APPENDIX D

SOURCE DETERMINATION STUDY WORK PLAN

1.0 Introduction

This work plan supports achievement of the objectives of the Remedial Investigation (RI) Addendum by conducting stable isotope and geochemical tracer analysis on select groundwater samples to determine the extent of dissolved perchlorate originating from the Jet Propulsion Laboratory (JPL). Samples collection will occur in February/March 2005. This work plan identifies procedures for collecting additional analytes.

2.0 Background

Stable isotope analyses were recommended by the United States Environmental Protection Agency (U.S. EPA) and the City of Pasadena's consultant, Geosyntec, based on their review of the Draft RI Addendum Work Plan. The National Aeronautics and Space Administration (NASA) then organized an expert team to evaluate the existing data and make recommendations for isotope analyses. Meetings were then conducted with members of the expert team on October 25, 2004 and November 2, 2004. The expert team consisted of the following members:

October 25, 2004 Meeting
- Dr. Bruce Sass (Battelle)
- Dr. Neil Sturchio (University of Illinois at Chicago)

November 2, 2004 Meeting
- Dr. Max Coleman (California Institute of Technology)
- Dr. Richard Hurst (Hurst and Associates)
- Mr. Michael Land (United States Geological Survey [USGS])
- Mr. Eric Reichard (USGS).

Dr. Sturchio and Dr. Hurst prepared technical memoranda to summarize recommendations made during the meetings. These memoranda are provided as Attachments 1 and 2 of this Work Plan. Recommendations from the expert team include the following isotope analyses:

- Perchlorate: chlorine ($\delta^{37}Cl$) and oxygen ($\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$),
- Groundwater: oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$), and inorganic chloride ($\delta^{37}Cl$)
- Strontium ($^{87}Sr/^{86}Sr$), and
- Tritium/helium ($^{3}H/^{3}He$).

Other recommended sampling includes chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), analysis for perchlorate-reducing microbial activity, dissolved oxygen (DO), oxidation-reduction potential (ORP), nitrite/nitrate, ferrous/ferric iron, sulfite/sulfate, dissolved organic carbon (DOC), and total organic carbon (TOC). CFCs and SF_6 are a useful complement to $^{3}H/^{3}He$ measurements to determine the age of groundwater ($\leq$50 years).

A microcosm study previously performed at the JPL site demonstrated that indigenous bacteria are capable of reducing perchlorate and identified the microbes cultured from the JPL site as *Dechlorosoma suillum* strain JPLRND (Hatzinger et al., 2002). The activity of these perchlorate-reducing bacteria will be assessed by conducting either a chlorite-dismutase-specific immunoprobe or a functional gene probe for the relevant perchlorate-reducing RNA. The additional geochemical analyses to be

performed as part of this study will also be used to evaluate if appropriate conditions are present within the aquifer to support biodegradation of the perchlorate.

3.0 Sampling Locations

The production wells and monitoring wells which have been selected as sample locations for this study are provided in Table D-1. A map showing the well locations is provided in Figure D-1. The selected sampling locations provide representation of the groundwater conditions both on and off the JPL facility:

- MW 1: a shallow monitoring well located east of the JPL facility; was chosen as an upgradient location representative of runoff from the San Gabriel Mountains.
- MW 24: a multiport well located within the JPL source area.
- MWs 17 and 18: multiport wells located outside the JPL facility and within the known perchlorate plume where other chemicals of interest from the JPL site have been detected (including carbon tetrachloride and trichloroethene).
- MWs 19, 20, and 21: multiport wells located south and southeast of the JPL facility representing the southernmost monitoring wells. Modeling indicates that groundwater from upgradient portions of the Monk Hill Subbasin flows to the south of the JPL facility; therefore, samples collected from these wells improve the understanding of groundwater origin and mixing.
- MW 25: a new multiport well located near the Sunset Reservoir wells.

Several municipal production wells are located in the vicinity of the JPL facility and are of interest to this study. Municipal production wells owned by the City of Pasadena, Lincoln Avenue Water Company (LAWC), Rubio Canyon Land and Water Association (RCLWA), and Las Flores Water Company (LFWC) are located hydraulically downgradient (or cross gradient) of JPL, and municipal production wells operated by Valley Water Company (VWC) are located hydraulically upgradient of JPL. Two City-of-Pasadena production wells (Bangham and Garfield) and two VWC production wells (VWC-2 and VWC-3) are constructed to serve as extraction and injection wells. Injected water was purchased from the Metropolitan Water District (MWD). A significant portion of the injected MWD water was obtained from the Colorado River, which contains low levels of perchlorate from industrial sources in Nevada. Therefore, samples will be collected from the following locations (if possible):

- VWC-1: located upgradient of JPL.
- LAWC-3: located downgradient of the JPL facility; perchlorate and volatile organic compounds (VOCs) in LAWC-3 are believed to originate from JPL. NASA funded installation, and operation of treatment has been installed as part of a CERCLA Removal Action for perchlorate and other chemicals of interest (including carbon tetrachloride and low levels of tetrachloroethene) associated with the JPL.
- RCLWA-7: located further south of LAWC wells. Low levels of perchlorate have been detected in RCLWA wells; however, other chemicals of interest from the JPL site have not been detected in these wells.
- LFWC-2: located further south and east of LAWC. Low levels of perchlorate have recently been detected in this well; however, higher levels of tetrachloroethene than those associated with the JPL site have historically been detected in this well.
- Garfield Well: City of Pasadena well located in the Sunset Reservoir area.
- Colorado River Water.

Table D-1. Monitoring and Production Wells Summary Table

Well	Screen Number	Perchlorate Detected in Screen	Depth of Screened Interval (ft bgs)	Elevation of Screened Interval (ft amsl)	Layer	Water Type (1)	Range Perchlorate Detected (µg/L)(2)
MW-1	1	No	70-110	1007-1047	1	1	—
MW-17	1	No	246-256	935-945	1	1	—
	2	Yes	366-376	815-825	2	1	3.4 – 15.7
	3	Yes	466-476	715-725	3	1	3.7 – 209.0
	4	Yes	578-588	603-613	4	1+2	6.5 – 17.0
	5	Yes	723-733	458-468	4	1+2	4.4 – 22.0
MW-18	1	No	266-276	950-959	1	1	—
	2	No	326-336	890-899	1	1	—
	3	Yes	421-431	794-804	2	1	1.3-5.2
	4	Yes	561-571	654-664	3	1+2	11.0-31.3
	5	No	681-691	534-544	4	2	—
MW-19	1	No	240-250	893-903	1	1	—
	2	Yes	310-320	823-833	2	3+1	4.3 – 4.5
	3	Yes	390-400	743-753	2	3+1	4.1 – 7.2
	4	Yes	442-452	691-701	3	1+3	4.9
	5	Yes	492-502	641-651	3	3+1	4.2 – 4.4
MW-20	1	Yes	228-238	927-937	1	3+1	4.4 – 7.8
	2	No	388-398	767-777	2	2	—
	3	No	558-568	597-607	3	2, 2+1	—
	4	Yes	698-708	457-467	4	2	20.0 – 124.0
	5	Yes	898-908	257-267	4	2	8.2
MW-21	1	Yes	86-96	963-973	1	3+1	3.1 – 19.0
	2	Yes	156-166	893-903	2	3	2.1 – 4.6
	3	Yes	236-246	813-823	2	3	2.7 – 4.8
	4	Yes	306-316	743-753	3	1+3	2.1 – 7.7
	5	Yes	366-376	683-693	3	3+1	2.6 – 5.8
MW-24	1	Yes	275-285	916-926	2	1+3	14.0 – 2,760.0
	2	Yes	370-380	821-831	2	2+3	11.6 – 700.0
	3	Yes	430-440	761-771	2	2	1.6
	4	No	550-560	641-651	3	2+1; 2	—
	5	No	657-685	516-526	4	2	—
MW-25(3, 4)	1	Yes	355-365	550-560	TBD	TBD	TBD
	2	Yes	420-430	485-495	TBD	TBD	TBD
	3	Yes	500-510	405-415	TBD	TBD	TBD
	4	Yes	630-640	275-285	TBD	TBD	TBD
	5	Yes	710-720	195-205	TBD	TBD	TBD
VWC-1(5)	1	Yes	155-432	730-1007	2	3	4.2
LAWC-3(5)	1	Yes	463-601	602-740	2,3	1	31.0
RCWLA-7(5)	1	Yes	290-510; 570-700	440-850	1,2,3	2+1	4.3
LFWC-2(5)	1	Yes	240-390; 474-510	765-915; 645-681	2,3	1, 1+3	5.9
Garfield(5)	1	Yes	192-257; 295-327; 355-360; 387-419; 602-620; 624-629	706-641; 603-571; 543-538; 511-479; 296-278; 274-269	3,4	3	6.9

(1) 1 = calcium bicarbonate; 2 = sodium bicarbonate; 3 = calcium-bicarbonate/chloride/sulfate
(2) Analytical results span sampling events from Aug/Sep 1996 to Oct/Nov 2003.
(3) Analytical data based on preliminary sampling results.
(4) Well depths and elevations approximate pending survey data.
(5) Analytical data based on latest sampling results.

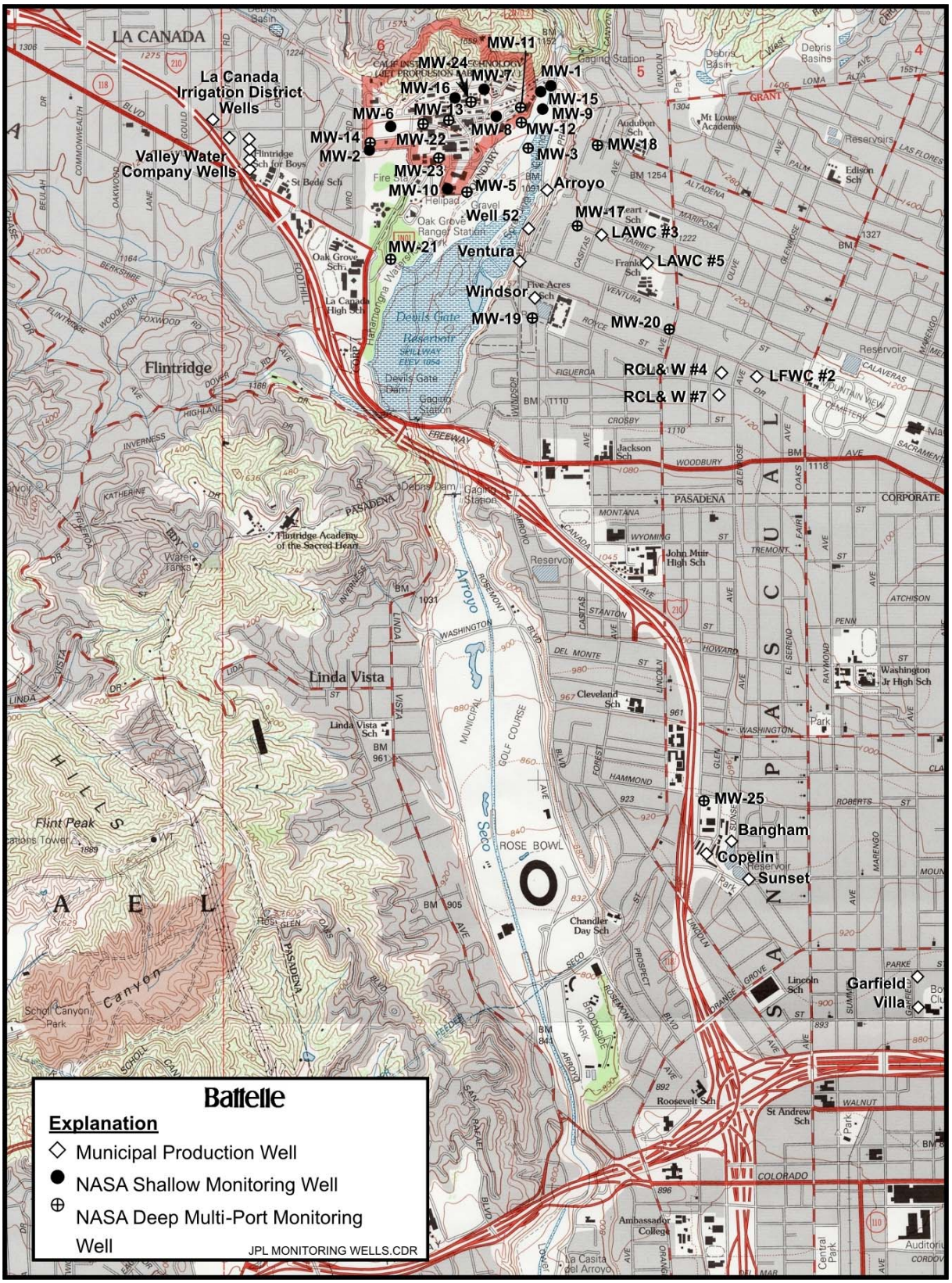

Figure D-1. Sample Locations

4.0 Laboratory Analytical Procedures

There are forty-two (42) sampling locations identified for this study. Samples collected from all locations will be analyzed for $\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$, $^{3}H/^{3}He$, CFCs, SF_6, DO, ORP, nitrite/nitrate, ferrous/ferric iron, sulfite/sulfate, DOC, and TOC. Thirty-one (31) of these locations will be sampled for perchlorate isotope analysis (i.e., $\delta^{37}Cl$, $\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$). Samples will also be collected for inorganic chloride analysis and microbial activity analysis from the 31 locations sampled for perchlorate isotopes, along with one upgradient location (MW-1).

Table D-2 outlines the method, sample volume requirement, sample preservation, and holding time for each analysis to be conducted. The field measurements will be conducted using the WTW Multi 340i handheld meter (or equivalent) and analyzed immediately at the site. All water quality parameters will be analyzed by California-certified laboratory. Nitrate only has a 48-hour holding time without preservatives, so samples must be shipped the day they are collected. Battelle will notify the laboratory prior to shipping.

The protocols for isotope analyses have been provided by the laboratories and are included in the Attachments 3A through 3F. Isotope analysis of perchlorate, groundwater ($\delta^{18}O$ and $\delta^{2}H$), and inorganic chloride will be conducted by the University of Illinois at Chicago. The tritium-helium analysis will be conducted by Columbia University, and the strontium isotope analysis will be conducted by Massachusetts Institute of Technology.

Table D-2. Analytical Methods, Sample Volumes, Practical Quantitation Limit, Preservations, and Holding Times

Constituent	Units	Method	PQL	Sample Container	Preservation Method	Maximum Holding Time
Field Measurements						
pH	S.U.	WTW Multi 340i handheld meter	None	50 mL, poly	Not required	Analyze immediately in field
Temperature	°C	WTW Multi 340i handheld meter	None	50 mL, poly	Not required	Analyze immediately in field
Dissolved Oxygen (DO)	mg/L	WTW Multi 340i handheld meter	None	50 mL, poly	Not required	Analyze immediately in field
Oxidation-reduction potential (ORP)	S.U.	WTW Multi 340i handheld meter	None	50 mL, poly	Not required	Analyze immediately in field
Water Quality Parameters (to be analyzed by a California-certified laboratory)						
Dissolved Organic Carbon (DOC)	mg/L	415.1	1.0	250 mL, glass	Cool, 4°C H_2SO_4 to pH<2	28 days
Total Organic Carbon (TOC)	mg/L	415.1	1.0	250 mL, glass	Cool, 4°C H_2SO_4 to pH<2	28 days
Ferrous iron	mg/L	SM3500	0.05	2x40 mL VOA vials	Cool, 4°C, Field Filtered[(i)] HCL	14 days
Ferric iron	mg/L	SM3500	0.05	250 mL Poly	Cool, 4°C Field Filtered[(i)] Nitric Acid to pH<2	28 days
Nitrite-Nitrogen (NO2-N)	mg/L	300.0	0.25	250mL, poly	Cool, 4°C Non preserved	48 hours
Nitrate-Nitrogen (NO_3-N)	mg/L	300.0	0.25	250 mL, poly	Cool, 4°C Nonpreserved	48 hrs
Sulfide	mg/L	376.2	0.10	250 mL, poly or Glass	Cool, 4°C Zn Acetate	14 days
Sulfate	mg/L	300.0	0.5	250 mL, poly	Cool, 4°C Nonpreserved	28 days
Stable Isotope Analysis of Perchlorate and Water (UIC Environmental Isotope Geochemistry Laboratory)						
$\delta^{18}O$, $\delta^{17}O$, $\Delta^{17}O$ [(a)]	ppt	UIC	1 ppb	Resin column	None	1 year
$\delta^{37}Cl$ [(a)]	ppt	UIC	1 ppb	Resin column	None	1 year
$\delta^{18}O$ [(b)]	ppt	UIC	None	20 mL glass with PolySeal cap	None	1 year
$\delta^{2}H$ [(c)]	ppt	UIC	None	20 mL glass with PolySeal cap	None	1 year

Constituent	Units	Method	PQL	Sample Container	Preservation Method	Maximum Holding Time
Inorganic Chloride ($\delta^{37}Cl$) [(d)]	ppt	UIC	None	125 mL ploy	Field filtered (0.45 micron); Cool, 4°C	1 year
Tritium-Helium Analysis of Water (Environmental Tracer Group, LDEO, Columbia University)						
$^{3}H/^{3}He$ [(e)]	TU	Columbia	0.5	2x500 mL, glass; 2 special copper tubes	Cool, 4°C	6 months
Isotope Analysis of Strontium (MIT Dept. of Earth, Atmospheric, and Space Science Laboratory)						
$^{87}Sr/^{86}Sr$ [(f)]		MIT	None	250 mL, poly	Not required	6 months
CFC and SF_6 analysis of water (USGS Reston CFC Laboratory)						
Chlorofluorocarbons (CFC-11, CFC-12) [(g)]	Picograms/L	USGS	0.3	5x125 mL, glass with special foil-lined caps	Not required	6 months
Chlorofluorocarbons (CFC-113) [(g)]	Picograms/L	USGS	1.0	5x125 mL glass with special foil-lined caps	Not required	6 months
Sulfur hexafluoride (SF_6) [(h)]	Femtomoles/L	USGS	0.1	2x1 L, glass	Not required	6 months
Analysis for Evidence of Perchlorate-Reducing Microbial Activity (BioInsite)						
perchlorate-reducing microbial activity [(j)]	active cells/mL	immunoprobe or functional gene probe	200	1 L glass	Cool, 4°C	48 hours

ppt = part per thousand (or per mil shift from reference)
PQL = practical quantitation limit
Femtomoles/L = 10^{-15} moles/L
TU = Tritium Units
Poly = polyethylene bottles

(a) The laboratory method protocol for perchlorate isotope analysis is included in Attachment 3A.
(b) The laboratory method protocol for oxygen isotope analysis in groundwater is included in Attachment 3B.
(c) The laboratory method protocol for hydrogen isotope analysis in groundwater is included in Attachment 3C.
(d) The laboratory method protocol for inorganic chloride isotope analysis in groundwater is included in Attachment 3D.
(e) The laboratory method protocol for tritium/helium isotope analysis is included in Attachment 3E.
(f) The laboratory method protocol for strontium isotope analysis is included in Attachment 3F.
(g) The laboratory method protocol for CFC analysis is included in Attachment 3G.
(h) The laboratory method protocol for SF_6 analysis is included in Attachment 3H.
(i) 50 cc filter syringes can be provided by laboratory.
(j) Samples will be analyzed by either the immunoprobe method or the functional gene probe method. The method will be chosen based on the level of sensitivity required, as determined by the laboratory.

5.0 Sampling Procedures

Each sample shall be designated with a unique identifier as discussed in Section 2.3.4 of Appendix A (Sampling and Analysis Plan). All samples will be collected in the appropriate sample containers provided by the laboratory and preserved as indicated in Table D-2. Unless otherwise noted, all samples should be collected in airtight, precleaned glass containers provided by the laboratory, which should be filled to the rim to avoid aqueous-air exchange.

Once collected, each containerized sample will be labeled and placed into a laboratory-specific sample cooler. The sample cooler will serve as the shipping container and will be provided by the laboratory. Samples are to be shipped to the laboratory promptly in order to provide ample time for analyses to be conducted within the established maximum holding times. The samples will be packed with shock-absorbent materials, such as bubble wrap, to prevent movement or breakage of the sample jars during transport. In addition, the samples shall be preserved with wet ice to meet the 4°C preservative requirement, if appropriate (see Table D-2). All samples shall be shipped under the chain-of-custody procedures discussed in Section 2.3.3 of Appendix A. Special sampling procedures for perchlorate ($\delta^{37}Cl$, $\delta^{18}O$, $\delta^{17}O$, $\Delta^{17}O$), $^{3}H/^{3}He$, CFC, and SF_6 are identified as follows:

$\delta^{37}Cl$, $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ (Perchlorate Isotope) – Extraction of perchlorate from groundwater samples is accomplished by sorption onto a highly selective bifunctional anion exchange resin. For each sample to be collected, the laboratory provides a sampling apparatus, consisting of a prefilter and a glass column packed with a mixture of bifunctional resin and glass beads (see Figure D-2). The amount of resin in the sampling apparatus is based on the expected perchlorate concentration in the groundwater, and optimized to recover approximately 20 mg of perchlorate. Therefore, a location-specific resin column will be used at each sample location. In the field, groundwater will be passed through the sampling apparatus at a maximum flowrate of 0.5 liter per minute. Table D-3 summarizes the estimated sample volume required at each location and the estimated time required for sample collection. Note that each bulk water sample collected for perchlorate isotope analysis will be analyzed for perchlorate concentration to determine the actual volume required for the perchlorate isotope sample. Once the total sample volume has passed through the resin column, the sampling apparatus will be disconnected, drained, plugged and returned to the UIC Environmental Isotope Geochemistry Laboratory for analysis (see also Attachment 3A).

Figure D-2. Perchlorate Sampling Apparatus

Table D-3. Perchlorate Sample Volumes

Sample Location	ClO_4^- Concentration in Latest Sampling Event (µg/L)	Total Sample Volume Required (L)	Estimate Sample Collection Time (hours)
MW-17 Screen 2	16.2	1,235	41.2
MW-17 Screen 4	4.0	5,000	166.7
MW-18 Screen 3	4.0	5,000	166.7
MW-18 Screen 4	11.0	1,820	60.7
MW-19 Screen 2	6.8	2,945	98.2
MW-19 Screen 4	3.5	5,715	190.5
MW-20 Screen 1	4.0	5,000	166.7
MW-20 Screen 4	4.0	5,000	166.7
MW-24 Screen 1	1120	20	0.7
MW-24 Screen 2	107	190	6.4
MW-24 Screen 3	4.0	5,000	166.7
MW-25 Screen 1	8.1	2,470	82.4
MW-25 Screen 2	12	1,670	55.7
MW-25 Screen 3	8.7	2,300	76.7
MW-25 Screen 4	8.1	2,470	82.4
VWC-1	4.2	4,765	158.9
LAWC-3	31	650	22
RCWLA-7	4.3	4,655	156
LFWC-2	5.9	3,390	113
Garfield	6.9	2,900	97

Tritium/Helium– Proper collection of a water sample for $^3H/^3He$ analysis requires (1) filling duplicate special copper sample tubes for helium analysis and (2) filling two 500-mL bottles for tritium analysis. The special copper sample tubes have a 3/8-inch diameter, 30-inch length, contain about 44 mL of water, and are fitted with stainless steel pinch-off clamps at each end. Safety coated 500-mL glass bottles with polycone seals will be used for the tritium sample. A headspace of several mililiters should be left in the bottle to prevent breakage when warming.

Damage to the ends of the copper tube may prevent proper attachment of the sample tube to the vacuum extraction line for sample preparation at the contract laboratory. The copper tube, which is fixed in an aluminum channel holding the stainless steel pinch-off clamps, is connected to a closed path from the well or pump. The connection to the well or pump can be of almost any material including plastic, rubber, or metal tubing, providing that all connections are airtight and will not come loose when back pressure is applied during closing of the copper tubes. Clear plastic tubing (Tygon) is preferred because one can observe if air bubbles are present in the water line. It is recommended that connections be secured with stainless steel hose clamps, again being careful not to damage the end of the copper tube. The length of the path from the well or pump discharge should not exceed about 5 feet to minimize the possibility of gas separation from the water sample prior to sealing the copper tube. Any trapped air or formation of gas bubbles in the helium water sample will produce erroneous results.

1. Flush and fill copper tube for He analysis, which can normally be done within 5 minutes.
2. Remove and discard the plastic caps that cover the ends of the copper tube, taking care not to scratch or bend or otherwise damage the ends of the copper tube.
3. Apply back pressure to the discharge end of the copper tube during flushing. A small valve and suitable compression type fittings to attach the valve to the discharge end of the copper tube will need to be obtained to aid in sample collection. Figures 1 and 2 in

Attachment 9 show diagrams of the copper tube and back-pressure valve assembly, respectively. The valve should not be closed completely during filling because a steady flow of water must be maintained through the copper tube during sealing.

4. Tap forcibly the entire line from the well through the copper tube to dislodge any gas bubbles that may be in the line or copper tube. Hold the copper tube at an approximate 45-degree angle with the discharge point up, to ensure that gas bubbles, if present, will be completely flushed. Tapping normally requires 1 minute to complete.
5. Once water flowing through the copper tube is free of any gas bubbles, the socket wrench is used to close the bolts on the pinch-off clamps, beginning with the bolts at the discharge end.
6. Before turning the bolts, be sure to position the copper tube in the approximate center of the pinch-off clamp. There are two bolts on each clamp. Turn the bolts in successive order (back and forth approximately four (4) times until firmly closed) so that the blades of the pinch-off clamp close as evenly as possible. A socket wrench with 13-mm (note metric bolt) socket is used to turn the bolts that close the pinch-off clamps.
7. The pinch-off clamps are machined to leave about a 1-mm space when the bolts are turned all the way down; however, care should be taken not to overtighten and strip the threads on the bolts.
8. After tightening the discharge end bolts, tighten the upstream bolts in the same manner, again centering the copper tube between the blade.
9. When done, double check to be sure that all bolts are tight. The sample is then complete and the copper tube can be disconnected from the well or pump.
10. Remove the back-pressure valve from the discharge end of the copper tube. Precautions should be taken not to scratch or otherwise damage the ends of the copper tubes. If waters are corrosive, such as seawater or other saline or acidic waters, the ends of the copper tubes should be washed with dilute water to prevent corrosion, which might prevent obtaining a proper seal when extracting the noble gases.
11. Care should be taken not to further bend the ends of the sealed copper tubes because they can easily break off. If the tubes were received with plastic caps protecting the ends, do not replace the caps after filling (see also Attachment 4B).

CFCs – 125-mL glass bottles and white metal caps with aluminum foil liners are required for sample collection. Discard any caps if the foil liner appears scratched, dented, or altered in any way. Refrigeration-grade copper tubing is required to fill the bottles from the groundwater pump. The filling procedure is carried out within a 2- to 4-liter beaker; a plastic beaker is fine. Five bottles will be collected for each sample, following the sample collection procedures outlined below (refer also to Attachment 3C for example figures):

1. After the well has been purged, place the bottle in the beaker and then insert the end of the copper tubing from the pump all the way into the bottom of the bottle. Also place the cap in the beaker.
2. Fill the bottle with well water until it overflows into the beaker.
3. Continue to overflow the bottle until the beaker overflows. Allow at least 2 liters of water to flow through the bottle and out of the beaker.
4. Tap the cap under water to dislodge air bubbles. Remove the copper tube from the bottle and tightly cap the bottle under water without allowing the water in the bottle to come in contact with air. Flushing the bottle with more water is far better than with less water.
5. Remove the capped bottle from the beaker, dry the bottle and retighten the cap. The tighter the cap the better.

6. Invert the bottle, tap it and check it for air bubbles. If there are bubbles, repeat the procedure from Step 2 above. If it is necessary to refill the bottle, a new cap must be used.
7. If there are no bubbles present, tape the cap securely to the bottle with electrical tape. Wrap the tape in a clockwise direction looking down from the bottle top. Two rounds of electrical tape are needed. Do not forget to label each bottle with the appropriate sample designation, and number each bottle in sequence as it is collected, 1 through 5.
8. Store bottles upside down until shipment.

SF_6 – A minimum of 1 liter of groundwater is required for the SF_6 analysis; therefore, two 1-L bottles will be filled for each sample. One-liter glass bottles with polyseal cone-lined cap will be used for sample collection. Safety coated glass bottles can also be used and are better for shipping. The following sampling procedures will be used for SF_6 sample collection (see also Attachment 3D):

1. Purge well.
2. Place tubing from pump in the bottom of 1-L bottle.
3. Fill bottle and allow it to overflow from the neck (about 2.5L).
4. Slowly remove tubing from the bottle while water is still flowing.
5. Cap bottle (do not leave any headspace) and tape cap in a clockwise direction with electrical tape.
6. Keep bottles in the cooler and not in the sun (water expands when heated and breaks the bottles).

6.0 Quality Control/Quality Assurance

The overall quality objectives for this project and the performance criteria necessary to meet these objectives are discussed in Section 1.7 of Appendix A.

As discussed in Section 2.5 of Appendix A, quality control (QC) requirements include both field and laboratory checks necessary to ensure the integrity of the analytical results. QC checks include proper sample acquisition and handling procedures, as well as proper laboratory quality assurance (QA).

6.1 Field Quality Control Checks

Typical field QC checks include the collection of field duplicates, equipment rinsate samples, trip blanks, and field blanks. Of these field QC samples, only the field duplicates are applicable to this isotope sampling program.

Duplicate samples will be collected by retaining consecutive samples from the sample pump. Field duplicate samples will be collected at a rate of 10% of the total number of samples collected during this sampling program. If fewer than 10 samples will be collected, one duplicate sample will be collected.

General water chemistry cation/anion (Ca, K, Mg, Na, Cl, CO_3/HCO_3) and total dissolved solids (TDS) samples will also be collected in association with the perchlorate isotope samples. One sample will be collected for these general water chemistry analytes from each bulk water sample collected for a perchlorate isotope sample. The results of the general water chemistry analyses will be compared against recent quarterly ground water monitoring results to demonstrate that the water type purged for the perchlorate isotope samples is consistent with the water type present during normal no-purge sampling of the monitoring wells.

The other field QC samples are not applicable to this isotope sampling program for the following reasons:

- Equipment rinsate blanks are collected to ensure that nondedicated sampling devices have been decontaminated effectively, and are only collected for VOC analysis;
- Trip blanks ensure that samples are not contaminated during shipping, and accompany samples to be submitted for VOC analysis only;
- Field blanks are collected to detect possible contamination of the samples from airborne hydrocarbons during sample collection.

6.2 Laboratory Quality Control Checks

Laboratory QC is addressed through the analysis of laboratory QC samples, documented internal and external laboratory QC practices, and laboratory audits. Laboratory blank samples and laboratory control samples (including matrix spike/matrix spike duplicates [MS/MSD]) for the water quality parameters listed in Table D-2 of this Attachment will be collected in accordance with the procedures listed in Section 2.5.1 of Appendix A.

Laboratory QC samples for the isotope analysis will include analysis of standard solutions to demonstrate the accuracy of the analytical method by measuring a known concentration. For the CFC/SF_6 analysis, gas and water blanks, as well as standard solutions, will be analyzed in accordance with the procedures outlined in Attachments 3G and 3H to demonstrate laboratory equipment and method precision and accuracy. In addition, laboratory duplicates will be analyzed to determine the precision of isotope and CFC/SF_6 measurements.

The following standard solutions will be used for laboratory QC purposes:

- All reported oxygen and hydrogen isotope compositions will be calibrated against Vienna Standard Mean Ocean Water (VSMOW);
- All reported chlorine isotope ratios will be calibrated against Standard Mean Ocean Chloride (SMOC);
- All reported $^3H/^3He$ results will be calibrated against standard atmospheric air;
- All reported strontium isotope compositions will be calibrated against the NBS-987 standard;
- All CFC analysis will be calibrated using Standard Marine Oregon Air and Niwot Ridge Colorado Air;
- All SF_6 analysis will be calibrated using either the Scott master gas standard or a National Oceanic and Atmospheric Administration (NOAA) air standard.

6.3 Instrument/Equipment Testing, Inspection, and Maintenance

A water quality meter will be used in the field during this sampling program. As discussed in Sections 2.6 and 2.7 of Appendix A, calibration of field equipment will be conducted according to manufacturer's recommendations. All field instruments will be calibrated before each day of use; and a calibration check at the end of the day will be performed to verify that the instrument remained in good working condition throughout the day. The calibration of all field equipment will be documented in the field logbook.

Laboratory instrument maintenance will be performed in accordance with standard preventive maintenance procedures and schedules. Laboratory instrument calibration will be performed as specified in the attached method documentation (Attachments 3A through 3I).

7.0 Data Evaluation

Analyses to be completed as part of this study include perchlorate isotopes ($\delta^{37}Cl$, $\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$), groundwater isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{37}Cl$), strontium ($^{87}Sr/^{86}Sr$), tritium dating ($^{3}H/^{3}He$), CFCs, SF_6, perchlorate-reducing microbial activity, and several geochemical parameters to evaluate biodegradation. The results of the perchlorate isotope analyses will be used to determine the extent of dissolved perchlorate originating from the JPL site. In addition, historical water chemistry data will be combined with the stable isotope analyses and groundwater dating ($\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$, $^{3}H/^{3}He$, CFCs, and SF_6) to trace fate and transport of the perchlorate and improve the understanding of groundwater flow conditions within the aquifer.

8.0 References

Hatzinger, P.B., M.D. Whittier, M.D. Arkins, C.W. Bryan, and W.J. Guarini. 2002. "In-Situ and Ex-Situ Bioremediation Options for Treating Perchlorate in Groundwater." *Remediation*, 12(2): 69-86.