Final
Work Plan for Chromium Sample Filtration Comparison Test PG&E Topock Groundwater Monitoring Program

Prepared for: Department of Toxic Substances Control

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Introduction

This work plan describes the objectives, scope, and methods for conducting a comparison test of the sampling procedures used for dissolved chromium analyses of groundwater samples at the Pacific Gas and Electric Company (PG&E) Topock Compressor Station, Needles, California. Dissolved hexavalent chromium [Cr(VI)] and dissolved total chromium [Cr(T)][1] are the primary constituents of concern in groundwater at the Topock site. Since 1997, groundwater investigation and monitoring have been conducted at the site under a RCRA Facility Investigation (RFI) and an ongoing groundwater and surface water monitoring program (GMP). The California Department of Toxics Substances Control (DTSC) is the lead agency directing and overseeing the RFI, GMP, and other corrective measures activities at the site.

In July 2004, at DTSC request, PG&E submitted a *Sampling and Analysis Plan, Groundwater and Surface Water Monitoring* (SAP) (CH2M HILL 2004) describing the GMP monitoring plan, sampling/analysis procedures, and quality assurance project plan (QAPP) to support water quality sampling and investigation for the GMP and corrective measures studies at the Topock site. Since late August 2004, with DTSC approval, groundwater and surface water monitoring at the Topock site has been conducted on quarterly, monthly, and bi-weekly schedules following the July 2004 SAP (currently in revision).

In January 2005, DTSC provided final comments on the water quality SAP. DTSC's comments included the requirement for PG&E to conduct a chromium sample filtration comparison test (initially proposed in the July 2004 SAP) during first quarter 2005 to assess the sample filtration and preservation methodology used for Cr(VI) and dissolved Cr(T) analyses. The draft work plan was prepared in response to DTSC's letter dated January 25, 2005. This final work plan is submitted in response to DTSC's March 1, 2005 conditional approval letter of the draft work plan.

Background

Under the ongoing GMP, water samples collected for dissolved Cr(VI) and dissolved Cr(T) analyses are filtered and preserved in the laboratory as opposed to filtering and preserving the samples in the field during sample collection. Due to the Cr(VI) 24-hour holding time

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[1] Dissolved total chromium [Cr(T)] includes the combined concentrations of trivalent and hexavalent chromium, as measured by U.S. EPA Method 6010B.

requirement, the Cr(VI) and Cr(T) samples collected for the GMP are delivered to the laboratory daily, and filtered and preserved upon receipt, within 8 to 24 hours after sample collection.

Since RFI investigations were initiated in 1997, water samples for Cr(VI) and Cr(T) have been filtered in the laboratory before analysis. For the monitoring period 1997-2004, Cr(VI) has been analyzed using Method **SW 7196A** (colometric analytical method, with a standard, undiluted, reporting limit [RL] of 0.010 milligrams per liter [mg/L]). Beginning in September 2003, groundwater samples from wells outside the plume area are analyzed for Cr(VI) using Method **SW 7199** (ion chromatography method, with standard RL of 0.0002 mg/L). Total dissolved solids (TDS) and other organo-metallic constituents potentially in the groundwater samples introduce matrix interference on the SW 7199 analyses requiring sample dilution and a corresponding increase in the RL.

Dissolved Cr(T) has been analyzed in the RFI through 2002 using Method **SW 6010A** (standard RL of 0.020 mg/L) and subsequently with Method **SW 6010B** (standard RL of 0.001 mg/L). Both SW 6010A and SW 6010B are inductively coupled plasma–atomic emission analytical methods.

The USEPA analytical method description for SW 7199 states that “filtration and pH adjustments should be performed at the time of sample collection or as soon thereafter as practically possible” (SW-846, USEPA 1996). Chapter 3 of SW-846 does not specify the requirements for collecting “dissolved” hexavalent chromium. According to SW-846, Method SW 7196A does not require field filtration or preservation adjustment of the sample (USEPA 1996).

The Cr(VI) and Cr(T) sample collection and analysis procedures initiated in the RFI have been maintained in the GMP for the following reasons:

- The Topock site is located in easternmost San Bernardino County, approximately 6 hours drive time from analytical laboratories in the Los Angeles area. Therefore, Cr(VI) sampling must be conducted between the general period 9 AM – 3 PM to ensure sufficient time for courier transport, laboratory receipt/log-in, and analyses within the 24-hour holding time requirement.
- In addition to its remote location, the Topock site is subject to harsh field conditions including daytime temperatures exceeding 100° F in May through September, and locally gusty winds. During the summer months, the effective daily sampling regime and capacity, outlined above, is limited.
- Additional sampling equipment and time is required for field filtration and sample preservation. When sampling is conducted under harsh field conditions (extreme heat, wind-blown sand and dust), the number of samples collected per day will be less than with the current sampling procedure, and the possibility of field contamination exists at the sampling sites.

Test Objective

The objective of this sample collection procedure test is to compare the dissolved Cr(VI) and dissolved Cr(T) analytical results for groundwater samples field-filtered and preserved versus laboratory-filtered and preserved to assess any differences in measured concentrations.

There are four possible outcomes for the data generated from this comparison test:

1. There are no appreciable differences between the dissolved Cr(VI) and dissolved Cr(T) concentrations measured in samples that are filtered and preserved in the field, versus samples that are filtered and preserved in the laboratory.
2. The field-filtered samples have overall higher concentrations than the laboratory-filtered samples.
3. The field-filtered samples have overall lower concentrations than the laboratory-filtered samples.
4. The test results are mixed; field-filtered samples yield both higher and lower concentrations relative to the laboratory-filtered samples.

Sampling Plan for Filtration Methods Comparison Test

The filtration methods comparison test and data evaluation proposed in this work plan involve the following steps and activities:

- Select a subset of GMP monitoring wells for the comparison test that are representative of chromium concentrations and geochemical conditions in the network of wells monitored at the Topock site.
- Collect duplicate Cr(VI) and Cr(T) samples from the selected wells; one set to be filtered and preserved in the field, and the second set to be filtered and preserved by the laboratory. The comparative sampling is proposed for two consecutive monthly sampling events.
- Statistically evaluate the test results to assess the significance of data variability, and then compare the test data with the chromium data set collected under the existing GMP.
- Prepare a test report that summarizes the filtration method comparison results, statistical analyses, and evaluation. Pending this evaluation, recommendations will be prepared regarding filtration sampling procedures to be used for the ongoing GMP.

To maintain consistency with the existing GMP data set, DTSC has confirmed that the filtration method comparative test be conducted and evaluated before modifying chromium sampling collection and preservation procedures used for the GMP. During the test period and agency review, all Cr(VI) and Cr(T) sampling will continue to be collected unfiltered and submitted for laboratory filtering, preservation, and analysis.

Well Locations for Filtration Test and Rationale

Sixteen monitoring wells are selected for this filtration methods test. Figure 1 shows the locations of the wells proposed for this test. Table 1 summarizes recent chromium, TDS, and oxidation-reduction potential (ORP) sampling data for the 16 monitoring wells. The wells were selected to evaluate Cr(VI) (using Methods SW 7199 SW 7196A) and dissolved Cr(T) test results for different areas of the site, including the floodplain, the IM extraction area, and interior site areas within and along the periphery of the chromium plume. The monitoring locations selected represent a range of TDS (high, medium, low) and ORP (reducing and oxidizing) groundwater conditions for the primary areas of the site.

The filtration method comparison test is scheduled to be conducted during the upcoming March 2005 quarterly monitoring event and subsequent April 2005 monthly monitoring event.

Sampling Methodology

Chromium samples will be collected from the selected wells during two consecutive monitoring events. Well purging and sample collection will be performed in accordance with the attached standard operating procedures (SOP): *Purging and Sampling of Groundwater Monitoring Wells, Well Volume Method* or *Purging and Sampling of 1-inch Diameter Groundwater Monitoring Wells, Modified Well Volume Method* (Attachment A).

Samples will be collected using both filtration methods from each well selected for this study. When three-casing volumes have been purged and field parameters have stabilized, a 0.45 micron in-line filter will be placed on the sample tubing and the bottles for Cr(T) and Cr(VI) will be filled and preserved in accordance with the SOP *Sample Field Filtration and Sample Preservation for Metals Analysis* (Attachment A).

After collection of the field-filtered samples, the in-line filter will be removed and a second set of sample bottles for Cr(T) and Cr(VI) will be filled and placed in an ice chest for laboratory filtration and preservation upon receipt. Both sets of samples (field-filtered and samples to be filtered and preserved by the laboratory) will be relinquished to the courier in the afternoon of the day of collection and transported to the laboratory in Tustin, California. The samples will be filtered and preserved by the laboratory chemists within 8 to 24 hours of collection. The filter size and preservatives used by the laboratory are the same as those described in the SOP *Sample Field Filtration and Sample Preservation for Metals Analysis* in Attachment A. This method is representative of the filtration and preservation procedures currently used in the GMP.

Each sample will be analyzed for dissolved Cr(T) using Method SW 6010B and Cr(VI) using either Method SW 7199 or SW 7196A (see Table 1). Descriptions of analytical methodology are included in Appendix D of the *Sampling, Analysis, and Field Procedures Manual* for the PG&E Topock program (CH2M HILL 2005).

Data Evaluation

After two rounds of sampling, 64 data points will be available for comparison and analysis, 32 for each test group. The results will be evaluated using applicable statistical analyses. The proposed data evaluation methods are discussed in Attachment B.

Schedule

The chromium sample filtration comparison is currently scheduled for the March and April 2005 GMP monitoring events, as requested by DTSC. The test results and evaluation report will be submitted to DTSC approximately six weeks after final sample collection. The report will include a summary of sampling activities, presentation of the analytical data collected during the study, summary of statistical analyses, and conclusions and recommendations. The results of the test and the appropriate sampling methodology will be incorporated into a revision of the *Monitoring Plan for Groundwater and Surface Water Monitoring Program* currently in preparation.

References

California Department of Toxic Substances Control (DTSC), 2005. Letter to PG&E. “Sampling and Analysis Plan, Groundwater and Surface Water Monitoring, dated July 14, 2004.” January 25.

CH2M HILL, 2004. *Sampling and Analysis Plan, Groundwater and Surface Water Monitoring PG&E Topock Compressor Stations Needles, California*. July 14.

CH2M HILL, 2005. *Sampling, Analysis, and Field Procedures Manual, PG&E Topock Program.* February 11. [includes SOPs and QAPP].

U. S. Environmental Protection Agency (USEPA), 1996. *Test Methods for Evaluating Solid Waste, Physical and Chemical Methods,* SW-846, 3rd Edition, Update III, Section 1. December. Includes methodology for Methods SW 7199, SW 7196A, SW 6010B.

U. S. Geological Survey (USGS), 1995. *Techniques of Water-Resources Investigations of the United States Geological Survey, Book 4 Hydraulic Analysis and Interpretation*