



**Pacific Gas and
Electric Company[®]**

Yvonne J. Meeks
Site Remediation - Portfolio Manager
Environmental Affairs

6588 Ontario Road
San Luis Obispo, CA 93405
Mailing Address
4325 South Higuera Street
San Luis Obispo, CA 93401

805.546.5243
Internal: 664.5243
Fax: 805.546.5232
E-Mail: YJM1@pge.com

May 23, 2005

Norman Shopay
Project Manager
California Department of Toxic Substances Control
Geology and Corrective Action Branch
700 Heinz Avenue, Suite 200
Berkeley, California 94710

Subject: Chromium Sample Filtration Comparison Test Report
Groundwater and Surface Water Monitoring Program
PG&E Topock Compressor Station, Needles, California

Dear Mr. Shopay:

Enclosed is the results report for the Chromium Sample Filtration Comparison Test for the Topock project. The sampling events were conducted in two separate events (March 7-11 and April 4-8 2005), and included the collection of split samples at 16 well locations during each sampling event. One set of the split samples was field filtered and preserved; the other was filtered and preserved upon receipt by the laboratory. If you have any questions on these results, please call me at (805) 546-5243.

Sincerely,

Cc: Kate Burger

Results of the Chromium Sample Filtration Comparison Test

**PG&E Topock Compressor Station
Needles, California**

Prepared for
Pacific Gas and Electric Company

May 23, 2005

CH2MHILL
155 Grand Avenue, Suite 1000
Oakland, CA 94612

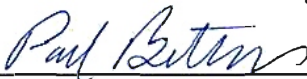
Results of Chromium Sample Filtration Test

PG&E Topock Compressor Station
Needles, California

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Pacific Gas and Electric Company

May 23, 2005

This report was prepared under supervision of a
California-Certified Engineering Geologist



Paul Bertucci, C.E.G.
Project Hydrogeologist



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Acronyms and Abbreviations

Cr(T)	total dissolved chromium
Cr(VI)	hexavalent chromium
DTSC	California Department of Toxic Substances Control
GMP	Groundwater and Surface Water Monitoring Program
IM	interim measures
mg/L	milligrams per liter
PG&E	Pacific Gas and Electric Company
PPCC	probability plot correlation coefficient
QAPP	Quality Assurance Program Plan
RFI	RCRA facility investigation
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedures
TDS	total dissolved solids
USEPA	United States Environmental Protection Agency

1.0 Introduction

This report describes the methods, results, and conclusions for the chromium sample filtration comparison study performed during March and April 2005 at the Pacific Gas and Electric Company (PG&E) Topock Compressor Station, Needles, California. The site location is depicted in Figure 1. 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 Toxic Substances Control (DTSC) is the lead agency directing and overseeing the RFI, GMP, and other corrective measures activities at the site. Since late August 2004, with DTSC approval, groundwater and surface water monitoring at the Topock site has been conducted on quarterly, monthly, and biweekly schedules following the July 2004 SAP. In February 2005, weekly well sampling was instituted at four floodplain sentry well locations (DTSC 2005a).

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 to support water quality sampling and investigation for the GMP and corrective measures studies at the Topock site.

In January 2005, DTSC provided final comments on the SAP (DTSC 2005a). DTSC's comments included the requirement for PG&E to conduct a chromium sample filtration comparative study to assess the sample filtration and preservation methodology used for hexavalent chromium [Cr(VI)] and dissolved total chromium [Cr(T)] groundwater analyses. The Work Plan for Chromium Sample Filtration Comparison Test, submitted on March 4, 2005, describes the objectives, scope, and methods for this study (CH2M HILL 2005a). The statistical methods proposed for the evaluation of data produced during the comparative study were presented in Appendix B to the Final Work Plan for Chromium Filtration Comparative Test (CH2M HILL 2005b). The Work Plan was approved by DTSC in a letter dated March 1, 2005 (DTSC 2005b).

1.1 Background

Since RFI investigations were initiated in 1997, water samples for Cr(VI) and Cr(T) have been filtered in the laboratory before analysis. Due to the Cr(VI) 24-hour holding time 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.

For the monitoring period 1997-2004, Cr(VI) has been analyzed using United States Environmental Protection Agency (USEPA) Method SW 7196A (colorimetric analytical method, with a standard, undiluted, reporting limit of 0.010 milligrams per liter [mg/L]). Beginning in September 2003, groundwater samples from wells with low concentrations of chromium are analyzed for Cr(VI) using Method SW 7199. Method 7199 is an ion chromatography method which provides a lower standard reporting limit of 0.0002 mg/L.

Dissolved Cr(T) was analyzed through 2002 using USEPA Method SW 6010A (standard reporting limit of 0.020 mg/L) and, subsequently, with USEPA Method SW 6010B (standard reporting limit 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” Cr(VI). Method SW 7196A and the supporting Chapter 3 of SW-846 do not specify a requirement for filtering samples undergoing analysis for dissolved Cr(VI) by this method. Method SW6010B allows sample filtration and preservation prior to analysis for dissolved metals but does not specify a requirement for field or laboratory filtration.

1.2 Study Objective

The objective of this sample collection procedure test is to determine if there are statistically significant differences in analytical results for groundwater samples that are filtered and preserved in the field versus filtered and preserved in the laboratory. If statistically significant differences are revealed between the two filtering methods, this study will evaluate how these differences might affect project decision-making.

There were three possible outcomes for the data generated from this comparative study:

1. There are no statistically significant 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. This is referred to as the “null hypothesis” in statistical tests.
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.

2.0 Sampling Methods for Filtration Comparative Test

As described in the work plan, the filtration methods comparative study and data evaluation proposed in the work plan involved the following steps and activities:

- A subset of GMP monitoring wells was selected for the comparative study that are representative of the range of chromium concentrations and geochemical conditions in the network of wells monitored at the Topock site.
- Duplicate Cr(VI) and Cr(T) samples were collected from the selected wells; one set was filtered and preserved in the field, and the second set was filtered and preserved by the laboratory.
- Test results were statistically evaluated to assess the significance of data variability, and then compared to the test data with the chromium data set collected under the existing GMP.

2.1 Well Locations for Filtration Test and Rationale

Sixteen monitoring wells were selected for this filtration methods test. Figure 2 shows the locations of the wells used for the study. Table 1 summarizes recent chromium, TDS, and oxidation-reduction potential sampling data for the 16 monitoring wells and presents the rationale for inclusion of each well in the study. The wells were selected to evaluate different areas of the site, including the floodplain, the Interim Measures (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 oxidation-reduction potential groundwater conditions for the primary areas of the site.

2.2 Sampling Methodology

Samples for chromium analysis were collected from the selected wells during the March 2005 quarterly and the April 2005 monthly monitoring events. Well purging and sample collection were performed in accordance with either Standard Operating Procedure (SOP) A-1 *Purging and Sampling of Groundwater Monitoring Wells, Well Volume Method* or SOP A-2, *Purging and Sampling of 1-inch Diameter Groundwater Monitoring Wells, Modified Well Volume Method*, which were included in Attachment A of the work plan (CH2M HILL 2005a). Purge forms from the field filtration study events will be provided as an attachment.

Prior to sampling, three-casing volumes were purged and field parameters stabilized, a 0.45 micron inline filter was placed on the sample tubing, and the bottles for Cr(T) and Cr(VI) were filled and preserved in accordance with the SOP A-6, *Sample Field Filtration and Sample Preservation for Metals Analysis* (CH2M HILL 2005a, Attachment A).

After collection of the field-filtered samples, the inline filter was removed, and a second set of sample bottles for Cr(T) and Cr(VI) analysis were filled for laboratory filtration and preservation upon receipt by the laboratory. Both sets of samples (field-filtered and samples to be filtered and preserved by the laboratory) were relinquished to the courier in the afternoon of the day of collection and transported to Truesdail Laboratory, Inc. in Tustin, California. The samples were 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 A-6, *Sample Field Filtration and Sample Preservation for Metals Analysis*.

Each sample was analyzed for dissolved Cr(T) using Method SW 6010B and Cr(VI) using either USEPA 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 2005c).

2.3 Deviations from the Work Plan

In the course of the March 2005 and April 2005 sampling events several deviations from the work plan occurred. Each is described below.

2.3.1 pH Degradation

During the March 2005 sampling event, the field preservation of the samples to be analyzed by USEPA Method 7199 was performed in accordance with SOP A-6. In general, after 5 ml of buffer was added in accordance with the SOP, each sample's pH measured between 9.0 and 9.5. However, the analytical laboratory reported that samples from wells MW-30-30 and MW-30-50, collected on March 9, 2005, for Cr(VI) analysis, arrived with a pH of 7. As recommended by the laboratory analyst, 12.5 ml of buffer was added to each sample, 5% by volume in a 250 ml container. After this modification, all subsequently-collected samples arrived at the laboratory within the appropriate pH range (Appendix C).

2.3.2 Field Procedure Errors

On March 8, 2005, the field crew mistakenly added nitric acid preservative to both the field-filtered and lab-filtered samples from well MW-39-50 that were to undergo analysis by Method 6010B, instead of just the field-filtered sample as required by the work plan. The error was discovered by the field sampler shortly after sample collection. Well MW-39-50 was re-sampled immediately and the samples preserved correctly.

The sample from well MW-09, collected on March 9, 2005, for Cr(VI) analysis by Method 7196A, was mistakenly preserved with nitric acid. Method 7196A does not require nitric acid preservation of samples. The error was discovered when the laboratory tested the pH of the sample before running the analysis. The well was re-sampled on March 23, 2005, to fill the data gap caused by the initial sample.

2.3.3 Missing Analysis

Lab-filtered and field-filtered samples for Cr(VI) analysis by Method 7196A and Cr (T) analysis by Method 6010B were collected from monitoring well MW-31-60 on March 9, 2005. All samples collected that day were relinquished to the courier and signed as received.

Later, it was discovered that the laboratory had lost the pair of bottles for the field-filtered sample from MW-31-60 when the laboratory final data report was delivered incomplete. Fortunately, a sample for Title 22 metals analysis by Method 6010B had also been collected at MW-31-60 on March 9, 2005, field-filtered and preserved, which was suitable for filling the Cr(T) data gap for the comparative study. However, there was no replacement sample for Method 7196A analysis for that well location during the March 2005 event.

3.0 Results

The analytical results from the field filtration comparative study are presented in Table 2. The sixteen wells were sampled twice over two events for a total of 32 samples analyzed for both Cr(VI) and Cr(T). The Cr(VI) data set is split between Method 7199 and 7196A for 16 samples each, with the exception of the missing sample from MW-31-60 described above. A statistical data evaluation is presented in Section 4.0.

3.1 Analytical Data Quality Review

The laboratory analytical data generated from the March 2005 event and the April 2005 event were independently reviewed by project chemists to assess data quality and identify deviations from analytical requirements. A detailed discussion of data quality for these samples is presented in the associated data validation reports, which are kept in the project file and are available upon request.

Holding Time Data Qualification: The hexavalent chromium analysis for samples MW-34-080-056FF, MW-39-050-060, MW-39-050-060FF, MW-30-30-060FF were analyzed just outside of hold time. The associated non-detect results in the samples were qualified as estimated and "UJ" flagged.

Quantitation and Sensitivity: Due to irregularities in laboratory analysis sensitivity criteria, the method reporting limit was raised by the laboratory for samples MW-27-085-056FF, MW-30-030-056FF, MW-30-050-056FF, MW-32-035-056FF, MW-34-080-056FF, MW-27-85-060, MW-27-85-060FF, MW-29-060, MW-30-30-060, MW-30-30-060FF, MW-34-80-060, and MW-34-80-060FF, all of which had non-detect results.

4.0 Statistical Data Evaluation

The field-filtered and laboratory-filtered data were compared using statistical analyses described in Appendix A and summarized below. These data were not evaluated for spatial distribution or temporal concentration trends.

4.1 Statistical Methods

The statistical methodology is described in detail in Appendix A. Below is a list of steps and brief descriptions of analytical methods used to evaluate the data from this study. The data from each laboratory analytical method will be evaluated separately.

1. **Test for Normality**

This test is performed to determine if the distribution of the data fit the normal, bell shaped distribution common to many sample data types. The probability plot correlation coefficient (PPCC) was calculated for each set of data to test for normality of the data set. In this instance, the differences between field and lab filtered samples were compared to their normal quantiles. The calculation produces an r value, which is an indication of the linearity of the data on a normal probability plot. The r value is compared to a critical r (r^*) from Table A1 in Appendix A. If $r > r^*$, then the data approximates normal distribution.

2. **Paired t-test**

Based on the result of the PPCC, if the differences between the field-filtered and lab-filtered data were normally distributed, the paired t-test was used to compare the data sets. The paired t-test is a common parametric analysis used to evaluate matched pairs of data. This test determines if the mean values of the paired data sets are equal. Therefore, the null hypothesis for the paired t-test is that the mean of the field-filtered data is equal to the mean of the lab-filtered data.

3. **Wilcoxon Ranked-Sum test**

If the differences between the field-filtered and lab-filtered were not normally distributed, then the Wilcoxon Ranked-Sum Test was used. This is a non-parametric test that does not require normally-distributed data. This test determines if there is a difference between the median values of the paired data. The null hypothesis for the Ranked-sum test is that the median of the field-filtered data is equal to the mean of the lab-filtered data.

The Ranked-Sum Test and the Paired t-Test were each performed as a two-tailed test at 95% confidence. In this case, an *a priori* alpha (α) of 0.1 was used for each paired analysis. The $\alpha = 0.1$ indicates 5% at each end of the two-tailed test. Probability values (p) were compared to the $\alpha = 0.1$ value to determine if the null hypothesis was rejected. Rejection of the null hypothesis indicates that there is a 95 percent chance that there is a real difference between field-filtered and laboratory-filtered data.

4.2 Data Evaluation

The data from the comparative study were separated into three categories:)1) Cr(VI) analyzed by USEPA Method 7199, (2) Cr(VI) analyzed by USEPA Method 7196A, and (3) Cr(T) analyzed by USEPA Method 6010B. Summaries of the statistical evaluations are provided in Tables 3 through 5. Tables of the complete statistical procedure are provided in Appendix B.

4.2.1 Cr(VI) Analyzed by Method 7199

During each event, eight of the well locations included in this study were sampled for Cr(VI) analysis by Method 7199. After two sampling events, the dataset consisted of 16 sets of field-filtered and lab-filtered pairs. Of those 16 sample pairs, seven were non-detect. Of the detections, three pairs showed lab-filtered results higher than the field-filtered sample, and six pairs had higher field-filtered results (Table 3).

The statistical analysis described in Section 4.1 was performed on the Method 7199 data set. The results of the analysis are summarized in Table 3. According to the PPCC, the data set was not normally distributed. Therefore, the Wilcoxon Rank Sum Test was used to compare the field-filtered and lab-filtered data. The p value resulting from the test is 1.0. This is far greater than the α value of 0.1. The null hypothesis of equal medians is preserved in this case, indicating no significant difference between field-filtered and lab-filtered samples.

4.2.2 Cr(VI) Analyzed by Method 7196A

Eight of the well locations included in this study had samples analyzed for Cr(VI) by Method 7196A. After two sampling events, data for a sample size of 15 sets of field-filtered and lab-filtered pairs were accumulated. Cr(VI) was detected in all 15 sample pairs. One pair showed lab-filtered results higher than the field-filtered sample, 10 sample pairs had higher field-filtered results, and four had no difference (Table 4).

The results of the statistical analysis are summarized on Table 4. According to the probability plot correlation coefficient, the data set was not normally distributed. Therefore the Wilcoxon Ranked-Sum test was used to compare the field-filtered and lab-filtered data. The p value resulting from the test is 0.002. This shows a high degree of confidence that there is a difference between the field-filtered and lab-filtered samples when compared to $\alpha = 0.1$. The null hypothesis of equal medians is rejected in this case, indicating that there is a significant difference between the field-filtered and lab-filtered samples.

4.2.3 Cr(T) Analyzed by Method 6010B

During each event, all 16 of the well locations included in this study were sampled for Cr(T) analysis by Method 6010B. After two sampling events, the dataset consisted of 32 field-filtered and lab-filtered pairs. Five of the sample pairs had no detection of Cr(T). Eight of the 32 pairs demonstrated higher concentrations in the lab-filtered samples while 18 samples showed higher concentrations in the field-filtered samples (Table 5). Lab-filtered samples from wells MW-30-50 and MW-27-85 were non-detect for Cr(T), but had Cr(T) detections in the field-filtered sample.

The results of the statistical analysis are summarized on Table 5. According to the PPCC, the data set was not normally distributed. Therefore the Wilcoxon Rank Sum test was used to compare the field-filtered and lab-filtered data. The p value resulting from the test is 0.09, less than the α of 0.1. The null hypothesis of equal medians is rejected in this case, indicating that there is a significant difference between the field-filtered and lab-filtered samples.

5.0 Conclusions and Recommendations

As stated in Section 1.2, the objective of this study was to determine if field filtering and preservation of chromium samples yields significantly different results when compared to laboratory filtering and preservation. Each of three chromium analytical methods was evaluated separately by comparing data from side-by-side preparation of samples from 16 wells.

5.1 Conclusions

The findings of this study are briefly described below.

1. Results for the **Cr(VI) Method 7199** analysis showed no statistically significant difference between field-filtered and preserved samples and those filtered and preserved at the lab.
2. Results for the **Cr(VI) Method 7196A** analysis showed that the field-filtered samples generally yield slightly higher results than the corresponding lab-filtered results. Statistical analysis showed that there was a significant difference between field-filtered and lab-filtered samples.
3. Results for the **Cr(T) Method 6010B** analysis showed that the field-filtered samples generally yield slightly higher results than the corresponding lab-filtered results.

5.2 Recommendations

Recommendations from the findings of this comparative test are based on two criteria:

1. Is there a significant difference in the chromium detections of the field-filtered and lab-filtered samples?
2. If there is a significant difference between the data from the sampling methods, is decision-making affected?

Results for the Cr (VI) Method 7199 analysis showed no significant difference between the samples that were field filtered and preserved and the samples that were filtered and preserved in the lab. Therefore, there would be no benefit derived from altering current sampling methods (i.e., filtration at the laboratory) for samples that undergo Cr(VI) analysis by Method 7199.

Results for Cr (VI) Method 7196A showed that field-filtered samples had slightly higher concentrations than lab-filtered samples. However, the difference of the concentrations detected would not impact project decision making for two reasons. First, the relative percent difference (RPD) between field filtered and lab filtered samples was less than 10% in all cases. The laboratory method allows up to 20% RPD analytical variability in associated quality control samples for the associated sample results to be valid; therefore, the difference between the field-filtered samples and the laboratory-filtered samples could be

considered insignificant compared to the laboratory quality control limits for Method 7196A. Second, only samples from wells with historic concentrations consistently greater than 100 µg/L are analyzed by Method 7196A. Since these wells are all well inside the plume delineated at 50 µg/L, the 10% RPD would not impact the delineation of the Cr(VI) plume. Further, it should be reiterated that EPA Method 7196A does not require filtration, either in the field or in the laboratory. Performing field filtration would represent a step beyond what is required by the EPA method.

The statistical evaluation for Cr(T) by Method 6010B showed a significant difference between field-filtered and laboratory-filtered samples. In general, the results for field-filtered samples were higher than results for the lab-filtered samples. Two samples had detections when field-filtered, but were non-detect when lab-filtered. In this case, the difference could impact the site evaluation, since samples from all wells, regardless of previous detection levels, are analyzed by this method. It is recommended that the filtration method that provides the more conservative results be used. Therefore, it is recommended that samples to be analyzed by Method 6010B be filtered and preserved in the field.

In summary, these are the recommendations derived for the data collected during the field filtration comparison test:

- Samples to be analyzed for Cr(VI) by EPA Method 7199 should continue to be filtered and preserved in the laboratory.
- Samples to be analyzed for Cr(VI) by EPA Method 7196A should also continue to be filtered in the laboratory as long as only samples from wells with historic detections greater than 100 µg/L are analyzed by this method.
- All samples to be analyzed for Cr(T) by EPA Method 6010B should be filtered and preserved in the field immediately after sample collection.

6.0 References

- California Department of Toxic Substances Control (DTSC). 2004. Letter to PG&E.
“Notification of Required Weekly Sampling and Analysis of Monitoring Well MW-33-90 and Submission of a Revised Water Quality Sampling and Analysis Plan, Pacific Gas & Electric Company, Topock Compressor Station, Needles, California.” May 3.
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Tables

Table 1
Wells Included in the Comparative Study of Sample Filtration Procedures
PG&E Topock Groundwater Monitoring, March-April 2005

Well Selected for Comparison Test		Hex. Chromium Results June-Dec 2004		Total Chromium Results June-Dec 2004		Total Dissolved Solids May-June 2004	Oxidation Reduction Potential June-Dec 2004	Rationale for Comparison Test
		Maximum Concentration mg/L	Minimum Concentration mg/L	Maximum Concentration mg/L	Minimum Concentration mg/L	maximum mg/L	Range of Measurements mV	
Wells / Locations Analyzed with Cr(VI) Method SW 7199								
MW-27-85	Floodplain	N/A (new well)		N/A (new well)		N/A (new well)	N/A (new well)	strongly reduced zone, floodplain
MW-34-80	Floodplain	ND (0.001)		0.0017	ND (0.001)	9,100	18 to -20	floodplain sentry well
MW-30-30	Floodplain	ND (0.005)		0.0017	0.0014	30,000	-74 to -207	high saline zone, shallow floodplain
MW-30-50	Floodplain	1.96	0.0262	2.07	0.0339	6,600	191 to -115	monitors Cr(VI) near aerobic/anaerobic boundary
MW-33-90	Floodplain	0.0176	0.012	0.0182	0.0120	4,800	34 to -199	low Cr(VI) concentrations, floodplain sentry well
MW-37S	Bat Cave Wash	0.0075	0.003	0.007	0.0027	2,400	16 to -60	low Cr(VI) concentrations, outside floodplain
MW-40S	Bat Cave Wash	0.0082	0.0047	0.0078	0.0047	1,200	51 to 79	low Cr(VI) concentrations, outside floodplain
MW-14	Interior	0.0336	0.0322	0.0363	0.0303	880	47 to 73	northwestern margin of chromium plume
Wells / Locations Analyzed with Cr(VI) Method SW 7196A								
MW-9	Bat Cave Wash	0.359	0.265	0.334	0.333	1,900	73 to 124	southern plume area, long sampling record
MW-12	Bat Cave Wash	1.56	1.39	1.57	1.49	2,600	26 to 67	intermediate Cr(VI) concentrations, southeastern margin of plume
MW-25	Bat Cave Wash	2.26	1.97	2.15	1.94	1,000	75 to 125	intermediate Cr(VI) concentrations, mid-plume
MW-36-100	Floodplain	2.8	1.75	2.49	1.57	9,500	-16 to -109	plume edge well, deep floodplain
MW-39-50	Floodplain	3.48	1.47	1.48	3.92	4,440	18 to -40	monitors Cr(VI) near aerobic/anaerobic boundary
MW-31-60	MW-20 Bench	3.51	3.09	3.3	3.07	1,700	80 to 85	IM extraction area, long sampling record
MW-20-70	MW-20 Bench	12.4	7.68	12.0	7.8	2,100	35 to 85	IM extraction area, high Cr(VI) shallow well
MW-20-130	MW-20 Bench	7.86	7.38	7.49	7.27	8,300	8 to 72	TW-2D extraction zone, high Cr(VI) deep well
NOTES: 1. For comparative study, duplicate set of samples collected at each location for hexavalent chromium [Cr(VI)] and total chromium [Cr(T)] analyses: sample set #1: field-filtered & preserved (FF samples), sample set #2: unfiltered/unpreserved for laboratory-filtering 2. Cr(VI) analyses by Methods SW 7199 and SW 7196A, Cr(T) analyses by Method SW 6010B 3. Concentrations in milligrams per liter (mg/L), ND = not detected at listed reporting limit, millivolts (mV)								

Table 2
Groundwater Chromium Sampling Results
Field Filtration Study
PG&E Topock, Groundwater Monitoring Program

Well ID	Sample Date	Hexavalent Chromium (SW7199)		Hexavalent Chromium (SW7196A)		Dissolved Total Chromium (SW6010B)	
		µg/L		µg/L		µg/L	
		Field Filtered ¹	Lab Filtered	Field Filtered ²	Lab Filtered	Field Filtered ⁴	Lab Filtered
MW-09	3/8/2005	---	---	338	343 ³	343	316
MW-09	4/7/2005	---	---	364	338	401	318
MW-12	3/10/2005	---	---	952	925	879	883
MW-12	4/6/2005	---	---	862	810	898	871
MW-14	3/9/2005	31.5	32.0	---	---	33.6	32.5
MW-14	4/7/2005	30.9	34.3	---	---	46.9	38.0
MW-20-070	3/10/2005	---	---	8570	8280	8020	8630
MW-20-070	4/7/2005	---	---	9190	8740	10200	9020
MW-20-130	3/9/2005	---	---	8920	8730	8630	8900
MW-20-130	4/7/2005	---	---	9420	8980	10500	8870
MW-25	3/9/2005	---	---	1740	1740	1590	1600
MW-25	4/7/2005	---	---	1670	1620	1640	1700
MW-27-085	3/8/2005	ND (1.0)	ND (2.0)	---	---	17.9	ND (1.0)
MW-27-085	4/5/2005	ND (1.0)	ND (1.0)	---	---	ND (1.0)	ND (1.0)
MW-30-030	3/10/2005	ND (5.0) ⁵	ND (5.0)	---	---	ND (1.0)	ND (1.0)
MW-30-030	4/6/2005	ND (2.0) J	ND (2.0)	---	---	ND (1.0)	ND (1.0)
MW-30-050	3/10/2005	ND (1.0) ⁵	ND (1.0)	---	---	3.70	ND (1.0)
MW-30-050	4/6/2005	28.5	18.5	---	---	35.2	15.5
MW-31-060	3/9/2005	---	---	---	2700 ⁶	2590	2550
MW-31-060	4/7/2005	---	---	1990	1910	2120	2030
MW-33-090	3/9/2005	19.4	18.6	---	---	20.2	18.2
MW-33-090	4/4/2005	20.5	21.3	---	---	17.0	17.2
MW-34-080	3/8/2005	ND (1.0) J	ND (1.0) J	---	---	ND (1.0)	ND (1.0)
MW-34-080	4/5/2005	ND (1.0)	ND (1.0)	---	---	ND (1.0)	ND (1.0)
MW-36-100	3/9/2005	---	---	1380	1380	1220	1200
MW-36-100	4/4/2005	---	---	1140	1110	921	981
MW-37S	3/11/2005	7.60	7.40	---	---	6.40	5.40
MW-37S	4/7/2005	6.30	5.90	---	---	5.90	5.40
MW-39-050	3/9/2005	---	---	422	422	412	372
MW-39-050	4/6/2005	---	---	282 J	282 J	396	237
MW-40S	3/10/2005	5.60	5.50	---	---	4.80	5.50
MW-40S	4/7/2005	4.70	4.60	---	---	4.70	4.40

Table 2
Groundwater Chromium Sampling Results
Field Filtration Study
PG&E Topock, Groundwater Monitoring Program

Notes:

- ¹ Field filtered samples analyzed by EPA Method 7199 were preserved with (NH₄)₂ SO₄/NH₄OH buffer to pH range of 9.0-9.5
- ² Field filtered samples analyzed by EPA Method 7196A were not preserved
- ³ Due to a sample preservation error during the 3/8/05 sampling event monitoring well MW-09 was resampled on 3/23
- ⁴ Field filtered samples analyzed by EPA Method 6010B were preserved with HNO₃ to pH<2
- ⁵ Samples for hexavalent chromium analysis from wells MW-30-030 and MW-30-050 collected on March 10, 2005, arrived at the laboratory with pH outside the 9.0-9.5 range. Additional buffer was added by the laboratory.
- ⁶ The sample for hexavalent chromium analysis from well MW-31-060 collected on March 9, 2005, was misplaced by the laboratory.

µg/L = micrograms per liter

ND = not detected at listed reporting limit

J = concentration or RL estimated by laboratory or data validation

Table 3
Statistical Analysis Summary for the Method 7199 Analysis
Comparison Test of Sample Filtration Procedures
PG&E Topock, Groundwater Monitoring Program

Well ID	Sample Date	Field Filtered µg/L	Lab Filtered µg/L	Difference µg/L	Relative Percent Difference (RPD) %
MW-14	3/9/2005	31.5	32.0	-0.5	2%
MW-14	4/7/2005	30.9	34.3	-3.4	10%
MW-27-085	3/8/2005	ND (1.0)	ND (2.0)	-0.5	67%
MW-27-085	4/5/2005	ND (1.0)	ND (1.0)	0.0	0%
MW-30-030	3/10/2005	ND (5.0)	ND (5.0)	0.0	0%
MW-30-030	4/6/2005	ND (2.0) J	ND (2.0)	0.0	0%
MW-30-050	3/10/2005	ND (1.0)	ND (1.0)	0.0	0%
MW-30-050	4/6/2005	28.5	18.5	10.0	43%
MW-33-090	3/9/2005	19.4	18.6	0.8	4%
MW-33-090	4/4/2005	20.5	21.3	-0.8	4%
MW-34-080	3/8/2005	ND (1.0) J	ND (1.0) J	0.0	0%
MW-34-080	4/5/2005	ND (1.0)	ND (1.0)	0.0	0%
MW-37S	3/11/2005	7.60	7.40	0.2	3%
MW-37S	4/7/2005	6.30	5.90	0.4	7%
MW-40S	3/10/2005	5.60	5.50	0.1	2%
MW-40S	4/7/2005	4.70	4.60	0.1	2%

Notes:

µg/L = micrograms per liter
ND = not detected at listed reporting limit.
J = concentration or RL estimated by laboratory or data validation
RPD = [field filtered]-[lab filtered] / ([lab filtered]+[field filtered])/2
1/2 of the reporting limit used for nondetect values

Statistical Results Summary

The Probability Plot Correlation Coefficient (PPCC)

r = 0.61
r* = 0.94

Conclusion: Non-Normal Distribution; Use Signed-Rank Test

Signed-Rank Test

α = 0.1 (95% confidence for two tailed test)
W+ = 27
p = 1.0

p > α , therefore Ho is not rejected

Conclusion: There is no significant difference between FF and LF samples

Table 4
Statistical Analysis Summary for the Method 7196A Analysis
Comparison Test of Sample Filtration Procedures
PG&E Topock, Groundwater Monitoring Program

Well ID	Sample Date	Field Filtered µg/L	Lab Filtered µg/L	Difference µg/L	Relative Percent Difference (RPD) %
MW-09	3/23/2005	338 ¹	343	-5	1%
MW-09	4/7/2005	364	338	26	7%
MW-12	3/10/2005	952	925	27	3%
MW-12	4/6/2005	862	810	52	6%
MW-20-070	3/10/2005	8570	8280	290	3%
MW-20-070	4/7/2005	9190	8740	450	5%
MW-20-130	3/9/2005	8920	8730	190	2%
MW-20-130	4/7/2005	9420	8980	440	5%
MW-25	3/9/2005	1740	1740	0	0%
MW-25	4/7/2005	1670	1620	50	3%
MW-31-060	4/7/2005	1990	1910	80	4%
MW-36-100	3/9/2005	1380	1380	0	0%
MW-36-100	4/4/2005	1140	1110	30	3%
MW-39-050	3/9/2005	422	422	0	0%
MW-39-050	4/6/2005	282 J	282 J	0	0%

Notes:

µg/L = micrograms per liter

J = concentration or RL estimated by laboratory or data validation

RPD = $[\text{field filtered}] - [\text{lab filtered}] / ([\text{lab filtered}] + [\text{field filtered}]) / 2$

1/2 of the reporting limit used for nondetect values

¹ Due to a sample preservation error during the 3/8/05 sampling event monitoring well MW-09 was resampled on 3/23

Statistical Results Summary

The Probability Plot Correlation Coefficient (PPCC)

r = 0.84

r* = 0.94

Conclusion: Non-Normal Distribution; Use Signed-Rank Test

Signed-Rank Test

α = 0.1 (95% confidence for two tailed test)

W+ = 65.0

p = 0.002

p < α, therefore Ho is rejected

Conclusion: There is a significant difference between FF and LF samples

Table 5
Statistical Analysis Summary for the Method 6010B Analysis
Comparison Test of Sample Filtration Procedures
PG&E Topock, Groundwater Monitoring Program

Well ID	Sample Date	Field Filtered µg/L	Lab Filtered µg/L	Difference µg/L	Relative Percent Difference (RPD) %
MW-09	3/8/2005	343	316	27	8%
MW-09	4/7/2005	401	318	83	23%
MW-12	3/10/2005	879	883	-4	0%
MW-12	4/6/2005	898	871	27	3%
MW-14	3/9/2005	33.6	32.5	1.1	3%
MW-14	4/7/2005	46.9	38.0	8.9	21%
MW-20-070	3/10/2005	8020	8630	-610	7%
MW-20-070	4/7/2005	10200	9020	1180	12%
MW-20-130	3/9/2005	8630	8900	-270	3%
MW-20-130	4/7/2005	10500	8870	1630	17%
MW-25	3/9/2005	1590	1600	-10	1%
MW-25	4/7/2005	1640	1700	-60	4%
MW-27-085	3/8/2005	17.9	ND (1.0)	17.4	189%
MW-27-085	4/5/2005	ND (1.0)	ND (1.0)	0	0%
MW-30-030	3/10/2005	ND (1.0)	ND (1.0)	0	0%
MW-30-030	4/6/2005	ND (1.0)	ND (1.0)	0	0%
MW-30-050	3/10/2005	3.70	ND (1.0)	3.2	152%
MW-30-050	4/6/2005	35.2	15.5	19.7	78%
MW-31-060	3/9/2005	NA	2550	NA	NA
MW-31-060	4/7/2005	2120	2030	90	4%
MW-33-090	3/9/2005	20.2	18.2	2	10%
MW-33-090	4/4/2005	17.0	17.2	-0.2	1%
MW-34-080	3/8/2005	ND (1.0)	ND (1.0)	0	0%
MW-34-080	4/5/2005	ND (1.0)	ND (1.0)	0	0%
MW-36-100	3/9/2005	1220	1200	20	2%
MW-36-100	4/4/2005	921	981	-60	6%
MW-37S	3/11/2005	6.40	5.40	1	17%
MW-37S	4/7/2005	5.90	5.40	0.5	9%
MW-39-050	3/9/2005	412	372	40	10%
MW-39-050	4/6/2005	396	237	159	50%
MW-40S	3/10/2005	4.80	5.50	-0.7	14%
MW-40S	4/7/2005	4.70	4.40	0.3	7%

Notes:

µg/L = micrograms per liter

ND = not detected at listed reporting limit

RPD = $[(\text{field filtered}) - (\text{lab filtered})] / ((\text{lab filtered}) + (\text{field filtered})) / 2$

1/2 of the reporting limit used for nondetect values

Table 5
Statistical Analysis Summary for the Method 6010B Analysis
Comparison Test of Sample Filtration Procedures
PG&E Topock, Groundwater Monitoring Program

Statistical Results Summary

The Probability Plot Correlation Coefficient (PPCC)

$r = 0.59$
 $r^* = 0.97$

Conclusion: Non-Normal Distribution; Use Signed-Rank Test

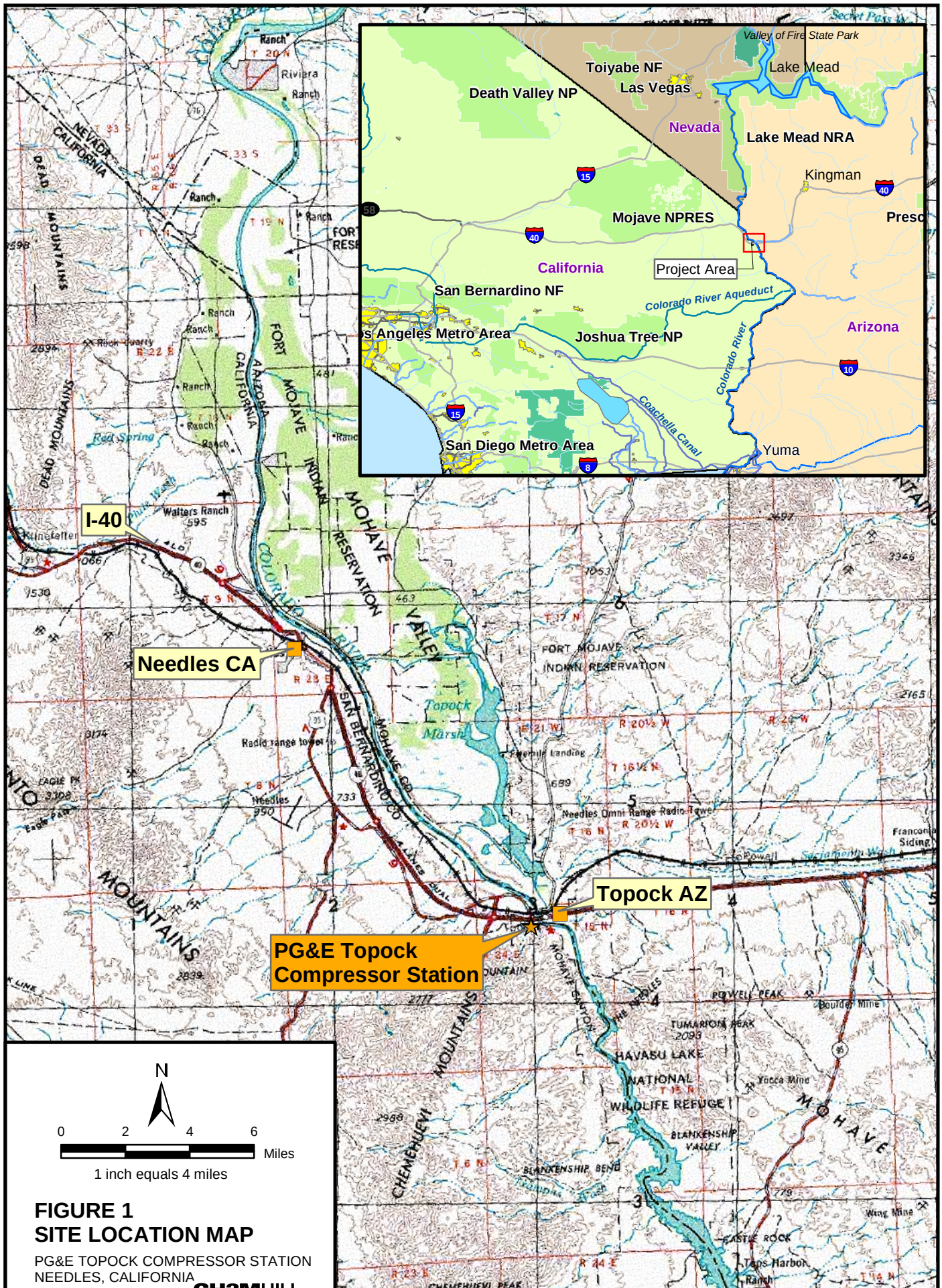
Signed-Rank Test

$\alpha = 0.1$ (95% confidence for two tailed test)
 $W+ = 265.5$
 $p = 0.09$

$p < \alpha$, therefore H_0 is rejected

Conclusion: There is a significant difference between FF and LF samples

Figures



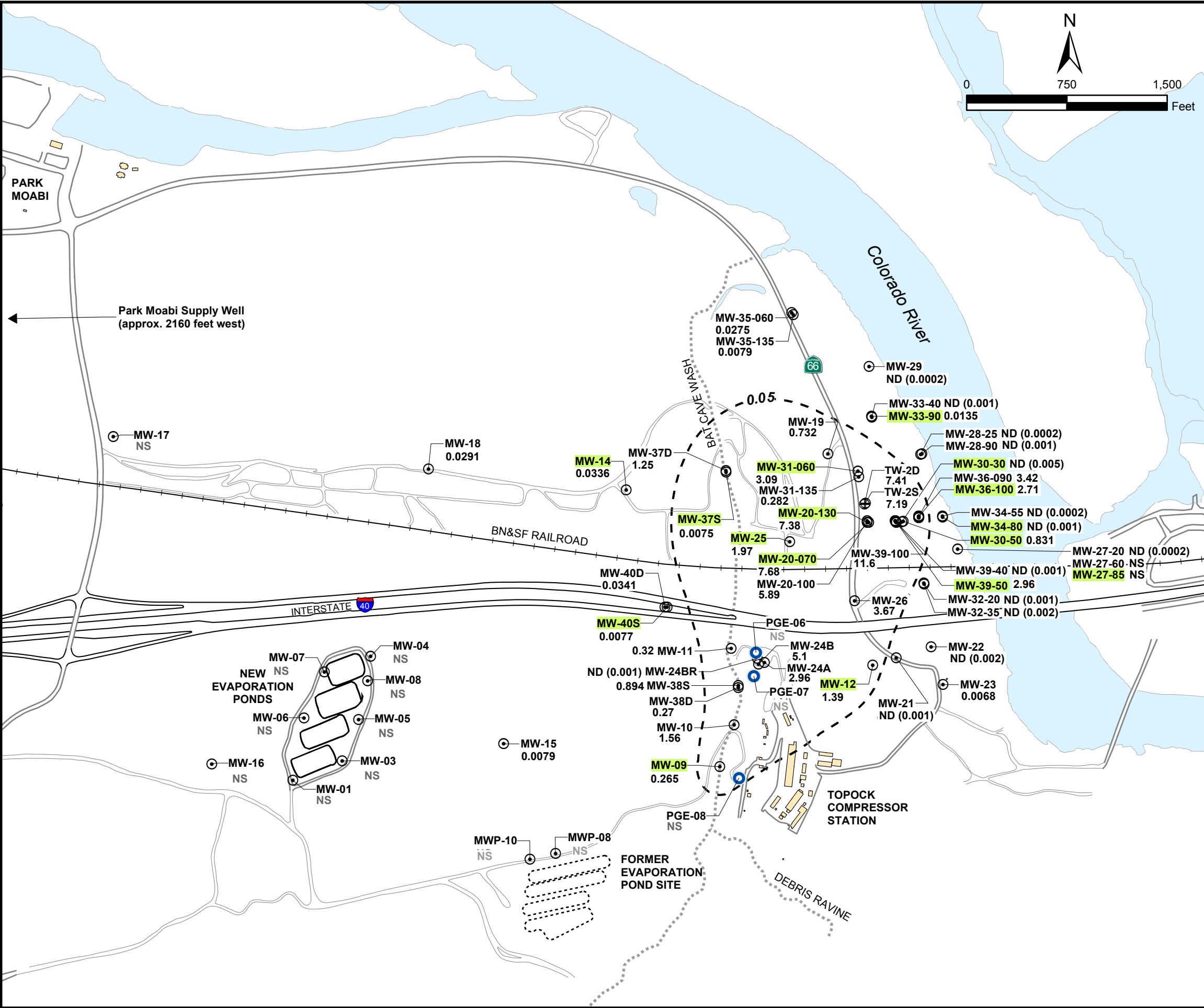


FIGURE 2
WELL LOCATIONS SAMPLED FOR CHROMIUM FILTRATION COMPARISON TEST, MARCH - APRIL 2005

GROUNDWATER MONITORING PROGRAM
PG&E TOPOCK COMPRESSOR STATION
NEEDLES, CALIFORNIA

CH2MHILL

Appendix A

Statistical Methods

Statistical Data Evaluation

A1. Introduction

PG&E performed a filtration comparative study in March and April 2005 in accordance with the Work Plan for the Chromium Sample Filtration Comparison Test, PG&E Topock Groundwater Monitoring Program (CH2M HILL, 2005). The Study was conducted in response to DTSC comments on the *Sampling and Analysis Plan, Groundwater and Surface Water Monitoring* (SAP) (CH2M HILL 2004) regarding the filtration and preservation of hexavalent and dissolved chromium samples. Duplicate samples were collected from 16 selected wells for Cr(VI) and Cr(T); one set to be filtered and preserved in the field, and the second set to be filtered and preserved by the laboratory. These samples were collected during two consecutive monthly sampling events. Samples were collected in accordance with the *Sampling, Analysis, and Field Procedures Manual* (CH2M HILL, 2005). This Attachment describes the statistical methodology to be used to evaluate the data from the filtration comparative study. The statistical tools that will be used are described in the *Techniques of Water-Resources Investigations of the United States Geological Survey, Book 4 Hydraulic Analysis and Interpretation* (USGS 1995).

A2. Data Evaluation

The comparative study generated three groups of data that will be evaluated independently; 1) hexavalent chromium analyzed by EPA Method SW7199, 2) hexavalent chromium analyzed by EPA Method SW7196A, and 3) total dissolved chromium analyzed by EPA Method 6010B. For each group the results from the field filtered and preserved samples will be compared to the data from the laboratory filtered and preserved samples.

The applicability of the statistical analyses will be determined using the stepwise approach. The statistical analysis that will be used will be based on the distribution of the data. If the data are normally distributed, then the paired t-test will be used. If the data are not normally distributed, then the Wilcoxon Signed-Rank Test will be used to determine if there is a statistically significant difference between the data sets. Normality will be determined by calculating the correlation coefficient.

The paired t-test is a common parametric analysis used to evaluate matched pairs of data. The test requires the normal distribution of data. The Wilcoxon signed-rank test is a nonparametric test used to determine whether the median difference between paired observations is zero. As a nonparametric test, the sign rank test is a good alternative to the paired t-test when the data distribution is not normal.

A3. Statistical Methodology

Normality will be determined using the probability plot correlation coefficient. The linearity will be tested by computing the correlation coefficient (r) between the data and their normal quantiles. For this test the closer the data are to normal distribution, the r will approach 1.0. The calculated r value will be compared to the critical r* on Table B-1. If it is

smaller than r^* , then the normality is rejected. If r is greater than or equal to r^* then the data set will be treated as normally distributed.

Paired t-Test

In the case of normally distributed data, the paired t-test will be used to compare field filtered and lab filtered sample data. This tests the hypothesis that two sets of data have the same mean assuming they have the same variance and shape. This null hypothesis is stated:

$H_0: \mu_x = \mu_y$, or the mean of group x is equal to the mean of group y

The alternative hypotheses are:

$H_1: \mu_x \neq \mu_y$, or the two groups have different mean values

$H_2: \mu_x > \mu_y$, or the mean of group x is greater than the mean of group y

$H_3: \mu_x < \mu_y$, or the mean of group y is greater than the mean of group x

Since there is no prior expectation of whether group x or y might be higher, alternative hypothesis H_1 will be used to evaluate the data for this study.

The paired t-statistic is computed by:

- 1) the differences between paired observations are computed
$$x_i - y_i = D_i$$
- 2) Compute the sample mean (μ_D) of the differences.
- 3) Compute the sample standard deviation (s) of the differences
- 4) The paired t-statistic is calculated: $t_p = (\mu_D \sqrt{n})/s$
- 5) Reject H_0 if $T_p < -t_{(1-\alpha/2), (n-1)}$ or $t_p > t_{(1-\alpha/2), (n-1)}$ from the t distribution table (Table B-2). For 95% confidence $\alpha = 0.05$.

The Signed-Rank Test

The signed-rank test will be used to compare the results from field filtered and lab filtered data if they are not normally distributed. This test compares the median difference between paired observations.

The Null hypothesis is that the median difference is zero'

$H_0: \text{median}[D] = 0$

Same as the paired t-test above, the alternate hypothesis was determined with no prior expectation of whether field filtered data are higher or lower than lab filtered data.

Therefore, the alternate hypothesis is stated:

$H_1: \text{median}[D] \neq 0$

The signed rank test is computed by:

- 1) Compute the absolute differences $|D_i|$, between paired data
- 2) Rank the $|D_i|$ from smallest to largest. If $D_i = 0$ then disregard the sample pair. If two non-zero differences are tied, assign the average rank to each difference involved in the tie.
- 3) Compute the signed rank

$$R_i = + \text{rank of } |D_i| \text{ for } D_i > 0$$

$$R_i = - \text{rank of } |D_i| \text{ for } D_i < 0$$
- 4) The test statistic (W^+) is the sum of all signed ranks having a positive sign.
- 5) H_0 is rejected if $W^+ \geq \alpha/2, n$ or $W^+ \leq -\alpha/2, n$ from Table B-3. Otherwise to not reject H_0

Decision Criteria

In the case of either the paired t-test or the rank-sum test, if the null hypothesis is rejected, then there is 95% probability that differences observed between field filtered and preserved samples and lab filtered and preserved samples are not due to random error. In that case, the current sampling procedures will have to be re-evaluated.

If the null hypothesis is not rejected, than there is no statistically significant difference between the results of the field filtered data set and the lab filtered data set.

Table A-1

Critical r^* Values for the Probability Plot Correlation Coefficient Test of Normality

Work Plan for Chromium Sample Filtration Comparison Test

PGE Topock Groundwater Monitoring Program

n	α -level					
	0.005	0.01	0.025	0.05	0.1	0.25
3	0.867	0.869	0.872	0.879	0.891	0.924
4	0.813	0.824	0.846	0.868	0.894	0.931
5	0.807	0.826	0.856	0.88	0.903	0.934
6	0.82	0.838	0.866	0.888	0.91	0.939
7	0.828	0.85	0.877	0.898	0.918	0.944
8	0.84	0.861	0.887	0.906	0.924	0.948
9	0.854	0.871	0.894	0.912	0.93	0.952
10	0.862	0.879	0.901	0.918	0.934	0.954
11	0.87	0.886	0.907	0.923	0.938	0.957
12	0.876	0.892	0.912	0.928	0.942	0.96
13	0.885	0.899	0.918	0.932	0.945	0.962
14	0.89	0.905	0.923	0.935	0.948	0.964
15	0.896	0.91	0.927	0.939	0.951	0.965
16	0.899	0.913	0.929	0.941	0.953	0.967
17	0.905	0.917	0.932	0.944	0.954	0.968
18	0.908	0.92	0.935	0.946	0.957	0.97
19	0.914	0.924	0.938	0.949	0.958	0.971
20	0.916	0.926	0.94	0.951	0.96	0.972
21	0.918	0.93	0.943	0.952	0.961	0.973
22	0.932	0.933	0.945	0.954	0.963	0.974
23	0.925	0.935	0.947	0.956	0.964	0.975
24	0.927	0.937	0.949	0.957	0.965	0.976
25	0.929	0.939	0.951	0.959	0.966	0.976
26	0.932	0.941	0.952	0.96	0.967	0.977
27	0.934	0.943	0.953	0.961	0.968	0.978
28	0.936	0.944	0.955	0.962	0.969	0.978
29	0.939	0.946	0.956	0.963	0.97	0.979
30	0.939	0.947	0.957	0.964	0.971	0.979
31	0.942	0.95	0.958	0.965	0.972	0.98
32	0.943	0.95	0.959	0.966	0.972	0.98
33	0.944	0.951	0.961	0.967	0.973	0.981
34	0.946	0.953	0.962	0.968	0.974	0.981
35	0.947	0.954	0.962	0.969	0.974	0.982
36	0.948	0.955	0.963	0.969	0.975	0.982
37	0.95	0.956	0.964	0.97	0.976	0.983
38	0.951	0.957	0.965	0.971	0.976	0.983
39	0.951	0.958	0.966	0.971	0.977	0.983
40	0.953	0.959	0.966	0.972	0.977	0.984

Note: This table is derived from Table B1 in

Geological Survey, Book 4 Hydraulic Analysis and Interpretation (USGS 1995)

Table A-2
Percentage Points of the t-Distribution
Work Plan for Chromium Sample Filtration Comparison Test
PGE Topock Groundwater Monitoring Program

	α	0.4	0.25	0.1	0.05	0.025	0.01	0.005	0.0005
df									
1		0.32492	1	3.077684	6.313752	12.7062	31.82052	63.65674	636.6192
2		0.288675	0.816497	1.885618	2.919986	4.30265	6.96456	9.92484	31.5991
3		0.276671	0.764892	1.637744	2.353363	3.18245	4.5407	5.84091	12.924
4		0.270722	0.740697	1.533206	2.131847	2.77645	3.74695	4.60409	8.6103
5		0.267181	0.726687	1.475884	2.015048	2.57058	3.36493	4.03214	6.8688
6		0.264835	0.717558	1.439756	1.94318	2.44691	3.14267	3.70743	5.9588
7		0.263167	0.711142	1.414924	1.894579	2.36462	2.99795	3.49948	5.4079
8		0.261921	0.706387	1.396815	1.859548	2.306	2.89646	3.35539	5.0413
9		0.260955	0.702722	1.383029	1.833113	2.26216	2.82144	3.24984	4.7809
10		0.260185	0.699812	1.372184	1.812461	2.22814	2.76377	3.16927	4.5869
11		0.259556	0.697445	1.36343	1.795885	2.20099	2.71808	3.10581	4.437
12		0.259033	0.695483	1.356217	1.782288	2.17881	2.681	3.05454	4.3178
13		0.258591	0.693829	1.350171	1.770933	2.16037	2.65031	3.01228	4.2208
14		0.258213	0.692417	1.34503	1.76131	2.14479	2.62449	2.97684	4.1405
15		0.257885	0.691197	1.340606	1.75305	2.13145	2.60248	2.94671	4.0728
16		0.257599	0.690132	1.336757	1.745884	2.11991	2.58349	2.92078	4.015
17		0.257347	0.689195	1.333379	1.739607	2.10982	2.56693	2.89823	3.9651
18		0.257123	0.688364	1.330391	1.734064	2.10092	2.55238	2.87844	3.9216
19		0.256923	0.687621	1.327728	1.729133	2.09302	2.53948	2.86093	3.8834
20		0.256743	0.686954	1.325341	1.724718	2.08596	2.52798	2.84534	3.8495
21		0.25658	0.686352	1.323188	1.720743	2.07961	2.51765	2.83136	3.8193
22		0.256432	0.685805	1.321237	1.717144	2.07387	2.50832	2.81876	3.7921
23		0.256297	0.685306	1.31946	1.713872	2.06866	2.49987	2.80734	3.7676
24		0.256173	0.68485	1.317836	1.710882	2.0639	2.49216	2.79694	3.7454
25		0.25606	0.68443	1.316345	1.708141	2.05954	2.48511	2.78744	3.7251
26		0.255955	0.684043	1.314972	1.705618	2.05553	2.47863	2.77871	3.7066
27		0.255858	0.683685	1.313703	1.703288	2.05183	2.47266	2.77068	3.6896
28		0.255768	0.683353	1.312527	1.701131	2.04841	2.46714	2.76326	3.6739
29		0.255684	0.683044	1.311434	1.699127	2.04523	2.46202	2.75639	3.6594
30		0.255605	0.682756	1.310415	1.697261	2.04227	2.45726	2.75	3.646

Table A-3

Critical test Statistic Values for the Sign Rank Statistic W^+
 Work Plan for Chromium Sample Filtration Comparison Test
 PGE Topock Groundwater Monitoring Program

Reject H_0 : when W^+ is $\leq$ table entry (small W)

n	α -level			
	0.005	0.01	0.025	0.05
5				0
6			0	2
7		0	2	3
8	0	1	3	5
9	1	3	5	8
10	3	5	8	10
11	5	7	10	13
12	7	9	13	17
13	9	12	17	21
14	12	15	21	25
15	15	19	25	30
16	19	23	29	35
17	23	27	34	41
18	27	32	40	47
19	32	37	46	53
20	37	43	52	60

Reject H_0 : when W^+ is $\geq$ table entry (Large W)

n	α -level			
	0.005	0.01	0.025	0.05
5				15
6			21	19
7		28	26	25
8	36	35	33	31
9	44	42	40	37
10	52	50	47	45
11	61	59	56	53
12	71	69	65	61
13	82	79	74	70
14	93	90	84	80
15	105	101	95	90
16	117	113	107	101
17	130	126	119	112
18	144	139	131	124
19	158	153	144	137
20	173	167	158	150

Note: This table is derived from Table B1 in
Geological Survey, Book 4 Hydraulic Analysis and Interpretation (USGS 1995)

Appendix B

Statistical Evaluation Calculations

Table B-1
Statistical Evaluation for EPA Method 7199
Comparison Test of Sample Filtration Procedure
PG&E Topock, Groundwater Monitoring Program

Correlation Coefficient

n	D
1	-3.4
2	-1
3	-0.8
4	-0.5
5	0
6	0
7	0
8	0
9	0
10	0
11	0
12	0.1
13	0.1
14	0.2
15	0.4
16	0.8
17	10
r =	0.613
r* =	0.944

Conclusion: Non-Normal Distribution; Use Signed-Rank Test

Signed-Rank Test

D	 D 	Remove Zeros	Ranked Order	Rank	Rank Sum
-3.4	3.4	0.0034	0.0001	1	1
-1	1	0.001	0.0001	2	2
-0.8	0.8	0.0008	0.0002	3	3
-0.5	0.5	0.0005	0.0004	4	4
0	0	0.0001	0.0005	5	
0	0	0.0001	0.0008	6	
0	0	0.0002	0.0008	7	7
0	0	0.0004	0.001	8	
0	0	0.0008	0.0034	9	
0	0	0.01	0.01	10	10
0	0				
0.1	0.1				
0.1	0.1				
0.2	0.2				
0.4	0.4				
0.8	0.8				
10	10				
				W+ =	27
				W(table)	45
				p =	1.0

W+ < W(table)

Conclusion: There is no significant difference between FF and LF samples
at 95% confidence ($\alpha = 0.1$)

Table B-2
Statistical Evaluation for EPA Method 7196
Comparison Test of Sample Filtration Procedure
PG&E Topock, Groundwater Monitoring Program

Correlation Coefficient

n	D
1	-5
2	0
3	0
4	0
5	0
6	26
7	27
8	30
9	50
10	52
11	80
12	190
13	290
14	440
15	450
r =	0.840
r* =	0.939

Conclusion: Non-Normal Distribution; Use Signed Rank Test

D	 D 	Remove Zeros	Ranked Order	Rank	rank sum
-5	5	0.005	0.005	1	
0	0	0.026	0.026	2	2
0	0	0.027	0.027	3	3
0	0	0.03	0.03	4	4
0	0	0.05	0.05	5	5
26	26	0.052	0.052	6	6
27	27	0.08	0.08	7	7
30	30	0.19	0.19	8	8
50	50	0.29	0.29	9	9
52	52	0.44	0.44	10	10
80	80	0.45	0.45	11	11
190	190			W+ =	65.0
290	290			W(table)	53
440	440			p =	0.002
450	450				

W+ > W(table)

**Conclusion: There is a significant difference between FF and LF samples
at 95% confidence ($\alpha = 0.1$)**

Table B-3
Statistical Evaluation for EPA Method 6010B
Comparison Test of Sample Filtration Procedure
PG&E Topock, Groundwater Monitoring Program

Correlation Coefficient

n	Difference
1	-610
2	-270
3	-60
4	-60
5	-10
6	-4
7	-0.7
8	-0.2
9	0
10	0
11	0
12	0
13	0
14	0.3
15	0.5
16	1
17	2
18	2.7
19	4.1
20	8.9
21	16.9
22	19.7
23	20
24	27
25	27
26	40
27	40
28	83
29	90
30	159
31	1180
32	1630

Correlation Coefficient

$r =$ 0.58
 $r^* =$ 0.97

Conclusion: Non-Normal Distribution; Use Signed Rank Test

Signed-Rank Test

D	D	Remove Zeros	Ranked Order	Rank	rank sum
27	27	27	0.2	1.0	
83	83	83	0.3	2.0	2
-4	4	4	0.5	3.0	3
27	27	27	0.7	4.0	
4.1	4.1	4.1	1	5.0	5
8.9	8.9	8.9	2	6.0	6
-610	610	610	2.7	7.0	7
1180	1180	1180	4	8.0	
-270	270	270	4.1	9.0	9
1630	1630	1630	8.9	10.0	10
-10	10	10	10	11.5	
-60	60	60	16.9	11.5	11.5
16.9	16.9	16.9	19.7	13.0	13
0	0	2.7	20	14.0	14
0	0	19.7	27	15.5	15
0	0	40	27	15.5	16
2.7	2.7	90	40	17.0	17
19.7	19.7	2	40	18.0	18
40	40	0.2	60	19.5	
90	90	20	60	19.5	
2	2	60	83	21.0	21
-0.2	0.2	1	90	22.0	22
0	0	0.5	159	23.0	23
0	0	40	270	24.0	
0	0	159	610	25.0	
20	20	0.7	1180	26.0	26
-60	60	0.3	1630	27	27
1	1			W+ =	265.5
0.5	0.5				
40	40				
159	159				
-0.7	0.7				
0.3	0.3				

Large Scale Approximation

$$W^+ = 265.5$$

$$\mu_W = 189$$

$$\sigma_W = 41.62331078$$

$$\mu_W = n(n+1)/4$$

$$\sigma_W = \sqrt{n(n+1)(2n+1)/24}$$

$$Z_{sr+} = 1.825899924$$

p (from table of normal distribution) = 0.07

$$\alpha = 0.1$$

$$Z_{sr+} = \frac{W - 0.5 - \mu_W}{\sigma_W}$$

$p \leq \alpha$. Therefore, H_0 is rejected. There is a significant difference between FF v. LF data

Appendix C

pH Summary Table

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~~Mark Binger~~Company: CH2M HillFax No.: (510) 622-9210From: Charles MorrowDate: 4/11/05No. of Pages: 6

Including cover page.

Hard Copy to Follow? Yes: X No: Comments: Shawn,pH values for Hex Cr, by 7199, and Tot Diss Cr for FF samples collected in
March plus for last week. Note for Hex Cr beginning with samples
analyzed last week, the pH data will be included in a spread sheet
with the Hex Cr raw data.Please let me know if you have any questions.Charles Morrow**Confidentiality Notice:**

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pH record for field filtered samples

CH2M Hill Samples

EPA Method 7199

TLI Sample No.	Date Sampled	CH2M Hill Number	Incoming pH	Adjustment	Comments
940538-9	3/8/05	MW-9-056	ok		
940541-3	3/8/05	MW-27-085-056FF	ok		
940541-4	3/8/05	MW-34-080-056FF	ok		
940586-2	3/9/05	MW-20-130-056FF	ok		
940588-3	3/9/05	MW-32-035-056FF	ok		
940588-7	3/9/05	MW-33-090-056FF	ok		
940588-9	3/9/05	MW-36-100-056FF	ok		
940591-5	3/9/05	MW-14-056FF	ok		
940619-1	3/10/05	MW-40S-056FF	ok		
940622-4	3/10/05	MW-30-030-056FF	Low	add NH4OH	
940622-5	3/10/05	MW-30-030-056FF	Low	add NH4OH	
940663-3	3/11/05	MW-37S-056FF	ok		

pH record for field filtered samples

CH2M Hill Samples

Metals/Mercury

TLI Sample No.	Date Sampled	CH2M Hill Number	Cr		Hg	T22 Met	Adjustment	Comments
			FF	LF				
940462-1 met	3/7/05	MW-43-025-055	7			2		
940462-3 met	3/7/05	MW-43-075-055	7			2		
940462-4 met	3/7/05	MW-43-090-055	7			2		
940538-6 met/hg	3/8/05	MW-11-056	7		2	2		
940538-7 met/hg	3/8/05	MW-10-056	7		2	2		
940538-8 met/hg	3/8/05	MW-90-056	7		2	2		
940538-9 met	3/8/05	MW-9-056	2					
940541-2 met/hg	3/8/05	MW-34-080-056			2	2		
940541-3 met	3/8/05	MW-27-085-056FF	2					
940541-4 met	3/8/05	MW-27-080-056FF	2					
940586-1 met/hg	3/9/05	MW-20-130-056	7		2	2		
940586-2 met	3/9/05	MW-20-130-056FF	7		2	2		

pH record for field filtered samples

CH2M Hill Samples

Metals/Mercury

TLI Sample No.	Date Sampled	CH2M Hill Number	Cr FF	Cr LF	Hg	Met	Adjustment	Comments
940586-3 met/hg	3/9/05	MW-93-056			2	7		T22 metals bottle, pH adjust
940588-3 met	3/9/05	MW-32-035-056FF	2					
940588-7 met	3/9/05	MW-33-090-056FF	2					
940588-9 met	3/9/05	MW-36-100-056FF	2					
940589-4 met	3/9/05	MW-39-050-056		7				
940589-9 met	3/9/05	MW-39-050-056FF	2					
940591-4met	3/9/05	MW-14-056		7				
940591-5 met	3/9/05	MW-14-056FF	2					
940591-6 met	3/10/05	MW-25-056FF	2					
940591-7 met/hg	3/10/05	MW-25-056		7	2	2		
940591-8 met/hg	3/10/05	MW-31-60-056		7	2	2		
940619-1 met	3/10/05	MW-40S-056FF	2					
940619-1 met	3/10/05	MW-40S-056		7				
940620-1 met/hg	3/10/05	MW-20-70-056		7	2	2		
940620-2 met	3/10/05	MW-20-70-056FF	2					
940620-3 met	3/10/05	MW-20-100-056		7				
940622-4 met	3/10/05	MW-30-030-056FF	2					
940622-5 met	3/10/05	MW-30-050-056FF	2					
940622-6 met/hg	3/10/05	MW-34-55-056FF			2	2		
940622-9 met/hg	3/10/05	MW-34-55-056FF			2	2		
940663-1 met/hg	3/11/05	MW-37D-056		7	2	2		
940663-2 met	3/11/05	MW-37S-056		7				
940663-3 met	3/11/05	MW-37S-056FF	2					

pH record for field filtered samples

CH2M Hill Samples

Metals/Mercury

TLI Sample No.	Date Sampled	CH2M Hill Number	Cr		Hg	Met	Adjustment	Comments
			FF	LF				
941393-3	4/5/05	MW-27-85-060FF	1					
941393-6	4/5/05	MW-34-080-060FF	1					
941444-4	4/6/05	MW-39-050-060		7				
941444-5	4/6/05	MW-39-050-060FF	2					
941447-2	4/6/05	MW-30-50-060		7				
941447-3	4/6/05	MW-30-50-060FF	2					
941447-5	4/6/05	MW-30-30-060		7				
941447-6	4/6/05	MW-30-30-060FF	2					
941447-8	4/6/05	MW-12-060		7				
941447-9	4/6/05	MW-12-060FF	2					

pH record for field filtered samples

CH2M Hill Samples

Metals/Mercury

TLI Sample No.	Date Sampled	CH2M Hill Number	Cr FF	LF	Hg	Met	Adjustment	Comments
941488-1	4/7/05	MW-40S-060		7				
941488-2	4/7/05	MW-40S-060FF	1					
941488-3	4/7/05	MW-37S-060		7				
941488-4	4/7/05	MW-37S-060FF	1					
941488-5	4/7/05	MW-31-060-060		7				
941488-6	4/7/05	MW-31-060-060FF	1					
941488-7	4/7/05	MW-25-060		7				
941488-8	4/7/05	MW-25-060FF	1					
941488-9	4/7/05	MW-14-060		7				
941488-10	4/7/05	MW-14-060FF	1					
941488-11	4/7/05	MW-09-060		7				
941488-12	4/7/05	MW-09-060FF	1					

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