



**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

March 3, 2006

Mr. Norman Shopay
California Department of Toxic Substances Control
Permitting and Corrective Action Branch
700 Heinz Avenue, Suite 200
Berkeley, California 94710-2721

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

Dear Mr. Shopay:

This letter transmits a work plan and schedule for performing a chromium isotope study in the vicinity of the PG&E Topock Compressor Station. The work plan and schedule are submitted in conformance with the California Department of Toxic Substances Control letter dated January 13, 2006, and modifications thereto as authorized by your email dated February 17, 2006.

If you have any questions, please do not hesitate to call me.

Sincerely,

Enclosure

cc: Kate Burger/DTSC

Chromium Isotope Study Workplan

DATE: March 3, 2006

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 to the southeast of Needles, California (Figure 1).

DTSC has directed PG&E to perform a groundwater study of stable chromium isotope signatures in and around the Topock Facility (DTSC 2006). The purpose of this Chromium Isotope Study is to provide an additional tool to be used potentially in distinguishing chromium releases associated with the Topock Compressor Station from natural chromium in local groundwater. This distinction possibly may enable better definition of the chromium plume, which will support selection of the final remedy for the Corrective Measures Study. CH2M HILL is coordinating with the U.S. Geological Survey (USGS) to plan and conduct the Chromium Isotope Study.

2.0 Background

2.1 Chromium Chemistry

Chromium (Cr) is the 17th most common element in rocks that compose the earth's crust (Hem 1970), and it can enter the environment naturally through weathering of chromium-containing minerals and leaching from soils as well as from discharges from industrial sources (Kimbrough and others, 1999). In aqueous solutions chromium exists as trivalent chromium (Cr[III]) and hexavalent chromium (Cr[VI]). Cr(III) is the predominant form under moderately oxidizing to reducing conditions over a wide range of pH (Ball and Nordstrom, 1998), though it readily forms insoluble precipitates and adsorbs strongly onto minerals in the aquifer matrix. As a result, Cr(III) concentrations are typically very low (i.e., less than 10 micrograms per liter [$\mu\text{g/L}$]) in near-neutral pH waters. Cr(VI) is the predominant form only under strongly oxidizing conditions (Rai and Zachara 1984). Sorption/desorption reactions on aluminum and iron oxide mineral surfaces govern chromium solubility. The different oxidation states have very different adsorption characteristics because of their oppositely charged valences. Cr(VI) forms negatively charged ions when dissolved in water, in contrast to Cr(III) which forms positively charged ions. Cr(III) is therefore much more strongly adsorbed than Cr(VI). Cr(III) sorption increases with increasing pH and is associated with iron-rich surface coatings (Rai and Zachara 1984). Cr(VI) sorption decreases at high pH, and in some studies sorption has been shown to decrease with increasing ionic strength (Rai and Zachara 1984). Reduction of Cr(VI) to Cr(III) can occur under a variety of conditions -- even in oxic environments; and reduction

of Cr(VI) to Cr(III) in anaerobic environments in the presence of sulfide or ferrous ions is almost instantaneous.

2.2 Chromium Isotope Theory

There are four stable isotopes of Cr having atomic masses of 50, 52, 53, and 54 (^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr), with 52 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; Ball et al. 2001).

Reduction of oxidized aqueous species of other redox sensitive elements such as sulfur (SO_4^{2-}) (Harrison and Thode 1957; Brüchert et al. 2001) and selenium (SeO_4^{2-}) (Johnson et al. 1999) tends to enrich the products in the light isotopes because they preferentially react, and the residual reactants become progressively enriched in the heavier isotopes as reduction proceeds. In these cases, the breakage of the bond with oxygen requires significant energy promoting the isotopic fractionation, and is the rate-limiting step in the reduction reaction. If Cr behaves the same way, then variations in the isotopic composition of Cr in groundwater along a flowpath from a suspected Cr source could be used to determine the extent of Cr reduction that has occurred.

Ellis et al. (2002) demonstrated that Cr isotopes are substantially fractionated during abiotic reduction of Cr(VI) to Cr(III). For example, progressive reduction of Cr(VI) in a magnetite slurry, buffered at pH~6 in order to minimize sorption of $\text{Cr}_2\text{O}_4^{2-}$ and HCr_2O_4^- , resulted in progressively increasing $\delta^{53}\text{Cr}$ of the remaining dissolved Cr(VI) ($\delta^{53}\text{Cr}$ is the per mil difference in measured $^{53}\text{Cr}/^{52}\text{Cr}$ relative to that of N.I.S.T. 979, an accepted Cr isotope standard). Using a Rayleigh fractionation model, in which Cr(III) once produced is immediately removed from further reaction (e.g., by sorption onto mineral surfaces), an instantaneous fractionation factor ($\alpha_{\text{Cr(III)-Cr(VI)}} = 0.9965$) was calculated for the reduction reaction. Using this factor, after the reaction progressed to 80 percent completion the remaining Cr(VI) had $\delta^{53}\text{Cr}$ 5.6 per mil greater than the original Cr(VI); at 90 percent completion, the difference was greater than 8 per mil; and so on. Cr reduction experiments utilizing natural magnetite-bearing and microbe-rich aquifer sediments, including autoclaved controls, gave essentially identical results, suggesting that at least for these sediments the reduction mechanism was abiotic.

Ellis et al. (2004) demonstrated that Cr isotopes are not significantly fractionated during sorption of Cr(VI) aqueous species onto Al_2O_3 and goethite substrates at circum-neutral pH. Similarly, no significant fractionation was observed during sorption of Cr(VI) onto Al_2O_3 at pH=4. In contrast, a kinetic isotope effect was observed during sorption of Cr(VI) onto goethite at pH=4, with $\delta^{53}\text{Cr}$ of the initial sorbed Cr(VI) being 3.5 per mil 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.

Equilibrium isotope fractionation between aqueous Cr(III) and Cr(VI) may be important in situations where the Cr(III)/Cr(VI) ratio of dissolved species is large (i.e., >1). Theoretical estimates of equilibrium Cr isotope fractionation between Cr aqueous species at 25°C

(Schauble 2004) indicate that $\delta^{53}\text{Cr}$ of Cr(VI) will be ~6.6 per mil greater than that of Cr(III). Experiments are currently underway at the USGS in Menlo Park, CA to determine the practical fractionation factors of the equilibrium process, as well as to determine if natural Cr oxidation mechanisms such as oxidation of Cr(III) on mixed-valence manganese oxide surfaces promote fractionation of the Cr isotopes. However, it is important to recognize that the equilibrium effect on $\delta^{53}\text{Cr}$ of Cr(VI) will decrease as the Cr(III)/Cr(VI) ratio of dissolved species decreases (i.e., at higher pH), due to isotope mass balance considerations.

2.3 Existing Data on Chromium Isotopes in the Mojave Basin

The USGS is beginning to establish a database of Cr isotope compositions in groundwater from both anthropogenic and natural settings. The database includes isotopic data from aquifers contaminated by Cr plating wastes associated with industry and military activities and aquifers in the Mojave Desert of Southern California where groundwater naturally contains elevated levels of dissolved Cr(VI). Based on existing USGS data, for groundwater samples collected nearest to sources of unambiguous anthropogenic Cr contamination, $\delta^{53}\text{Cr}$ of dissolved Cr(VI) is approximately 0.0 per mil, similar to Cr in igneous minerals (Ellis et al. 2002; Johnson and Bullen 2004) and thus to potential mineral sources of the Cr. Cr(VI)-bearing groundwater downgradient from the contamination sources consistently has $\delta^{53}\text{Cr} > 0.0$ per mil, with values generally increasing as Cr(VI) concentrations decrease, indicating that Cr(VI) reduction is probably occurring as the contaminant plume migrates through the aquifer materials. Groundwater samples collected by the USGS from the Mojave Desert containing naturally elevated levels of Cr(VI) (Ball and Izbicki 2004) likewise have $\delta^{53}\text{Cr}$ ranging from around 0 to over 4 per mil (Ball et al. 2001 and other unpublished analyses determined at USGS, Menlo Park). This indicates that either Cr(VI) reduction or equilibrium between Cr(III) and Cr(VI) aqueous species has occurred along flowpaths between the recharge zone and the sample locations in this arid region. The USGS has rarely analyzed a groundwater sample that has $\delta^{53}\text{Cr} < 0.0$ per mil, which has been interpreted to indicate a considerable store of isotopically light Cr exists, bound to aquifer mineral surfaces.

2.4 Application of Cr Isotope Analyses to Evaluate Potential Sources

The spatial distribution of Cr isotope compositions in groundwater throughout a Cr plume may be evaluated based on potential fractionation patterns. It appears that reduction of dissolved Cr(VI) is an important mechanism that causes measurable Cr isotope fractionation in aquifers. Therefore, if the concentration and Cr isotope composition of the suspected source of Cr along a flowpath is known, then the Cr isotope composition of downgradient samples possibly can be predicted based solely on their measured Cr(VI) concentrations using a simple Rayleigh model and the fractionation factor reported by Ellis et al. (2002). For example, if $\delta^{53}\text{Cr}$ of the suspected source of Cr(VI) is 0 per mil and the concentration is 1 part per million (ppm), then a downgradient groundwater sample having 0.1 ppm Cr(VI) (i.e., 90 percent completion of the reduction reaction) would have $\delta^{53}\text{Cr}$ of about 8 per mil if reduction of Cr(VI) was the only process causing decreasing Cr concentrations along the flowpath. If the Cr isotope composition of the downgradient water sample is not as great as that predicted by the fractionation model, then the Cr in that downgradient water sample possibly was not derived from the suspected Cr source or the sample has been diluted by Cr having a different isotopic composition from another source. Because both uncontaminated groundwater and contaminated groundwater that has been reduced can have $\delta^{53}\text{Cr}$ greater than 4.5 per mil, Cr isotopes cannot be used alone to determine the source of Cr in an

aquifer system. The use of Cr isotopes assumes that hydrologic factors that can cause decreasing concentrations of dissolved constituents (e.g., dispersion, diffusion, mixing) can be taken into account using additional geochemical parameters. A possible approach to compensate for these effects would be to index the Cr(VI) concentration to that of a conservative constituent of the plume water that is absent or is known to be different in the uncontaminated regional groundwater.

2.5 Study Limitations

As the above discussions indicate, studies of ^{53}Cr in the environment have only recently been conducted. This is a relatively new science, in which stable isotopes of environmentally sensitive elements have been applied to test sites. Investigators in environmental isotope studies for selenium, which has undergone more isotopic study than chromium, caution that effects of all important processes on isotopic fractionation must be understood before more quantitative use of stable isotopic ratios may be realized (Johnson and Bullen 2004). For example, adsorption of Cr(VI) may cause significant isotopic fractionation in areas of low Cr(VI) concentrations, such as background areas or plume edges (Ellis et al. 2002). In addition, the Cr(VI) historically added to Topock facility cooling tower water may have a different isotopic signature from chromium plating solutions, which are thus far the only published source of anthropogenic chromium isotope values.

These observations provide perspective that although the use of chromium isotopes may provide a useful tool for the present study, the science is in a relatively early stage and its use may have significant limitations at the Topock site.

3.0 Study Approach

3.1 Samples to be Collected

To determine the isotopic composition of Cr in groundwater underlying the PG&E Topock Compressor Station and surrounding area, groundwater samples will be collected from 26 monitoring and water-supply wells. Of the total, samples will be collected from nine wells within the plume in the alluvial fan deposits, from four wells in the plume in the floodplain deposits, and from 13 wells considered to be background wells in both California and Arizona. Table 1 at the end of this memorandum provides a listing of the wells to be sampled. Figure 1 shows the locations of wells to be sampled for this study.

The objective of this sampling is to determine whether there is a clear distinction in the Cr isotope signature between plume samples and background samples. Other tools will be used in conjunction with the Cr isotopes to assist in making this distinction, including general chemistry, field parameters, and stable isotopes of oxygen and hydrogen.

If the analysis shows a clear distinction between plume and background wells, a second phase of sampling will be conducted in which selected wells near the plume margin will be sampled and analyzed.

3.2 Sample Collection and Analysis

USGS personnel will accompany the CH2M HILL field team during its regular sampling rounds. The CH2M HILL field team will purge the wells under the standard operating

procedure (CH2M HILL 2005), and the USGS will be responsible for collection, transport, and analysis of all Cr isotope samples collected for this study.

The USGS sample will be filtered using a 0.2-micrometer filter. A small aliquot of each sample will be taken for measurement of total Cr. The remainder of each sample will then be processed in the field using the cation exchange method for field speciation of Cr(VI) (Ball and McCleskey 2003). Cr(III) will be sorbed on cation exchange resins leaving only Cr(VI) in the liquid fraction. All liquid samples will be preserved to pH <2 using ultra-clean hydrochloric acid. Both the unspicated and speciated liquid samples will be sent to the USGS laboratory in Boulder, CO for analysis of total Cr by USEPA method 218.6 (Arar and others 1991). The sample processed using the cation-exchange method contains only Cr(VI). The second sample will contain Cr(total); therefore, Cr(III) will be determined by difference.

The chromium isotope composition of the Cr(VI) liquid sample will be determined in the USGS laboratory in Menlo Park, CA. The Cr(III) fraction retained on the cation exchange resin may be determined if sufficient Cr is scavenged by the resin column. Analysis will be accomplished using thermal-ionization mass spectrometry (TIMS) by application of purified Cr to a solid source filament using the silica gel technique to enhance production of thermal ions (Ball 1996). This technique has been applied successfully in the groundwaters from the Mojave Desert. Analyses of samples of water from 16 wells in the Twenty-Nine Palms area of the Mojave Desert show $\delta^{53}\text{Cr}$ values range from 0.1 to 4.5 per mil, with an average precision of ± 0.1 per mil. Duplicate samples will be collected from a minimum of 10 percent of the wells (i.e., at least three wells).

The water quality and isotopic data will be coupled with detailed geologic data available at the site to evaluate changes in chromium concentration, speciation, and isotopic composition in the zone of contamination, both areally and with depth as groundwater moves away from the contamination source. It is expected that the stable isotopes of oxygen and hydrogen can be used to help identify the mixing of groundwater of different sources.

Standard well purging procedures to be used in association with study are presented in the Field Procedures Manual (CH2M HILL 2005). The Field Procedures Manual presents standardized protocols for field investigation and data collection activities for the several investigation, monitoring, and interim measure programs performed at the Topock Compressor Station.

3.3 Quality Control and Data Management

Quality control procedures will be 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* (QAPP) (Appendix D of the Topock Field Procedures Manual [CH2M HILL 2005]). The quality control procedure used during laboratory purification of Cr fractions and measurement of Cr isotopic compositions involves processing of the NIST 979 Cr reference metal through the entire analytical procedure several times over the course of the study, and demonstrating consistency and accuracy of derived Cr isotopic compositions.

3.3.1 Data Validation

The analytical results of groundwater and surface water samples will be evaluated to verify whether the data are sufficiently accurate, precise, and representative of site conditions for decision-making purposes in support of ongoing site investigation and remediation activities. Details regarding data validation are provided in the QAPP (CH2M HILL 2005).

3.3.2 Data Management

Management of data generated from the study will be 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, quality assurance/quality control procedures associated with data management, and reporting formats.

3.4 Project Schedule

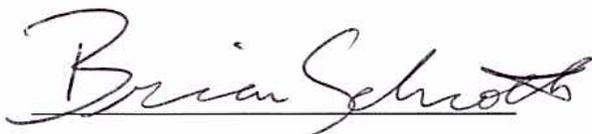
Samples will be collected during regularly scheduled sampling events at the wells listed in Table 1, either as part of the Groundwater Monitoring Program, or Groundwater Background Study. Currently the wells included in the Groundwater Background Study are sampled on a bi-monthly basis (through April 2006), and the wells in the Groundwater Monitoring Program are sampled on either a bi-weekly, monthly, or quarterly basis. Analysis for chromium speciation and chromium isotopes in the USGS laboratories should be completed within 45 days of sample collection. Data will be interpreted by a consultation between the USGS and CH2M HILL, and will utilize other chemical data and possibly the groundwater model in testing hypotheses.

Conclusions of data analysis will be reported to and discussed with the TWG. If, as a result of this discussion, it is concluded there is a clear distinction between plume and background wells, a second phase of sampling will be conducted in which selected wells near the plume margin will be sampled and analyzed.

A report of study results will be provided to DTSC within 120 days of completion of laboratory analysis.

4.0 Certification

This work plan was prepared by CH2M HILL under the supervision of the professional whose seal and signature appears hereon, in accordance with currently accepted professional practices; no warranty, expressed or implied, is made.



Brian Schroth, Professional Geologist #7423

5.0 References

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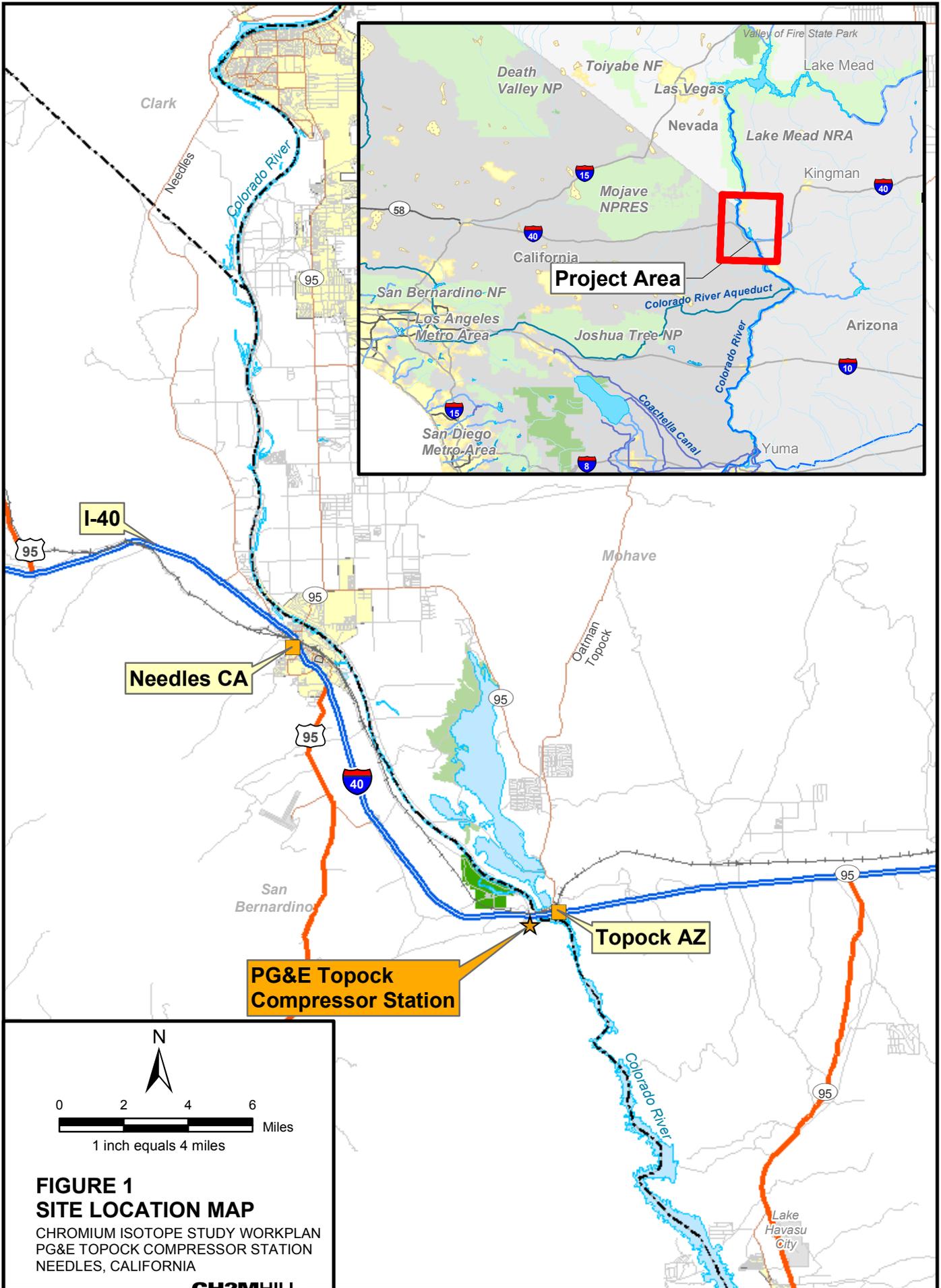
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TABLE 1
Chromium Isotope Study – Proposed Sample Locations

Location, Sampling Plan	Depth Interval	Reason
California -- Background		
Taylor PG&E background well	360 to 400' bgs	Avg. 0.5 µg/L Cr(VI),
Needles MW-11	Well depth of 280' (screened interval unknown)	Avg. 2.3 µg/L Cr(VI), Needles Municipal Well
Lily Hill PG&E background well	20 to 220' bgs	Avg. 10.5 µg/L Cr(VI), irrigation well for Needles apartment complex
CA Agricultural Station PG&E background well	Well depth of 202' (screened interval unknown)	Avg. 2.0 µg/L Cr(VI), irrigation well for Agricultural Station
Arizona – Background		
TMLP-2	750 to 880' bgs	Avg. 16.0 µg/L Cr(VI), monitoring well.
GSRV-2 (also known as RPGS) PG&E Background Study well and part of ADEQ Topock GW Study	205 to 245' bgs	Avg. 29.1 µg/L Cr(VI), AZ side of river, should be background and is upgradient of plume.
Langmaack PG&E Background Study well	Well depth of 240' (screened interval unknown)	Avg. 21.4 µg/L Cr(VI), AZ side of river, should be background and is upgradient of plume, expected to be screened in alluvium (no log available)
GSWC-1 PG&E Background Study well	Well depth of 250' (screened interval unknown)	Avg. 12.8 µg/L Cr(VI), expected to be screened in alluvium (no log available)
GSWC-2 PG&E Background Study well	Well depth of 500' (screened interval unknown)	Avg. 4.5 µg/L Cr(VI), screened in alluvium
GSWC-3 PG&E Background Study well	Well depth of 500' (screened interval unknown)	Avg. 9.9 µg/L Cr(VI), screened in alluvium
GSWC-4 PG&E Background Study well	352 to 522' bgs	Avg. 10.1 µg/L Cr(VI), screened in alluvium
EPNG-2 PG&E Background Study well	322 to 482' bgs	Avg. 8.7 µg/L Cr(VI), screened in alluvium
New ADOT (ADOT-2) PG&E Background Study well	330 to 530' bgs	Avg. 8.5 µg/L Cr(VI), screened in alluvium
Plume: Alluvial Fan Deposits		
MW-10 GMP	74 to 94' bgs	Avg. 1,800 µg/L Cr(VI), adjacent to plant, shallow well
MW-38S GMP	75 to 95' bgs	Avg. 740 µg/L Cr(VI), downgradient of MW-10, shallow well
MW-24B GMP	194 to 214' bgs	Avg. 5,200 µg/L Cr(VI), downgradient from MW-38 cluster; shallow well

TABLE 1
Chromium Isotope Study – Proposed Sample Locations

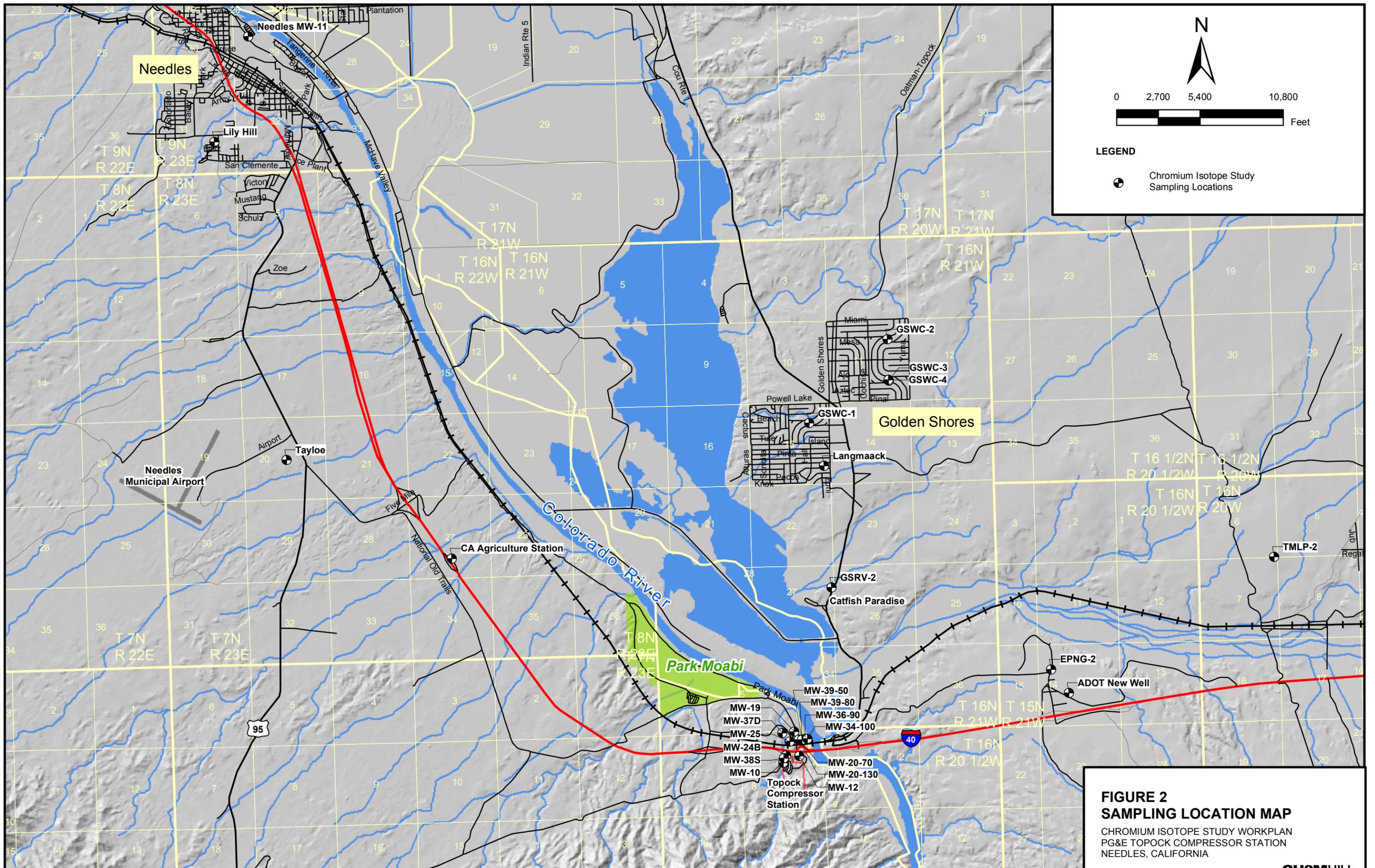
Location, Sampling Plan	Depth Interval	Reason
MW-25 GMP	84 to 104' bgs	Avg. 1,900 µg/L Cr(VI), upgradient of MW-20 bench, shallow well
MW-20-130 GMP	121 to 131' bgs	Avg. 8,600 µg/L Cr(VI), highest concentrations, near base of alluvial aquifer, may be most similar to initial isotopic composition; deep well
MW-20-70 GMP	50 to 70' bgs	12,400 µg/L decreased to 4,640 µg/L Cr(VI), may show partial reduction signature; shallow well
MW-19 GMP	46 to 65' bgs	Avg. 960 µg/L Cr(VI), north of MW-20 bench, has increased somewhat in past two years; shallow well
MW-12 GMP	51.5 to 71.5 bgs	1,560 µg/L decreased to 626 µg/L Cr(VI), south of MW-20 bench, may show partial reduction signature; shallow well
MW-37D GMP	180 to 200' bgs	Avg. 1,400 µg/L Cr(VI), beneath Bat Cave Wash downgradient from MW-38; deep well
Plume: Floodplain Deposits		
MW-39-80 GMP	70 to 80' bgs	10,900 µg/L decreased to 2,060 µg/L Cr(VI), may show partial reduction signature
MW-39-50 GMP	47 to 52' bgs	3,500 µg/L Cr(VI) decreased to 66 µg/L, lies just below MW-39-40 which never had any Cr(VI), decrease in concentration could be combination of dilution plus reduction, decrease in ORP values observed
MW-36-90 GMP	80 to 90' bgs	3,500 µg/L Cr(VI) decreased to 700 µg/L, lies just below MW-36-70 which does not contain Cr(VI)
MW-34-100 GMP	88 to 98' bgs	350 to 880 µg/L Cr(VI)



**FIGURE 1
SITE LOCATION MAP**

CHROMIUM ISOTOPE STUDY WORKPLAN
PG&E TOPOCK COMPRESSOR STATION
NEEDLES, CALIFORNIA

CH2MHILL



**FIGURE 2
SAMPLING LOCATION MAP**

CHROMIUM ISOTOPE STUDY WORKPLAN
PG&E TOPOCK COMPRESSOR STATION
NEEDLES, CALIFORNIA