The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale, California Ground Water Supply:

Phase III
Demonstration-Scale
WBA Resin
Treatment Technology Evaluation

QUALITY ASSURANCE PROJECT PLAN

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Michael MacPhee, Ph.D., MMP	Date
Laurie McNeill, Ph.D., Utah State University	Date
Gary Amy, Ph.D., UNESCO	Date
Mel Suffet, Ph.D., UCLA	Date

Distribution List of Principal Project Participants

Each organization included in this project is to receive and retain a copy of this QAPP.

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1 Project Description and Objectives

The City of Glendale's groundwater supply in the San Fernando Valley has been contaminated with a wide variety of chemicals, including hexavalent chromium [Cr(VI)], trichloroethylene (TCE), perchloroethylene (PCE), 1,2,3-trichloropropane (TCP), and others, mainly as a result of the improper disposal of industrial waste products. Extraction and treatment of volatile organic compounds (VOCs) is underway in the San Fernando Valley using air stripping and granular activated carbon (GAC), and the treated water is served to customers. Although Cr(VI) was also found in the groundwater supplies, levels were below the total Cr maximum contaminant level (MCL) of 50 μg/L in California. No Cr(VI) treatment was included with the VOC facilities at the time they were constructed.

Until June 2007, the health effects of Cr(VI) in drinking water were uncertain; Cr(VI) was a proven carcinogen by inhalation but little evidence existed to demonstrate the impact of Cr(VI) ingestion. However, a recent study conducted by the National Toxicology Program (NTP) showed that Cr(VI) is a carcinogen by ingestion in animal studies (NTP 2007). Even prior to this study, the Legislature of California mandated that the California Department of Public Health (DPH) establish a Cr(VI) MCL. First, the Office of Environmental Health Hazard Assessment (OEHHA) must set a public health goal (PHG), which will likely be based on the new NTP findings. In Glendale, public concern about Cr(VI) in the groundwater supply led the city to embark on a multi-phase study to identify and install Cr(VI) treatment in anticipation of a Cr(VI) MCL lower than the current total Cr MCL in California.

In the year 2000, the City of Glendale, along with the Cities of Los Angeles, Burbank, and San Fernando, initiated a testing program to develop a full-scale Cr(VI) treatment system capable of removing Cr(VI) to low parts-per-billion levels. The **Phase I Bench-scale study** was conducted to improve the understanding of fundamental chromium chemistry and to screen promising technologies for their ability to treat and remove Cr(VI) to very low levels. The Phase I study is complete and the final report was published by AwwaRF (Brandhuber et al. 2004). The **Phase II Pilot-scale study** was initiated in the summer of 2003 to further test the promising Cr(VI) removal technologies at the pilot scale (i.e., several gallons-per-minute flows) using Glendale groundwater. A final report on the Phase II pilot-scale study was completed in 2005 (MEC 2005). Selected results were also published in peer-reviewed scientific journals (Qin et al. 2005, McGuire et al. 2006).

The **Phase III Demonstration-scale study** will finalize the treatment evaluation, residuals assessment, and cost estimate development by implementing one or more Cr(VI) removal technologies. The initial part of the Phase III effort was designated as the Phase III Bridge Project, which included additional studies to finalize testing of weak-base anion exchange resins for Cr(VI) treatment, refinement of treatment technology cost estimates based on Phase III Bridge Project results, and assembly of an expert panel to recommend one or more treatment processes for demonstration-scale testing. The Phase III Bridge Project was completed in early 2007.

The Phase III Demonstration-scale study will test weak-base anion (WBA) exchange using a 425 gpm well. Depending on additional funding availability, the City of Glendale may also construct a reduction-coagulation-filtration (RCF) treatment system on one or more other wells. This QAPP covers only the WBA treatment system, which is funded in part by the USEPA State and Tribal Assistance Grant (STAG).

The purpose of this project is to demonstrate the effectiveness of WBA resin in removing Cr(VI) to low part-per-billion levels. The system will be operated for one year under the STAG grant, and treated water will be put to beneficial use by serving Glendale’s consumers. Treatment cost information developed in the Phase II Pilot-scale and Phase III Bridge studies will be updated as a result of this effort. This information is intended to be of use to other utilities requiring Cr(VI) treatment and to the state of California in setting a Cr(VI) MCL.

1.1 Treatment System Description

Cr(VI) removal by WBA resin is a novel application of ion exchange for drinking water treatment. Originally, WBA resin was believed to behave similarly to strong-base anion exchange (SBA) resins in terms of removal mechanism, except that the WBA resins are only useful in the acidic pH range where the functional groups are protonated and thus have positively charged exchange sites to attract Cr(VI) as chromate or bichromate ion. However, the WBA resin tested in the Phase II pilot study (Duolite A7, now called PWA7, resin provided by Rohm & Haas) showed a 20 times higher Cr(VI) removal capacity compared with five SBA resins tested. Other observations, such as leakage of Cr(III) during periods in which pH values were lower than 5.5, indicated that an ion exchange mechanism alone was not likely responsible for all of the Cr(VI) removal by WBA resin.

As part of the Phase III Bridge study, five other WBA resins were tested to evaluate Cr(VI) removal. In addition, the impact of pH on the performance of the top resins was assessed to minimize acid addition requirements. PWA7 resin again showed a high Cr(VI) capacity along with another WBA resin (ResinTech SIR-700, which did not perform as well as the PWA7 initially but improved over time). Testing confirmed that more than 95% of the Cr(VI) retained on both resins was in the form of Cr(III), as observed directly by x-ray absorption spectroscopy. The true mechanism of Cr(VI) removal and retention by the WBA resins is hypothesized to first involve adsorption followed by reduction and retention perhaps by the resin backbone (SenGupta and Sarkar, 2007).

To date, WBA has only been tested in bench- and pilot-scale studies. The proposed demonstration-scale WBA system will be the first installation of this technology in a drinking water treatment application.

The WBA system that will be constructed and tested in the Phase III Demonstration-scale study will consist of the following major components:

- Ion exchange vessels (two 8-ft. diameter vessels each containing 185 cubic feet of WBA resin)
- Bag filters (two parallel filter housings containing 10-micron filters),

- Carbon dioxide (CO_2) storage tank (14 tons), and
- CO_2 feed and control system.

Figure 1-1 provides a process flow schematic for the WBA system. The system will consist of a pair of lead/lag vessels with upstream CO_2 addition for pH depression. Due to the resin's high capacity and difficulty in regeneration, WBA resin will be used as a once-through, non-regenerable media.

The WBA system will be located at the GS-3 well site adjacent to Goodwin Street in the City of Los Angeles. The GS-3 well was selected for testing the WBA demonstration-scale system for two primary reasons: (1) GS-3 is one of the high Cr(VI) wells, with a current Cr(VI) concentration of approximately 50 μg/L (historical peak of 69 μg/L); and (2) a pair of unused GAC vessels exist at the GS-3 well site and can be retrofitted for WBA resin, thus minimizing capital costs for ion exchange vessels.

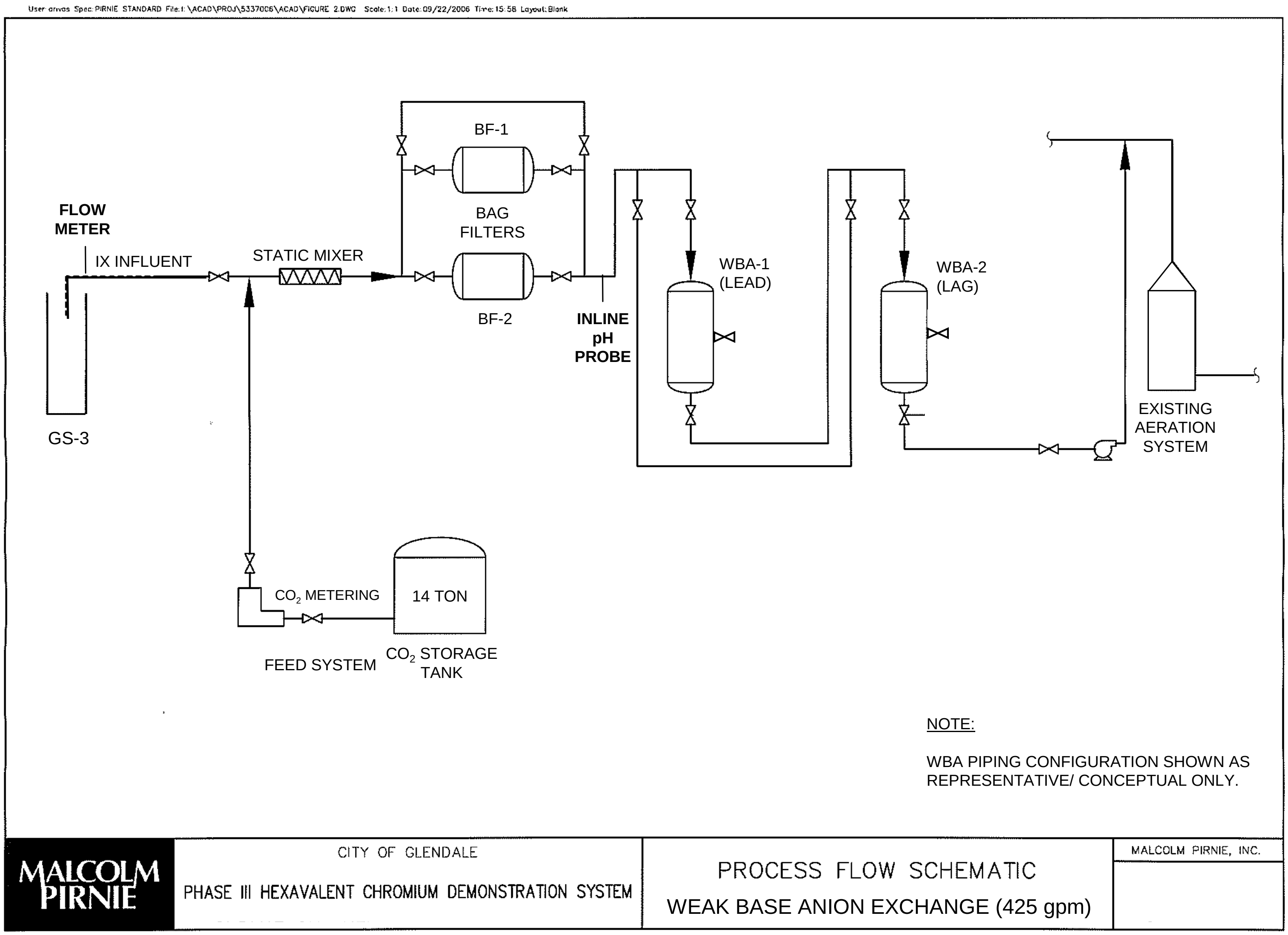

Figure 1-1. Process Flow Schematic of the WBA Exchange System

1.2 Project Objectives

The objectives of the Phase III Demonstration-scale study include the following:

- Evaluate Cr(VI) removal capacity of WBA resin at the demonstration-scale (approximately 425 gpm) and the ability to scale-up bench and pilot results;
- Quantify demonstration treatment performance with respect to Cr(VI) removal over extended periods of time (i.e., at least one year);
- Assess the impact of WBA resin treatment on finished water quality, including any leaching of nitrosamines, and develop mitigation strategies;
- Optimize day-to-day operations of the WBA treatment system and develop a comprehensive operations and maintenance manual;
- Assess the reliability of the demonstration-scale WBA technology during a year of operations and identify necessary backwashing or fluffing frequency;
- Confirm residuals optimization and disposal strategies identified in the Phase III Bridge project;
- Verify unit cost information developed in the pilot study with actual treatment costs; and
- Publicly disseminate project plans and findings to a wide audience, including water agencies also concerned with Cr(VI) in water supplies, California DPH, the USEPA, and consumers.

Glendale's goal of the WBA treatment system is to reduce Cr(VI) concentrations to less than 5 ppb using the WBA resin. Since a Cr(VI)-specific MCL does not currently exist and the total Cr concentrations in the blended water are below the total Cr MCL, the success or failure of the project cannot be defined as a specific concentration. Nevertheless, the change-out criteria for the WBA resin will be when Cr(VI) or total Cr exceeds 5 ppb in the lag bed effluent or 50% in the lead bed effluent (whichever occurs first).

For residuals disposal, critical values that may trigger hazardous waste restrictions in this treatment system include:

- total chromium (5 mg/L by California Waste Extraction Test, or CWET, and 5 mg/L by the Toxicity Leaching Characteristic Procedure, TCLP)
- uranium (total by kinetic phosphorescence analysis, KPA).

The WBA resin may initially leach N-Nitrosodimethylamine (NDMA), as shown in the Phase III Bridge Project. Each bed of resin will be rinsed during the initial backwash for approximately 9-10 minutes. Subsequently, the vessels will be put into normal operation, which includes dilution with approximately 4,575 gpm of water from the other wells at the GWTP, followed by an approximately 50% dilution with MWD water at the Grandview Pumping Station. Overall, the GS-3 water will be diluted to approximately 5% of the total flow before the water is served to customers, providing sufficient mitigation of nitrosamines leached from the resin upon startup to yield a finished water level below the Notification Level of 10 ppt.

2 Project Organization

2.1 Key Points of Contact

Refer to the above Distribution List of Principal Project Participants for the key points of contact at each organization.

2.2 QA Managers

The QAPP dictates procedures that will be used by two primary organizations: McGuire Malcolm Pirnie and the ELAP-certified laboratories (Montgomery Watson Harza (MWH) Laboratories and Test America). With respect to data quality assurance, Malcolm Pirnie is charged with the tasks of sample collection, handling, field analysis of selected parameters, data management, data reduction, and data validation. McGuire Malcolm Pirnie's QA Manager will be Dr. Michael MacPhee. He is independent of Project Management and his only role in the project is as QA Manager. The QA Manager at MWH Labs will be Ms. Linda Geddes, Quality Assurance Officer. The QA Manager at Test America will be Marti Ward.

2.3 Responsibilities of Project Participants

Each project participant responsible for critical components in this project is listed in Table 2-1. Team members' affiliations and overall project involvement roles are also listed. Project involvement roles specified here include: Planning, Coordination, Sample Collection, Sample Custody, Measurements (Analytical, Physical, and Process), Data Reduction, Data Validation, and Report Preparation. The project team organization is illustrated in Figure 2-1.

The majority of the project team was significantly involved in Phase II testing, which was covered by the QAPP entitled *The Treatment of Hexavalent Chromium (Cr(VI)) in the City of Glendale Ground Water Supply: Phase II Demonstration of Pilot Scale Treatment Technologies* (dated July 31, 2003). Dr. Bruce Macler has been the EPA Project Manager of the Phase II and Phase III efforts and is up-to-date on the historical study progress. Peter Kavounas and Don Froelich have also been key participants in the previous projects representing the City of Glendale. Dr. Michael J. McGuire, currently the Project Manager, was the Principal-in-Charge of the last study. Dr. Michael J. MacPhee will serve in the same role as in Phase II, as Technical Advisor and Quality Assurance Manager. Dr. Nicole Blute will plan, coordinate, oversee the field operations, and prepare reports. In the Phase II effort, Dr. Blute conducted the pilot-scale operations along with Dr. Danny Qin, who will conduct the field testing in the demonstration study. Dr. Qin is highly experienced in field sampling and analysis, having worked on the Phase II Pilot Study and Phase III Bridge Study and Additional RCF Testing, among other compliance testing and pilot testing efforts for other clients. The three university technical advisors, Dr. Mel Suffet, Dr. Laurie McNeill, and Dr. Gary Amy, have all been part of the Phase I and Phase II efforts. The two laboratories selected for this effort have been used in the prior work or in other projects with the City of Glendale.

Table 2-1.
Project Participant Roles

Team Member	Title and Organization	Overall Project Involvement	Specific Involvement
Bruce Macler, Ph.D.	USEPA, Project Manager	Project Manager	Project Management
Peter Kavounas, PE	City of Glendale	Glendale Principal Investigator	Planning Coordination
Don Froelich, PE	City of Glendale	Glendale Project Management	Planning Coordination
Leighton Fong, PE	City of Glendale	Glendale Project Management	Coordination
Michael McGuire, Ph.D., PE	Vice President, MMP	MMP Project Manager	Experimental Design Report Preparation
Michael MacPhee, Ph.D.	Vice President, MMP	MMP Technical Advisor	MMP Quality Assurance Manager
Nicole Blute, Ph.D.	Project Engineer, MMP	MMP Deputy Project Manager	Planning Coordination Data Reduction and Validation Report Preparation
Danny Qin, D.Env.	Engineer, MMP	Study Field Testing	Study Operations Sample Collection Sample Custody Field Measurements (analytical, physical, process) Data Management
Yolanda Martin	Project Manager, MWH Labs	Analytical Support	Coordination of Analytical Laboratory Measurements
Linda Geddes	QA Officer, MWH Labs	Laboratory Quality Assurance	Laboratory Quality Assurance
Kay Clay	Project Manager, Test America Labs	Analytical Support	Coordination of Analytical Laboratory Measurements
Marti Ward	QA Officer, Test America Labs	Laboratory Quality Assurance	Laboratory Quality Assurance
Gary Amy, Ph.D.	Professor, UNESCO	Technical Advisor	Experimental Design
Laurie McNeill, Ph.D.	Associate Professor, USU	Technical Advisor	Experimental Design

Mel Suffet, Ph.D.	Professor, UCLA	Technical Advisor	Experimental Design
To Be Determined	To Be Determined	To Be Determined	Construction

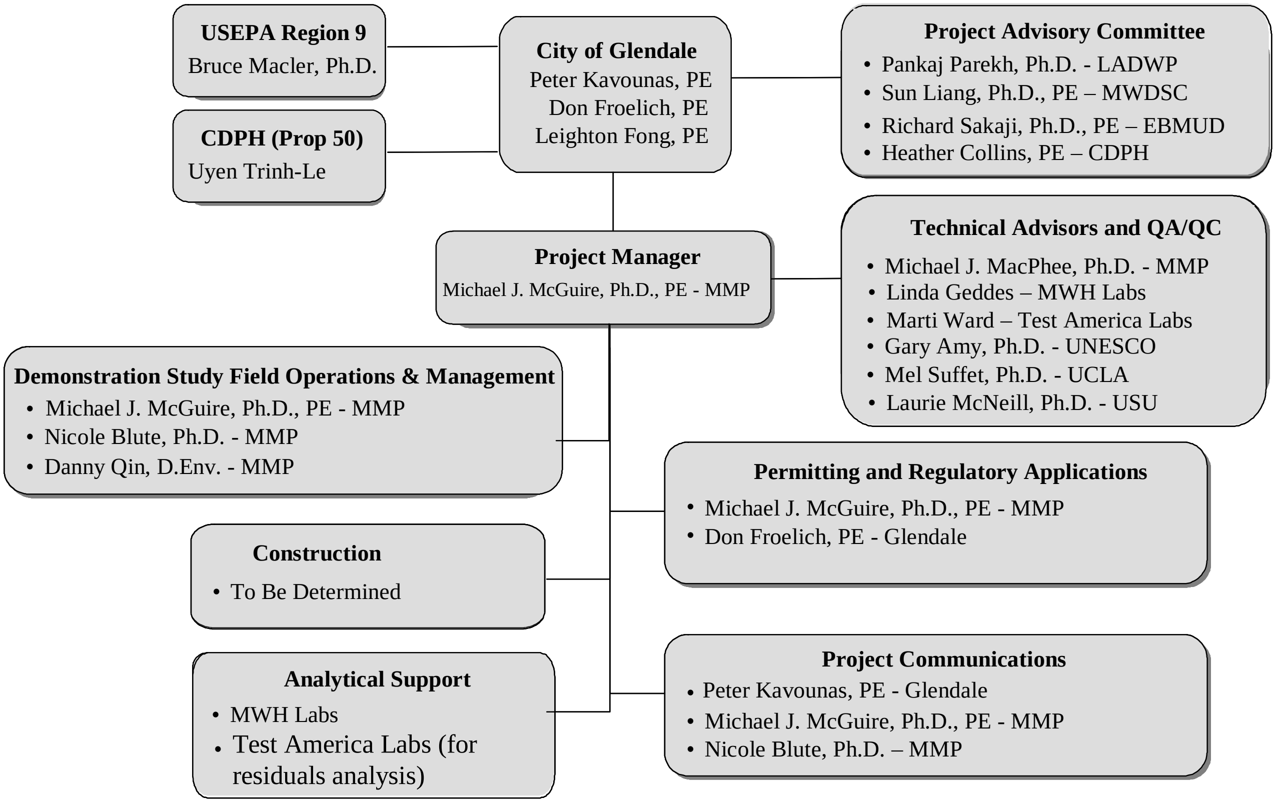

Figure 2-1. Demonstration Study Team Organization and Lines of Communication

2.4 Laboratory Certification Requirements

Each of the laboratories that will be used is certified by the California Department of Public Health under the State's Environmental Laboratory Accreditation Program (ELAP; certifications in Appendix B). Each laboratory's QA and Project Managers will be responsible for ensuring that the laboratory staff are appropriately trained and qualified to conduct the analyses.

3 Experimental Approach

3.1 General Approach and Test Conditions

Evaluation of WBA resin for Cr(VI) removal at the demonstration scale will focus on the measurement of key chemical and process parameters described in this section. Of critical importance, the project team will closely monitor Cr(VI) and total Cr concentrations in influent, mid-treatment train, and effluent water samples. In addition, other process-related parameters and water quality constituents described below will be measured to assess operational effectiveness and the impact of the WBA technology on water quality.

3.2 Sampling Strategy

Table 3-1 lists the proposed sampling parameters for the WBA demonstration-scale testing. In addition to chemical and physical analytical measurements, process-related parameters listed in Table 3-2 will be assessed.

3.2.1 Aqueous Samples

Critical sampling parameters in the demonstration study include Cr(VI), total Cr [ie., Cr(VI) plus Cr(III)], and pH. Other chemical and physical parameters, including temperature, conductivity, turbidity, and alkalinity will be routinely measured. Anions such as sulfate, nitrate, phosphate, and silicate may impact ion exchange treatment; consequently periodic measurements of these parameters will also be obtained. Nitrosamines, which have been found to leach from ion exchange resins, will be monitored in the start-up period of the demonstration-scale study to identify strategies to mitigate initial releases (e.g., flushing the resin for a specified period of time).

3.2.2 Residuals

Treatment residuals, including exhausted ion exchange resin and backwash water, will also be assessed to confirm disposal options using the Toxicity Characteristic Leaching Procedure (TCLP, EPA Method 1311 as mandated by 40 CFR 261) and the California Waste Extraction Test (CWET). Pilot-scale testing indicated that the spent WBA resins would be classified a hazardous waste in the State of California based on total chromium concentrations leached during the California WET test. Uranium accumulated on the spent WBA resin will also be determined throughout the testing; PWA7 resin may need to be replaced prior to 50% resin breakthrough to avoid uranium concentrations exceeding 500 mg/kg (i.e., the threshold above which the waste could be classified a low-level radioactive waste).

During the demonstration study, a vendor will be contracted to provide resin delivery and disposal services. Since the spent resin will likely be a hazardous waste according to CWET, the vendor will be required to appropriately dispose of the resin in accordance with the prevailing hazardous waste restrictions in California.

3.3 Sampling/Monitoring Locations

All of the samples collected for analysis will be obtained from the demonstration-scale study site at GS-3. Samples will be collected from sample ports shown in Figure 3-1. Sample types collected at each of these locations are highlighted in Table 3-1.

For the WBA treatment systems, sampling locations include the raw GS-3 well water (pre-CO_2 addition), influent water to the lead ion exchange vessel (post-CO_2 addition and bag filtration), lead vessel midpoint (50% depth), lead vessel effluent, lag vessel midpoint (50% depth), and lag vessel effluent.

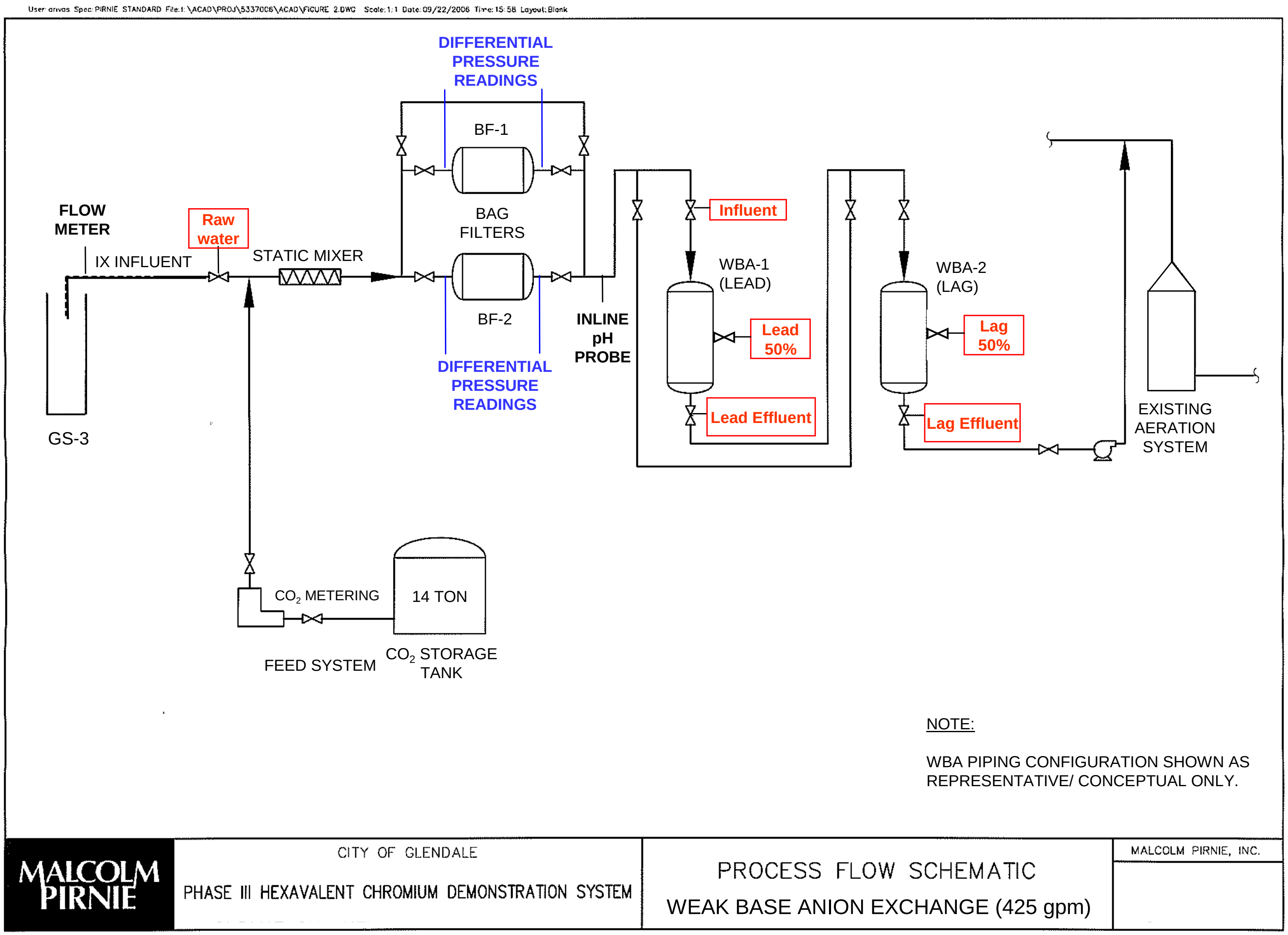

Figure 3-1. Sampling Locations for Chemical and Process Parameters (highlighted in red)

Table 3-1. Analytical Measurements for the WBA Demonstration-Scale Study, Identified as Critical (C) and Non-Critical (N/C) Measurements

Sampling Types and Locations	Cr(VI)	Total Cr	pH	Temp.	SO_4^{2-}	NO_3^-	PO_4^{3-}	SiO_2	Alk-alinity	Cond-uctivity	Turb-idity	Nitros-amines	TCLP, WET tests	Ura-nium
Raw water (before pH adjustment)			N/C											
Influent (after pH adjustment)	C	C	C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	C		
Lead Vessel 50% bed depth	N/C	N/C												
Lead Vessel Effluent	C	C	C	N/C										
Lag Vessel 50% bed depth	N/C	N/C												
Lag Vessel Effluent	C	C	C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	N/C	C		
Residuals (spent resin)													C	C
Backwash Water		C												

Table 3-2. Process-Related Measurements

	Flow rates	Pressure loss through BF-1	Pressure loss through BF-2	Backwash frequency	EBCT	# Bed volumes to breakthrough (> 5 µg/L)	# Bed volumes to 50% saturation of the lead vessel	CO_2 feed rate and volume use rate
WBA	C	C	C	C	C	C	C	C

3.4 Sampling/Monitoring Frequency

The planned sampling frequency for chemical and physical parameters, shown in Table 4-1, is based on treatment process design and the expected one year duration of testing. Samples will be collected at a sufficient frequency to provide enough information to achieve the project's stated objectives. For a predicted bed life of 207 days (based on maximum uranium accumulation), the weekly chromium sampling frequency will capture an approximately 29-point breakthrough curve. Process-related parameters, such as flow rate and pressure loss, will be taken on a daily basis to determine when bag filters should be changed and backwash initiated. Other chemical and physical analyses of influent and treated water will be collected at least monthly or more frequently as deemed necessary.

A weekly Cr(VI) and total Cr sampling frequency will be established for the following key sampling points:

- Influent
- Lead vessel 50% depth
- Lead vessel effluent
- Lag vessel effluent

Once breakthrough occurs such that the lead bed effluent Cr concentration exceeds 5 μg/L, the lag vessel 50% depth location will be added to the list of sampling points monitored weekly and the lead vessel 50% depth sampling curtailed (until the next bed is installed and the lead and lag vessel order is changed).

pH, which is a critical parameter due to its impact on WBA resin treatment, will be measured continuously at a point near the influent sampling point to the vessels. Note that sufficient mixing is necessary to enable capture of stable pH values representative of the influent to the WBA resin; thus, CO_2 will be added upstream of the bag filters and samples collected after the bag filters and before the lead vessel inlet.

Nitrosamines will be measured during the first day of startup according to California DPH permit requirements.

Non-critical parameters, including temperature, sulfate, nitrate, phosphate, silicate, alkalinity, conductivity, and turbidity, will be measured monthly at the following sampling points:

- Influent
- Lag vessel effluent.

Bag filter changes will be triggered by a drop in the treatment system flow rate below 425 gpm or differential pressure greater than 10 psi, whichever occurs first. Besides the initial bed washing, vessel backwashing will be conducted when the flow rate drops below 425 gpm, if the system has been recently shutdown, and the bag filters have a low differential pressure (level to be determined based on operational experience gained during the initial weeks of testing).

3.5 Identification of Measurements

Tables 3-1 and 3-2 identify analytical and process-related measurements and specify whether they are critical (C) or non-critical (N/C) analytes.

3.6 Evaluation of Project Objectives

Treatment technology success will primarily be judged by the effectiveness of the process for removing Cr(VI) and total Cr from the water supply. This objective will be assessed by calculating the difference between influent and effluent chromium concentrations during the demonstration-scale study. Efficiency of removal will be calculated as follows:

$$\text{Removal (\%)} = (1 - [\text{Cr}_{\text{effluent}}]/[\text{Cr}_{\text{influent}}]) * 100\%.$$

Effluent Cr(VI) and total Cr will be measured and plotted as a function of time to determine when breakthrough occurs. Number of bed volumes (i.e., volume of water treated per volume of the resin bed) of water treated will be calculated at breakthrough of the lead vessel (i.e., defined as Cr concentrations of greater than 5 μg/L) and also 50% saturation.

Operations and maintenance (O&M) issues associated with the WBA resin will be assessed, as listed in Table 3-2. For example, pressure drop through the beds and resultant backwashing frequency for the resin will be determined in the demonstration-scale study.

The Phase III Bridge study indicated that the spent WBA resin was classified as hazardous in the state of California due to the California Waste Extraction test (WET -- CCR Title 22 §66261.24) but not in states governed only by the federal Toxicity Characteristic Leaching Procedure (TCLP – EPA Method 1311 as mandated by 40 CFR 261). Subsamples of disposable spent media from the demonstration test will be analyzed to verify the hazardous nature of the residuals and, subsequently, the disposal options.

A broader purpose of the demonstration testing is to develop a technology that can be applied in other water utilities needing Cr(VI) treatment. Glendale’s demonstration study will therefore foster a better understanding of the WBA treatment technology for Cr(VI) removal from groundwater.

4 Sampling Procedures

4.1 Methods to Establish Steady-State Conditions

Achievement of steady-state conditions will be determined on the basis of process operating parameters rather than water quality. For WBA resin, dynamic water quality conditions will occur during operation, whereby the treated water quality will change over time as the media becomes exhausted. Therefore, sampling conditions that reflect steady-state operations will be based on the consistency of flows and chemical feed conditions (in particular, a stable pH within plus or minus 0.2 pH units).

4.2 Known Site-Specific Factors Affecting Sampling and Monitoring Procedures

The GS-3 well site will have dedicated space, power, and water from the GS-3 well. The effluent will be pumped into the transmission line leading to the GWTP for VOC treatment. The ion exchange vessels and piping will be designed with sampling ports to enable appropriate sampling for technology performance assessment as detailed in Section 3.

Limited hours of site accessibility (approximately 8 hours per day) will affect the possible time on site. However, the system will be tied into the existing SCADA system and will be alarmed. Operators are available around the clock in case the system experiences problems. The WBA resin is expected to last for at least 6 months prior to reaching 50% breakthrough on the lead vessel, which supports a weekly sampling periodicity.

4.3 Site Preparation Prior to Sampling

The demonstration-scale facility will be located at the GS-3 well site, as shown in Figure 4-1. The City of Glendale has an easement within the Ralph’s Grocery warehouse property located in the City of Los Angeles. The GS-3 well site is located on the Ralph’s property just off of Goodwin Street.

Site preparations that will be conducted before the demonstration-scale study commences include the following tasks:

- retrofitting the existing GAC vessels with different screens to support ion exchange media,
- construction of a concrete pad and installation of a CO_2 feed system,
- preparation of necessary electrical power supplies,
- integration of the treatment system with the existing Supervisory Control And Data Acquisition (SCADA),
- piping of the raw GS-3 well water to the treatment system, and
- piping of the ion exchange treated water to the transmission pipeline serving the GWTP.

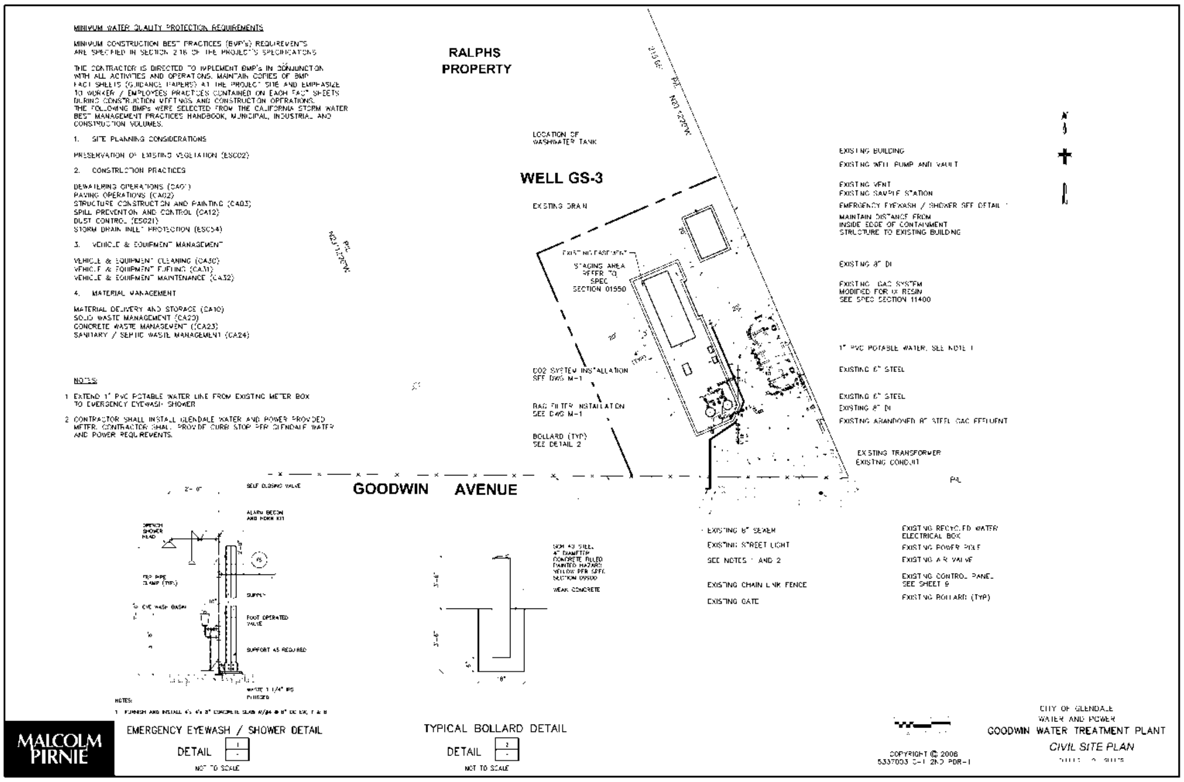

Figure 4-1. GS-3 Well Site and Property Easement Boundaries

4.4 Sampling/Monitoring Methods

Chemical and physical analytes will be measured in this demonstration-scale study either in the field or in a laboratory. The analytical methods and locations of analyses are shown in Table 4-1.

Laboratory analytical measurements will be sent to one of two labs:

- MWH Labs for Cr(VI), total Cr, nitrate, and nitrosamines
- Test America Labs – for TCLP, CWET, and uranium in residuals

The laboratory analyses of total chromium (a California DPH regulated constituent) will be performed by ICP-MS using EPA Method 200.8. Cr(VI) will be analyzed using EPA Method 218.6, which is an ion chromatography method. Nitrate will be analyzed using Method 300.0. Nitrosamines will be measured with EPA Method 521. Treatment residuals from the WBA treatment process will be analyzed for TCLP (metals – specifically, chromium levels will be of concern), CWET (metals – specifically, chromium levels will be of concern), and uranium analyses prior to disposal. All other parameters will be analyzed using the methods shown in Table 4-1.

Quality assurance field sampling includes field-collected duplicate samples and field blanks (refer to Section 6.1 for full details). Generally, field-collected duplicate samples will be collected for at least 10% of all samples. These duplicates will not be identified as QA samples when sent to the laboratory.

Field-collected blanks will include metal-free deionized water added to a sample bottle in the field and shipped to the laboratory for analysis (testing field sample handling, transport, and storage, including preservative reagents). Blanks submitted to the laboratory for analysis will not be identified as QA samples.

Samples will not be composited to amplify sample volume or average samples over time. Sufficient sample volume will be available for the required analyses. To achieve the project objective of evaluating Cr(VI) removal efficiency as a function of time, sample compositing is not desirable.

In addition to chemical and physical analytical measurements, process measurements listed in Table 3-2 will be recorded daily. Flow rate and pressure drop across the vessels will be monitored throughout the demonstration-scale testing to determine when backwashing is needed. Empty bed contact time (EBCT) will be calculated by dividing the media volume in a vessel by the flow rate. The number of bed volumes of water treated will then be calculated as the volume of treated water divided by the resin bed volume.

Table 4-1.
Sampling Frequency, Analytical Methods, & Analytical Location

Sample Analysis	Analytical Method	Analysis Location	Sampling Frequency
Cr(VI)	EPA 218.6 (IC)	MWH Labs	Weekly
Total Cr	EPA 200.8 (ICP-MS)	MWH Labs	Weekly
Sulfate	Hach 8051 (Turbidimetric)	Field	Monthly
Nitrate	EPA 300.0 (IC)	MWH Labs	Monthly
Phosphate	Hach 8048 (Colorimetric)	Field	Monthly
Silicate	Hach 8185 (Colorimetric)	Field	Monthly
Alkalinity	Hach 8203 (Titration)	Field	Weekly
Conductivity	SM 2510B (Conductance)	Field	Weekly
pH	SM 4500H+ B (Electrometric)	Field	Continuous online monitoring
Temperature	SM 2550 (Thermometric)	Field	Weekly
Turbidity	SM 2130 B	Field	Weekly
Nitrosamines	EPA 521	MWH Labs	Start of test[a]
Residuals – TCLP	EPA 1311 – Extraction EPA 6010B – Total Cr	Test America Labs	End of lead vessel life
Residuals – CWET	CWET Test (Title 22) – Extraction EPA 6010B – Total Cr EPA 7196A – Cr(VI)	Test America Labs	End of lead vessel life
Residuals: Uranium	ASTM5174-91 (KPA method)	Test America Labs	Monthly on lead vessel

[a] Nitrosamines will be analyzed at a frequency required by the DPH permit

4.5 Calibration of Sampling/Monitoring Equipment

Field equipment calibration will be performed in accordance with manufacturer specifications for each instrument. Calibration procedures for field equipment will be included in the Operations Manual developed for this project. Certified standard solutions will be used to test the functionality and accuracy of each piece of analytical instrument within the range of measurements and at a frequency specified by the manufacturer, or at least once per month.

Process instruments, such as flow meters and pumps, will be calibrated before the demonstration-scale treatment unit is brought online, at one intermediate time during operations (minimally), and at the conclusion of the test. Calibration procedures for process instruments will be included in the Operations Manual developed for this project. Calibration results and date and time of calibration will be recorded in the Field Sampling Log Book.

Trained operators will determine whether the calibrations are acceptable based on the allowed drift specified by the manufacturer. If an instrument is not functioning properly (e.g. calibration attempts are unsuccessful or the standard curve is unacceptable), the operator will obtain a calibrated back-up instrument for interim use and will send the malfunctioning instrument for repair.

4.6 Avoidance of Cross-Contamination

Sample contamination will be avoided by practicing clean sampling techniques. Water samples will be collected from dedicated sampling ports by directly filling pre-cleaned sample bottles Sample collections staff will avoid contact with the interior surfaces of the bottles. Hosing from the sampling ports will initially be acid-cleaned to remove any contaminants. Between collected samples, the ends of the hoses will be covered with clean polyethylene coverings to prevent contamination. Prior to sample collection, the sampling port and hose will be flushed for at least 1 minute to clean out the lines.

California DPH recommends *not* filtering drinking water samples to avoid potential sorption of Cr(VI) on the filter membranes and cross-contamination (CA DHS, 2001). Cr(VI) samples will therefore remain unfiltered in the field.

4.7 Selection of Representative Samples

Samples collected in this demonstration-scale study will be representative of the whole study based on consistent sampling at established sampling locations indicated in Table 3-1 and sampling frequencies shown Table 4-1.

Solid resin samples for TCLP, WET, and uranium analyses will be collected during a fluidized backwashing of the resin to obtain a representative sample of the bed.

4.8 Sample Amounts Required for Analysis

Table 4-2 lists the sample analysis methods, sample amounts required for analysis according to each method (including QA aliquots except field-collected duplicates), preservatives, and maximum holding times. The same amounts will be required for each analysis at each sampling location. Field-collected duplicate sample quantities discussed in Section 4.4 will be in addition to the bottles below.

To determine if spent media will be classified as a hazardous waste, TCLP and WET tests will be performed on the media. The Federal TCLP test requires a minimum of two 100-gram samples: one sample to determine percent solids, and one sample on which the extractions will be performed. California WET mandates a 50 gram sample for analysis.

4.9 Sample Containers

All samples will be collected using containers pre-cleaned and approved by the USEPA for the analytes of interest. Samples for the critical Cr(VI) and total Cr analyses will be collected in pre-cleaned plastic bottles provided by the laboratory or, for field testing, those shown to be clean of contamination in the Phase II testing. Bottle types for other analyses of interest may be plastic or glass (EPA 1997), although plastic will be used to eliminate breakage during shipping (refer to Table 4-2). Empty containers will be stored in the original packaging until use. Once collected, samples will be shipped to the laboratories for analysis according to the protocol for sample custody.

4.10 Sample Identification

Samples will be identified using a standardized code that imparts sampling information to each party. Each sample location will be assigned an ID as follows (referring to Figure 3-1):

- Raw water: SP-1
- Influent: SP-2
- Lead Bed 50%: SP-3
- Lead Bed Effluent: SP-4
- Lag Bed 50%: SP-5
- Lag Bed Effluent: SP-6

Next, the appropriate sample type (e.g. raw water, lead bed effluent) will be recorded. The date and time will then be recorded using the convention of military time. The analyte(s) to be measured in that sample will be recorded on the label, as will the preservative used. Finally, the field sample collector’s initials will be added.

An example identification label is as follows:

Sample Location ID ___________________
Sample Type ___________________
Date and Time ___________________
Analyte(s) ___________________
Preservative, if any ___________________
Field Sampler Initials ___________________

Table 4-2.
Sample Handling Requirements

Sample Analysis	Sample Size Required, including QC Aliquots	Container Material	Preservative	Maximum Holding Time
Cr(VI)	250 mL	P[1]	$(NH_4)_2SO_4$/ NH_4OH to pH 9-9.5	24 hours[4]
Total Cr	250 mL	P	HNO_3 to pH <2	6 months
Sulfate	60 mL	P, G[2]	4ºC	28 days
Nitrate	50 mL	P	4ºC	48 hours
Phosphate	60 mL	P	4ºC	48 hours
Silicate	60 mL	P	4ºC	28 days
Alkalinity	200 mL	P, G	4ºC	14 days
Conductivity	500 mL[3]	P, G	4ºC	28 days
pH	500 mL[3]	P, G	None	Analyze Immediately
Temperature	500 mL[3]	P, G	None	Analyze Immediately
Turbidity	500 mL[3]	P, G	None	Analyze Immediately
Nitrosamines	2 L	Amber glass	At or below 10ºC[5]	14 days until extraction; 28 days after extraction
Residuals: TCLP	200 g	P	4ºC	180 days (metals)
Residuals: CWET test	50 g	P	4ºC	180 days (metals)
Residuals: Uranium	100 g	P	4ºC	28 days

[1] P = Plastic. [2] G = Glass. [3] Combined 500 mL bottle for conductivity, pH, temperature, and turbidity.

[4] Although samples preserved with ammonium sulfate/ammonium hydroxide buffer (pH 9 to 9.5) can be held for 28 days, analyses will be conducted within 24 hours..

[5] Chill nitrosamine samples prior to shipment if they are greater than 10ºC at the time of collection.

4.11 Sample Preservation Methods

Table 4-2 lists the preservation requirements for each of the methods that will be used in the demonstration study. Details of sample preservation include whether the sample needs to be chilled, if an acid, base, or buffer is required, the type of container required for sample collection and storage, and the maximum holding time.

As the critical analytes, more details for Cr(VI) and total Cr are provided here. Samples for total Cr will be preserved with 2% nitric acid (HNO_3). It is intended that Cr(VI) samples will be analyzed within 24 hours of sample collection, thereby avoiding the need for preservative. However, samples will be preserved with ammonium sulfate/ ammonium hydroxide buffer (extending the hold time to 28 days) in case the samples cannot be measured within 24 hours. During each weekly sampling event, the pH of one sample for Cr(VI) analysis and one for total Cr after preservative addition will be verified by pouring out a small amount of the preserved sample onto pH paper. This approach to testing pH will reduce the volume removed from the sampling bottles.

4.12 Sample Holding Time Requirements

Maximum holding times for each of the analytes are shown in Table 4-2.

4.13 Sample Shipment

Samples will be shipped by courier from the site of collection (GS-3) to the appropriate contract laboratory using a reputable shipping company or lab courier. Shipping containers will consist of coolers with ice packs to chill samples and bubble wrap to protect the bottles during transit.

4.14 Sample Chain-of-Custody

Samples will be considered “in custody” when they are in someone’s physical possession or view, locked up, or stored in a secure area accessible only by authorized personnel. A minimal number of persons participating in sample handling and custody is desirable.

Samples collected for analyses will be recorded in a Field Sampling Log Book using waterproof, permanent ink. The log will contain the following information: Sample ID (as described in Section 4.11), results of field measurements, and descriptions of incidents that may have affected operations.

After samples have been collected for laboratory measurements, the field staff person will complete the Sample Chain-of-Custody form in ink, affix and sign Custody Seals, place the completed Chain-of-Custody in a sealed plastic bag affixed to the inside lid of the cooler, and surrender the samples to the ELAP-certified lab courier or authorized shipper for shipment. Upon arrival at the contract laboratory, laboratory personnel will immediately log the samples in on the Chain-of-Custody form, inspect for damage and sample integrity, and store the samples as appropriate until analysis. Problems encountered during sample shipping will be reported to the analytical manager.

4.15 Sample Archives

Samples will be stored at 4°C after analysis until personnel at the laboratory and McGuire Malcolm Pirnie review sample data and associated quality control analyses. In general, samples are kept by MWH or Test America Laboratories for two years. Unless directed otherwise, samples will then be disposed of in accordance with appropriate environmental health and safety regulations for hazardous chemical waste.

5 Testing and Measurement Protocols

5.1 Measurement Methods

The analytical methods for the water quality parameters and treatment residuals will conform to EPA guidelines and recommended test methods, including those in *Standard Methods for the Examination of Water and Wastewater* (APHA 1999). Standard Operating Procedures (SOPs) to be used for all measurements are included in Appendix A.

At MWH Laboratories, total chromium analyses will be performed using the ICP-MS method (EPA Method 200.8). Ion chromatography (EPA Method 218.6) will be used to analyze Cr(VI). Nitrate will be measured using EPA Method 300.0 (IC). Nitrosamines will be measured using EPA Method 521. Treatment residuals from each process will be shipped to a certified laboratory (Test America Labs) for TCLP, California WET, and uranium analyses prior to disposal.

Other water quality parameters will be measured in the field by trained operators (as discussed in Section 4.6) using SOPs provided in Appendix A.

5.2 Verification of Unproven Methods

No unproven laboratory methods will be used in this project.

5.3 Calibration Procedures

For Cr(VI) analysis, the ion chromatograph at MWH Labs will be calibrated each analysis day using a 6-point calibration curve ranging from 0.1 to 50.0 μg/L. Acceptance criteria include a correlation coefficient for the linear calibration curve of greater than 0.999. The method detection limit (MDL) at the laboratory is reported to be 0.015 μg/L. However, the method reporting limit (MRL) is 0.1 μg/L. Samples falling within the range of the MDL and MRL will be flagged as “J values”. An external laboratory control sample (LCS) at 2 μg/Lwill be analyzed for every batch of 20 samples or less. The acceptance percent recovery range for the LCS sample is within 90-110%. A 20 ppb instrument performance check (IPC) sample will be run after the initial calibration and subsequently after every 10 samples, with an acceptable percent recovery range of 95 to 105%. A laboratory reagent blank (LRB) will also be measured after every 10 samples and should be below the MRL of 0.1 μg/Leach time.

Total Cr samples will be analyzed by ICP-MS, which includes daily calibration using a 3-point calibration curve (plus a blank) ranging from 1 to 250 μg/L. Acceptance criteria include a correlation coefficient for the linear calibration curve of greater than 0.999. The laboratory-reported MDL for total Cr is 0.192 μg/L, and the MRL is 1 μg/L. An initial calibration verification standard (ICV) will be analyzed immediately after the calibration curve with an acceptance percent recovery range of 95 to 105%. A continuing calibration verification standard (CCV) will be run subsequently after every 10 samples, with an acceptable percent recovery range of 90 to 11%. A continuing calibration blank (CCB) will also be measured after every 10 samples and should be below one-half of the MRL of 1.0 μg/Leach time.

If the laboratory calibration check criteria are not met, the analysis run will be stopped and the instrument recalibrated. Additional details are available in the Appendix A SOPs.

Nitrosamine analysis will be conducted by capillary column gas chromatograph with large volume injection and chemical ionization trap mass spectrometry. The daily calibration curve will consist of 6 samples ranging from 2 to 100 ng/L, and acceptance criteria for each calibration standard will be within 70-130% (or 50-150% for the lowest standard). A continuing calibration check (CCC) sample will be run after the initial calibration curve and after every 10 samples, with acceptance criteria of between 70-130% of the true value.

Leachate metal concentrations using the TCLP and CWET methods will be measured using ICP-AES. Details of the standards used to calibrate the ICP-AES for the various metals are shown in Appendix A. In general, at least 3 standards and a blank are used to calibrate the instrument daily, with acceptance criteria of greater than 0.995 for the correlation coefficient. Following the calibration, an initial calibration verification (ICV) sample will be run, with acceptance criteria of 95-105%. An initial calibration blank (ICB) will subsequently be run and should fall within +/- of the MRL from zero. CCV and CCB samples will then be run every 10 samples with acceptance levels of 90-110% and +/- the MRL from zero, respectively.

Total uranium concentrations accumulated on the resin will be tested using kinetic phosphorescence analysis (KPA). Solid samples will be digested during sample preparation. Seven standards ranging from 1 to 300 μg/Lare used in the instrument calibration procedure, with acceptance criteria of a correlation coefficient greater than 0.995. After the calibration curve, ICV and ICB samples will be run, with acceptance criteria of 90-110% for the ICV. CCV and CCB samples will then be analyzed after every 10 samples and must fall within 90-110% for the CCV sample and within +/- the MRL from zero for the CCB sample.

Other analyses run at the ELAP-certified laboratories (e.g., nitrate) will conform to the calibration procedures described in the SOPs (Appendix A). Standard calibration curves run on the field instrument will be sufficient to ensure that the instrument is operational and large deviations in concentrations are real phenomena.

6 QA/QC Checks

6.1 Quantitative Acceptance Criteria for Data

QA/QC sampling, which includes field-collected duplicate samples and blanks, as well as laboratory, split samples (i.e., replicate analyses) and matrix spikes will be used to verify consistency in sample collection and handling and analytical accuracy.

6.1.1 Field QA/QC Samples

Field-collected duplicate samples will be obtained for at least 10% of all samples collected and will be co-located samples taken one right after the other. Duplicates will not be identified as QA/QC samples when sent to the laboratory. Field-collected duplicates will serve to ensure acquisition of representative samples, consistency of sampling, and precision of the analytical methods. Acceptance criteria for the field-collected duplicate samples will be within the analytical acceptance criteria for the specific analytical method (Appendix A).

Field blank samples will be prepared by filling metal-free distilled water in the sample bottles provided by the lab (with added preservatives, if necessary); these samples will be sent for analysis to test any possible contamination during sample handling, transport, and storage. At least one field blank sample per method will be prepared for each shipment. The routine frequency for the field blanks will be approximately one in ten samples to be shipped (i.e., 10% field blanks). Field blanks submitted to the laboratory for analysis will not be identified as QA/QC samples. The proposed QA/QC sampling and analysis frequency is listed in Table 6-1. Acceptance criteria for the field blanks will be +/- the MRL from zero.

For field-measured chemical parameters (sulfate, phosphate, silicate), accuracy and precision acceptance criteria will be based on manufacturer specifications, which will be tested using standards prepared in the water matrices. In general, acceptance criteria for these analytes will be less than 20% for field-collected duplicate samples. For the field methods, precision will be analyzed every 20 samples from repeat analyses on known-concentration accuracy check standards, with an acceptance criteria of 80 to 120%.

6.1.2 Laboratory QA/QC Samples

Calibration curve development and CCV samples were discussed in Section 5.3. Additional QA/QC samples to test for accuracy and precision are described below.

Accuracy (a combination of random and systematic error) in Cr(VI) and total Cr analyses will be evaluated by determining percent recoveries in samples spiked in the laboratory. A matrix spike (MS) will be performed on 10% of samples (or at least one sample per run), chosen at random. MS recoveries should be between 90 and 110% of the expected value for Cr(VI) and between 70 to 130% for total Cr. National Institute of Standards and Technology (NIST) traceable Cr(VI) solutions and ICS total Cr standard solutions will be used for matrix spikes. Accuracy will also be tested throughout the runs and after every 10 samples by analyzing a mid-range IPC sample and a laboratory reagent blank (LRB). The acceptance criteria for the IPC sample is between 95 and 105%. The LRB should be below ½ the MRL. If concentrations are outside of these ranges, corrective actions will be performed as detailed in the SOPs for Method 218.6 or 200.6 (Appendix A).

Precision (random error) will be investigated by performing repeat analyses on the same analytical instruments. For every batch of twenty samples, a LCS and a MS will be run. The acceptable ranges for these sample results are between 90 and 110% for Method 218.6 and 70 to 130% for Method 200.8. Laboratory replicates and matrix spike duplicates (MSD) will be analyzed for every batch of twenty samples with an acceptance criteria of < 20% relative percent difference (RPD).

Table 6-1.
Quality Assurance Sampling and Measurement Frequency

Sample Analysis	**Sampling QA/QC Frequency**			
	Sample Frequency	**Field-Collected Duplicates**	**Laboratory Matrix Spikes**	**Field Blanks**
Cr(VI)	Weekly	10% of samples	5% of samples	1/week
Total Cr	Weekly	10% of samples	5% of samples	1/week
Sulfate	Monthly	10% of samples	None	1/month
Nitrate	Monthly	10% of samples	None	1/month
Phosphate	Monthly	10% of samples	None	1/month
Silicate	Monthly	10% of samples	None	1/month
Alkalinity	Weekly	10% of samples	None	None
Conductivity	Weekly	10% of samples	None	None
pH	Continuous online monitoring	Weekly	None	None
Temperature	Weekly	10% of samples	None	None
Turbidity	Weekly	10% of samples	None	None
Nitrosamines	Start of test[a]	10% of samples	5% of samples	1/sample shipment
Residuals: TCLP	End of resin bed life	10% of samples	5% of samples	None

Sample Analysis	**Sampling QA/QC Frequency**			
	Sample Frequency	**Field-Collected Duplicates**	**Laboratory Matrix Spikes**	**Field Blanks**
Residuals: CWET	End of resin bed life	10% of samples	5% of samples	None
Residuals: Uranium	Monthly on lead vessel	10% of samples	5% of samples	None

[a] Nitrosamines will be analyzed at a frequency required by the DPH permit

As the critical parameters in evaluating the success of the project, total Cr and Cr(VI) concentration data quality will also be subjected to paired sample analyses (i.e., Cr(VI) and total Cr samples collected at the same time). Paired samples will be used to assess the chromium speciation and verify that the two concentrations are similar, as observed in the Phase III Bridge Project. Discrepancies between the total Cr and Cr(VI) values will be investigated more closely to ensure that no bias exists for the total Cr analyses (as was observed in the Phase III Additional RCF Testing project).

6.2 Additional Project-Specific Quality Assurance Objectives

In addition to the primary objective of evaluating the effectiveness of Cr(VI) removal from water using the WBA resin, this demonstration-scale study will test the operations and maintenance (O&M) requirements for this technology. Table 3-2 highlights the critical process-related measurements that will be obtained during testing. To ensure quality data are collected to evaluate these objectives, flow rates and pressures will be measured and assessed within the acceptance criteria set forth by manufacturer specifications for the instrumentation.

6.3 Procedures to Assess QA Objectives

Quality assurance objectives will be assessed as detailed throughout this QAPP. Field measurements will be tested for accuracy by frequent calibration of equipment, for precision by obtaining replicate analyses of parameters, and for any contamination that may occur during sample handling and transfer by analyzing blanks.

Laboratory analyses, including critical chromium measurements, will be subjected to numerous procedures to assess quality assurance objectives. Sample accuracy will be tested by comparing sample concentrations to matrix spike concentrations and laboratory control samples. Relative percent differences on replicate samples will be used to determine instrumental precision. The examination of QA parameters including accuracy, precision, and sample contamination will enable us to have confidence in data and trends observed throughout the demonstration-scale study.

7 Data Reporting, Data Reduction, & Data Validation

7.1 Data Reporting Requirements

Table 7-1 details the reporting requirements (units, MDL, and MRL) for each of the analyses to be performed. All of the analyses in Table 7-1 for water samples are expressed in mg/L or µg/L. Data reporting requirements for residuals analyses are also listed in Table 7-1.

7.2 Field and Data Deliverables

Field data to be collected includes pH, temperature, conductivity, turbidity, alkalinity, sulfate, phosphate, and silicate. Measurements will be recorded in the Field Sampling Log Book and entered into Microsoft Excel.

Laboratory data for Cr(VI), total Cr, nitrate, and nitrosamines will be reported to McGuire Malcolm Pirnie by the contract laboratories. The data will be stored in the project data management system as well as at the contract laboratory. Routine analytical QC data will also be stored electronically.

McGuire Malcolm Pirnie will gather all data and prepare summary tables and graphics to characterize the findings from the demonstration-scale study. Quality assurance procedures (refer to Section 7.4) will be used to validate and confirm the data.

7.3 Data Reduction Procedures

In the laboratory and in the field, analytical measurements will be converted to concentrations by running appropriate calibration curves on the same instrument and interpolating the sample values.

Sample and QC concentrations received from the labs will be entered manually into a Microsoft Excel spreadsheet, from which efficiencies of Cr(VI) removal will be calculated. A minimum of 10% of data entered will be checked by the Malcolm Pirnie Quality Assurance Manager or Deputy Project Manager to ensure that transcription errors have not occurred.

Table 7-1.
Measurement Data Reporting

Sample Analysis	Analytical Method	Units	Method Detection Level (MDL)	Method Reporting Level (MRL)
Cr(VI)	EPA 218.6	µg/L	0.015	0.1
Total Cr	EPA 200.8 (ICP-MS)	µg/L	0.192	1
Nitrate	300.0 (IC)	mg/L	0.009	0.100
Sulfate	Hach 8051 (Turbidimetric)	mg/L	5	5
Phosphate	Hach 8048 (Colorimetric)	mg/L	0.5	0.5
Silicate	Hach 8185 (Colorimetric)	mg/L	1	1
Alkalinity	Hach 8203 (Titration)	mg/L (as $CaCO_3$)	10	10
Conductivity	SM 2510B (Conductance)	µmho/cm	TBD	TBD
pH	SM 4500H+ B (Electrometric)	pH units	N/A	N/A
Temperature	SM 2550 (Thermometric)	ºC	N/A	N/A
Turbidity	SM 2130 B	NTU	0.02	0.02
Nitrosamines	EPA 521	ng/L	NDMA – 0.476 NMEA – 0.393 NDEA – 0.758 NDPA – 0.785 NDBA – 0.719 NPYR – 0.361	NDMA – 2 NMEA – 3 NDEA – 5 NDPA - 7 NDBA – 4 NPYR – 2
Residuals: TCLP	EPA 1311 (TCLP) EPA 6010B (ICP): Total Cr	µg/L	2.466	10
Residuals: STLC	CA WET Test (Title 22:§66261.126) EPA 7196A: Cr(VI) EPA 6010B (ICP): Total Cr	mg/L mg/L	2.985 2.466	10 10
Residuals: TTLC	CA WET Test (Title 22:§66261.126) EPA 7196A: Cr(VI) EPA 200.7 (ICP-MS): Total Cr	mg/kg mg/kg	2.985 2.466	10 10
Residuals: Uranium	ASTM 5174-91 (KPA method)	mg/kg	0.00403	0.010

N/A = Not Applicable; TBD = To Be Determined.

7.4 Data Validation Procedures

Depending on the analytical measurement, the types of QA/QC samples may include the following:

- Laboratory matrix spike samples that are used to assess the accuracy of laboratory procedures in at least 5% of the samples;
- Laboratory blank samples that are used to determine the MDL of the analytical procedure and to detect potential laboratory contamination;
- Laboratory control samples that are subjected to multiple analyses to determine laboratory precision in at least 5% of the samples;
- Field-collected duplicate samples to assess how representative samples are and the degree to which the samples reflect actual field conditions; and
- Field-collected blank samples to detect potential problems in the sample collection, handling, and preservation methods.

Operational data will be routinely collected onsite using standardized log sheets. Log sheets will contain information about operational conditions and will be transferred into Microsoft Excel each week.

At the contract laboratory, a person other than the analyst will compare ten percent of all spreadsheet data to original hard-copy printouts. The analyst will ensure that all QC criteria are met, and the analysis manager will review all QC data monthly. The contract labs also conducts an annual performance evaluation for all methods.

Field data entered manually will be validated internally by qualified MMP personnel. Calculations performed in a spreadsheet will be carefully examined to ensure the accuracy of the formulas, data input, and results. After data have been validated and reduced, the MMP QA Manager will review the files to ensure that the data are not suspicious. Any quality control data that do not meet the acceptance criteria, either in the field or in the laboratory, will be flagged and either reported with an explanatory note or excluded from the data reduction.

7.5 Data Storage Requirements

Project data will be generated and duplicated in several locations. Operational data and water quality data generated on site will be recorded on standardized sheets in the Field Sampling Log Book. Water quality samples collected will be labeled to ensure correct identification of sample results returned from off-site laboratories. Information collected on water quality samples will include: sample identification number, name of person who collected the sample, date, time, sample volume, and sample preservation method.

Electronic and hard copies of data will be sent to McGuire Malcolm Pirnie by the contract labs. Project data in the Field Sampling Log Book and off-site laboratory reports will be entered into and will reside in the main project data files. The project data files will serve many purposes, including validation of data entry, central storage of all project data, and routine reduction and reporting of operational and water quality data. In addition, the contract labs will keep the electronic data for at least 5 years.

The main project data files will be hosted on the data server at the McGuire Malcolm Pirnie-Santa Monica office. This data server is routinely backed up on daily, weekly, and monthly schedules, with weekly off-site backups. The server is protected with hardware firewall, and the data files are protected from viruses with reputable anti-virus software.

7.6 Project Documentation

The product documents from this project include an operations and maintenance manual and a final report. However, monthly reports will also be produced for this project to provide updates, including discussion of any QA/QC issues and any necessary resolutions.

8 Assessments

8.1 Audit Schedule

Internal audits are not scheduled for this project. However, the Quality Assurance managers at McGuire Malcolm Pirnie and the contract laboratories will review all QC data monthly to ensure that QC objectives are being met.

8.2 Corrective Action Procedures

The need for corrective action may be identified by assessing standard QC procedures. The essential steps in the corrective action system are detailed below.

<u>Identification and definition of the problem</u>
Corrective action will be required if analytical data are determined to be out-of-control. An analytical batch will be considered to be out-of-control when replicate samples, matrix spiked samples, calibration blanks, the standard curve, calibration check samples, or external reference samples fail to meet the QC criteria.

<u>Investigation and determination of the cause of the problem</u>
When an analysis is determined to be out-of-control, steps will be taken to determine the cause. First, it must be determined whether a calculation error has occurred. Then the instrument used in the analysis will be checked against performance specifications. The indicators of being out-of-control will be a clue to the problem. For example, wrong readings of laboratory control samples may indicate the instrument is not properly set-up or standards are bad; if replicates are not within precision limits, contamination may be a problem; if spike recovery is outside acceptable limits, matrix interferences may have occurred; or if blanks are too high, contamination has probably occurred.

<u>Determination of a corrective action to eliminate the problem</u>

- Calibration check samples
  If results of the daily calibration sample check are out-of-control, as indicated by flagged values, causes may include instrument malfunction or improper set-up, bad standards, or operator error. The first step will be to check instrument performance. The instrument will be restarted. If this does not bring the system back into control, then standards will be re-made and analyzed. If the problem is operator error, the analyst will be re-trained and put through a rigorous QC check before he/she can continue with the sample analyses.

- Accuracy

  When a result is out-of-control as indicated by flagged values for spiked samples, the following steps will be taken to determine the cause. First, calculations will be checked. Then the instrument will be checked for proper set-up. The sample(s) will be reanalyzed. If these steps do not bring the analysis under control, then the spiked sample will be prepared again and analyzed. It may be necessary at this time to prepare fresh standards. If all of the above procedures do not bring the analysis into control, analysis will be performed by standard addition. All samples analyzed in the batch containing the out-of-control sample will be re-analyzed by the procedure used to bring the analysis back into control.

- Precision

  When a result for replicate analysis is out-of-control as indicated by flagged values, steps will be taken to determine the cause. First calculations will be checked. Then instrument performance will be evaluated. The sample(s) will be reanalyzed. If these procedures do not bring the samples back into control, then all samples in the analytical batch will be prepared again and analyzed.

- Blank contamination

  If the laboratory control blank shows contamination (i.e. concentrations greater than ½ the MRL during analysis, materials and reagents used to make that blank will be replaced before additional samples are prepared. Also, glassware and sample preparation will be re-evaluated to ensure that contamination is not occurring during these processes. Standards prepared with contaminated reagents will be discarded, and samples will be reprocessed.

- External reference sample analysis

  The inability of the laboratory to accurately analyze an external reference sample is indicative of analytical problems related to sample preparation procedures, instrument operation, or calibration. If the calibration check sample within the same analytical batch analysis is also out-of-control, a problem with the instrument or operator performance is indicated. Corrective action will be taken as described earlier. If the calibration check sample is within the control limits, the problem may be with the sample preparation procedure. At this point the calibration standards will be prepared again and analyzed. If this fails to bring the measurement back into control, the procedure will be reevaluated to determine if there are points within the procedure likely to be the source of contamination or the cause of a loss of the analyte. All samples analyzed in the batch with the out-of-control sample will be re-analyzed by the procedure used to bring the check samples back into control.

8.3 Implementation of Corrective Action

Analysts at the contract laboratories will have the authority to implement corrective action (described in Section 8.2 Investigation and Determination of the Cause of the Problem) during an analysis run if quality control samples are determined to be out-of-control. The Quality Assurance managers and Project Managers at McGuire Malcolm Pirnie and the contract laboratories will review QC logs monthly and will consult with the analyst if further corrective action is identified as necessary. Following any corrective action, the primary investigators will ensure that the analysis is truly back in control, as indicated by consistently meeting quality control criteria.

9 References

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10 Appendices

Appendix A – SOPs

Appendix B – ELAP Certifications

Appendix A - SOPs

1. Cr(VI)– EPA Method 218.6

2. Total Cr– EPA Method 200.8

3. Nitrate – EPA Method 300.1

4. Sulfate – Hach Method 8051

5. Phosphate – Hach Method 8048

6. Silicate – Hach Method 8185

7. Alkalinity – Hach Method 8203

8. Conductivity – Standard Method 2510B

9. pH – Standard Method 4500H+ B

10. Temperature – Standard Method 2550

11. Turbidity – Standard Method 2130B

12. Nitrosamines – Standard Method 521

13. TCLP – EPA Methods 1311 (leaching), SW-846 6010C (and EPA Method 200.7) for metals, and SW-846 7470A (mercury)

14. California WET – CWET (Title 22)

15. Uranium – ASTM5174-9

Appendix B – ELAP Certifications

1. MWH Labs
2. Test America Labs