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May 20, 2008

Mr. Aaron Yue Project Manager California Department of Toxic Substances Control 5796 Corporate Avenue Cypress, CA 90630

Subject: Chromium Isotope Study Summary Report PG&E Topock Compressor Station, Needles, California

Dear Mr. Yue:

This letter transmits the Chromium Isotope Study Summary Report, at the PG&E Topock Compressor Station. This study was conducted as required by DTSC's letter date January 13, 2006, and was performed in two phases; Phase I data were collected in 2006 and Phase II data were collected in 2007. PG&E and its consultant CH2M HILL coordinated with the United States Geological Survey (USGS) to plan and conduct the Chromium Isotope Study at the Topock site.

PG&E appreciates your consideration of the attached report. Please contact me at (805) 234-2257 with any questions or concerns.

Sincerely,

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Yvonne Meeks Topock Project Manager

cc: Chris Guerre/DTSC Karen Baker/DTSC Kris Doebbler/DOI Peter Martin/USGS

Enclosure

# Chromium Isotope Study Summary Report

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

Prepared for

## California Department of Toxic Substances Control

On Behalf of Pacific Gas and Electric Company

May 20, 2008

Prepared by CH2MHILL 155 Grand Avenue, Suite 1000 Oakland, CA 94612

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This report was prepared under the supervision of a California Professional Geologist

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# Acronyms and Abbreviations

µg/L	micrograms per liter
‰	parts per thousand
CF-IRMS	continuous flow isotope ratio mass spectrometry
CIS	Chromium Isotope Study
Cr	chromium
Cr(III)	trivalent chromium
Cr(T)	total chromium
Cr(VI)	hexavalent chromium
DTSC	California Environmental Protection Agency Department of Toxic Substances Control
FD	field duplicate
LCS	Laboratory Control Samples
RPD	relative percent difference
PG&E	Pacific Gas and Electric Company
QAPP	Quality Assurance Project Plan for Water Quality Sampling and Analysis
QA/QC	quality assurance/quality control
RL	reporting limit
TLI	Truesdail Laboratories, Inc.
TWG	Technical Work Group
USGS	United States Geological Survey

# 1.0 Introduction

Pacific Gas and Electric Company (PG&E) is addressing chromium in groundwater at the Topock Compressor Station in Needles, California under the oversight of the California Environmental Protection Agency, Department of Toxic Substances Control (DTSC). The Topock Compressor Station is located in eastern San Bernardino County, approximately 15 miles southeast of Needles, California, as shown in Figure 1-1.

DTSC has directed PG&E to perform a groundwater study of stable chromium isotope signatures in and around the Topock facility (DTSC, 2006a). The objectives of this Chromium Isotope Study (CIS), as stated in the workplan, were to:

- Assess whether chromium isotopes can be used to distinguish anthropogenic chromium from naturally occurring chromium in groundwater.
- If chromium isotopes can be used to distinguish anthropogenic and naturally occurring chromium, determine whether chromium isotopes can assist with delineation of the chromium plume.
- Evaluate the utility of chromium isotopes for the assessment of the degree of chromium reduction that is occurring in the floodplain area.

It should be stressed that chromium isotopes are employed as a potential tool to help distinguish groundwater sources and pathways, in tandem with flow modeling, general chemistry, and other tools. They are not intended to be used independently from the other tools to determine groundwater origin.

CH2M HILL coordinated with the United States Geological Survey (USGS) to plan and conduct the CIS. The CIS consisted of two phases of sampling and analysis, Phase I and Phase II.

Phase I of the CIS was implemented in 2006 as approved by DTSC (DTSC, 2006b-c). Phase I activities were performed in accordance with the work plan dated April 7, 2006 (CH2M HILL, 2006a). Phase I samples were collected from 26 existing wells in May 2006, and analytical results were reported to DTSC in August 2006 (CH2M HILL, 2006b). Following laboratory analysis and data interpretation by both CH2M HILL and USGS, results were discussed at Topock project Technical Workgroup (TWG) meetings in September and December 2006 and were summarized at the Topock project Consultative Workgroup meeting in December 2006.

The Phase I study was determined to be inconclusive. Additional data were needed to determine if stable chromium isotopes could provide a useful tool for distinguishing between natural and anthropogenic chromium in groundwater at the Topock site. In a January 22, 2007 meeting, CH2M HILL and USGS collaborated to identify a set of potential wells to be sampled in a Phase II isotope study. This list of wells was discussed in the TWG meeting on February 21, 2007, and DTSC responded with a formal request for a Phase II work plan (DTSC, 2007a).

Phase II of the CIS was implemented in 2007 in accordance with the Phase II work plan (CH2M HILL, 2007a), as approved by DTSC (DTSC, 2007b). Phase II samples were collected from 26 existing wells between April 30 and May 4, 2007, with one well sampled July 10, 2007. Analytical results were reported to DTSC in November 2007 (CH2M HILL, 2007b). Following laboratory analysis and data interpretation, results were discussed at meetings between CH2M HILL and USGS in November 2007 and January 2008 and at the TWG Meeting in December 2007.

This report presents the data collected in both phases of work and provides interpretation of the chromium isotope data with the support of general chemistry and hydrogeologic data. The concept and methodology of chromium isotopic analysis is discussed in Section 2.0, a presentation of the selected wells and sampling protocol are provided in Section 3.0, and Section 4.0 provides a presentation, discussion and interpretation of the data. Conclusions of the study are summarized in Section 5.0.

# 2.0 Chromium Stable Isotope Theory

There are four stable isotopes of chromium (Cr) having atomic masses of 50, 52, 53, and 54 ( ${}^{50}$ Cr,  ${}^{52}$ Cr,  ${}^{53}$ Cr and  ${}^{54}$ Cr); 52 is by far the most common. There are no stable isotopes of any other element having atomic masses of 52 or 53. Small variations in the ratio of  ${}^{53}$ Cr to  ${}^{52}$ Cr are expected to occur in nature and may have the potential to identify specific chromium sources or chemical processes involving Cr (Ball and Bassett, 1999; Izbicki et al., 2008). The  ${}^{53}$ Cr/ ${}^{52}$ Cr ratio is measured on a mass spectrometer and compared to an international standard (NIST SRM 979; procedure described in Ellis et al., 2002). The difference between the ratio in a sample and that in this standard is expressed as  $\delta {}^{53}$ Cr, in parts per thousand (‰).

Both natural mineral and industrial sources of hexavalent chromium [Cr(VI)] have  $\delta^{53}$ Cr values around 0.0 ‰. The changing of a  $\delta^{53}$ Cr value due to a process or reaction is also referred to as fractionation. In order to use chromium isotope values to differentiate natural and industrial sources, the  $\delta^{53}$ Cr values would need to fractionate differently in the environment for each source.

Ellis et al. (2002) demonstrated that Cr isotopes are substantially fractionated during abiotic reduction of Cr(VI) to trivalent chromium [Cr(III)]. For example, progressive reduction of Cr(VI) in a magnetite slurry, buffered at pH~6 in order to minimize sorption of Cr<sub>2</sub>O<sub>4</sub><sup>2-</sup> and HCr<sub>2</sub>O<sub>4</sub><sup>-</sup>, resulted in progressively increasing  $\delta^{53}$ Cr of the remaining dissolved Cr(VI). Using a Rayleigh fractionation model, in which Cr(III) once produced is immediately removed from further reaction (e.g., by precipitation or sorption onto mineral surfaces), an instantaneous fractionation factor ( $\propto_{Cr(III)-Cr(VI)} = 0.9965$ ) was calculated for the reduction reaction. Using this factor, after the reaction progressed to 80 percent completion, the remaining Cr(VI) had  $\delta^{53}$ Cr 5.6 ‰ greater than the original Cr(VI); at 90 percent completion, the difference was greater than 8 ‰ and so on.

Ellis et al. (2004) demonstrated that Cr isotopes are not significantly fractionated during sorption of Cr(VI) aqueous species onto Al<sub>2</sub>O<sub>3</sub> and goethite substrates at circum-neutral pH. Similarly, no significant fractionation was observed during sorption of Cr(VI) onto Al<sub>2</sub>O<sub>3</sub> at pH=4. In contrast, a kinetic isotope effect was observed during sorption of Cr(VI) onto goethite at pH=4, with  $\delta^{53}$ Cr of the initial sorbed Cr(VI) being 3.5 ‰ less than that of the coexisting aqueous Cr(VI); however, the isotopic contrast essentially disappeared as the 12-hour experiment progressed. Thus, these investigators concluded that sorption of Cr(VI) probably has only a secondary effect on the isotopic composition of dissolved Cr along groundwater flowpaths in most natural aquifer systems, although effects may be magnified at plume edges or fronts.

If partial reduction of Cr(VI) to Cr(III) is assumed to be the only process that fractionates  $\delta^{53}$ Cr values in the environment, then natural groundwater would be expected to have higher values of  $\delta^{53}$ Cr than industrial sources. Over the long course of natural groundwater flowpaths, naturally occurring Cr(VI) is expected to develop a higher  $\delta^{53}$ Cr value that reflects episodes of partial reduction along the flowpath. Reduction selectively removes the lighter fraction of chromium (i.e., the most common isotope, <sup>52</sup>Cr). This has the effect of

slightly enriching the fraction of <sup>53</sup>Cr in groundwater and thereby increasing the  $\delta^{53}$ Cr value above zero. Natural groundwater samples in the Mojave Desert region of California have been reported to range in  $\delta^{53}$ Cr value between 0.5 and 5.1 ‰ (Izbicki et al., 2008). By contrast, the value of  $\delta^{53}$ Cr in any anthropogenic chromium in groundwater would be expected to remain around zero, since the flowpath of anthropogenic chromium in groundwater is generally much shorter than that of natural chromium in groundwater, resulting in fewer opportunities for chromium reduction along the way. It should be noted, however, that groundwater samples collected from recharge areas showed that  $\delta^{53}$ Cr values are elevated above zero (i.e. around 2 ‰) very close to the aquifer source, possibly indicating reaction with reduced iron minerals or other electron donors in the parent rock (Izbicki et al., 2008). This demonstrates that there are many factors involved in the determination of the chromium isotope value, and some may not yet be fully explained.

### 3.1 Data Collection Strategy

Groundwater samples were collected from 49 existing wells during Phase I and Phase II of the CIS. Table 3-1 provides a listing of wells from each phase of sampling, with descriptions of well characteristics and well selection criteria.

The CIS Phase I sampling was designed to examine data from three groups: reference wells not affected by site activity, plume wells, and plume "margin" wells. The margin wells were designated by DTSC on the basis of geographic proximity to the plume, as defined by the 50 micrograms per liter ( $\mu$ g/L) Cr(VI) contour at the time, while lying outside of the plume. Twenty-six wells were sampled, including eight reference, ten plume, and eight margin wells. Differentiation of margin wells from reference wells proved to be inconclusive, and the spread of isotope values among plume wells was smaller than anticipated.

As a result, Phase II sampling was designed to add more reference wells and more plume wells so as to increase the variety of Cr(VI) concentrations. All of the margin wells were sampled in Phase I; therefore, no more could be added for Phase II. Fourteen reference wells were sampled during Phase II, along with nine plume wells. In addition, three wells (one margin, one plume, and one reference) that were sampled in Phase I were resampled in Phase II to check for consistency of analytical method and to monitor any changes that might have occurred over the previous year.

### 3.2 Sample Collection and Analysis

In both phases of the CIS study, the wells were sampled concurrently with a routine Topock site sampling event under the Groundwater Monitoring Program, the Compliance Monitoring Program, and/or the Groundwater Background Study. Standard well purging and sample collection and management procedures used for the study were in accordance with the Field Procedures Manual (CH2M HILL, 2005a), and the Topock Background Study Work Plan Supplement (CH2M HILL 2005b).

Duplicate samples were collected from a minimum of 10 percent of the wells during each phase. Duplicates were collected at wells from the lower, middle, and upper ranges of the Cr(VI) concentration distribution in order to avoid biasing the duplicate sampling toward any one portion of the concentration range. In Phase II, collected samples were assigned a numerical identification number so that the analytical laboratories could not tell which well each sample was collected from.

A sample from each well was shipped to the USGS laboratory in Menlo Park, California for chromium isotope analysis. In Phase I, this sample was collected by USGS personnel; whereas, in Phase II, CH2M HILL personnel collected the samples. Upon arrival at the USGS laboratory, the Cr(VI) fraction was extracted by passing the sample through an anion exchange resin. Extracted Cr(VI) was then flushed off the resin and used in isotope analysis.

Chromium isotope analysis was accomplished using thermal-ionization mass spectrometry by application of extracted chromium to a solid source filament using the silica gel technique to enhance production of thermal ions (Ball, 1996).

During Phase I, USGS personnel collected a sample using a 0.2-micrometer filter. A small aliquot of each USGS sample was taken for measurement of Cr(T). The remainder of each sample was then processed in the field using the cation exchange method for field speciation of Cr(VI) (Ball and McCleskey, 2003). In this method, Cr(III) is sorbed on cation exchange resins leaving only Cr(VI) in the liquid fraction. Both the unspeciated and speciated liquid samples were also sent to the USGS laboratory in Boulder, Colorado for analysis of Cr(T) by graphite furnace atomic absorption spectroscopy. The sample processed using the cation exchange method contains only Cr(VI). The concentration of Cr(III) was determined by the difference between Cr(T) and Cr(VI). In Phase II, unpreserved, filtered samples were sent for analysis to the Menlo Park laboratory only. Samples were initially analyzed for Cr(VI) by a non-standard method solely to determine proper exchange column length. They were then sent through the exchange column to isolate Cr(VI) and subsequently run for isotopic analysis.

In addition to analysis by USGS laboratories, samples collected during both phases of the CIS were also sent to California Department of Health Services certified laboratories for analytical testing. Analytical testing by California Department of Health Services certified laboratories included total chromium [Cr(T)], Cr(VI), general chemistry parameters, trace metals and stable isotopes. The laboratories used for the CIS were Truesdail Laboratories, Inc. (TLI) of Tustin, California, Emax Laboratories, Inc. of Torrance, California, and Zymax Forensics of San Luis Obispo, California. All laboratories are certified by the California Department of Health Service's Environmental Laboratory Accreditation Program for the analyses included in Appendix A where appropriate. The analysis included Cr(T), Cr(VI), general chemistry parameters, trace metals and stable isotopes. Holding times and quality assurance/quality control (QA/QC) procedures for the general chemistry and metals analyses followed standard procedures outlined in the *Quality Assurance Project Plan for Water Quality Sampling and Analysis* (QAPP) (CH2M HILL, 2005a).

Holding times and quality assurance/quality control (QA/QC) procedures for the general chemistry and metals analyses followed standard procedures outlined in the Quality Assurance Project Plan for Water Quality Sampling and Analysis (CH2M HILL, 2005a).

### 3.3 Quality Control and Data Management

Quality control procedures were implemented for both field activities and laboratory work associated with the study. Detailed descriptions of quality control procedures specific to water quality sampling at the Topock site are provided in the *Quality Assurance Project Plan for Water Quality Sampling and Analysis* (Appendix D of the Topock Field Procedures Manual [CH2M HILL, 2005a]).

### 3.3.1 Analytical Data Quality Review

The laboratory analytical data generated from the chromium isotope study, Phase I and II were independently reviewed by project chemists to assess data quality and identify deviations from analytical requirements. The quality assurance and quality control

requirements are outlined in the QAPP for the PG&E Topock Program, which is Appendix D of the *Sampling, Analysis, and Field Procedures Manual, Revision 1* (CH2M HILL, 2005b). A detailed discussion of data quality for CIS sampling data is presented in the data validation reports, which are kept in the project file and are available upon request.

### 3.3.1.1 Hexavalent Chromium Matrix Interference

No Matrix interference was encountered in the groundwater samples affecting the sensitivity for Chromium (VI) when analyzed by Method SW7199.

### 3.3.1.2 Matrix Spike Samples

Five samples had matrix spike and /or matrix spike duplicate results recovered outside the control limits (SW6020A – one or more of the following analytes - boron, calcium, chromium, magnesium, potassium, and sodium). The detected sample results were qualified as estimated and flagged "J", unless the sample concentration was more than four times the spike concentration. One sample had a matrix spike result that exceeded the control limits for nitrate (E300.0). The detected sample result was qualified as estimated and flagged "J". All other matrix spike acceptance criteria were met.

### 3.3.1.3 Quantitation and Sensitivity

Two beryllium, one chromium, and four ammonia non-detect samples were diluted prior to analysis and did not meet the project reporting limit objects. All other method and analyte combinations met the project reporting limit objectives.

### 3.3.1.4 Holding Time Data Qualification

For Phase II CIS one nitrate sample was analyzed outside the recommended holding time. The detected sample was qualified as estimated and flagged "J".

Based on the March 2007 EPA Ruling pH has a 15 minute holding time. As a result pH (SM4500-HB) samples analyzed in a certified lab require qualification. Therefore, pH results for samples collected after March 2007 (Phase II) were qualified as estimated and "J" flagged.

### 3.3.1.5 Field Duplicates

One field duplicate (FD) pair had results that exceeded the relative percent difference (RPD) criteria for Isotopes (CF-IRMS) and a second FD pair had results that exceeded the RPD criteria for zinc (SW6020A). The samples were qualified as estimated and the detected results were flagged "J".

All other FD acceptance criteria were met for the CIS samples.

### 3.3.1.6 Method Blanks

Method blanks (MB) were analyzed at the method required frequency. Manganese (SW6020A) was detected above the reporting limit (RL) in one sample delivery group. The associated sample detect result was more than five times the MB result and was not qualified. The associated non-detect result also was not qualified. All other MB acceptance criteria were met.

### 3.3.1.7 Equipment Blanks

For the CIS Phase I and II sampling events, equipment blank acceptance criteria were met.

### 3.3.1.8 Laboratory Duplicates

For the CIS Phase I and II sampling events, laboratory duplicate acceptance criteria for the methods were met.

### 3.3.1.9 Laboratory Control Sample

Laboratory Control Samples (LCS) were analyzed at the required frequency and were recovered within QC limits with the following exceptions:

Fourteen boron, two chromium, and two nickel (SW6020A) sample results were qualified as estimated because the LCS recovery was greater than the upper control limit. Detect results were flagged "J".

Four zinc (SW6020A) results were qualified as estimated because the LCS recovery was greater than the upper control limit. Detect results were flagged "J". Twelve additional non-detect sample results were not qualified.

Two zinc (SW6020A) results were qualified as estimated because the LCS RPD criterion was exceeded. Non-detect results were flagged "UJ".

Eight Total Dissolved Solid (E160.1) sample results were qualified as estimated because the LCS RPD criterion was exceeded. The detect results were flagged "J".

### 3.3.1.10 Calibration

For the CIS Phase I and II sampling events, initial and continuing calibrations were performed as required by the methods. All calibration criteria were met, with the following exceptions:

One chloride and three sulfate (E300.0) sample detected results were qualified as estimated and "J" flagged due to continuing calibration verification recoveries greater than the upper control limit.

### 3.3.1.11 Conclusion

For the CIS Phase I and II sampling events, the completeness objectives were met for all method and analyte combinations. The analyses and data quality met the QAPP and laboratory method quality control criteria except as noted above. Overall, the analytical data are considered acceptable for the purpose of the CIS.

### 3.3.2 Data Comparison

The USGS Cr(VI) and Cr(T) data results were compared to validated results from California certified laboratories (Table 3-2). The data was evaluated using the FD RPD criterion of less then or equal to 20% for Cr(VI) and Cr(T) analysis. Three Cr(VI) sample results did not meet the RPD criterion.

As part of the QC procedures, USGS used Standard 979 Cr (National Institute of Standards and Testing) as a reference metal throughout the entire analytical procedure. The USGS

analyzed the standard several times over the course of the study demonstrating consistency and accuracy of the Cr isotopic compositions. Quality control procedures followed by USGS personnel are described in McCleskey et al. (2004).

As part of the QC, double blind samples for Phase II were sent to all labs. Certified lab sample results were all consistent with historical data.

### 3.3.3 Data Management

Management of data generated from the study was conducted in accordance with the *PG&E Program Data Management Plan* (CH2M HILL, 2004). The Data Management Plan outlines standardized procedures for field data collection and review, analytical data loading into the information system (environmental database), verification of the uploaded data, QA/QC procedures associated with data management, and reporting formats.

### 4.1 Results

A map view of all wells sampled in Phases I and II is provided on Figure 4-1 (regional scale) or Figure 4-2 (local site scale), which also display the chromium isotope values. All data collected in the study are listed in Table 4-1 (isotopes). Table 4-2 (general chemistry), and Table 4-3 (trace elements). A complete data set is provided in Appendix A, including laboratory QA/QC data (e.g., duplicate and blank samples). All sample results met laboratory QA/QC standards, based on established protocol (CH2M HILL, 2005a). Forty-nine wells were sampled during the two phases, including three wells that were sampled in both phases.

The 22 reference wells correspond to (1) 13 wells that were included in the Topock Groundwater Background Study (CH2M HILL, 2008), and (2) nine site wells that, although not used in the Background Study, were considered outside the area of possible influence of historical discharges from the Topock compressor station. The latter group consisted of well MW-15, plus eight wells used in the Compliance Monitoring Program, with those wells having either OW- or CW- designations. The Tayloe well, a background well located about 4 to 5 miles northwest of the site (Figure 4-1), was sampled in Phase II but its concentration of Cr(VI) was too low to reliably report a  $\delta^{53}$ Cr value.

The eight margin wells were all sampled in Phase I, and none was left unsampled. Nineteen plume wells were sampled over the two phases, with Cr(VI) concentration ranging from 46.1 up to 5,760  $\mu$ g/L. There were also two "plume" samples taken from wells that have displayed plume concentrations in the past but were below background levels<sup>1</sup> at the time of sampling: MW-47-55 (30.3  $\mu$ g/L) and MW-39-60 (1.1  $\mu$ g/L).

Three wells were sampled in both phases.

- The sample from well OW-3M showed a  $\delta^{53}$ Cr value of 0.88 ‰ in Phase I and, for a reference well, this value appeared to be very low at the time. Previous studies of natural groundwater  $\delta^{53}$ Cr ranges in Mojave Desert, California samples showed only one sample below 1 ‰ that was not believed to have been influenced by human activity (Izbicki et al., 2008). Well OW-3M was sampled again in Phase II to verify the low  $\delta^{53}$ Cr value, and the measured value of 0.63 ‰ was even lower and in general agreement with the first given analytical uncertainty.
- Well MW-34-100 is a plume well screened in the deep fluvial material near the Colorado River (Figure 4-2). Because the concentration of Cr(VI) had been dropping in this well since mid-2006, the well was sampled again in Phase II to see if the decreasing trend was coupled with a change in δ<sup>53</sup>Cr. The Phase I δ<sup>53</sup>Cr value of 0.89 ‰ was considered to be essentially the same as the Phase II value of 0.71 ‰, within analytical uncertainty.

<sup>&</sup>lt;sup>1</sup> Background concentrations at the Topock site documented in the Revised Groundwater Background Study Steps 3 and 4: Report of Results (CH2M HILL 2008).

Well MW-35-135 had its Cr(VI) concentration rise above 30 μg/L in the months following the collection of the Phase I sample. A Phase II sample was proposed to investigate the correlation with δ<sup>53</sup>Cr. In this case, there was a significant change observed between Phase I (2.76 ‰) and Phase II (0.91 ‰). The influence of IM pumping is believed to be responsible for this change, as discussed below.

A plot of  $\delta^{53}$ Cr vs. Cr(VI) concentrations is provided in Figure 4-3. The Cr(VI) concentrations are plotted on a logarithmic scale so that lower concentrations will not all plot as a cluster near the y-axis. Figure 4-3 shows the plume wells with  $\delta^{53}$ Cr values in the range of 0 to 1.5 ‰. This observation follows the expected model of plume groundwater described above (i.e., it should be near zero due to limited opportunities for reduction to occur). When Phase I and II data are combined, reference wells range in  $\delta^{53}$ Cr between 0.0 and 3.2 ‰. The margin wells range between 0.6 and 4.0 ‰, and this large range was the subject of the most interpretation, as described further below.

Figure 4-4 is a Piper Diagram of general chemistry parameters, with different symbols for the same categories as in Figure 4-3. A Piper diagram shows, for each sample, relative percentages of cations on the left triangular plot and anions to the right, with a central diamond-shaped field showing the combined plot of overall water chemistry. Locations of samples on the three fields may be compared to note distinctions between different groups of samples. Most samples are dominated by sodium and chloride, plotting in the right corner of the diamond field, regardless of plume or non-plume location. Most of the Arizona samples plot in the middle of the diamond field, reflecting a more bicarbonate-rich chemistry than the other samples. Other notable samples are from Lily Hill and Needles MW-11, two reference wells that show a river-influenced chemistry with a mixed-ion composition, and reference well MW-17, unique in its sodium-sulfate chemical quality.

Stable isotopes of oxygen and hydrogen, expressed as  $\delta^{18}$ O and  $\delta^{2}$ H, respectively, are plotted against each other in Figure 4-5. The samples are plotted relative to the Global Meteoric Water Line, along which most global rainfall would plot. Samples from wells Lily Hill and Needles MW-11 plot to the left or "lighter" side of the diagram, reflecting a similar isotopic signature to Colorado River water. Plume wells plotting to the far right reflect the heavier isotopic signature of partially evaporated water potentially associated with early cooling tower blowdown water. As shown on Figure 4-5, there is a great deal of overlap between plume and non-plume groundwater in terms of isotopic signature. This is due to (1) natural advective mixing within the plume and around the plume edge and (2) recent Interim Measures extraction that has caused mixing between plume water and non-plume waters.

### 4.2 Data Interpretation

### 4.2.1 Plume Wells

As described in Section 2.0, plume well samples were expected to produce  $\delta^{53}$ Cr values in the range of 0.0 to 1.0 ‰, reflecting the limited degree of reduction that would occur within the plume. This is generally what was observed, as plume samples ranged between slightly below 0.0 and 1.5 ‰. The values are plotted on Figure 4-3 and are split between "plume center" and "plume downgradient" to highlight differences between samples that were collected along the plume's main flow axis and those that represent more peripheral and

downgradient flanks of the plume, respectively. Based on the site conceptual groundwater model, the main axis of flow from the original Bat Cave Wash discharge follows a curve running generally through well/well cluster locations MW-10, MW-38, MW-24, and MW-20 (Figure 4-2).

Although the alluvial aquifer has limited quantities of reducing material, especially compared to the shallow- and medium-depth fluvial material, there are believed to be enough scattered pockets of this material to partly reduce the modest concentrations of naturally-occurring Cr(VI), resulting in more elevated  $\delta^{53}$ Cr values in non-plume wells. However, the plume is a case where elevated Cr(VI) levels have been present for many years, and it is possible that the elevated concentrations of Cr(VI) in the plume may have relatively quickly exhausted the modest reducing capacity of the alluvial material. If this possibility is accurate, the present-day samples would not be expected to be fractionated by partial reduction because they would be passing through a zone of the alluvial aquifer where all the reducing capacity has been previously exhausted. The parts of the plume away from the main plume axis show somewhat elevated  $\delta^{53}$ Cr values (0.5 to 1.5 ‰, yellow boxes on Figure 4-3) potentially as a result of advective mixing with some non-plume water during the plume's evolution.

The sample from MW-39-60 was expected to demonstrate a rise in  $\delta^{53}$ Cr in this floodplain location, where Cr(VI) is known to be dropping and high-reducing capacity fluvial deposits are nearby. A distinct decrease in Cr(VI) has been observed at all wells in the MW-39 cluster between 2004 and 2008. The MW-39-60 sample, which contained only 1.1 µg/L Cr(VI) in the Phase I sample (May 2006), was expected to show an elevated  $\delta^{53}$ Cr value because it was thought to contain the very last of the Cr(VI) that had not yet been chemically reduced. The concentration of Cr(VI) in this well dropped from 3,810 µg/L in September 2004 to below detection limit in October 2006, apparently accelerated by Interim Measures extraction drawing non-plume fluvial groundwater westward and downward through this area. The measured  $\delta^{53}$ Cr value for MW-39-60 was 1.26 %, only slightly higher than the range of the other plume wells. Based on this result, it was postulated that the drop in concentration at MW-39-60 and other nearby wells has been driven mainly by advective flushing with nonplume water. The fractionation that would occur with reduction of Cr(VI) is not evident, possibly due to the process of dilution in these floodplain wells. This interpretation is supported by  $\delta^2$ H data: in June 2004, the  $\delta^2$ H value at MW-39-60 was -42 ‰, consistent with values in many plume wells, and by May 2006 (Phase I) the  $\delta^2$ H value had dropped to -72 ‰, a typical value for shallow fluvial non-plume wells. These data suggest the groundwater at this well has been replaced by non-plume groundwater.

### 4.2.2 Reference Wells

The 22 reference wells sampled during Phases I and II showed a range in  $\delta^{53}$ Cr values from 0.0 to 3.2 ‰. As described in Section 2, existing literature for natural groundwater in the Mojave Desert, California region reports a range of 0.5 to 5.1 ‰ (Izbicki et al., 2008). In addition to verifying the one Phase I sample that was found to be near the bottom of this range (OW-3M, described in Section 3.0), there were several Phase II samples that were even lower. The same USGS Menlo Park, California laboratory analyzed both the Mojave Desert and Topock samples, so the results should be comparable. The Topock site data suggest that

natural alluvial groundwater, far from its original source, can have  $\delta^{53}$ Cr values as low as 0.0 ‰.

Very low  $\delta^{53}$ Cr values appear to be associated with reference wells with deeper screen intervals (e.g., P-2 and CW-3M on Figure 4-3 and Table 4-1). These were the deepest site reference wells in the CIS, and they had the lowest  $\delta^{53}$ Cr values in the study. The data appear to support the idea of decreasing  $\delta^{53}$ Cr with depth in site reference wells, as illustrated on Figure 4-6. A possible explanation is that the aquifer solids lose their reductive material over time and so the oldest (deepest) materials have very little or no reductive material left. Without reductive material, the Cr(VI) cannot be reduced and its  $\delta^{53}$ Cr could remain near zero.

All reference wells are screened in alluvial material with one exception: Needles MW-11, which is the only river-influenced fluvial well in the area that contains detectable Cr(VI). The Needles MW-11  $\delta^{53}$ Cr value of 1.1 ‰ may be indicative of the fluvial-alluvial interface zone of the floodplain areas.

One of the objectives of Phase II sampling was to determine if reference samples in the area would have  $\delta^{53}$ Cr values as high as some of the margin well samples from Phase I (i.e., between 3.5 and 4.0 %). This was not observed in Phase II. A possible explanation for this is that the groundwater sampled in this study represents an equilibrium between natural reductive material in the alluvium and ion exchange of Cr(VI) between the dissolved phase and the mineral surfaces of the alluvium. In this theory, natural Cr(VI) would not achieve a  $\delta^{53}$ Cr value above about 3.2 ‰ because (1) there is not enough reducing material to drive the fractionation further, and (2) chromate ions (CrO<sub>4</sub><sup>2-</sup>) with lower  $\delta^{53}$ Cr exchange off of mineral surfaces with higher  $\delta^{53}$ Cr chromate ions removed from solution to take their places. This would create an equilibrium between natural dissolved Cr(VI), adsorbed Cr(VI), and the modest reducing material in the alluvium. This theory cannot be tested with any analysis yet developed, but it is noted that the only samples in the Mojave Desert study with  $\delta^{53}$ Cr values above 3.2 were from a sub-oxic groundwater environment (Izbicki et al., 2008), which does not exist in the Topock area.

### 4.2.3 Margin Wells

The margin wells are all located outside of the plume but relatively close to the plume. The large range of  $\delta^{53}$ Cr values observed for this group (0.62 to 3.9 ‰) indicates that this collection of wells represents a variety of environments, potentially within and outside of the plume's influence.

Well MW-37S is screened in a zone immediately above the current plume, with the sample from MW-37D being clearly a plume well with Cr(VI) at 1,970  $\mu$ g/L. The  $\delta^{53}$ Cr value for MW-37S is similar to plume samples at 0.62 ‰, suggesting advective mixing (and not chemical reduction) as the likely mechanism for the low Cr(VI) concentration of 8.1  $\mu$ g/L in this well.

A well in a similar plume margin position to that of MW-37S is MW-40S, located above the western edge of the plume, above well MW-40D (Cr(VI) = 78  $\mu$ g/L). In stark contrast to MW-37S, MW-40S has a very high  $\delta^{53}$ Cr value of 3.65 ‰. A possible explanation for this disparity is that MW-37S is located in Bat Cave Wash, where periodic local storms provide fresh water infiltration that could dilute shallow Cr(VI) concentrations in this area. Dilution

would lower the Cr(VI) concentration without significantly changing the  $\delta^{53}$ Cr value, resulting in the low observed  $\delta^{53}$ Cr value for MW-37S. In contrast, MW-40S is located in an area that likely does not receive significant recharge, so the most likely mechanisms for lowering Cr(VI) concentration may be advective mixing at the plume fringe plus reduction (as will be described in more detail below). Under those potential mechanisms, the  $\delta^{53}$ Cr value would be expected to be elevated.

Well MW-35-135 showed a distinct drop in  $\delta^{53}$ Cr from 2.76 ‰ in Phase I to 0.91 ‰ in Phase II. The earlier value is typical of  $\delta^{53}$ Cr in reference wells around the region (e.g., Lily Hill, EPNG-2, MW-18), while the Phase II value of 0.91 ‰ is closer to that of fluvial wells influenced by Colorado River water (Needles MW-11, at 1.15 ‰). These data suggest that IM pumping may be drawing river-influenced groundwater through the MW-35-135 screen, resulting in a lower  $\delta^{53}$ Cr value. Stable oxygen and deuterium isotope data from this well support this assumption, with lighter, more river-like values evident in the Phase II sample from MW-35-135 compared to the sample from Phase I (Figure 4-5, Table 4-1).

Margin wells MW-14, MW-35-60, and MW-35-135 (Phase I sample) have  $\delta^{53}$ Cr values between 2.46 and 3.20 ‰. These values are within the upper range of values described above for reference wells. All other geochemical characteristics of these samples are similar to reference well properties, and the site groundwater data and resulting conceptual/numerical model indicate that these wells do not lie within the expected flowpath of historic discharge water. Based on the propensity of data, these locations are believed to represent background alluvial groundwater conditions at the site.

The remaining four margin well samples, MW-13, MW-33-90, MW-33-210, and MW-40S, all collected in Phase I, remain the only samples with  $\delta^{53}$ Cr values above 3.5 ‰. There were no distinctive properties of these four wells based on general chemistry, trace elements, or oxygen-hydrogen isotopes. Two hypotheses may explain the elevated  $\delta^{53}$ Cr values in the four wells:

- 1. They represent the upper end of natural variation in reference wells and may be regarded as such.
- 2. They represent chromium from the plume that has been advectively mixed at the edge of the plume and then partly reduced.

Hypothesis 1 was considered because values in this range (3.5 – 3.9 ‰) were observed in naturally-occurring Mojave Desert groundwater samples (Izbicki et al., 2008). However, elevated values in the Mojave represented sub-oxic samples from either a dry lake environment or deeper flow system, where active reduction would be expected to take place. The four Topock wells exhibit characteristics of an oxic environment (mostly elevated dissolved oxygen, positive oxidation-reduction values, nitrate as dominant nitrogen form) and so it may not be likely that the naturally elevated  $\delta^{53}$ Cr values would be expected in the alluvial material of the Topock site. In addition, no reference well samples from the Topock site were found in this range in Phase I or II, so these four samples have greater values than the rest of the site samples. Conversely, there are still limited data in the literature on stable chromium isotope data in natural groundwater samples. Just as some low  $\delta^{53}$ Cr values in this study have extended the lower range of natural groundwater, these four elevated  $\delta^{53}$ Cr values may represent the upper end of the natural range. Variability in mineralogy present

in the subsurface may have localized effects on isotope fractionation, either via adsorption/desorption or by dissolution. Lack of adsorption effects has been documented only for aluminum oxide and the iron oxide goethite (Ellis et al., 2004), and other minerals may have stronger influences.

Hypothesis 2 assumes Ralyeigh fractionation would create isotopically heavy values as proposed during the study design. The high  $\delta^{53}$ Cr values associated with this process are not apparent in the margin wells at the site, potentially due to advective mixing. The advective mixing with natural alluvial groundwater on the west and north sides of the plume could create lower Cr(VI) values without greatly altering the  $\delta^{53}$ Cr value. An illustration of this process is shown in Figure 4-7, in which a hypothetical sample originally at high Cr(VI) concentration (point "A") follows the line towards lower concentration (point "B"). In the central area of the plume, it is assumed that all natural reductive material in the alluvium was removed long ago by the high concentrations of Cr(VI), a strong oxidant, in the plume, so there would be no increase in  $\delta^{53}$ Cr by reductive fractionation. Point "B" is assumed to be within but near the edge of the plume at a Cr(VI) concentration of about  $100 \,\mu g/L$  and will begin to be partly reduced as it encounters native aquifer matrix that still contains reductive material. As this reduction occurs, the  $\delta^{53}$ Cr rises along a Rayleigh fractionation line, sloping up and to the left in the plot shown in Figure 4-7 (to Point "C", at a similar position as the four wells in question). Because the plume contains more Cr(VI) than the natural groundwater, the natural system would work to reduce the Cr(VI) to the background level (about 30  $\mu$ g/L)<sup>2</sup>, which would be buffered by ion exchange as described in the previous section. This would be accomplished by chemical reduction to Cr(III), and the remaining Cr(VI) would be enriched in <sup>53</sup>Cr. This extra reduction would result in the plume margin groundwater having a higher  $\delta^{53}$ Cr value than native groundwater. The hypothetical process shown on Figure 4-7 could be accomplished with various combinations of reduction and advective mixing; this scenario is illustrated for simplicity of explanation.

The net effect of this process would be to create an "apparent" fractionation factor significantly lower than that observed in laboratory studies (Ellis, 2002; Kitcher et al., 2004). This apparent fractionation is illustrated by the dashed line between points "A" and "C" in Figure 4-7. Hypothesis 2 provides a plausable geochemical explanation to reconcile field data with expected behavior from laboratory data.

Because these four wells are located along the edge of the plume, Hypothesis 2, if true, provides supporting evidence for the groundwater model calibration by acting to "frame" the plume and constraining the model parameters so that the model duplicates this plume geometry. By the same token, the hydrogeologic conceptual model of the site helped to constrain the chromium isotope interpretation: Well MW-14 shows an elevated  $\delta^{53}$ Cr value (3.2 ‰) which is consistent with reference wells. Coupled with geologic and hydraulic data that do not indicate that well MW-14 is located near a plume flowpath, the isotopic data confirms the interpretation that this margin well is actually a reference well with alluvial groundwater from outside the plume. This illustrates how the hydraulics and geochemistry may be used together to support site interpretations.

<sup>&</sup>lt;sup>2</sup> Background concentrations at the Topock site documented in the Revised Groundwater Background Study Steps 3 and 4: Report of Results (CH2M HILL 2008).

# 5.0 Summary

Groundwater samples from 49 wells were collected and analyzed for the stable chromium isotope <sup>53</sup>Cr during two phases of sampling in 2006 and 2007. Three wells were sampled in both phases, so that a total of 52 samples were collected and analyzed. The samples were also analyzed for general chemistry parameters, trace elements, and stable isotopes of oxygen and hydrogen.

Natural groundwater  $\delta^{53}$ Cr values likely range between 0.0 and 3.2 ‰ at the Topock site. Plume samples ranged between 0.0 and 1.5 ‰. Margin wells ranged between 0.62 and 3.9 ‰. Elevated values between 3.5 and 3.9 ‰ were observed in four of the margin wells: MW-13, MW-33-90, MW-33-210, and MW-40S.

### 5.1 Initial Study Objectives

- Study data showed too much overlap in δ<sup>53</sup>Cr sample results between plume wells and natural groundwater to be used directly or independently to distinguish anthropogenic chromium from naturally occurring chromium in groundwater. Only when used in tandem with other data were they useful in helping to identify possible plume influence in some well samples.
- Chromium isotopes appear to have utility in confirming the reaction pathway of the plume and supporting other data to assist with delineation of the chromium plume. That is, the hydraulics and geochemistry can be used together to support site interpretation. For example, the hydrogeologic conceptual model and elevated  $\delta^{53}$ Cr values for wells MW-33-90 and MW-33-210 both support the likelihood of some degree of plume water contribution to Cr(VI) concentrations in this well cluster.
- In this study, chromium isotopes appeared to have limited utility for the assessment of the degree of chromium reduction that is occurring in the floodplain area. For example, using chromium isotope data together with stable isotopes and other data, it is possible to qualitatively interpret that a most of the cr6 concentration decrease at MW39-60 is due to advective mixing with river water while more of the concentration decrease at MW-33-90 appears to be related to a combination of mixing and reduction.

### 5.2 Additional Interpretation

The most likely explanation for the four elevated  $\delta^{53}$ Cr values in the margin wells appears to be Hypothesis 2 as described above, where a combination of mixing at the plume edge and partial reduction results in elevated  $\delta^{53}$ Cr values. It should be noted that available data are not sufficient to definitively support this explanation. Because these wells are on the margins of the plume flowpaths, the interpretation lends support for the site conceptual model and on the limits of the plume extent. Hypothesis 2 also provides a potential explanation for the lack of elevated  $\delta^{53}$ Cr values that would be predicted by published laboratory data, which did not include the advective mixing process. However, as discussed above, the variation in mineralogy and potential influences on natural isotopic fractionation have not been fully explored, making interpretation of these data tentative.

There appears to be a relationship between groundwater depth and  $\delta^{53}$ Cr values among reference samples, with higher values at shallow depth and lower values in deep wells (Figure 4-6). The absence of reducing material at depth appears to be the most likely explanation for this relationship, and the very low  $\delta^{53}$ Cr values observed in deep wells indicate that natural groundwater samples can maintain near-zero  $\delta^{53}$ Cr values far away from their original mineral sources.

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Figures



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Note:

Refer to Figure 4-1 for regional well locations.



CHROMIUM ISOTOPE STUDY SUMMARY REPORT PG&E TOPOCK COMPRESSOR STATION NEEEDLES CALIFORNIA



CH2MHILL



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### Tables

# TABLE 3-1 Chromium Isotope Study Well Listing Chromium Isotope Study Summary Report

Plume Wells         MV-09         534         77         87         Shallow         Alluvial         CA         Bat Cave Wash near original discharge         II           MV-10         529         74         94         Shallow         Alluvial         CA         Bat Cave Wash near original discharge         II           MV-11         521         62.5         82.5         Shallow         Alluvial         CA         Bat Cave Wash near original discharge         II           MW-19         499         46         66         Shallow         Alluvial         CA         North of MV-20 bench         I           MW-20070         499         50         70         Shallow         Alluvial         CA         North of MV-20 bench         I           MW-25         541         B4.5         104.5         Shallow         Alluvial         CA         North of ormpresor station near original discharge         I           MW-31.35         495         113         133         Deep         Alluvial         CA         North of ormpresor station near original discharge         I and II           MW-37D         444         180         200         Deep         Alluvial         CA         Bat Cave Wash near original discharge         I and II	ase
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MW-31-135         495         113         133         Deep         Alluvial         CA         North end of MW-20 bench         II           MW-34-100         459         89.5         99.5         Deep         Alluvial         CA         Eastern Floodplain near river         I and II           MW-37D         484         180         200         Deep         Alluvial         CA         Bat Cave Wash north of RR tracks         I           MW-38S         523         75         95         Shallow         Alluvial         CA         Bat Cave Wash north of RR tracks         I           MW-38D         523         163         183         Deep         Alluvial         CA         Bat Cave Wash near original discharge         II           MW-38D         523         163         183         Deep         Alluvial         CA         Bat Cave Wash near original discharge         II           MW-38D         523         163         183         Deep         Alluvial         CA         Bat Cave Wash near original discharge         II           MW-38D         523         163         183         Deep         Alluvial         CA         Floodplain near MW-20 bench         I           MW-405         567         240	
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MW-39-0704656070Mid-depthAlluvialCAFloodplain near MW-20 bench1MW-40D567240260DeepAlluvialCAWestern edge of plume at 1-40 medianIIMW-44-125471114124DeepAlluvialCAEastern floodplain well north of PE-1IIMW-45-0954678393DeepFluvialCAEastern floodplain well near PE-1IIMW-46-175481165175DeepAlluvialCAEastern floodplain at north edge of plumeIIMW-47-0554834555ShallowAlluvialCAPark Moabi road at northern edge of plumeIIMW-1348728.582.5ShallowAlluvialCAAdjacent to northern edge of Bat Cave WashI	
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MW-46-175481165175DeepAlluvialCAEastern floodplain at north edge of plumeIIMW-47-0554834555ShallowAlluvialCAPark Moabi road at northern edge of plumeIIMargin WellsMW-1348728.582.5ShallowAlluvialCAAdjacent to northern end of Bat Cave WashI	
MW-47-0554834555ShallowAlluvialCAPark Moabi road at northern edge of plumeIIMwellsMW-1348728.582.5ShallowAlluvialCAAdjacent to northern end of Bat Cave WashI	
Margin Wells         Alluvial         CA         Adjacent to northern end of Bat Cave Wash         I	
MW-13         487         28.5         82.5         Shallow         Alluvial         CA         Adjacent to northern end of Bat Cave Wash         I	
MW-14 570 111 131 Shallow Alluvial CA Between Bat Cave Wash and East Mesa injection well area I	
MW-33-090 485 69 89 Mid-depth Alluvial CA Eastern floodplain north of plume edge I	
MW-33-210 485 190 210 Deep Alluvial CA Eastern floodplain north of plume edge I	
MW-35-060 481 41 61 Shallow Alluvial CA Edge of northern floodplain off Park Moabi Road I	
MW-35-135 481 116 136 Deep Alluvial CA Edge of northern floodplain off Park Moabi Road I and II	II
MW-37S 484 64 84 Mid-depth Alluvial CA Bat Cave Wash north of RR tracks II	
MW-40S         566         115         135         Shallow         Alluvial         CA         Western edge of plume at I-40 median         I	
Reference Wells	
CW-01M       563       140       190       Mid-depth       Alluvial       CA       South of East Mesa injection well area       I	
CW-02M       547       155       205       Mid-depth       Alluvial       CA       East of East Mesa injection well area       I	

# **TABLE 3-1**Chromium Isotope Study Well ListingChromium Isotope Study Summary Report

Well Name	Ground Surface Elevation <sup>1</sup>	Depth to Top of Screen <sup>2</sup>	Depth to Bottom of Screen <sup>2</sup>	Site Aquifer Depth Zone <sup>3</sup>	Geologic Material at Screen	State	Location	CIS Phase
CW-03M	532	172	222	Mid-depth	Alluvial	CA	Northeast of East Mesa injection well area	II
CW-04M	516	119	169	Mid-depth	Alluvial	CA	West of East Mesa injection well area	II
MW-15	640	180.5	200.5	Shallow	Alluvial	CA	West of the compressor station	П
MW-16	655	198	218	Shallow	Alluvial	CA	Southwest of new evaporation ponds	I
MW-17	588	130	150	Shallow	Alluvial	CA	West end of site off Park Moabi access road	I
MW-18	544	85	105	Shallow	Alluvial	CA	Between West Mesa and East Mesa injection well area	I
CA Agriculture Station	NA	NA	NA	NA	Alluvial	CA	Northwest of compressor station	I
GSRV-2	NA	NA	NA	NA	Alluvial	AZ	Northeast of compressor station	П
GSWC-2	NA	NA	NA	NA	Alluvial	AZ	Northeast of compressor station	П
GSWC-4	NA	NA	NA	NA	Alluvial	AZ	Northeast of compressor station	П
Langmaack	NA	NA	NA	NA	Alluvial	AZ	Northeast of compressor station	П
Lily Hill	NA	NA	NA	NA	Alluvial	CA	Northwest of compressor station	I
Needles MW-11	NA	NA	NA	NA	Fluvial	CA	Northwest of compressor station	П
Tayloe	NA	NA	NA	NA	Alluvial	CA	Northwest of compressor station	I
TMLP-2	NA	NA	NA	NA	Alluvial	AZ	East of compressor station	I
OW-02S	546	71	101	Shallow	Alluvial	CA	East Mesa near injection well area	П
OW-03M	556	108	200	Mid-depth	Alluvial	CA	West Mesa	I and II
OW-03S	556	86	116	Shallow	Alluvial	CA	West Mesa	I
OW-05S	549	70	110	Shallow	Alluvial	CA	East Mesa near injection well area	I

Note:

<sup>1</sup> Aquifer depth zone is based on screen elevation and not hydrostratigraphy. It provides a relative comparison of screened intervals of Topock Site Wells.

<sup>2</sup> Feet above mean sea level

<sup>3</sup> Feet below ground suface

NA Not available

See Figures 4-1 and 4-2 for locations of the wells listed above.

### TABLE 3-2

Comparison of USGS and Truesdail Laboratory Results

Chromium Isotope Study Summary Report

			USG	S Lab	TLI La	b
Well	Sample Date		Hexavalent Chromium μg/L	Dissolved Chromium µg/L	Hexavalent Chromium µg/L	Dissolved Chromium µg/L
CA Agriculture Station	05/01/2006		3.00	3.00	2.80	3.33
CW-1M	05/02/2006		13.0	16.0	15.1	17.1
CW-2M	05/02/2006		14.0	16.0	15.5	15.7
Lily Hill	05/01/2006		3.00	3.00	2.60	3.06
MW-10	05/04/2006		1650	1680	1610	1780
MW-13	05/02/2006		21.0	22.0	21.4	22.5
	05/02/2006	FD			21.2	20.5 ^
MW-14	05/02/2006		28.0	31.0	32.6	33.1
MW-16	05/03/2006		7.00	8.00	8.20	9.72
	05/03/2006	FD			8.10	9.88
MW-17	05/09/2006		14.0	16.0	14.6	15.8 J
	05/09/2006	FD			14.4	16.3 J
MW-18	05/01/2006		33.0	34.0	37.6	37.4
MW-19	05/02/2006		1170	1200	1130	1130
MW-20-70	05/05/2006		4600	4770	4100	4670
MW-24B	05/04/2006		6610	6640	5760	6260
	05/04/2006	FD			5760	6200
MW-33-90	05/03/2006		16.0	19.0	16.1	17.8
	05/03/2006	FD			19.3	15.3 ^
MW-33-210	05/05/2006		11.0	14.0	10.0	11.5
MW-34-100	05/03/2006		815	856	900	877
	05/03/2006	FD			920	881
MW-35-60	05/02/2006		26.0	26.0	25.7	38.0
MW-35-135	05/02/2006		15.0	15.0	21.0	19.6
MW-37D	05/03/2006		1780	1940	1970	1750 J
MW-37S	05/04/2006		8.00	9.00	8.10	ND (10)
MW-38S	05/04/2006		750	781	812	846
MW-39-60	05/02/2006		2.00	4.00	1.10	4.07
MW-40S	05/03/2006		4.00	5.00	5.70	6.63
	05/03/2006	FD			5.60	7.20 ^
OW-3M	05/04/2006		15.0	17.0	18.0	20.0

NOTES:

not detected at listed reporting limit (RL) field duplicate data not collected ND

FD

(---)

µg/L micrograms per liter
 J concentration or reporting limit estimated by laboratory or data validation
 ^ dissolved chromium analyzed by Truesdail Laboratories. All other chromium samples analyzed by Emax Laboratories.

#### TABLE 4-1

Chromium Isotope and Hexavalent Chromium Values

Chromium Isotope Study Summary Report

			USGS Lab	TLI Lab	
Well	Sample Date		δ <sup>33</sup> Cr (‰ )	Hexavalent Chromium (µg/L)	
CIS Phase 1					
CA Agriculture Station	05/01/2006		3.16	2.80	
CW-1M	05/02/2006		2.14	15.1	
CW-2M	05/02/2006		2.64	15.5	
Lily Hill	05/01/2006		2.56	2.60	
MW-10	05/04/2006		-0.12	1610	
MW-13	05/02/2006 05/02/2006	FD	3.95 	21.4 21.2	
MW-14	05/02/2006		3.20	32.6	
MW-16	05/03/2006 05/03/2006	FD	1.75 	8.20 8.10	
MW-17	05/09/2006 05/09/2006	FD	2.49 	14.6 14.4	
MW-18	05/01/2006		2.69	37.6	
MW-19	05/02/2006		0.58	1130	
MW-20-70	05/05/2006		-0.11	4100	
MW-24B	05/04/2006 05/04/2006	FD	-0.16 	5760 5760	
MW-33-90	05/03/2006 05/03/2006	FD	3.57 	16.1 19.3	
MW-33-210	05/05/2006		3.90	10.0	
MW-34-100	05/03/2006 05/03/2006	FD	0.89	900 920	
MW-35-60	05/02/2006		2.46	25.7	
MW-35-135	05/02/2006		2.76	21.0	
MW-37D	05/03/2006		0.94	1970	
MW-37S	05/04/2006		0.62	8.10	
MW-38S	05/04/2006		-0.02	812	
MW-39-60	05/02/2006		1.26	1.10	
MW-40S	05/03/2006 05/03/2006	FD	3.65	5.70 5.60	
OW-3M	05/04/2006		0.88	18.0	
CIS Phase 2					
CW-3M	05/02/2007 05/02/2007	FD	0.01 1.12	11.4 11.4	
CW-4M	05/01/2007		0.41	20.8	
EPNG-2	05/02/2007		2.94	9.60	
GSRV-2	07/10/2007		0.93	25.0	
GSWC-2	05/02/2007		1.20	1.50	
GSWC-4	05/02/2007		0.54	10.7	

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#### TABLE 4-1

Chromium Isotope and Hexavalent Chromium Values

Chromium Isotope Study Summary Report

			USGS Lab	TLI Lab	
Well	Sample Date		$\delta^{53}$ Cr (‰)	Hexavalent Chromium (μg/L)	
CIS Phase 2					
Langmaack	05/02/2007		1.50	18.1	
MW-9	05/03/2007		1.24	286	
MW-11	05/03/2007 05/03/2007	FD	0.72 0.54	350 356	
MW-15	05/04/2007		0.63	21.1	
MW-31-135	05/01/2007		1.47	46.1	
MW-34-100	04/30/2007 04/30/2007	FD	0.71 0.84	626 632	
MW-35-135	05/04/2007 05/04/2007	FD	0.91 0.79	27.2 27.8	
MW-38D	05/03/2007		0.08	68.9	
MW-40D	05/04/2007		1.38	78.0	
MW-44-125	05/03/2007 05/03/2007	FD	1.27 1.06	254 300	
MW-45-095a	05/04/2007		1.21	169	
MW-46-175	05/04/2007		0.22	86.4	
MW-47-55	05/04/2007		0.62	30.3	
Needles MW-11	05/02/2007		1.15	2.40	
OW-2S	04/30/2007		1.79	35.0	
OW-3M	05/01/2007		0.63	17.8	
OW-3S	04/30/2007		1.68	20.0	
OW-5S	04/30/2007		2.48	24.1	
P-2	05/02/2007		0.05	2.50	
Tayloe	05/02/2007		^	1.20	
TMLP-2	05/03/2007		0.59	20.2	

### NOTES:

% reported in parts per thousand difference from international chromium isotope standard NST 979

μg/L micrograms per liter FD field duplicate

(---) data not collected

Λ The Tayloe well's very low Cr(VI) concentration prevented an accurate chromium isotope measurement.

		Dissolved Metals							Alkalinity, Alkalinity,				Total Total Dissolved Kieldahl					<b>NP</b>	Total	Oxygen 18	Deuterium
	Sample	Sodium	Potassium	Calcium	Magnesium	Manganese	Iron	Boron	as Bicarbonate	as Carbonate	Sulfate	Fluoride	Silica	Dissolved Solids	Kjeldani Nitrogen	Ammonia	Chloride	Nitrate as N	Organic Carbon	(δ <sup>18</sup> 0)	(δ <sup>2</sup> Η)
Well	Date	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(‰)	(‰)
CIS Phase 1																					
CA Agriculture Station	05/01/2006	235	5.52	60.9	17.6	0.00124	ND (0.1)	0.603	90.6	ND (5.0)	219	1.27	31.4	825	ND (0.5)	ND (0.5)	265	1.80	ND (1.0)	-9.3	-63.1
CW-1M	05/02/2006	1,310	9.59	106	8.94	ND (0.001)	ND (0.1)	1.08 J	49.0	ND (5.0)	355	2.72	17.8	3670 J	ND (0.5)	ND (0.5)	1760	0.832	ND (1.0)	-10.1	-69.8
CW-2M	05/02/2006	1,450	10.5	113	8.72	0.00119	ND (0.1)	1.11 J	51.7	ND (5.0)	372	2.82	17.8	3630 J	ND (0.5)	ND (0.5)	1900	0.821	ND (1.0)	-10.2	-71.1
Lily Hill	05/01/2006	293	12.0	93.8	43.9	0.00794	ND (0.1)	0.506	217	ND (5.0)	418	1.52	34.9	1390	ND (0.5)	ND (0.5)	299	1.85	ND (1.0)	-14.1	-98.7
MW-10	05/04/2006	639	9.01	74.7	12.7	ND (0.001)	ND (0.1)	1.96 J	261	ND (5.0)	392	10.9	36.7	1790	ND (0.5)	ND (0.5)	552	10.6	1.12	-5.7	-44.4
MW-13	05/02/2006	288	6.05	95.7	13.3	ND (0.001)	ND (0.1)	0.343 J	87.1	ND (5.0)	161	1.28	23.6	1100 J	ND (0.5)	ND (0.5)	396	4.57	ND (1.0)	-9.4	-65.6
MW-14	05/02/2006	242	8.02	73.0	10.9	ND (0.001)	ND (0.1)	0.352 J	87.1	ND (5.0)	126	2.20	22.7	1160 J	ND (0.5)	ND (0.5)	312	5.37	ND (1.0)	-9.9	-63.3
MW-16	05/03/2006	205	4.04	28.4	4.85	ND (0.001)	ND (0.1)	0.364	107	ND (5.0)	114	2.20	22.2	605	ND (0.5)	ND (0.5)	193	2.72	ND (1.0)	-9.5	-62.7
MW-16	05/03/2006 FD	205	4.19	28.9	5.13	ND (0.001)	ND (0.1)	0.363	104	ND (5.0)	117	1.68	22.5	620	ND (0.5)	ND (0.5)	196	2.95	ND (1.0)	-9.5	-65.1
MW-17	05/09/2006	249	9.41	122	18.8	ND (0.001)	ND (0.1)	0.213	53.2	ND (5.0)	694	1.92	19.4	1330	ND (0.5)	ND (0.5)	104	4.06	ND (1.0)	-8.4	-57.7
MW-17	05/09/2006 FD	258	9.37	118	18.0	ND (0.001)	ND (0.1)	0.22	53.2	ND (5.0)	708	1.88	19.2	1360	ND (0.5)	ND (0.5)	105	4.22	ND (1.0)	-8.3	-56.6
MW-18	05/01/2006	147	7.12	71.3	12.7	ND (0.001)	ND (0.1)	0.184	96.1	ND (5.0)	86.6	0.546	21.7	750	ND (0.5)	ND (0.5)	269	3.75	ND (1.0)	-10.2	-61.9
MW-19	05/02/2006	358	8.15	118	18.8	ND (0.001)	ND (0.1)	0.43 J	81.6	ND (5.0)	191	2.26	23.2	1380 J	ND (0.5)	ND (0.5)	502	4.86	ND (1.0)	-8.3	-61.7
MW-20-70	05/05/2006	461	9.55	162	49.2	ND (0.001)	ND (0.1)	0.476	74.5	ND (5.0)	376	1.34	22.9	1750	ND (0.5)	ND (0.5)	696	9.86	ND (1.0)	-8.2	-55.9
MW-24B	05/04/2006	3,380	32.9	296	7.75	0.0266	ND (0.1)	2.90 J	53.2	ND (5.0)	1260	2.08	22.4	9220	ND (0.5)	ND (0.5)	4450	11.4	1.64	-4.4 J	-53
MW-24B	05/04/2006 FD	3,370	32.9	301	7.59	0.0264	ND (0.1)	2.92 J	45.3	ND (5.0)	1260	2.12	22.3	8630	ND (0.5)	ND (0.5)	4380	11.5	2.02	-5.1 J	-52.9
MW-33-90	05/03/2006	1,900	14.9	323	37.2	0.00211	ND (0.1)	1.15	55.9	ND (5.0)	496	1.79	18.1	5690	ND (0.5)	ND (0.5)	3020	1.09	ND (1.0)	-10.6	-73.5
MW-33-210	05/05/2006	3,980	35.1	633	92.0	0.0822	ND (0.1)	1.22	63.9	ND (5.0)	1300	ND (0.5)	20.1	12200	ND (0.5)	ND (0.5)	6250	1.05	ND (1.0)	-11.3	-75.4
MW-34-100	05/03/2006	3,890	31.1	162	12.0	0.0567	ND (0.1)	2.73	133	ND (5.0)	1200	0.527	19.5	9940	ND (0.5)	ND (0.5)	5060	1.34	2.17	-10.5	-74.5
MVV-34-100	05/03/2006 FD	3,900	31.3	166	12.2	0.0572	ND (0.1)	2.77	136	ND (5.0)	1230	0.643	19.5	9990	ND (0.5)	ND (0.5)	5170	1.33	2.22	-10.6	-71.9
MVV-35-60	05/02/2006	1,180	12.6	297	40.5	ND (0.001)	ND (0.1)	0.68 J	76.2	ND (5.0)	353	1.92	20.3	4000 J	ND (0.5)	ND (0.5)	2110	1.93	ND (1.0)	-9.6	-70.2
NIN 27D	05/02/2006	2,240	14.3	339	41.0	0.00223	ND (0.1)	0.79 J	49.0	ND (5.0)	805	1.70	17.1	6460 J	ND (0.5)	ND (0.5)	3160	2.20	ND (1.0)	-10.6	-79.7
NIN/ 279	05/03/2006	3, 130 J	21.7 J	401 J	23.7 J	ND (0.001)	ND (0.1)	2.00 J	42.0	ND (5.0)	000	1.11	19.2	8790	ND (0.5)	ND (0.5)	4770	3.33	ND (1.0)	-10.5	-70
M/W/-38S	05/04/2006	000 770	9.51	133	20.2	0.00376	ND(0.1)	0.014 J 2 50 J	173	ND (5.0)	240 523	2.15	20.0	2000	ND (0.5)	ND (0.5)	852	1.43 8.73	ND(1.0)	-7.5	-00.1
M/M/-30-60	05/04/2000	2 400	9.09	372	100	0.00370	ND(0.1)	2.50 J	256	ND (5.0)	973 873	2.50	20.0	2390 4600 I	ND (0.5)	ND (0.5)	3510		3.80	-4.3	-42.0
MW-40S	05/02/2000	2,430	7 31	031	10.0	0.103	ND(0.1)	0.357	71.9	ND (5.0)	158	2.50	23.2	4000 3	ND (0.5)	ND (0.5)	523	A 60	0.00 ND (1 0)	-9.7	-68.1
0W-3M	05/04/2006	1 1 2 0	7.80	75.6	7.67	ND (0.001)	ND(0.1)	0.007	58.6	ND (5.0)	329	1 56	16.9	2830	ND (0.5)	ND (0.5)	1510	0.886	ND (1.0)	-7.8	-69.7
CIS Phase 2	00/04/2000	1,120	7.00	70.0	1.01	110 (0.001)	ND (0.1)	0.027 0	00.0	110 (0.0)	020	1.00	10.0	2000	ND (0.0)	ND (0.0)	1010	0.000	ND (1.0)	7.0	00.1
	05/02/2007	1 760	13.0	221	18.3			1 1 /	45.0		401	3 /7	18.5	5730			2000	5 08		-10.8	-80.1
CW-3M	05/02/2007 ED	1,700	13.9	221	18.1	ND (0.001)	ND (0.5)	1.14	45.0	ND (5.0)	308	3.58		5900	ND (0.5)	ND (0.3)	2300	0.617 \	ND (0.3)	-10.0	-00.1
CW-4M	05/01/2007	1,700	10.3	137	11.5	ND (0.001)	ND (0.5)	0.804	55.0	ND (5.0)	289	2 27	18.6	3460	ND (0.5)	ND (0.5)	1780	1 77	ND (0.3)	-10.4	-77
EPNG-2	05/02/2007	165.1	5 28	35.5	6 84	ND (0.001)	ND (0.1)	0.004	103	ND (5.0)	64.4	4 28	24.2	604	ND (0.5)	ND (0.5)	201	2 19 *	ND (0.3)	-11.5	-79 4
GSRV-2	07/10/2007	55.2	4.63	39.2	12.6	ND (0.001)	ND (0.1)	0.149	160	ND (5.0)	42.6	2.12	34.4	370	ND (0.5)	ND (0.5)	59.4	3.42	0.742	-9.6	-70.7
GSWC-2	05/02/2007	116	5.63	29.9	11.3	0.00948	ND (0.1)	0.285	153	ND (5.0)	54.9	0.663	34.2	489	ND (0.5)	ND (0.5)	134	1.69 *	0.332	-10.4	-76.7
GSWC-4	05/02/2007	85.7	4.85	25.6	8.75	ND (0.001)	ND (0.1)	0.224	155	ND (5.0)	37.8	0.835	35.1	348	ND (0.5)	ND (0.5)	51.8	2.21 J	ND (0.3)	-10.4	-73.8
Langmaack	05/02/2007	67.7	5.42	30.3	12.3	0.00123	ND (0.1)	0.20	140	ND (5.0)	36.2	0.842	36.8	351	ND (0.5)	ND (0.5)	50.9	4.06	ND (0.3)	-10.7	-74.7
MW-9	05/03/2007	415	12.2	152	44.3	ND (0.001)	ND (0.1)	0.666	128	ND (5.0)	246	ND (0.5)	22.9	1680	ND (0.5)	ND (1.0)	733	22.6	0.325	-10	-65.8
MW-11	05/03/2007	286	8.31	128	18.5	ND (0.001)	ND (0.1)	0.479	92.5 J	ND (5.0)	282	1.02	22.1	1340	ND (0.5)	ND (1.0)	469	9.64 J	0.661	-9.5	-66.2
MW-11	05/03/2007 FD	288	8.41	130	18.5	ND (0.001)	ND (0.1)	0.473	148 J	ND (5.0)	324	0.998	22.4	1350	ND (0.5)	ND (1.0)	466	16.4 J	1.00	-9.0	-65.4
MW-15	05/04/2007	191	9.90	139	32.8	ND (0.001)	ND (0.1)	0.268	72.5	ND (5.0)	185	0.54	22.4	1270	ND (0.5)	ND (0.5)	542	9.73	0.433	-10	-70.1
MW-31-135	05/01/2007	2,120	15.0	230	14.5	ND (0.001)	ND (0.1)	1.32	39.0	ND (5.0)	244	4.05	18.5	6550	ND (0.5)	ND (0.5)	3380	0.797	ND (0.3)	-11.5	-81.7
MW-34-100	04/30/2007	3,840	31.5	186	12.0	0.0267	ND (0.1)	2.39	123	ND (5.0)	1040	1.78	19.7	10600	ND (0.5)	ND (0.5)	5920	1.38	ND (0.3)	-10.9	-80.7
MW-34-100	04/30/2007 FD	3,920	32.1	189	12.0	0.0278	ND (0.1)	2.40	123	ND (5.0)	1050	1.72	20.0	11900	ND (0.5)	ND (0.5)	5880	1.37	ND (0.3)	-11.2	-82.1
MW-35-135	05/04/2007	2,200	13.8	316	36.9	0.00276	ND (0.1)	0.894	52.5	ND (5.0)	854	1.95	16.3	6900	ND (0.5)	ND (0.5)	3360	2.39	ND (0.3)	-12	-87.1
MW-35-135	05/04/2007 FD	2,100	13.1	301	35.7	ND (0.001)	ND (0.1)	0.786	52.5	ND (5.0)	856	1.92	16.9	7100	ND (0.5)	ND (0.5)	3330	2.38	ND (0.3)	-11.9	-87
MW-38D	05/03/2007	4,760	44.1	351	8.51	0.00479	ND (0.1)	2.85	32.0	ND (5.0)	760	4.58	21.2	13600	ND (0.5)	ND (1.0)	7510	14.7	ND (0.3)	-11	-82.7
MW-40D	05/04/2007	3,310	25.7	375	45.4	0.123	ND (0.1)	2.05	51.0	ND (5.0)	682	2.79	20.7	9660	ND (0.5)	ND (0.5)	5280	19.7	ND (0.3)	-10.7	-80.6
MW-44-125	05/03/2007	2,650	19.7	142	16.6	0.777	ND (0.1)	1.85	82.5	ND (5.0)	678	2.87	14.3	7090	ND (0.5)	ND (0.5)	3690	6.43	ND (0.3)	-10.8	-80.2
MW-45-095	05/04/2007	2,240	18.0	164	16.9	0.00235	0.129	1.52	198	ND (5.0)	739	2.24	20.5	6040	ND (0.5)	ND (0.5)	3100	ND (1.0)	0.36	-11.1	-81.2

				C	issolved Meta	ls			Alkalinity,	Alkalinity,				Total Dissolved	Total Kieldahl			Nitrate	Total Organic	Oxygen 18	Deuterium
Well	Sample Date	Sodium (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Manganese (mg/L)	lron (mg/L)	Boron (mg/L)	Bicarbonate (mg/L)	Carbonate (mg/L)	Sulfate (mg/L)	Fluoride (mg/L)	Silica (mg/L)	Solids (mg/L)	Nitrogen (mg/L)	Ammonia (mg/L)	Chloride (mg/L)	as N (mg/L)	Carbon (mg/L)	(δ°O) (‰)	(δ <sup>∠</sup> Η) (‰)
CIS Phase 2																					
MW-46-175	05/04/2007	3,970	29.9	73.8	2.20	0.0176	ND (0.1)	2.22	43.0	ND (5.0)	680	3.99	15.1	10200	ND (0.5)	ND (0.5)	5650	ND (1.0)	ND (0.3)	-11.5	-87.6
MW-47-55	05/04/2007	654	10.2	166	24.5	ND (0.001)	ND (0.1)	0.564	72.5	ND (5.0)	248	2.32	20.7	2450	ND (0.5)	ND (0.5)	1170	2.00	ND (0.3)	-10.1	-74.3
Needles MW-11	05/02/2007	328	12.6	102	44.2	0.0194	ND (0.1)	0.53	215	ND (5.0)	468	1.68	43.1	1510	ND (0.5)	ND (0.5)	316	1.91 *	0.952	-14.9	-111
OW-2S	04/30/2007	331	5.84	36.9	4.97	0.0011	ND (0.5)	0.737	103	ND (5.0)	131 J	5.23	20.2	985	ND (0.5)	ND (0.5)	474 J	4.25 J	ND (0.3)	-10	-70.4
OW-3M	05/01/2007	1,080	7.81	75.2	6.86	ND (0.001)	ND (0.1)	0.938	57.0	ND (5.0)	266	2.58	17.1	3120	ND (0.5)	ND (0.5)	1510	1.31	ND (0.3)	-10.4	-77.2
OW-3S	04/30/2007	203	9.19	112	16.2	0.00943	ND (0.1)	0.181	62.5	ND (5.0)	90.9 J	3.25	21.0	1120	ND (0.5)	ND (0.5)	564	3.25	ND (0.3)	-9.5	-70
OW-5S	04/30/2007	273 J	6.88	59.2 J	9.12	ND (0.001)	ND (0.5)	0.416 J	87.5	ND (5.0)	114 J	2.82	21.0	983	ND (0.5)	ND (0.5)	480	4.25	ND (0.3)	-9.9	-70.8
P-2	05/02/2007	780	10.9	297	55.4	ND (0.001)	ND (0.1)	0.561	51.0	ND (5.0)	224	2.63	22.7	3360	ND (0.5)	ND (0.5)	1670	16.2	ND (0.3)	-10.8	-76.3
Tayloe	05/02/2007	146	4.25	34.8	5.23	ND (0.001)	ND (0.1)	0.357	110	ND (5.0)	90.9	0.881	22.8	508	ND (0.5)	ND (2.5)	140	2.14 *	ND (0.3)	-9.6	-64
TMLP-2	05/03/2007	50.4	5.94	21.7	9.51	0.00112	ND (0.1)	0.125	148	ND (5.0)	14.7	1.22	38.2	267	ND (0.5)	ND (0.5)	27.5	15.9	ND (0.3)	-10.5	-74.9

Notes:

mg/L milligrams per liter

μg/L micrograms per liter parts per thousand difference from international chromium isotope standard NST 979

ND parameter not detected at the listed reporting limit

concentration or reporting limit estimated by laboratory or data validation J

not collected ----

FD field duplicate

^ Total nitrate/nitrite as nitrogen

\* Nitrate as nitrogen was reanalyzed 7/25/2007. The reanalysis results are shown.

### TABLE 4-3

### Trace Elements Concentrations Chromium Isotope Study Summary Report

Well	Sample Date		Arsenic	Barium	Hexavalent Chromium	Chromium	Copper	Molybdenum	Nickel	Lead	Selenium	Vanadium	Zinc
CIS Phase 1			1										
CA Agriculture Station	05/01/2006		3.57	34.3	2.80	3.33	1.72	23.4	ND (1.0)	ND (1.0)	2.99	15.3	22.7
CW-01M	05/02/2006		2.22	69.6	15.1	17.1	1.21	23.9	1.73	ND (1.0)	ND (1.0)	4.19	ND (10)
CW-02M	05/02/2006		2.79	58.6	15.5	15.7	ND (1.0)	24.7	ND (1.0)	ND (1.0)	ND (1.0)	5.13	ND (10)
Lily Hill	05/01/2006		7.69	68.6	2.60	3.06	20.5	17.2	2.33	4.04	3.97	13.1	32.7
MW-10	05/04/2006		8.31	58.1	1610	1780	1.18	122	1.96	1.06	3.91	37.9	ND (10)
MW-13	05/02/2006		2.20	54.3	21.4	22.5	ND (1.0)	9.15	4.48	ND (1.0)	3.96	6.44	ND (10)
MW-13	05/02/2006	FD			21.2	20.5 *							
MW-14	05/02/2006		1.40	104	32.6	33.1	ND (1.0)	11.6	4.61	ND (1.0)	4.26	5.02	ND (10)
MW-16	05/03/2006		9.87	30.2	8.20	9.72	ND (1.0)	10.9	8.53	ND (1.0)	1.49	34.7	ND (10)
MW-16	05/03/2006	FD	10.0	30.8	8.10	9.88	ND (1.0)	11.4	9.24	ND (1.0)	1.55	35.4	ND (10)
MW-17	05/09/2006		1.36	37.5	14.6	15.8 J	ND (1.0)	14.6	2.23 J	ND (1.0)	12.8	4.08	56.0
MW-17	05/09/2006	FD	1.18	35.0	14.4	16.3 J	ND (1.0)	16.8	2.08 J	ND (1.0)	12.6	4.05	44.4
MW-18	05/01/2006		1.08	62.5	37.6	37.4	ND (1.0)	4.71	ND (1.0)	ND (1.0)	3.13	4.29	ND (10)
MW-19	05/02/2006		1.32	81.2	1130	1130	ND (1.0)	7.72	20.2	ND (1.0)	4.21	5.02	ND (10)
MW-20-070	05/05/2006		2.01	39.9	4100	4670	ND (1.0)	22.4	ND (1.0)	ND (1.0)	10.1	9.66	ND (10) J
MW-24B	05/04/2006		8.43	38.5	5760	6260	ND (1.0)	64.9	ND (1.0)	ND (1.0)	14.3	8.13	12.7
MW-24B	05/04/2006	FD	8.34	38.6	5760	6200	ND (1.0)	64.4	ND (1.0)	ND (1.0)	14.1	8.21	11.2
MW-33-090	05/03/2006		1.89	66.2	16.1	17.8	ND (1.0)	36.9	2.33	ND (1.0)	1.06	5.25	17.0
MW-33-090	05/03/2006	FD			19.3	15.3 *							
MW-33-210	05/05/2006		2.03	52.5	10.0	11.5	ND (1.0)	15.1	ND (1.0)	ND (1.0)	ND (1.0)	1.79	ND (10) J
MW-34-100	05/03/2006		1.85	25.7	900	877	ND (1.0)	36.0	ND (1.0)	ND (1.0)	ND (1.0)	2.02	14.0 J
MW-34-100	05/03/2006	FD	2.01	25.9	920	881	ND (1.0)	36.7	ND (1.0)	ND (1.0)	ND (1.0)	2.15	45.7 J
MW-35-060	05/02/2006		1.50	87.5	25.7	38.0	1.21	8.56	2.15	ND (1.0)	1.19	3.11	23.3 J
MW-35-135	05/02/2006		1.37	53.4	21.0	19.6	ND (1.0)	20.9	1.01	ND (1.0)	1.27	1.84	18.2 J
MW-37D	05/03/2006		3.79	44.0	1970	1750 J	ND (1.0)	47.5	ND (1.0)	ND (1.0)	3.66	6.25	ND (10)
MW-37S	05/04/2006		2.26	61.0	8.10	ND (10)	ND (1.0)	19.9	ND (1.0)	ND (1.0)	1.37	8.99	ND (10)
MW-38S	05/04/2006		3.62	38.7	812	846	ND (1.0)	63.7	ND (1.0)	ND (1.0)	5.10	18.8	ND (10)
MW-39-060	05/02/2006		2.21	87.8	1.10	4.07	ND (1.0)	10.9	1.20	ND (1.0)	ND (1.0)	9.27	ND (10)
MW-40S	05/03/2006		1.60	103	5.70	6.63	ND (1.0)	8.59	ND (1.0)	ND (1.0)	7.37	9.21	ND (10)
MW-40S	05/03/2006	FD			5.60	7.20 *							
OW-03M	05/04/2006		2.71	89.0	18.0	20.0	1.12	16.1	ND (1.0)	ND (1.0)	1.03	5.00	ND (10)
CIS Phase 2			1										
CW-03M	05/02/2007		1.22	54.2	11.4	11.2	ND (1.0)	21.4	ND (1.0)	ND (1.0)	ND (1.0)	2.31	ND (10)
CW-03M	05/02/2007	FD	1.30	53.7	11.4	11.4	ND (1.0)	21.0	1.21	ND (1.0)	ND (1.0)	2.43	ND (10)
CW-04M	05/01/2007		2.46	75.8	20.8	21.8	ND (1.0)	11.3	2.19	ND (1.0)	1.04	3.40	ND (10)
EPNG-2	05/02/2007		4.59	89.4	9.60	9.43	ND (1.0)	7.22	ND (1.0)	ND (1.0)	1.09	11.4	10.3 J

#### TABLE 4-3

#### Trace Elements Concentrations Chromium Isotope Study Summary Report

	Sample			Hexavalent								
Well	Date	Arsenic	Barium	Chromium	Chromium	Copper	Molybdenum	Nickel	Lead	Selenium	Vanadium	Zinc
CIS Phase 2												
GSRV-2	07/10/2007	5.40	55.2	25.0	25.6	ND (1.0)	5.63	ND (1.0)	ND (1.0)	1.61	16.7	ND (10)
GSWC-2	05/02/2007	7.25	56.9	1.50	2.99	3.25	6.25	ND (1.0)	ND (1.0)	1.31	15.6	24.3 J
GSWC-4	05/02/2007	7.79	45.0	10.7	11.0	ND (1.0)	5.75	ND (1.0)	ND (1.0)	1.21	19.2	ND (10)
Langmaack	05/02/2007	5.38	28.6	18.1	18.0	1.59	ND (2.0)	ND (1.0)	ND (1.0)	1.72	14.7	ND (10)
MW-09	05/03/2007	1.90	52.2	286	341	4.06	ND (2.0)	2.31	3.17	6.22	12.3	19.1
MW-11	05/03/2007	1.54	36.9	350	321	1.28	8.94	ND (1.0)	1.17	5.61	7.43	ND (10)
MW-11	05/03/2007 F	D 1.64	37.2	356	337	2.29	8.82	ND (1.0)	1.23	5.71	7.88	ND (10)
MW-15	05/04/2007	1.58	80.7	21.1	21.0	1.11	9.69	3.08	1.27	4.58	10.9	ND (10)
MW-31-135	05/01/2007	4.64	37.5	46.1	47.4	ND (1.0)	30.9	ND (1.0)	ND (1.0)	ND (1.0)	10.8	ND (10)
MW-34-100	04/30/2007	1.53	25.3	626	590	ND (1.0)	34.7	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (10)
MW-34-100	04/30/2007 F	D 1.75	25.8	632	599	ND (1.0)	36.2	1.09	ND (1.0)	ND (1.0)	1.12	16.8
MW-35-135	05/04/2007	1.09	46.1	27.2	26.2	ND (1.0)	21.1	ND (1.0)	ND (1.0)	1.25	1.40	ND (10)
MW-35-135	05/04/2007 F	D 1.07	44.2	27.8	25.2	ND (1.0)	20.3	ND (1.0)	ND (1.0)	1.20	1.48	ND (10)
MW-38D	05/03/2007	8.44	48.2	68.9	69.6	ND (1.0)	79.7	ND (1.0)	ND (1.0)	ND (1.0)	6.15	ND (10)
MW-40D	05/04/2007	4.36	64.0	78.0	79.6	1.12	45.8	1.40	ND (1.0)	2.12	5.49	ND (10)
MW-44-125	05/03/2007	2.99	70.8	254	326	ND (1.0)	125	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (10)
MW-44-125	05/03/2007 F	D		300	309 *							
MW-45-095	05/04/2007	3.76	19.6	169	140	6.45	26.8	ND (1.0)	1.53	ND (1.0)	6.14	42.2
MW-46-175	05/04/2007	2.71	29.0	86.4	114	ND (1.0)	196	ND (1.0)	ND (1.0)	ND (1.0)	3.56	ND (10)
MW-47-055	05/04/2007	1.35	54.4	30.3	31.6	ND (1.0)	8.05	ND (1.0)	ND (1.0)	1.46	2.40	ND (10)
Needles MW-11	05/02/2007	6.35	27.8	2.40	2.45	2.15	15.0	ND (1.0)	ND (1.0)	4.03	9.66	ND (10)
OW-02S	04/30/2007	2.45	50.3	35.0	37.4	ND (1.0)	40.0	1.73	ND (1.0)	2.77	5.80	ND (10)
OW-03M	05/01/2007	2.34	85.8	17.8	18.2	ND (1.0)	15.2	ND (1.0)	ND (1.0)	ND (1.0)	3.06	ND (10)
OW-03S	04/30/2007	ND (1.0)	162	20.0	23.4	ND (1.0)	4.43	6.01	ND (1.0)	2.26	1.55	ND (10)
OW-05S	04/30/2007	1.33	59.4	24.1	25.6	1.14	22.6	3.00	ND (1.0)	2.69	3.70	ND (10)
P-2	05/02/2007	2.13	166	2.50	2.70	ND (1.0)	4.23	ND (1.0)	ND (1.0)	1.86	11.2	ND (10)
Tayloe	05/02/2007	5.11	55.5	1.20	1.26	1.03	9.54	ND (1.0)	2.53	2.26	8.29	50.3 J
TMLP-2	05/03/2007	6.54	10.7	20.2	23.0	ND (1.0)	5.39	ND (1.0)	ND (1.0)	ND (1.0)	19.5	ND (10)

Notes:

ND

parameter not detected at the listed reporting limit concentration or reporting limit estimated by laboratory or data validation J

not collected or not available ----

field duplicate FD \*

dissolved chromium analyzed by Truesdail Laboratories. All other dissolved chromium samples analyzed by EMAX Laboratories.

All results are dissolved metals concentrations in micrograms per liter ( $\mu$ g/L).

Appendix A Chromium Isotope Study Data Set

### TABLE 1

### Comparison of USGS and Truesdail Laboratory Results *Chromium Isotope Study Summary Report*

			USG	S Lab	TLI Lab				
Well	Sample Date		Hexavalent Chromium µg/L	Dissolved Chromium µq/L	Hexavalent Chromium μg/L	Dissolved Chromium µg/L			
CA Agriculture Station	05/01/2006		3.00	3.00	2.80	3.33			
CW-1M	05/02/2006		13.0	16.0	15.1	17.1			
CW-2M	05/02/2006		14.0	16.0	15.5	15.7			
Lily Hill	05/01/2006		3.00	3.00	2.60	3.06			
MW-10	05/04/2006		1,650	1,680	1,610	1,780			
MW-13	05/02/2006		21.0	22.0	21.4	22.5			
	05/02/2006	FD			21.2	20.5 ^			
MW-14	05/02/2006		28.0	31.0	32.6	33.1			
MW-16	05/03/2006		7.00	8.00	8.20	9.72			
	05/03/2006	FD			8.10	9.88			
MW-17	05/09/2006		14.0	16.0	14.6	15.8 J			
	05/09/2006	FD			14.4	16.3 J			
MW-18	05/01/2006		33.0	34.0	37.6	37.4			
MW-19	05/02/2006		1,170	1,200	1,130	1,130			
MW-20-70	05/05/2006		4,600	4,770	4,100	4,670			
MW-24B	05/04/2006		6,610	6,640	5,760	6,260			
	05/04/2006	FD			5,760	6,200			
MW-33-210	05/05/2006		11.0	14.0	10.0	11.5			
MW-33-90	05/03/2006		16.0	19.0	16.1	17.8			
	05/03/2006	FD			19.3	15.3 ^			
MW-34-100	05/03/2006		815	856	900	877			
	05/03/2006	FD			920	881			
MW-35-135	05/02/2006		15.0	15.0	21.0	19.6			
MW-35-60	05/02/2006		26.0	26.0	25.7	38.0			
MW-37D	05/03/2006		1,780	1,940	1,970	1,750 J			
MW-37S	05/04/2006		8.00	9.00	8.10	ND (10)			
MW-38S	05/04/2006		750	781	812	846			
MW-39-60	05/02/2006		2.00	4.00	1.10	4.07			
MW-40S	05/03/2006		4.00	5.00	5.70	6.63			
	05/03/2006	FD			5.60	7.20 ^			
OW-3M	05/04/2006		15.0	17.0	18.0	20.0			

#### NOTES:

ND = not detected at listed reporting limit (RL)

FD = field duplicate

(---) = data not collected

 $\mu g/L =$  micrograms per liter

J = concentration or reporting limit estimated by laboratory or data validation

^ = dissolved chromium analyzed by Truesdail Laboratories. All other chromium samples analyzed by Emax Laboratories.

### TABLE 2

		Sample		Primary <sup>53</sup> Cr	Reanalysis <sup>53</sup> Cr
Well	Sample ID	Date		δ (‰)	δ (‰)
CW-3M	CIS-001	05/02/2007		0.01	-0.09
	MW-91-012	05/02/2007	FD	1.12	
CW-4M	CIS-007	05/01/2007		0.41	
EPNG-2	CIS-010	05/02/2007		2.94	2.51
GSRV-2	CIS-015	07/10/2007		0.93	
GSWC-2	CIS-019	05/02/2007		1.2	
GSWC-4	CIS-025	05/02/2007		0.54	
Langmaack	CIS-002	05/02/2007		1.5	
MW-9	CIS-003	05/03/2007		1.24	
MW-11	CIS-021	05/03/2007		0.72	
	CIS-089	05/03/2007	FD	0.54	
MW-15	CIS-026	05/04/2007		0.63	
MW-31-135	CIS-012	05/01/2007		1.47	
MW-34-100	CIS-004	04/30/2007		0.71	
	CIS-096	04/30/2007	FD	0.84	
MW-35-135	CIS-027	05/04/2007		0.91	
	CIS-085	05/04/2007	FD	0.79	
MW-38D	CIS-017	05/03/2007		0.08	
MW-40D	CIS-005	05/04/2007		1.38	
MW-44-125	CIS-013	05/03/2007		1.27	
	CIS-087	05/03/2007	FD	1.06	
MW-45-095a	CIS-009	05/04/2007		1.21	
MW-46-175	CIS-022	05/04/2007		0.22	
MW-47-55	CIS-006	05/04/2007		0.62	
Needles MW-11	CIS-020	05/02/2007		1.15	
OW-2S	CIS-011	04/30/2007		1.79	
OW-3M	CIS-023	05/01/2007		0.63	
OW-3S	CIS-014	04/30/2007		1.68	
OW-5S	CIS-018	04/30/2007		2.48	
P-2	CIS-016	05/02/2007		0.05	0.29
TMLP-2	CIS-024	05/03/2007		0.59	0.57

#### NOTES:

FD field duplicate

<sup>%</sup> reported in parts per thousand difference from international chromium isotope standard NST 979

--- not applicable