILL, 2007). Dernbach (2008) noted that the chromium plume was detected only in the Upper Aquifer. At the time of this review in 2011, the Lower Aquifer had been found to contain elevated Cr(T) and Cr(VI) in one area north of Highway 58 as shown on the Stantec Figure 3, in the report *Chromium in Groundwater Lower Aquifer*, by Stantec, dated August 1, 2011.

Since the Upper Aquifer is likely to contain the majority of the Cr(T) and Cr(VI), collecting samples where the well screens are unknown provides little useful information. Although video camera surveys in wells and geophysical logging can assess the screened areas and well construction information based on the large number of wells screened in both Upper and Lower Aquifer, the agricultural wells with unknown screen depths are likely to have been screened in both aquifer zones. Data from wells that are screened in more than one aquifer or having unknown screen depths should not be used in studies to establish background concentrations of Cr(T) and Cr(VI). Installation of new monitoring wells with proper screens in specific and isolated aquifer zones is the best way to get accurate data on groundwater concentrations of Cr(T) and Cr(VI).

In summary, the natural Cr(VI) and Cr(T) levels will be difficult to assess since the entire area has had intense agricultural pumping from both Upper and Lower Aquifers for up to eight decades. Artificial recharge has also been occurring in certain locations, affecting the natural background conditions of Cr(T) and Cr(VI). The background study for both Cr(T) and Cr(VI) in the current form is inadequate and inaccurate for reasons given above.

2. Quality of temporal sampling of background chromium in the 2007 Background Study Report

<u>Background: To address the potential to introduce bias into the overall summary statistics due to the temporally unbalanced nature of the data set (not all wells sampled in each quarter), the</u>

arithmetic average value of Cr (VI) and Cr(T) concentrations from each well were used; Each well is represented by one arithmetic mean result, not the actual number of samples taken at that well.

Comments: As noted above, in **Table 1**, for discrete data from specific areas or specific aquifer zones, there are only three wells from the West Cross Gradient area and one well from the Southern Upgradient Area that are known to be screened specifically in the Upper Aquifer. Regardless, one to three wells in specific aquifer zones do not provide enough information to evaluate background concentrations or even current concentrations. From my field experience and given the size of the Hinkley area, a minimum of 20 to 40 properly constructed groundwater monitoring wells should provide the minimal number of groundwater sampling locations for a scientifically reasonable background study. Each new monitoring well should be sealed so the screens and well design sample only one aquifer zone. Detailed statistical evaluation of geochemical data coming from a majority of wells with unknown screen intervals or of screens covering commingled aquifers does not provide much scientific value.

Background: Was the integrity of the study lost by the addition of wells mid-course/mid-year?

Comments: It was noted that 14 background study wells were sampled for 4 quarters. Various additional wells were added to the study. Statistical analyses should be run on the data from the original 14 wells. Statistics from one dataset cannot be combined with statistics from another dataset. These two datasets should be reported separately.

3. Assumption of statistical normality

Background: The Shapiro-Wilk normality test was applied to only a subset of the data, the detected chromium values in the dataset. The P-values (both higher than 0.05) suggest that the data subset (all detections of chromium, leaving out the non-detect values) are normally distributed.

Comment: Aquifer-specific information and detailed statistics from wells screened in specific aquifers is required to put the laboratory analytical data into a geologic perspective. Properly performed statistics on inaccurate geochemical data are not valid.

4. Quality of groundwater modeling

The plume core, Cr(VI) above the Maximum Contaminant Level (MCL) of 50 parts per billion (ppb), migrated (based on October 2007 data) approximately 300 feet to the west along at least a one-half-mile length of the northwestern plume boundary; Are the background study wells representative of naturally occurring chromium, given the data showing plume expansion?

a) *Location of background wells must be upgradient and outside the range of influence of wells drawing the plume in*. Wells screened in unknown or multiple aquifer zones provide only limited information.

In addition to the issues listed above regarding the wells being screened in more than one aquifer, the chosen set of 'background' wells are not located adequately upgradient and outside the range of influence of actively pumping (historically or currently) extraction wells (which could be drawing the Cr(VI) plume in an upgradient direction) to be representative of background conditions. Virtually all of the chosen wells are located in a cross gradient position from the main plume with poorly defined cross gradient Cr(T) and Cr(VI) plume boundaries. As noted, well data should reflect specific aquifer zones, not mixed zones. Given the eight decades of intense agricultural pumping, it is possible that with preferred flow pathways (high permeability zones due to lithologic characteristics or geologic faults (Lockhart) or other potential conduits), some of the Cr(T) and Cr(VI) from the Core Area may have migrated over the past decades toward the east or west into the East Cross Gradient Area or the West Cross Gradient Area, respectively (see **Figure 1**).

b) *The role of actively pumping of current wells in the migration of the plume*
Groundwater flow and transport modeling are needed. Range of influence of individual pumping or injection wells should be mapped and modeled.

c) *Role of irrigation with Cr(VI) water in the increase of the plume*
Deposition of Cr(VI) throughout the basin land surface has not been mapped. Correlation between land irrigation of Cr(T) and Cr(VI) impacted groundwater at the Land Treatment Units and the presence of chromium in the underlying soil and groundwater needs more focused investigation. The mechanism of remediation of spraying Cr(VI) onto the soil and the conversion of the oxidized Cr(VI) into the reduced Cr(III) and ultimately into chromium hydroxide using soil as a treatment media are not well documented or verified. Peroxide and acids may clean the drip or irrigation lines, but may also help to mobilize and carry the Cr(T) and Cr(VI) deeper into the subsurface environment if the acids or peroxide are spilled onto the soil.

d) *Lack of control of groundwater extraction throughout the basin*
There has been none, and there is currently no hydraulic control over the groundwater basin, so the plume will continue to migrate. The Cr(VI) plume is expanding both laterally to the north, as well as vertically, as evidenced by plume maps from 2001 to current consultant studies.

e) *Historic patterns of Cr(VI) migration*
There may be historic patterns of Cr(VI) migration which have left residue available for future recapture and migration.

f) *Lack of site conceptual model*

A detailed site conceptual model of the Cr(T) and Cr(VI) initial release(s), migration in the subsurface soils and aquifers, extraction at Land Treatment Units, and application of this untreated Cr(VT) and Cr(VI) impacted water onto the land surface should be developed. There is a concern that the lack of above-ground treatment of Cr(T) and Cr(VI), in which the extracted groundwater is removed from the aquifers at the Land Treatment Units and dripped or (historically) sprayed onto surface soils, is potentially creating another Cr(T) and Cr(T) release, albeit, at lower Cr(T) and Cr(VI) concentrations. The concepts of groundwater extraction of Cr(T) and Cr(VI) impacted groundwater and the reapplication of this water onto the land without treatment has not been well proven or well documented as a method to immobilize Cr(T) and Cr(VI). Documentation should be provided showing the soil in these areas where untreated Cr(T) and Cr(VI) impacted groundwater is being released onto the land surface is a safe and effective remediation method for Cr(T) and Cr(VI) in groundwater. The documentation should also evaluate the potential for hyperaccumulation or uptake of Cr(T) and Cr(VI) in plants or deposition and concentration of Cr(T) and Cr(VI) in the shallow soil.

Although regionally the rain water has been low over the period of historic record keeping, large changes in climate and rain patterns could occur in the future, creating higher risks of remobilization of the Cr(T) and Cr(VI) in the shallow soil near the groundwater drip or spray systems at the Land Treatment Units. Sources at the PG&E Compressor Station must be mapped and plotted in relationship to the release and the current location of the contaminants in both the shallow soils as well as the Upper Aquifer and the Lower Aquifer.

g) *Well construction details and depth discrete sampling are critical*

Samples from agricultural or domestic wells which cross the Upper Aquifer and Lower Aquifer have little value in defining Cr(T) or Cr(VI) background concentrations based on aquifer or geologic units. Correlating the flows from the two different aquifer zones, one unconfined and the other confined, is not an appropriate or satisfactory method for determining background levels of Cr(T) and Cr(VI). Mixing within the wells that were screened over two aquifers is likely to occur by diffusion, and possibly by other mechanisms. If filter packs are part of the well construction, then additional groundwater flow pathways exist for mixing of two originally separated groundwater aquifers. Using decades old domestic and agricultural wells which were readily available but designed for water production is not appropriate for background studies of Cr(T) or Cr(VI) which are associated with two vertically discrete aquifer units.

Discussion:

Background: 4a) Background levels - Location of wells

The background wells were chosen by the following criteria (BSP2 2002 Workplan): “The position of the 0.05 mg/L limit line shown on BSP2 Figure 3 represents the *inferred extent of the* *water bearing intervals that contain Cr(T) above the MCL within the Upper Aquifer*."

Background Study Criteria:

- Wells were in Hinkley Valley
- Wells were Cross/Upgradient of the 0.05 mg/L plume
- Wells were 500-2,000' outside of plume influence
- Wells were Historic Non-detect of Cr(VI) at 500' cross gradient
- Downgradient wells were excluded
- Criteria was based on 1995 study samples
- Wells chosen were only in the upper aquifer; they were chosen in the upper aquifer because the lower aquifer is confined and there is an upward vertical gradient; 'only upper aquifer should be used to establish the cleanup goal'.
- One of the 2004 reviewers (Harmon) states, "The Mojave River aquifer is the most logical source of groundwater flowing under and around the compressor station. Obtaining chromium levels in that water appears essential for determining the background chromium levels."

Comments: Background wells were not excluded or screened for their proximity to extraction wells. If the background wells chosen for sampling were inside the radius of influence (ROI) of wells extracting contaminated groundwater, then they cannot be identified as background wells. A background well should not lie within the zone of influence of a pumping well, or within the influence of the wells in the Hinkley Compressor station or Land Treatment Unit extraction systems. In addition, the wells to be used as background wells should have screens in one of the aquifer zones, but not both.

Background: 4b) Groundwater modeling - One of the 2004 reviewers noted the following: Synthesis of existing data in a quantitative model would be beneficial to verify the current plume direction. Also, it was noted that the 2003 Appendices were not utilized.

Comment: All groundwater extraction volumes and their ROIs should be mapped. The above mapping should be evaluated with the ROI information. In the 2002 report, "...the Upper Aquifer hydraulic gradient...reflects no known pumping from irrigation wells or groundwater extraction wells." pg 5. The Lockhart Fault and other faults in the Hinkley, California area may affect groundwater migration or influence preferred groundwater flow pathways. These elements should be evaluated in future hydrogeologic studies.

Background: 4c) Influence of land application of groundwater - Is there any relationship between the land-applied Cr(VI) water and the levels of Cr(VI) in the groundwater below those fields? What level of Cr(T) and Cr(VI) in spray (LTU's) was being aerosolized on the alfalfa fields.

Comment: All water applications from the Land Treatment Units should be mapped with detail on duration in time and volume of water of the applications. The deposition of wind-borne contaminants is discounted since there is low rainfall, yet Cr(VI) in dust can be an important exposure pathway if concentrations of Cr(VI) are high. In areas where Cr(T) and Cr(VI) are high in the shallow soil, plant hyperaccumulation of Cr(T) and Cr(VI) and the potential of livestock accumulation of chromium from ingesting impacted plants or impacted soil should be verified and documented with laboratory analysis.

Background: 4d) Groundwater recharge - How were the groundwater recharge areas mapped?

Comment: All injection wells and their ROI should be mapped for the whole basin.

Background: 4e) Historic groundwater migration - Previous patterns of migration
One of the 2004 reviewers (Harmon) noted the following: That historical groundwater flow patterns during, for example, remedial pumping periods or extreme climate events (drought and wet periods) may have produced a different plume than is now observed ...left behind anthropogenic Cr which could impact background concentration estimates which would be figured out with a groundwater modeling effort.

Comments: Heavy groundwater extraction since the 1930's supports this concept that the Cr(T) and Cr(VI) plume has migrated cross gradient through preferred flow pathways. Major geochemical changes in the Hinkley Valley caused by large water movements, including extraction, are likely to have occurred over the past several decades, altering background levels of Cr(T) and Cr(VI).

Background: 4f) Site Conceptual Model of the release - A site conceptual schematic of the release and migration of the Cr(VI) projected in cross section from 0-90' below ground surface (bgs).

Comments: A scientific site conceptual model of the release, migration, extraction, and reapplication of the impacted waters onto soil should be carefully and methodically performed. If needed, additional geologic cross sections should be prepared. To help establish well construction details and depths of screened intervals, well condition and other downhole information should be documented using a video camera and geophysical logging tools. This will help to establish whether the wells are acting as vertical conduits. All migration pathways should be mapped.

Background: 4g) Producing contaminant concentration contours - Sampling of equivalent depths is critical.

Comments: The discrete depth sampling dataset is not sufficient. New monitoring wells should be constructed solely for the purpose of groundwater sampling. I recommend that 20 to 40 new groundwater monitoring wells be constructed to current California standards in the Upper Aquifer and Lower Aquifer. The wells should be constructed so only one aquifer is screened for each well.

Task II - List other scientific issues that are not addressed in Report BSP3 or in **Task I**, above.

Comments: The extraction of groundwater containing Cr(T) and Cr(VI) and application of this impacted water on to the land surface without above-ground treatment of the chromium-impacted water should be rigorously evaluated and scientifically justified and documented. The concern is whether the Cr(T) and Cr(VI) are really being cleaned up, or whether the Cr(T) and Cr(VI) are being smeared in the shallow subsurface and ultimately being allowed to impact deeper soil horizons and groundwater resources. Groundwater resources in the area are heavily used for agricultural and domestic water supplies. Any additional impact from Cr(T) and Cr(VI) on soil and groundwater resources should be examined, tested, and documented in a careful and systematic manner. The drip lines for the Land Treatment Units are being cleaned with hydrogen peroxide and acid. These chemicals, if in contact with heavy metals, including Cr(T) and Cr(VI), might allow for more impacts in the shallow soils by increasing heavy metal solubility and enhancing mobilization of Cr(T) and Cr(VI) in the shallow soils.

Task III- Critique of the scientific portion of the 2007 Background Study Report, for the following parameters: a) scientific knowledge, b) scientific methods, c) scientific practices.

Comments: On the basis of my understanding of the well construction information (or lack thereof) of the wells used for the background study of Cr(T) and Cr(VI), the scientific approach to this study is seriously flawed if wells used in the study do not have proper screens in one discrete aquifer zone. If these mixed-aquifer wells are used for the overall concentration maps for Cr(T) and Cr(VI), the maps will be in error and likely to underestimate the Cr(T) and Cr(VI) concentrations, since the wells screened over both the Upper and Lower Aquifer will have most of the water in the well bore derived from the cleaner Lower Aquifer.

The wells currently in the background study were not designed for high-quality geochemical sampling, but rather they were probably designed for maximum water production. Applying detailed statistics to laboratory sample data from domestic and agricultural wells with ‘mixed aquifer’ water does not provide accurate results and likely underestimates the Cr(T) and Cr(VI) concentrations for reasons described above.

Although it might be economically attractive to use existing and available domestic and agricultural wells for a purpose for which they were not designed, the study does not meet the scientific objectives of trying to determine background concentrations of Cr(T) and Cr(VI). The use of statistical methods on the chemical data as well as averaging laboratory concentrations of Cr(T) and Cr(VI) from these wells does not provide accurate or correct results for background information.

RECOMMENDATIONS:

Natural background levels of Cr(T) and Cr(VI) for specific aquifers in the Hinkley, California, area can be determined with a significant drilling program of new wells with well screens limited to one aquifer zone in upgradient areas unaffected by historical pumping. It is possible that undisturbed hydrogeologic areas in the Hinkley, California, area do not exist due to the excessive groundwater pumping in the area. Samples upgradient toward the Mojave River may provide the best chance at finding what might be considered background Cr(T) and Cr(VI) concentrations.

Background levels are important to establish, but are very different from remediation goals or drinking water standards. The remediation goals are influenced by the best available technology to achieve a specific cleanup with regulatory oversight and public input. Maximum Contaminant Levels (MCLs) for Cr(T) and Cr(VI) or other drinking water standards are health based and provided by federal and state regulatory agencies. Together, these different levels (groundwater background levels, best available technology remediation levels, and the various drinking water standards and other exposure and toxicity concentrations) must be integrated to develop an appropriate and realistic remediation or cleanup goals for the site. After ten years of assessment and monitoring, remediation has been limited and the Cr(T) and Cr(VI) plume is expanding northward in the Upper Aquifer and there has been recent vertical migration into the Lower Aquifer as well (Stantec, 2011).

In summary, the following tasks are required:

a. Site Conceptual Model - Create a scientifically valid site conceptual model of the release, migration, extraction, and reapplication to land of the groundwater containing Cr(T) and Cr(VI).

b. Land Treatment Units - Map all the surface areas where groundwater containing chromium has been historically discharged to the land surface for irrigation purposes at the Land Treatment Units. Identify what levels (concentrations) of Cr(T) and Cr(IV) are in the shallow soil and the groundwater (besides the 5 foot lysimeters). Evaluate and verify the Land Treatment Unit extraction and water application process to document that Cr(T) and Cr(VI) are being properly immobilized.

c. Pumping Influence - Map the radius of influence of pumping wells located within the Hinkley Valley and the extracted waters discharge areas.

d. Obtain aquifer-specific background level data – Construct and install 20 to 40 new monitoring wells in accordance with current California well standards that are screened in one aquifer so that the Cr(T) and Cr(VI) aquifer contamination can be directly measured. A representative number of wells should be installed upgradient and outside the range of influence of historic or current pumping.

e. Plume control - Gain hydraulic control on the chromium plume in the Upper Aquifer which appears to be expanding northward. Gain hydraulic control of the Lower Aquifer which appears to be impacted from vertical movement of the Cr(T)- and Cr(VI)-containing groundwater sourced from the Upper Aquifer. The vertical migration and spreading of the chromium plume are a concern and should be addressed.

f. Identify background concentrations for Cr(T) and Cr(VI) in the area, and develop remediation goals.

g. Initiate more aggressive hydraulic control and remediation to contain and shrink the currently expanding Cr(T) and Cr(VI) groundwater plume in both the Upper Aquifer and Lower Aquifer.

I hope these comments are helpful to the Lahontan Regional Board. Please call me at (510) 590-1098 if you have any questions.

Sincerely,
CLEARWATER GROUP

James a Jacobs

JAMES ALAN JACOBS
NO. 88

James A. Jacobs, P.G.#4815, C.H.G.#88
Chief Hydrogeologist

References Cited

CH2MHILL, 2002, *Scope of the Background Chromium Study at the PG&E Compressor Station, Hinkley California*, (BSP1).

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US EPA, 1995, Establishing Background Levels, Office of Solid Waste and Emergency Response, Directive 9285.7-19FS, EPA/540/F-94/030, September 1995, 7 p.

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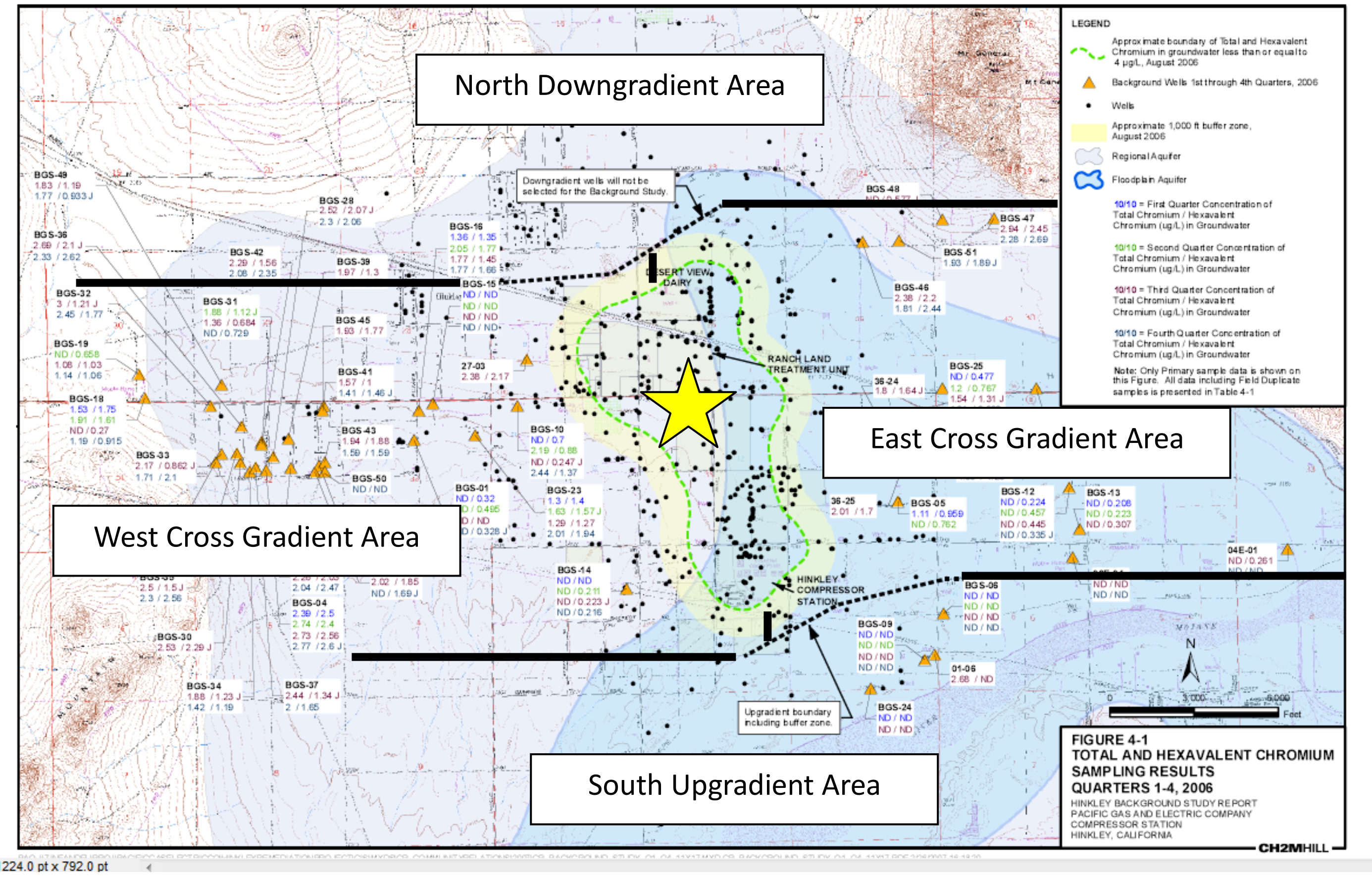

★

Core Area; green line shows approximate boundary of Cr(T) and Cr(VI) in groundwater less than or equal to 4 µg/L, August 2006.

Figure 1 Map of Cr(T) and Cr(VI) Sampling Results; Background Study

Hinkley, California

(Modified after CH2MHILL, 2007, Figure 4-1)

Date: 10/5/11; James Jacobs, P.G., C.H.G., Clearwater Group

A1-2: Stuart J. Nagourney, The College of New Jersey

TCNJ

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Peer Review of Pacific Gas and Electric Company's Chromium Background Study Report, Hinckley Compressor Station

Question 1. Quality of Spatial Sampling of Background Chromium

The sampling design is questionable. The purpose of this study was not to identify the primary source of Cr(VI) contamination, but to define the extent of the plume. To that end, more sampling should have occurred in the direction that the plume was believe to be directed toward rather than nearer to the known source. The sampling that did take place provides much more data than was required from sampling sites that were closest to the source, which biases the data summaries higher. This could seriously impact any conclusions based upon this data set regarding the extent and migration of the plume.

Question 2. Quality of Temporal Sampling of Background Chromium

The approach used in this study relative to the temporal trends appears to be reasonable. The use of an arithmetic mean to express the average concentrations of both total and hexavalent chromium is appropriate.

Question 3. Assumption of Statistical Normality

No comment, since this subject is outside my area of technical expertise

Question 4. Quality of Groundwater Modeling

As stated in the response to Question 1 above, the spatial sampling design that was used in this study is questionable.

The Big Picture – Additional Scientific Issues

The majority of my comments here are related to the efficacy and quality of the programmatic decisions regarding the choice of analytical methodologies and the quality of the data that was obtained.

The following questions were posed EMAX and Truesdale Laboratories, which were the two analytical laboratories that contributed adapt for this study. The questions that were posed were:

1. What calibration ranges were used for Methods 6010B, 6020A and 7199?
2. For Method 6020A, what was the value of the CRQL Check Standard (CRI) and the method control limits?
3. Were Reporting Limit (RL) check samples analyzed for Methods 7199 and 6010B?; if

so what are the control limits and what were the actual recoveries?
4. How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the Method Detection Limit (MDL) & RL for each method?
5. What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.
6. Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the expected sample concentrations for all analytical methods?

EMAX's responses to these questions were:

1. Responses are satisfactory
2. Response is satisfactory

3,4. Information on the RLs for Method 6020A were provided, but no information was supplied for Method 7199 or on how these limits were derived.

5. Response is satisfactory
6. This response was not satisfactory. The laboratory should have chosen the concentration level of matrix spikes for both Cr(T) and Cr(VI) to closer to the actual sample levels (usually a multiple of 3-5 the expected value is applied). The choice of much higher spiking levels means that the calculated recoveries have little value in assessing the quality of the actual sample concentrations and the impact to those results from possible matrix interferences.

Truesdale's responses to these questions were:

1. It is unclear from the response if the low level calibration ranges cited in the response for Methods 6010B and 6020A was used for the analyses in this study. If not, the data for this study for Cr(T) would be questionable.
2. Truesdale admitted in their response that they failed to perform this quality assurance as required by the method during the time that data for this study were obtained.
3. Truesdale admitted in their response that they failed to analyze a RL check sample during the time that data for this study were obtained.
4. Truesdale's response of varying criteria for a quantitative relationship between the MDL and RL is too vague to be acceptable.
5. The use of a mid-range check sample is NOT acceptable as a QC material as per the criteria for quality control specified in Method 7199. This would make the data for this study for Cr(VI) questionable.
6. This response was not satisfactory. The laboratory should have chosen the concentration level of matrix spikes for both Cr(T) and Cr(VI) to closer to the actual sample levels (usually a multiple of 3-5 the expected value is applied). The choice of much higher spiking levels means that the calculated recoveries have little value in assessing the quality of the actual sample concentrations and the impact to those results from possible matrix interferences

Other concerns with the analytical data that directly impact the conclusions of the study are:

1. No criteria were provide from with either laboratory as to the criteria for data assigned U or J flags
2. Based upon my experience with examining data for the analysis of Cr(VI) in water samples and soil extracts, this data set showed an unusually high percentage of samples failed the quality control criteria for the Continuing Calibration Verification (CCV). An explanation for this anomaly should be provided so as to show that the conclusions drawn from these data have not been compromised.
3. How were samples chosen for matrix spiking (was this procedure randomized so as to not bias the results?)
4. The workplan (Item #2 of Additional Materials) specifies the use of Method 6010 for the analysis of Cr(T); Method 6020A was used instead. This may impact the ability to quantify for Cr(T) at low concentration levels since the RL for Method 6020A is much lower than that for Method 6010.
5. Some data for Cr(VI) in this study was reported by the USEPA determinative method 218.6, other data was reported by Method 7196A and still other data was reported by Method 7199. These methods all have different sensitivities and different capabilities to report Cr(VI) without analytical interferences. Why were different methods used to measure Cr(VI)?
6. The rationale for using median vs. mean for data summaries was never provided.
7. The authors of the report chose to use a method from the United States Geological Survey (USGS) to attempt to define specific Cr species present in samples, any specie interconversion [either oxidation of Cr(III) to Cr(VI) or reduction of Cr(VI) to Cr(III)]. This method is not certified by any State or national laboratory accreditation authority. Information that was supplied suggests that this USGS method has only been applied to speciation of As. USEPA Method 6800, Elemental and Speciated Isotope Dilution Mass Spectrometry allows the identification individual Cr species, the extent of any specie interconversion, and can correct final results for up to 80% conversion. USEPA Method 6800 is certified by State and national laboratory accreditation authorities. Why was Method 6800 not used for this application?

Respectfully submitted,

Stuart Nagourney
Adjunct Professor of Chemistry
The College of New Jersey
Hillwood Lakes Campus
Ewing, New Jersey 08628
609-448-6440
nagourne@tcnj.edu

October 11, 2011

Attachments

From Truesdail Laboratory:

1) What calibration ranges were used for Methods 6010B, 6020A and 7199?

SW 6010B: Standard Calibration: 0.01 to 10 ppm
Low Level Calibration: 0.001 to 0.100 ppm

SW 6020A: Normally 0.2 to 500 ppb, or 0.2 to 100 or 200 ppb.

SW 7199: 0.2 to 50 ppb

2) For Method 6020A, what was the value of the CRI and the method control limits?

We were following the QAAP and there was no mention of this criteria. We started performing the CRI on September 12, 2011 and the criteria is ±30%

3) Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?

SW 7199: Yes, control limits of ±20%. The raw data was provided to CH2M Hill for these analysis but we were not asked to report them. A PQL sample was analyzed at 0.15 ug/L with control limits of ± 20%. The recoveries for the PQL in the data packages of interest were 108%, 110%, 103%, and 108%.

SW 6010B: We were not analyzing RL check sample. The Initial calibration starts with the PQL level and every 24 hours we run a calibration curve.

4) How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL & RL for each method?

The RL is 2 to 10 times the MDL depending on the noise level.

5) What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.

The mid-range calibration check standard (MRCCS) is a second QC source and is our QCS. It is the same thing but named differently and it is included in the package.

6) Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the expected sample concentrations for all analytical methods?

For Cr(VI), we spike the sample using concentrations of 1, 5, 10, 25, etc., and use the spike concentration that is the next increment that is greater than or equal to the sample concentration. Ex. a sample concentration of 4.2 is spiked with 5 ppb.

For **Cr(T):** From the PG&E QAPP: "The spike levels will be less than or equal to the mid-point of the calibration range."
From SW 6020A: The spike levels should be "at approximately the mid-point of the linear dynamic range".

Re: Clarification of Analytical Issues

From: Anne Holden
To: Nagourney, Stuart
CC: Dernbach, Lisa; Kemper, Lauri
Date: Friday - September 16, 2011 3:33 PM
Subject: Re: Clarification of Analytical Issues

Hi Stuart
Hopefully now you have everything you need from Emax. I have let Truesdail lab know we are still expecting their responses, and to email them to Lisa Dernbach and Lauri Kemper, my supervisors. I will be out of the office until Oct 23! Thank you for your diligence in conducting the peer review.

If you have any other clarifications/questions, please email Lisa (ldernbach@waterboards.ca.gov) and Lauri (lkemper@waterboards.ca.gov). When they get the responses to your outstanding questions from Truesdail, they will forward them on to you and help transmit any followup questions you may have.

thanks again,
Anne

Anne Holden, P.G.
Engineering Geologist
Lahontan Water Board
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South Lake Tahoe, CA 96150
530-542-5450 tel
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aholden@waterboards.ca.gov

>>> Stuart Nagourney <nagourne@tcnj.edu> 9/14/2011 3:53 AM >>>
Ask the lab. to provide the data that shows that they are full compliance with Section 10.2.3.1 of USEPA Method 6020A.
----- Original Message -----
From: "Anne Holden" <AHolden@waterboards.ca.gov>
To: "Stuart Nagourney" <nagourne@tcnj.edu>
Sent: Tuesday, September 13, 2011 5:05:56 PM GMT -05:00 US/Canada Eastern
Subject: Re: Clarification of Analytical Issues

Please see attached, and the text below [the lab's response to your additional questions (apparently they were able to figure out what samples you were referring to)]:

I was able to locate one of the SDGs 06K142. Please see attached file.
Included in the attached file are:
1. LCS report for 06K142 Method 6020A - Lab sample IDs for LCS/LCSD are IMK021WL and

IMK021WC respectively.
2. Analytical sequence - proof that LCS are analyzed with the samples
3. Digestion log - proof that the LCS are prepared the same way as the samples
4. Certificate of Analysis - proof that the standards used for LCS are purchased as certified standards from CPI

Please note that all samples received at EMAX are processed the same way. Should you have any question or need additional info please let me know.

>>> Stuart Nagourney <nagourne@tcnj.edu> 9/13/2011 11:09 AM >>>
I have this info. @ home; I will get it to you later today.
----- Original Message -----
From: "Anne Holden" <AHolden@waterboards.ca.gov>
To: "Stuart Nagourney" <nagourne@tcnj.edu>
Sent: Tuesday, September 13, 2011 1:55:12 PM GMT -05:00 US/Canada Eastern
Subject: Re: Clarification of Analytical Issues

Hi Stuart
Here is the lab's response - can you provide the needed information to help them narrow down the research?

--I need some specific info to help me go through archived records. We archive records per SDG and all related document from the SDG including preplogs (will prove that LCS was digested with the field samples) and standard logs(to trace for the LCS vendor)can be located. If you can provide me the SDG or at least the sample ID then it will be easier to search.

>>> Stuart Nagourney <nagourne@tcnj.edu> 9/13/2011 7:48 AM >>>
Thanks.

For Question 5, please ask EMAX for 2 additional pieces of information: (1) what vendor was used for the lab. control sample and (2)for documentation that this lab. control sample sample was prepared in an identical manner to which the samples were subjected.

So you know, several of EMAX's responses are factually incorrect and that may compromise their data. I will include this information as part of my testimony.

I look forward to other laboratory's comments.

----- Original Message -----
From: "Anne Holden" <AHolden@waterboards.ca.gov>
To: "Stuart Nagourney" <nagourne@tcnj.edu>
Sent: Tuesday, September 13, 2011 10:09:42 AM GMT -05:00 US/Canada Eastern
Subject: Re: Clarification of Analytical Issues

Hello Stuart
Below are responses to your questions from EMAX labs: Truesdail is still working on their responses, I will forward those to you ASAP.

1) What calibration ranges were used for Methods 6010B, 6020A and 7199?
Response: Method 6020A (please note that EMAX did not use method 6010B for this project)
for CAM metals and others, calibration ranges are: 10, 50 and 100 ug/L.
for Cations, Al and Fe, the calibration ranges are: 1000, 5000 and 10000 ug/L.
Method 7199: calibration ranges are: 0, 0.2, 2.0 and 5.0 ug/L.

2) For Method 6020A, what was the value of the CRI and the method control limits?

Response: CRI is not required for method 6020A hence it was not performed. All method QC requirements are applied, e.g., IECs, LDRs, ICSA, ICSAB, ICV, CCVs, LCS, MB, MS/MD, Dilution Test, Analytical Spike.

3) Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?

Response: RL check was not required by the project QAPP or method 7199 hence no RL check was performed for this project. All method QC requirements were performed, e.g., ICV, CCVs(90-110% recovery),MB, LCS, MS/MD.

4) How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL & RL for each method?

Response: RLs are derived from the lowest calibration point.

5) What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.

Response: EMAX reported LCS (lab control samples) purchased as certified standards from independent source ~ SRM

6) Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the exected sample concentrations for all analytical methods?

Response: Spiking levels are not specified by the method and the project QAPP, hence lab SOP was applied. Furthermore, for practical reasons LCS/MS laboratory spike levels are set the same for all samples. Sample concentration levels are unknown, hence analyzing samples to determine levels for spiking are deemed greatly onerous (and can be translated to a more costly analysis) with no scientific added value. If the analytical run is under control the sample result will be the same whether or not the spike level were (or were not) within the expected concentration levels.

>>> Stuart Nagourney <nagourne@tcnj.edu> 8/29/2011 12:03 PM >>>
Just the questions w/introduction will suffice for now. If it turns out that I need more detail, we can always ask for that later,

Thanks!
----- Original Message -----
From: "Anne Holden" <AHolden@waterboards.ca.gov>
To: "Stuart Nagourney" <nagourne@tcnj.edu>
Sent: Monday, August 29, 2011 2:24:31 PM GMT -05:00 US/Canada Eastern
Subject: Re: Clarification of Analytical Issues

thanks Stuart - is it necessary (or helpful) for me to provide the labs with the chain of custody or lab analytical results for context, or just send the questions with an introductory paragraph?

>>> Stuart Nagourney <nagourne@tcnj.edu> 8/29/2011 10:57 AM >>>
Please ask the analytical laboratories to clarify the following issues:

- What calibration ranges were used for Methods 6010B, 6020A and 7199?
- For Method 6020A, what was the value of the CRI and the method control limits?
- Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?
- How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL & RL for each method?
- What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.
- Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the exected sample concentrations for all analytical methods?

>>> Michael Ngo <michaeln@truesdail.com> 10/06/11 2:34 PM >>>
Hi Anne,
Sorry for the long delay. Attached is list of QC questions and their
answers.
>>>
>>>
>>
On 9/16/2011 3:15 PM, Anne Holden wrote:
> Hello Mona and Michael--
> We'll be looking forward to receiving Truesdail lab's responses. I will be out of the office from Sept 16 through Oct 23. In my absence, please email the responses to Lisa Dernbach (ldernbach@waterboards.ca.gov) and Lauri Kemper (lkemper@waterboards.ca.gov), both of whom are cc'ed on this email.
>
> thank you
> --Anne
>
> ____________________
> Anne Holden, P.G.
> Engineering Geologist
> Lahontan Water Board
> http://www.waterboards.ca.gov/lahontan/
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> aholden@waterboards.ca.gov
>
>
>
>>>> Mona Nassimi<mona@truesdail.com> 9/12/2011 10:09 AM>>>
>>>>
> Dear Anne,
> This project is very high profile and we are waiting for our client to
> obtain their permission to respond to your questions. We apologize for
> any inconvenient and delay.
>
> Sincerely,
>
>
> Mona Nassimi
> Truesdail Laboratories, Inc
> Manager Analytical Service Division
> 714-730-6239
> 714-730-6462 Fax
> mona@truesdail.commailto:mona@truesdail.com
> 14201 Franklin Ave
> Tustin, CA 92780
>
> >>
>>>>> Michael Ngo<michaeln@truesdail.com> 8/29/2011 3:43 PM>>>
>>>>>
>> Hi Anne,

>> We are working on getting those answers for you. I should be able to
>> send you answers for all of your questions by tomorrow.
>>
>>
>> Sincerely
>> Michael Ngo
>> Project Manager/Quality Assurance Manager
>> Truesdail Laboratories Inc.
>> Environmental Services
>> (714)730-6239
>> michaeln@truesdail.com
>>
>>
>> -------- Original Message --------
>> Subject: Re: QC questions
>> Date: Thu, 8 Sep 2011 17:38:18 -0400
>> From: Anne Holden<AHolden@waterboards.ca.gov>
>> To: Michael Ngo<michaeln@truesdail.com>
>>
>>
>>
>> Hi Michael
>> just following up on the status of your answers - any ETA?
>> thanks!
>>
>> ______________________
>> Anne Holden, P.G.
>> Engineering Geologist
>> Lahontan Water Board
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>> aholden@waterboards.ca.gov
>>
>>
>>
>>>>> Michael Ngo<michaeln@truesdail.com> 8/29/2011 3:43 PM>>>
>>>>>
>> Hi Anne,
>> We are working on getting those answers for you. I should be able to
>> send you answers for all of your questions by tomorrow.
>>
>>
>> On 8/29/2011 1:18 PM, Anne Holden wrote:
>>
>>> Hello Mr Ngo:
>>>
>>> I work for the Lahontan Regional Water Quality Control Board, a state of California agency. Our agency oversees the cleanup of chromium contamination in groundwater at the Pacific Gas and Electric Company Hinkley Compressor Station in Hinkley, CA. In 2006, PG&E conducted groundwater sampling to examine background chromium concentrations in the Hinkley area. We are reviewing the quality control

data for this sampling effort, which took place over four quarters of calendar year 2006. Your lab performed analytical chemistry services for the groundwater sampling, and we have the following questions regarding the analytical testing.
>>>
>>> 1) What calibration ranges were used for Methods 6010B, 6020A and 7199?
>>> 2) For Method 6020A, what was the value of the CRI and the method control limits?
>>> 3) Were RL check samples analyzed for Methods 7199 and 6010B?; if so what are the control limits and what were the actual recoveries?
>>> 4) How were RLs established for Methods 6010B, 6020A and 7199? What is the relationship between the MDL& RL for each method?
>>> 5) What SRM was used for QC for 7199 as per Section 5.4? This data was apparently not reported.
>>> 6) Why were the spiking levels for both Cr(T) and Cr(VI) analyses MUCH higher than the exected sample concentrations for all analytical methods?
>>>
>>> Please reply to each question above as they pertain to the services your lab performed. I would very much appreciate your reply as soon as possible. Please contact me with any questions or if you need more information to respond to this request.
>>>
>>> Regards,
>>>
>>>
>>> ____________________
>>> Anne Holden, P.G.
>>> Engineering Geologist
>>> Lahontan Water Board
>>> http://www.waterboards.ca.gov/lahontan/
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A1-3: Yoram Rubin, University of California-Berkeley

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October 7th, 2011

Ms. Lauri Kemper, PE
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Re: Peer Review of PG&E's Chromium Background Study Report, Hinkley Compressor Station

This review provides my opinions on several questions related to the documents provided to me. The review is organized following the sequence of questions raised in the Scientific Peer Review Request (Sections 1-4). Additional comments of a more general nature are provided in Section 5. If I missed or misinterpreted any information, I would be glad to be informed about it.

1. Comments on quality of spatial sampling of background chromium

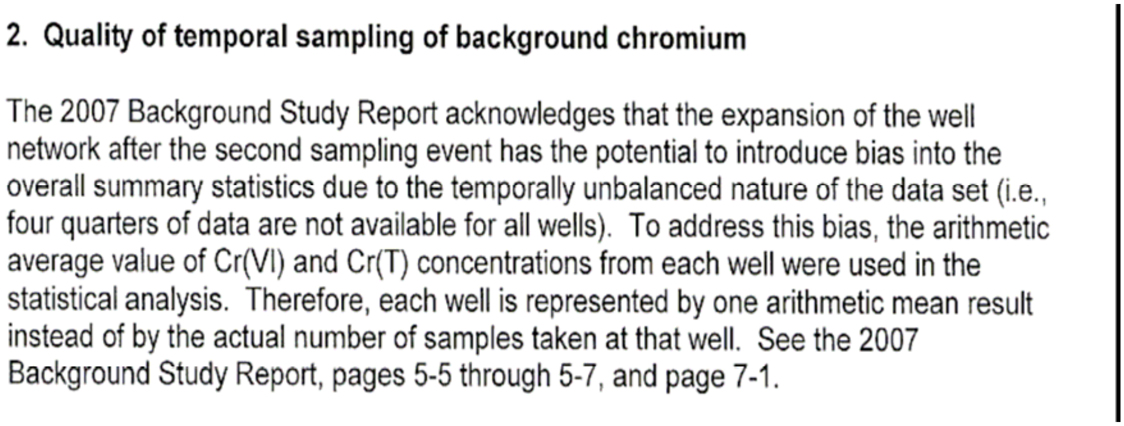
The first issue raised in the "Scientific Peer Review Request" concerns the large number of wells installed (and measurements taken) in the vicinity of well BGS-04. Looking at Figures 4-1 and 4-2, it is obvious to me that there are many measurements collected all over the site, and altogether they form a good basis for analysis and for making predictions. The challenge of course is how to analyze the data and how to use it for predictions. Specifically, there is a need to apply analysis that would take into consideration that uneven spatial distribution of the measurement locations (i.e., the sampling wells). Without taking this into account, the concentrations at a particular area (e.g., BGS-04) could be assigned a disproportionately large weight. If many or all the wells around BGS-04 sample a particularly high concentration area, the high concentration in that area could pull the spatial average higher (creating a positive bias), leading to averages that are not representative of the site. It could also happen that they all sample small values, and that would create a negative bias. This is knows in geostatistics as the clustering effect. The clustering effect could be removed through declustering. It does not appear that declustering was applied to the data. To summarize, the uneven distribution of wells could lead to bias. There are known techniques that could handle the clustering effect, but none was carried out, to my understanding.

Additional comments:

1. The Background Study mentions on page 1-4 that “To compensate for the lack of discrete-depth-samples, PG&E proposed to expand the background study well network”. In response to that statement, this approach cannot work unless the concentration field is stationary and statistically isotropic, which cannot be the case. So, expanding the area being sampled cannot compensate for the lack of discrete-depth samples.
2. Table 3-1 indicates that several of the wells are screened over the upper (floodplain) and lower (regional) aquifer. From my understanding of the sampling procedures (Section 3.2), the concentrations represent (flux-) averages over the entire screen. This could lead to ambiguity as to what the concentration averages actually represent (i.e., which geological unit?). Furthermore, it could also lead to bias: it may be that a well that is screened over the two aquifers would mix clean water from one unit with contaminated water from the other unit, which would lead to biases when trying to assign the measured value to a particular aquifer and to biases in assessing the average concentrations. This ambiguity could be removed, to a large degree, through appropriate modeling, but to my understanding this has not been done.
3. Spatial averages are of little predictive value in the case of non-stationary variables such as the concentration. The population sample mixes measurements taken upstream (potentially low values) and downstream (potentially larger values) of the compression area. There also appears to be a trend of the concentrations increasing from east to west. All this could lead to biases. A physically-based analysis could take the trends in the concentration into account and provide better predictions.

2. Comments on quality of temporal sampling of background chromium.

The procedure used to account for gaps in the temporal sampling is described as follows (Scientific Peer Review Request, Attachment 2)



2. Quality of temporal sampling of background chromium

The 2007 Background Study Report acknowledges that the expansion of the well network after the second sampling event has the potential to introduce bias into the overall summary statistics due to the temporally unbalanced nature of the data set (i.e., four quarters of data are not available for all wells). To address this bias, the arithmetic average value of Cr(VI) and Cr(T) concentrations from each well were used in the statistical analysis. Therefore, each well is represented by one arithmetic mean result instead of by the actual number of samples taken at that well. See the 2007 Background Study Report, pages 5-5 through 5-7, and page 7-1.

I find this approach lacking in several respects, and I would recommend against it. My reasons are as follows. Averaging is known to alter the statistical nature of the variables being averaged. The primary effect is reducing variability. The consequence of that is that the averaged variables provide a "smoother" version of reality, and as a result the high and low values are averaged out. The elimination of high values of the concentration from consideration is obviously of concern in the context of this study because it would lead to biased estimates.

Appendix I of the Background Study Report refers to this issues and mentions the "..dampening the effect of the most elevated values in the sample set by averaging those results with lower results from other sampling" (page 7-1). I cannot see why dampening would be a desired outcome. To explain this issue consider the following example: if you are searching for gold, you will not average gold concentrations from your soil samples, because that one sample with very high concentrations could be very important in telling you where to dig. Similarly, the samples with high concentrations could indicate the presence of high-concentration areas and should not be averaged out.

There is another problem with averaging of measurements that is related to the test of statistical normality (discussed further in Section 3 below). Statistical tests are generally performed (unless stated otherwise) based on statistically homogenous populations (population samples), meaning that all samples in the population sample are drawn from (or representative of) the same underlying distribution. In many cases, the samples are assumed to be independent and identically distributed (what's known in the statistical literature as i.i.d). The assumption of homogeneity is a key element of statistical inference. Averaging as done in the Background Study is inconsistent with this requirement, because the averaged concentrations and the non-averaged concentrations do not belong in the same underlying statistical distribution. I will discuss this issue further in Section 3, but in brief summary, the mixing of variables from different distributions violates one of the assumptions used to construct the Shapiro-Wilk test. The consequences of this violation were not evaluated and so cannot be ignored.

3. Comments on the assumption of statistical normality.

The normal distribution is a favorite model selection in applications because of its simplicity: one needs to infer only 2 parameters (the mean and variance) to be able to define the entire distribution, which could then be used for making predictions and associating them with confidence intervals. Given that in groundwater applications there is not a lot of data to begin with, and that inference of multi-parameter models is a challenge, there's no wonder why one would want to adopt the normal model, as was done in the background study.

In order to test whether or not a normal model is acceptable, the background study elected to use the formalism of hypothesis testing. The underlying theory is documented in many textbooks. The approach is to state a null hypothesis (in this case, that the concentrations are normally distributed) and then to apply a test that would indicate whether this assumption could be rejected or not. A fundamental tenet of hypothesis testing is that the test can only determine whether there's enough evidence to reject the null hypothesis. Hypothesis testing does not provide conclusive evidence that the null hypothesis is the right one. It can only determine whether or not there's enough evidence to reject it. Based on this, the statement made in Appendix I that "the probabilities (p-values) from the Shapiro-Wilk test (W test) provide evidence about whether the background total and hexavalent chromium concentrations are normally or log-normally[1] distributed" is very doubtful. The test does not provide such evidence, its power is only to state whether there's enough evidence to reject the assumption of normality.

Not having enough evidence to reject the null hypothesis (normality) does not mean that the normal model is the best one. It also does not mean that other evidence cannot be used. To use an analogy, not finding conclusive evidence with fingerprints does not mean that DNA samples cannot be used and shed a different light. In the case of the normal model assumption, it should be noted that the concentration is by definition non-negative, and hence non-normal by definition (exceptions can be made but I am not sure they are applicable here). There is evidence for asymmetry in Table 6.1 where differences between the mean and median of the distribution are shown to exist: in normal distributions these values should be equal (or at least very close to each other). Hence, there are indications against the assumption of normality.

The practice of hypothesis testing brings another issue to the surface. In hypothesis testing, the common thinking is that the null hypothesis should be a "safe" assumption, meaning an assumption that would not lead to damage if it is not rejected. This is because it is difficult to reject the null hypothesis: it is rejected only in the face of overwhelming evidence against it. Let me explain this with an example from the criminal law. I am not a jurist, but this example is commonly used and I think I understand it pretty well. The point is that legally a person is assumed innocent until proven guilty. So the null hypothesis in the legal system is that the person is innocent. The assumption of innocence is selected to be the safe assumption (null hypothesis) in most legal systems, and it will be rejected only in the face of overwhelming evidence to the contrary. How is that related to the Background Study? The question is whether the assumption of normality is the safe assumption and should it be used as the null hypothesis. In my opinion it is not a safe assumption because it could underestimate the probabilities of high concentrations. For example, a lognormal distribution has a longer "tail" and it assigns higher probabilities to the high concentrations, and so it could possibly be a safer assumption. This option and perhaps others need to be considered.

The quality of the sample population is obviously of primary consideration. Shapiro and Wilk (1965) assume that their samples are identically distributed. Section 2.2 in the Shapiro-Wilk paper states that "The objective is to derive a test for the hypothesis that this is a sample from a normal distribution with unknown mean μ and unknown variance σ^2." As discussed in Section 2, the sample population includes measured concentrations and averaged measured concentrations. Because averaging alters the statistical nature of the underlying distribution, the population sample appears to be is inappropriate for this

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[1] Shapiro and Wilk (1965) mention only the normal option, not lognormal. The log-normal option is a possibility after log-transformation of the measurements.

kind of test because differences in temporal averaging procedures (e.g., averaging over 2, or 3 or 4 measurements) will lead to different statistical distributions for the various samples within the population sample, in a violation of the requirements of the test. The consequences of such violation need to be analyzed, but in principle, inferences from such a hybrid sample population are not suitable for determining the nature of the underlying distribution.

The Background Study does not assume correlation between the concentration measurements. In other words, the measurements are assumed to be spatially-uncorrelated. This assumption, although not unreasonable for measurements with large distances in between, is not justified theoretically, and is particularly challenging for measurements at close proximity. It needs to be supported with evidence. I could not find such evidence in the study and I am concerned that the test is inconsistent with the underlying physics.

In another direction, the test of normality addresses the question of whether or not the population sample could be described as normally-distributed. It does not address the question of whether or not the normal model inferred from the population sample is a good model for prediction of regional or local averages of the concentration and its confidence intervals. More on that is provided in Section 5.

In light of this discussion, I believe that the outcome of the Shapiro-Wilk test is questionable. Additional comments on this matter are provided in Section 5.

4. Comments on quality of groundwater modeling

The groundwater model is discussed in Appendix B. Model calibration is discussed in Section B.1.4. Very little information is provided and whatever is given is not enough to confirm the adequacy of the calibration effort. Particular issues to consider are as follows:

1. The model was calibrated based on groundwater levels only. This raises several issues of concern:
    a. Water levels alone cannot be used for calibrating the spatial distribution of the hydraulic conductivity because there is no unique relationship between water levels and conductivity. Without sound calibration of the hydraulic conductivity field and porosity, the groundwater model cannot be used to predict velocities, and concentrations.
    b. No information is provided on the quality of the match between measured head and model-based predictions. It is important to remember in this context that even small errors in the predicted heads could lead to very large errors in the head gradients, and all that is related like velocities and concentrations.
    c. Without reliable estimates for the hydraulic conductivity, the reliability of the water budget analysis cannot be established.
2. No attempt is reported to test the model against the concentration data. This could be a useful strategy to establish the credibility of the model. Methods for using concentration data are available (see Rubin, 2003 and Rubin et al., 2010).

3. No attempt to model spatial variability of the hydrologic parameters is reported. Assuming the hydraulic conductivity to be uniform within each of the hydrostratigraphic units would neglect the possible consequences of channeling effects that could be introduced by the "….interbedded gravels, sands, silts, and minor amounts of clay " (Section B.1.2). One possible consequence is that the channels could act as fast flow channels. Such channels would lead to faster downstream migration of chemicals.

My conclusion is that more work is needed in order to align the model calibration efforts with modern concepts on this topic. As discussed in Section 5, uncertainty quantification (UQ) should be an important part of the study. A groundwater model is the main vehicle for UQ. This line of thinking was not pursued here and no UQ that meets acceptable norms was carried out, to my understanding.

5. General comments

In Section 3 I addressed questions related to the normality test. Here I would like to provide additional perspective. The first point I would like to make is that, regardless of whether or not the Shapiro-Wilk test is applicable or not, there is a need to evaluate the predictive capabilities of the normal model, and that is a different issue altogether. In other words, even if one accepts that the population sample is normal (see Section 3 for discussion on the difficulties with this), this does not constitute a confirmation that the normal model could actually be used for predicting (at best) anything but the statistics of that population sample, until the predictive capability itself is tested. The main reason for that is the issue of ergodicity. For spatial averages to be representative, the population sample must be ergodic (see Rubin, 2003). That means that the population sample must cover all the possible states of the sampled system, and in the right proportions. If this condition is met, then the population sample would be sufficient for making inferences about spatial averages. For stationary problems, satisfying the condition of ergodicity requires extensive spatial sampling. How large the sampled domain needs to be? This can only be established through physically-based modeling of the aquifer, including modeling of the spatial variability of the hydraulic conductivity and the flow and transport fields related to the spatial variability model. The added complication here is that the concentration field is non-stationary. This could be compensated through physically-based stochastic modeling strategies (Rubin, 2003). Another strategy to evaluate the model's predictive capability is through cross-validation (Rubin, 2003).

Another issue to consider is the no-detect concentrations. Figures 5-4 and 5-5 and associated discussion indicate that locations where the concentrations were measured below the detect limits were assigned values equal to half the detection limit. This is speculative. It may be a good speculation, but it is still a speculation, nonetheless. The speculation is in considering and analyzing the concentration from the perspective of a spatially-uncorrelated variable rather than a spatially-correlated variable. The point is that if one adopts the spatial correlation perspective, the no-detects could be interpreted in different ways. For example, one could also speculate that the no-detects could be indications of fast-flow channels with very high concentrations further downstream

(Wilson and Rubin, 2002), or that the wells with no-detects were placed in low-conductivity areas with by-pass flow nearby.

At times one must resort to speculations when it comes to groundwater applications, but there is a need to establish their likelihood. What is needed here is to substantiate this speculation by evaluating it using a physically-based flow and transport model. Another important point is that including speculative values in the population sample used to test normality is not warranted. Without accounting for the uncertainty around this speculation, one cannot assign any confidence intervals to any prediction that is based on a population sample that includes these values. This adds further doubts to the value of the normality test (see Section 3 for additional discussion).

The next comment is with regard to uncertainty quantification (UQ). UQ is the idea that all sources of uncertainty must be accounted for when making predictions. It is known that the sources for uncertainty are spatial variability and data scarcity, and the challenge is how to quantify that uncertainty. To be specific with regard to the analysis carried out in the Background Study, we would want to model the model uncertainty (in other words, how likely or unlikely is the normal model and alternative models?) and the parameter uncertainty (in other words, what is the uncertainty associated with the parameters of the normal model?). UQ is a fundamental concept in modern hydrogeology and its importance is in that it allows us to assess the quality of the prediction. In the Background Study, once a decision was made to accept the normal model, it was viewed as a certain model and that does not model realistically the uncertainty.

Respectfully,

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