ATTACHMENT B
Sampling and Analysis Plan

COUNTY SANITATION DISTRICTS
OF LOS ANGELES COUNTY

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STEPHEN R. MAGUIN
Chief Engineer and General Manager

November 10, 2011
File No. 20-04.01-55

Harold Singer
California Regional Water Quality Control Board
Lahontan Region - Victorville Branch Office
14440 Civic Drive, Suite 200
Victorville, CA 92392-2359

Dear Mr. Singer:

Submittal of the Revised Sampling and Analysis Plan (SAP) for the Palmdale Water Reclamation Plant (PWRP), WDID No. 6B190107069

In compliance with the requirements set forth in the Monitoring and Reporting Program No. R6V-2011-0012 (MRP), issued by the California Regional Water Quality Control Board, Lahontan Region (Regional Board) and transmitted to County Sanitation District No. 20 of Los Angeles County (Sanitation District) in a letter dated April 8, 2011, the Sanitation District submits the enclosed Revised Sampling and Analysis Plan (SAP) for the Palmdale Water Reclamation Plant (PWRP). This SAP is submitted to reflect altered sampling requirements in anticipation of start-up operations of the PWRP tertiary treatment facilities.

If you have any questions or comments, please contact the undersigned at (562) 908-4288 extension 2855 or Peter Navas at extension 2847.

Very truly yours,

Stephen R. Maguin

Thomas E. Weiland
Supervising Engineer
Monitoring Section

TW:pmn
Enclosure
cc: Linda Stone
Mike Coony

SANITATION DISTRICTS OF LOS ANGELES COUNTY

REVISED SELF-MONITORING SAMPLING AND ANALYSIS PLAN (SAP)

Palmdale Water Reclamation Plant
County Sanitation District No. 20 of Los Angeles County

November 2, 2011

DOC #2005255

CONTENTS

Overview

This document describes the self-monitoring plan prepared by the County Sanitation District No. 20 of Los Angeles County (Sanitation District) for the Palmdale Water Reclamation Plant (PWRP) to satisfy the conditions specified in Board Order No. R6V-2011-0012, WDID No. 6B190107069, which delineates the Waste Discharge Requirements (WDR) and the Monitoring and Reporting Program (MRP). This order was adopted by the California Regional Water Quality Control Board, Lahontan Region (Regional Board) on March 9, 2011.

Constituent concentrations will be monitored at the following locations[1] in accordance to the requirements of the MRP and WDR as well as additional sampling requirements stated within this SAP:

a) Influent to the treatment facilities
b) Disinfected secondary – treated effluent [2]
c) Disinfected tertiary – treated effluent
d) Groundwater monitoring wells
e) Groundwater supply wells
f) Groundwater extraction wells
g) Vadose zone lysimeters

Flows will be monitored or calculated at a frequency described in Table 1 according to conditions specified in the WDR and the MRP:

a) Influent to the treatment facilities
b) Effluent from the treatment facilities
c) Recycled water flow sent to the Agricultural Site
d) Recycled water flow to the Storage Reservoirs
e) Recycled water flow to each center irrigation pivot or other irrigation system
f) Recycled water flow utilized for reuse purposes (other than internally–recycled process water) at Reclamation Plant and Storage Reservoir Sites
g) Extraction well flow

In addition to flow metering, freeboard in each storage reservoir will be monitored weekly.

An overview of the plant treatment process as well as illustrations, diagrams, and/or photos of selected monitoring locations can be found in Appendix A.

Reason for Updating the SAP

The SAP has been updated to reflect altered sampling requirements due to the completion and operation of the activated sludge and tertiary treatment facilities.

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[1] Biosolids and sludge disposal offsite will be managed and monitored in accordance with applicable Federal, State, and Local permits and regulations (e.g., 40CFR503 for land application)

[2] Samples for Disinfected Secondary-Treated Effluent will only be taken when secondary treatment is the final level of treatment.

Sampling Schedule

The complete self-monitoring schedule is shown in Tables 1, 2 and 3. Tables 1 and 2 list the compiled monitoring requirements as outlined in the MRP and WDR. Table 3 lists additional monitoring not required by the MRP or WDR but these analyses will be completed whenever samples can be obtained. Typically, annual, semiannual, or quarterly monitoring events will be conducted concurrently with monthly events.

Sampling Constituents and Analytical Methods

Table 4 provides a compilation of the sampling and analytical protocols for all constituents requiring self-monitoring, as accepted in the MRP. The analytical methods and sampling techniques used may change if alternative methods are found to provide better results. The Sanitation District will seek Regional Board approval for any changes in analytical methods and sampling techniques prior to implementation.

Quality Assurance/Quality Control (QA/QC)

The Quality Assurance (QA) Group of the Sanitation Districts of Los Angeles County (Sanitation Districts) Laboratories Section is responsible for ensuring the validity and quality of analytical data produced in all laboratories operated by the Sanitation Districts. In order to accomplish this goal, a quality assurance plan prepared by the QA Group is strictly followed. The plan includes routine QA activities that are performed in the laboratories in order to assure the defensibility of data reported.

1. A routine practice of running laboratory control samples, duplicates and matrix spikes or duplicate spikes for every ten samples, or every analytical batch of less than ten samples, is maintained. Control limits have been established for both precision and accuracy, and quality control data are plotted on control charts for trend analyses. For situations where the data are outside of the control limits, corrective action is initiated and maintained at the bench level until the problems are solved.
2. A reagent or method blank is routinely run with each batch of samples as a contamination check.
3. Calibration standards are analyzed as required. For some tests, a daily calibration verification standard is used to check the initial calibration curve. For other tests, a multi-point calibration curve is prepared on each day of analysis.
4. For some organic constituents, surrogate standards are added to every sample, duplicate, spike, and blank. The results are compared to established acceptance limits. When unacceptable QA results are obtained, corrective action is performed.
5. Instrument QA is also performed (e.g., mass calibration and tuning are performed on gas chromatography-mass spectrometry (GC/MS) equipment to meet ion abundance criteria).
6. The Sanitation Districts' San Jose Creek and Joint Water Pollution Control Plant (JWPCP) Water Quality Laboratories participate in the United Sates Environmental Protection Agency's (EPA) Discharge Monitoring Report (DMR) QA by analyzing chemistry samples purchased from one of the EPA certified suppliers. Overall performance is satisfactory.
7. The Lancaster Treatment Plant Laboratory participates in the California Department of Public Health (CDPH) Environmental Laboratory Accreditation Program Branch (ELAPB) Performance Evaluation studies. Overall performance is satisfactory.

8. Any subcontract commercial laboratories are required to participate in the CDPH ELAPB Performance Evaluation studies. Overall performance must be satisfactory.

9. Quality control samples in the form of QC check standards, either prepared in-house or purchased from commercial sources, are issued by the QA Group to all Sanitation Districts' laboratories. In situations where the results are not acceptable, the analysts and their supervisors are informed and error resolutions are performed. This consists of checking calculations, data transcription, instrumentation, methodology, etc. Follow-up check samples are issued to verify that the analyses are back in control.

10. The QA Group also issues split samples collected from one of the water reclamation plants to assess analysis in a real environmental matrix. Results of these analyses are also submitted to the QA Group for statistical evaluation.

Sampling Procedures

Samples are collected and handled in the manner specified in the appropriate analytical method, as described in 40 Code of Federal Regulations (CFR) Part 136. Table 4 provides additional sampling information, including sample bottle material, holding times, and type of sample preservation.

Flow-weighted 24-hour composite samples are currently utilized by PWRP and are preferred whenever possible. However, there are situations where grab samples are more appropriate or specified by standard procedures (e.g., oil & grease monitoring, groundwater sampling). Standard Operating Procedures (SOPs) for the applicable sampling procedures can be found in Appendix B.

Sample Chain of Custody

With the names of specific individual staff, chain of custody (COC) forms are used to track the handling of samples. The COC forms also contain the complete analytical request and full documentation of the sample origin including sample date, sample time, sample location, preservation method, and the sampling staff individual's name. An example of the COC form can be found in Appendix C. This paper trail is archived along with the sample analytical results.

Groundwater Monitoring Network

Survey and completion information for the monitoring wells and lysimeters, which make up the existing ground water monitoring system, are provided in Appendix A. Groundwater monitoring is performed according to the MRP.

Low flow sampling of monitoring wells is of utmost importance in order to maintain the integrity and representative nature of the sample. Two procedures are provided in the appendices to guide the samplers in proper techniques. The Sanitation District has developed a standard operating procedure entitled *Low-Flow Purging and Sampling for Groundwater*, which is based on the more detailed Cal/EPA guidance. The Cal/EPA Department of Toxic Substances Control issued a revised (Feb 2008) sampling methodology entitled *Representative Sampling of Groundwater for Hazardous Substances*. Both documents can be found in Appendix B. Upon any disagreement between the two documents, the Cal/EPA guidance shall be considered correct. If more reference material is required, see the USEPA document, *Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers* (http://www.epa.gov/tio/tsp/download/gw_sampling_guide.pdf). The recommended allowable drawdown of any well being sampled is 0.33 feet.

As required by Section I.F.2 of the MRP, the Sanitation District's *Revised Groundwater Delineation and Monitoring Plan for Proposed Storage Reservoir Site*, dated May 30, 2008 (Doc #1042486) has been incorporated into this SAP by reference, except that monitoring for total dissolved solids (TDS) has been

replaced with monitoring of conductivity per the MRP due to the volume requirements for TDS sample analysis. This document describes the intended soil moisture monitoring system and sampling lysimeters at the recycled water storage reservoirs site. The system has since been installed and sampling operations have commenced.

As noted in the *Revised Groundwater Delineation and Monitoring Plan for Proposed Storage Reservoir Site*, Section 5.4 (page 24), when sufficient water is obtained from a lysimeter, the sample collection will be prioritized in order of the following chemical analyses: nitrate (as nitrogen), conductivity, nitrite (as nitrogen), total Kjeldahl nitrogen (TKN), and ammonia-nitrogen. Analysis for conductivity has replaced the TDS analysis as noted above.

Results Reporting

Analytical results are reported following a review of the QA/QC data. Monitoring reports are to be submitted according to the due dates specified in the permit.

Table 1. Flow Monitoring Schedule[a]

Parameter	Units	Facility Influent[b]	Facility Effluent[c]	To Storage Reservoirs	Reuse at WRP Site & SRS	To AS[d]	Individual Center Pivot	Extraction Wells[e]
Average Daily Flow Rate	MGD	D	D	D	D	D[e]		D
Total Volumetric Flow	MG	D	D	M	M	M	M	M
Max. Inst. Flow Rate	MGD	D						D

Where: AS = Agricultural Site
D = Daily monitoring
M = Monthly monitoring
MG = million gallons
MGD = million gallons per day
SRS = Storage Reservoir Site

Notes:

a) Flow monitoring and recording shall be conducted at a frequency according to R6V–2011–0012. Symbols in the table represent recording frequency, which may or may not be the same as reporting frequency.
b) Facility influent flows are measured in the influent pump force main.
c) Facility effluent refers to flows produced from the facility only. These flows will be calculated if a portion of the effluent produced is diverted to the SRS or if flow from the SRS is mixed with plant effluent before the combined flow is measured at the AS pump station.
d) Total flow to the AS is metered on the effluent line of the AS pump station, which sends flow to all irrigation pivots.
e) For extraction well pumping, average daily flow rate and maximum instantaneous flow rate to be reported in gallons per minute (gpm).

Table 2. Schedule for Self-Monitoring of Constituents as Required by the MRP

Parameter	Influent	Disinfected Secondary-Treated Effluent	Disinfected Tertiary Treated Effluent	Monitoring Wells[a,b]	Extraction Wells[c]	Lysimeters[d]
Flow			C			
Modal contact time			D			
CT Value			D			
Turbidity			C	Q		
Static water depth				Q		
Electrical conductivity				Q		Q
Color				Q		
Total chlorine residual		W	C			
Total coliform		D	D			
Dissolved oxygen		W	W	Q		
pH		W	W	Q		
Temperature		W	W	Q		
Biochemical oxygen demand (BOD)	W	W	M			
Total suspended solids		W				
Chemical oxygen demand (COD)	W	W	M			
Ammonia nitrogen	M	M	M	Q	Q	Q
Kjeldahl nitrogen	M	M	M	Q	Q	Q
Nitrate nitrogen	M	M	M	Q	Q	Q
Nitrite nitrogen			M			Q
Chloride		M	Q	Q		
Sodium		M	Q	Q		
Sulfate		M	Q	Q		
Calcium			Q			
Magnesium			Q			
MBAS		M	Q	Q		
Total organic carbon (TOC)		Q[e]	Q	Q		
Total dissolved solids (TDS)	S	M	Q	Q	Q	
Total trihalomethanes	S	Q	Q	T		
Bromodichloromethane	S	Q	Q	T		A (AS only)
Bromoform	S	Q	Q	T		A (AS only)
Chloroform	S	Q	Q	T		A (AS only)
Dibromochloromethane	S	Q	Q	T		A (AS only)
Haloacetic acids[f]			Q	T		
monochloroacetic acid			Q	T		
dichloroacetic acid			Q	T		
trichloroacetic acid			Q	T		
monobromoacetic acid			Q	T		
dibromoacetic acid			Q	T		
N-nitrosodimethylamine			Q			

Parameter	Influent	Disinfected Secondary-Treated Effluent	Disinfected Tertiary Treated Effluent	Monitoring Wells[a,b]	Extraction Wells[c]	Lysimeters[d]
bis(2diethylhexyl)phthalate (DEHP)			Q	Q[i]		
TPH - Gasoline range	Q	Q	Q	Q		
TPH - Diesel range	Q	Q	Q	Q		
Oil and grease		Q				
Total chromium			A			
Hexavalent chromium			A			
Total phenols	A	A	A	T		
Inorganics[g, h]	A	A	A	T		
Total cyanides, (cyanide)	A	A	A	T		
Volatile organics[g]	A	A	A	T		
Semi-volatile organics[g]	A	A	A	T		
Pesticides-PCBs[g, h]	A	A	A	T		
Methyl tertiary butyl ether (MTBE)		A	A	T		

Where:
C = Continuous monitoring
D = Daily monitoring
W = Weekly monitoring
M = Monthly monitoring
Q = Quarterly monitoring
S = Semiannual monitoring
PCB = polychlorinated biphenyls
A = Annual monitoring
T = Tri-Annual (sampling once every three years)
AS = Agricultural Site vadose zone lysimeters
SRS = Storage Reservoir Site vadose zone lysimeters
MBAS = methylene blue active substances
TPH = total petroleum hydrocarbons

Notes:

a) Monitoring wells included in the sampling schedule are as follows: MW1, MW2, MW4, MW15R, MW16, W18R, MW19, MW21, MW22, MW23, MW24R, MW25, MW26, MW27, MW28, MW29, MW31, MW32, MW33, MW40, MW46, MW51, MW52, MW53, MW54, MW55, MW56, MW57, and MW58. Monitoring wells MW17, MW20, and MW37 shall be sampled quarterly for depth to water only. Monitoring wells MW38 and MW39 shall be sampled tri-annually for the constituents marked with either "Q" or "T."

b) Supply wells included in the sampling schedule are as follows: DW4-2, 17D1, LAWA-7, and SW2.

c) Extraction wells included in the sampling schedule are as follows: EW-1(R-10), EW-2(R-2), EW-3(R-3), EW-4(R-4), EW-5(R-9), and EW-6(R-8).

d) Monitoring at site(s) indicated (AS or SRS lysimeters). Lysimeters may not yield enough sample volume to perform all the specified analyses. In such situations, the Sanitation Districts will analyze for as many constituents as possible.

e) Monitor dissolved organic carbon in filtered sample of effluent.

f) Sum of five haloacetic acids – monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid.

g) Refer to Appendix D for a complete list of constituents, based on the priority pollutants listed in Attachment E of the MRP. Semi-volatile Organics include Base/Neutral Extractable Organics & Acid Extractable Organics.

h) Monitoring for Arochlors (PCBs) 1016, 1221, 1232, 1242, 1248, 1254, 1260; Dioxin (2,3,7,8-TCDD); and asbestos is not required per Section I.K.4 of the MRP.

i) Quarterly monitoring for DEHP [bis(2diethylhexyl)phthalate] is only required in the following monitoring wells: MW2, MW4, MW16, MW22, MW28, and MW32. After a minimum of four quarters of groundwater monitoring for DEHP, the Discharger may present the findings and recommendations regarding whether to continue, modify, or cease DEHP monitoring.

Table 3. Schedule for Additional Self-Monitoring

Constituent	MW17, MW20, and MW37
Color	S
Dissolved oxygen	S
pH	S
Temperature	S
Depth to water	S
Electrical conductivity	S
Turbidity	S
Sodium	S
Chloride	S
Sulfate	S
Kjeldahl nitrogen (TKN)	S
Ammonia nitrogen	S
Nitrate nitrogen	S
Nitrite nitrogen	S
Total nitrogen	S
Total dissolved solids (TDS)	S
Total organic carbon (TOC)	S
Nethylene blue active substances (MBAS)	S

Where: S = Semiannual monitoring

Table 4. Sample Handling and Analytical Methods

Constituent	Method	Preservative	Holding Time[a]	Units	Sample Type	Sample Bottle[b]	Analytical Lab[c]
Ammonia Nitrogen	SM 4500-NH_3	H_2SO_4 to pH<2; Cool, 4°C	28 days	mg/L	composite	P/G	LACSD
Bis(2diethylhexyl)phthalate	EPA 625	sodium thiosulfate in presence of chlorine; Cool, 4°C	7 days; 40 days	µg/L	composite	Amber G, TFE lined cap	LACSD
BOD	SM 5210B	Cool, 4°C	48 hours	mg/L	composite	P/G	LACSD
Calcium	EPA 200.7	HNO_3 to pH<2; Cool, 4°C	6 months	µg/L	composite	P/G	LACSD
Chloride	EPA 300.0	Cool, 4°C	28 days	mg/L	composite	P/G	LACSD
Chlorine Residual	SM 4500-CL C	None	immediately	mg/L	grab	P/G, zero headspace	LACSD
COD	SM 5220D	Analyze ASAP, or add H_2SO_4 to pH<2; Cool, 4°C	28 days	mg/L	composite	P/G	LACSD
Color	N/A	N/A	N/A	N/A	N/A	N/A	Field
Dissolved Organic Carbon (DOC)	SM 5310 C	Filtered, H_3PO_4 to pH<2; Cool to 4°C	28 days	mg/L	composite	G, TFE lined cap	LACSD
Dissolved Oxygen	SM 4500-OG	None	immediately	mg/L	grab	G- BOD bottle	LACSD
Electrical Conductivity	N/A	N/A	N/A	N/A	N/A	N/A	Field
Haloacetic acids (five)	EPA 552.2	Ammonium chloride, Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	commercial lab
Monochloroacetic acid	EPA 552.2	Ammonium chloride, Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	commercial lab
Dichloroacetic acid	EPA 552.2	Ammonium chloride, Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	commercial lab
Trichloroacetic acid	EPA 552.2	Ammonium chloride, Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	commercial lab
Monobromoacetic acid	EPA 552.2	Ammonium chloride, Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	commercial lab
Dibromoacetic acid	EPA 552.2	Ammonium chloride, Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	commercial lab
Inorganics (Heavy Metals)[d]	EPA 200.8 et al[e]	HNO_3 to pH<2; Cool, 4°C	6 months	µg/L	composite	P/G	LACSD
Hexavalent Chromium	EPA 218.6	Cool, 4°C	24 hours	µg/L	grab	P/G	commercial lab[f]
Kjeldahl Nitrogen	SM 4500-NORGB	H_2SO_4 to pH<2; Cool, 4°C	28 days	mg/L	composite	P/G	LACSD
Magnesium	EPA 200.7	HNO_3 to pH<2; Cool, 4°C	6 months	µg/L	composite	P/G	LACSD
MBAS	SM 5540C	Cool, 4°C	48 hours	mg/L	composite	P/G	LACSD
Mercury	EPA 245.1	HNO_3 to pH<2; Cool, 4°C	28 days	ug/L	composite	G	LACSD
Mercury	EPA 1631	Acidified in laboratory clean room	90 days	ng/L	composite	G	commercial lab

Constituent	Method	Preservative	Holding Time[a]	Units	Sample Type	Sample Bottle[b]	Analytical Lab[c]
Methyl tertiary-Butyl Ether	EPA 624	sodium thiosulfate in presence of chlorine; Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	LACSD
Nitrate Nitrogen	SM 4500 NO_3E	Cool, 4°C	48 hours	mg/L	composite	P/G	LACSD
Nitrite nitrogen	SM4500-NO_2-B	Cool, 4°C	48 hours	mg/L	composite	P/G	LACSD
N-nitrosodimethylamine	EPA 1625	sodium thiosulfate in presence of chlorine; Cool, 4°C	7 days; 40 days	ng/L	composite	Amber G, TFE lined cap	LACSD
Oil & Grease	EPA 1664A	HCl to pH<2; Cool, 4°C	28 days	mg/L	grab	G	LACSD
pH	SM 4500-HB	None	2 hours	pH unit	grab	P/G	LACSD
Sodium	EPA 200.7	HNO_3 to pH<2; Cool, 4°C	6 months	mg/L	composite	P/G	LACSD
Static Water Depth	N/A	N/A	N/A	N/A	N/A	N/A	Field
Sulfate	EPA 300.0	Cool, 4°C	28 days	mg/L	composite	P/G	LACSD
Temperature	SM 2550B	None	immediately	ºC	grab	P/G	LACSD
Total Coliform	SM 9221B	sodium thiosulfate in presence of chlorine	6 hours	MPN/100 mL	grab	Sterile plastic	LACSD
Total Cyanides	SM 4500-CNC, E	Sodium thiosulfate in presence of chlorine; NaOH pH>12; Cool, 4°C	14 days	µg/L	grab	P/G	LACSD
Total Dissolved Solids	SM 2540C	Cool, 4°C	7 days	mg/L	composite	P/G	LACSD
Total Organic Carbon (TOC)	SM 5310 C	Filter sample to measure dissolved organic carbon, H_3PO_4 to pH<2; Cool, 4°C	28 days	mg/L	composite	G, TFE lined cap	LACSD
Total Petroleum Hydrocarbons: Diesel Range	EPA 8015B	HCl to pH<2; Cool, 4°C	7 days	mg/L	composite	G, TFE lined cap	commercial lab
Total Petroleum Hydrocarbons: Gasoline Range	EPA 8015B	HCl to pH<2; Cool, 4°C	7 days	mg/L	composite	G, TFE lined cap	commercial lab
Total Phenols	EPA 420.1	H_3PO_4 to pH<4; Cool, 4°C	28 days	µg/L	composite	P/G	LACSD
Total Suspended Solids	SM 2540D	Cool, 4°C	7 days	mg/L	composite	P/G	LACSD
Total trihalomethanes	EPA 624	sodium thiosulfate in presence of chlorine; Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	LACSD
Bromoform	EPA 624	sodium thiosulfate in presence of chlorine; Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	LACSD
Chloroform	EPA 624	sodium thiosulfate in presence of chlorine; Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	LACSD

Constituent	Method	Preservative	Holding Time[a]	Units	Sample Type	Sample Bottle[b]	Analytical Lab[c]
Dibromochloromethane	EPA 624	sodium thiosulfate in presence of chlorine; Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	LACSD
Dichlorobromomethane	EPA 624	sodium thiosulfate in presence of chlorine; Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap	LACSD
Turbidity	N/A	N/A	N/A	N/A	N/A	N/A	Field
Volatile Organics[d]	EPA 624	sodium thiosulfate in presence of chlorine; Cool, 4°C	14 days	µg/L	grab	G, TFE lined cap (zero headspace)	LACSD
Semivolatile Organics: Acid Extractable Organics[d]	EPA 625	sodium thiosulfate in presence of chlorine; Cool, 4°C	7 days; 40 days	µg/L	composite	Amber G, TFE lined cap	LACSD
Semivolatile Organics: Base/Neutral Extractable Organics[d]	EPA 625	sodium thiosulfate in presence of chlorine; Cool, 4°C	7 days; 40 days	µg/L	composite	Amber G, TFE lined cap	LACSD
Pesticides and PCBs[d]	SM6630B, EPA 608, EPA 8081 & 8082	sodium thiosulfate in presence of chlorine; Cool, 4°C	7 days; 40 days	µg/L	composite	Amber G, TFE lined cap	LACSD

Notes:

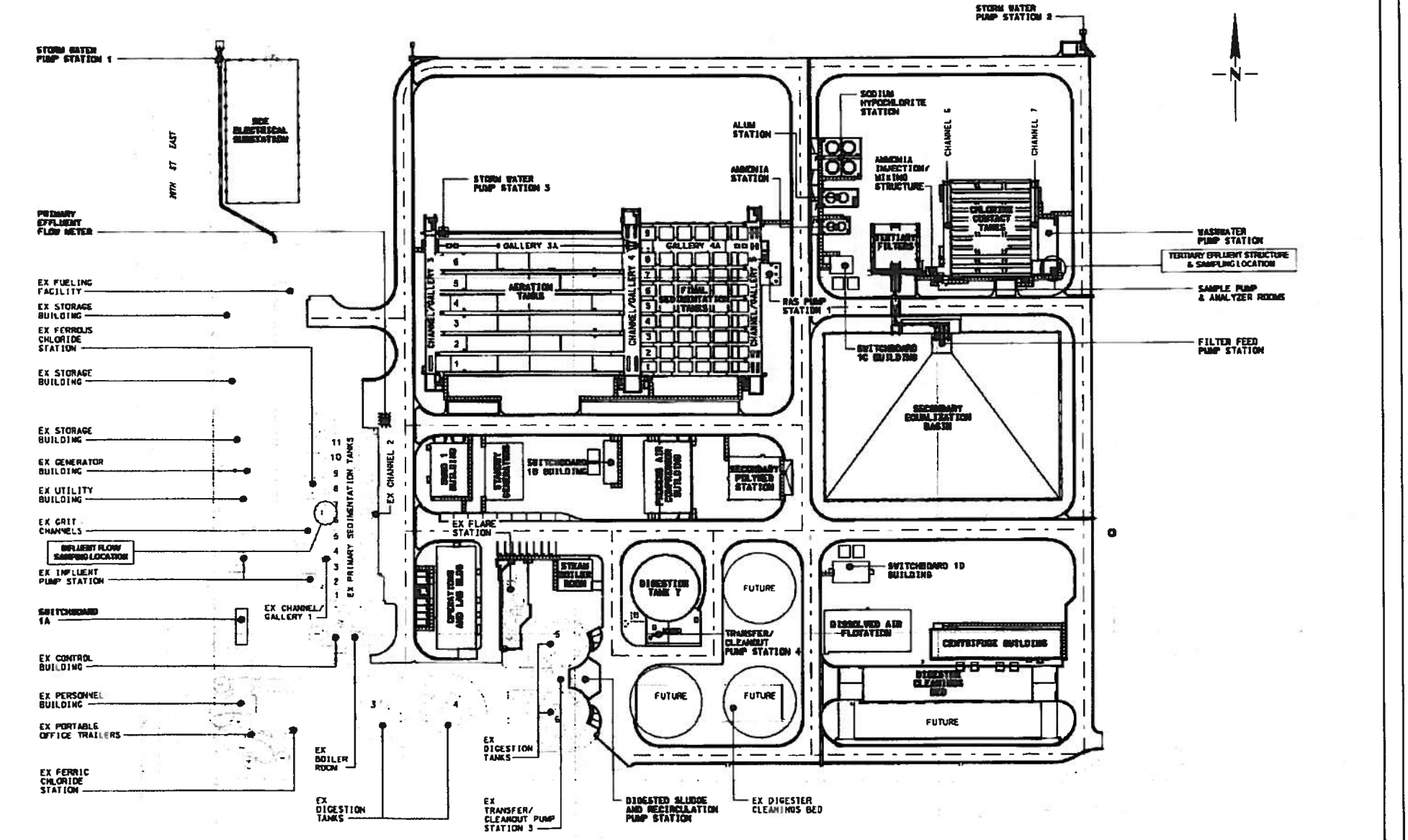
NA = Not Applicable

a) Maximum holding times, per Standard Methods/EPA specifications
b) G = Glass, P = Plastic; Types of glass/plastic containers and rinsing techniques will vary depending on types of constituents being analyzed.
c) In general, the Sanitation Districts (LACSD) laboratories will perform all analyses. However, the Sanitation Districts will occasionally send samples to commercial laboratories for analysis.
d) Please see Appendix D for specific individual parameters.
e) Other methods are: antimony by EPA SW-846 Method 7062, arsenic by SM 3114 B 4,d, and selenium by SM 3114B.
f) Upon completion of the new laboratory facilities at Palmdale, hexavalent chromium analysis is planned to be performed in-house.

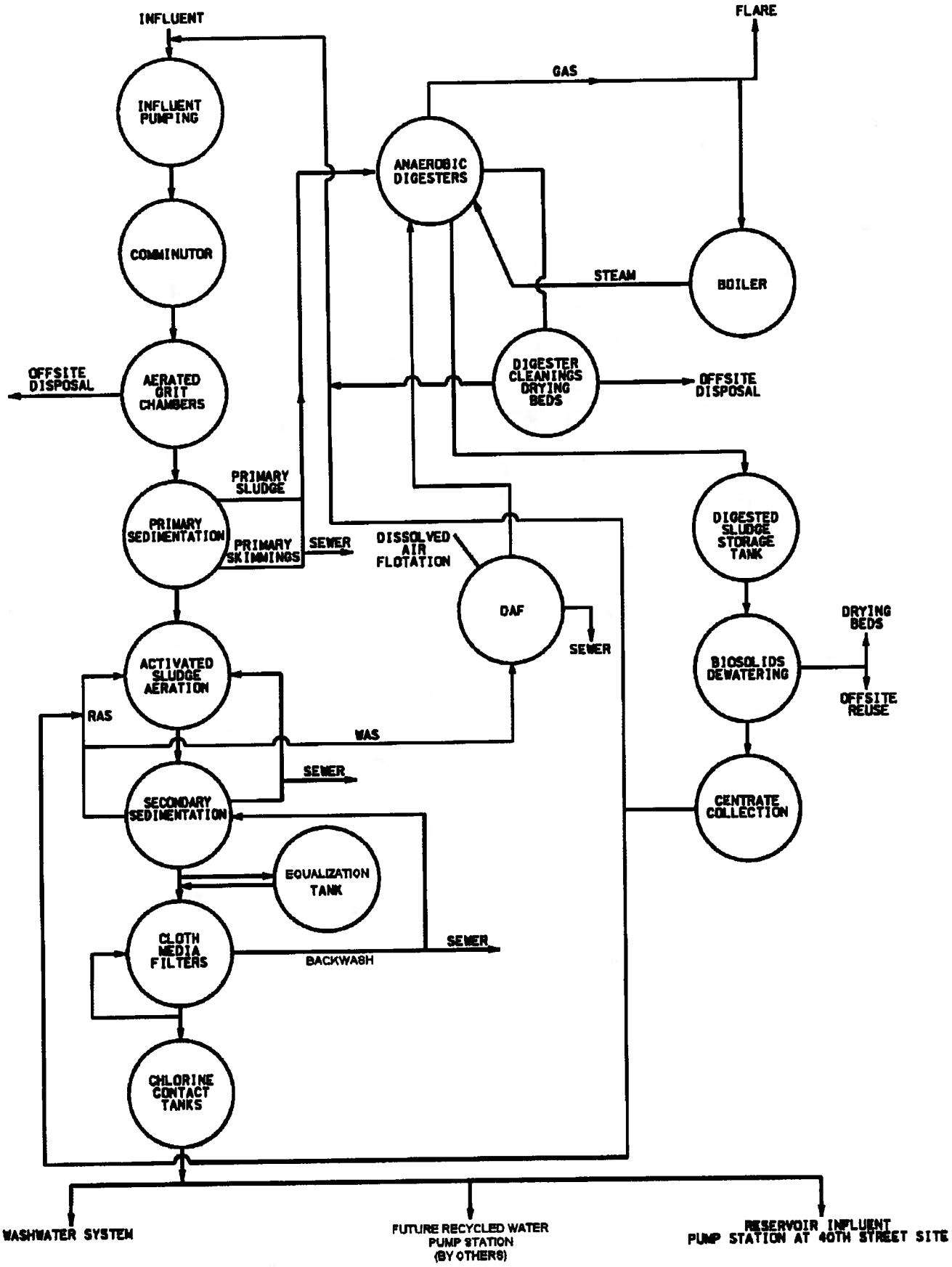
Appendix A

Sample Locations: Maps, Diagrams, and Photographs

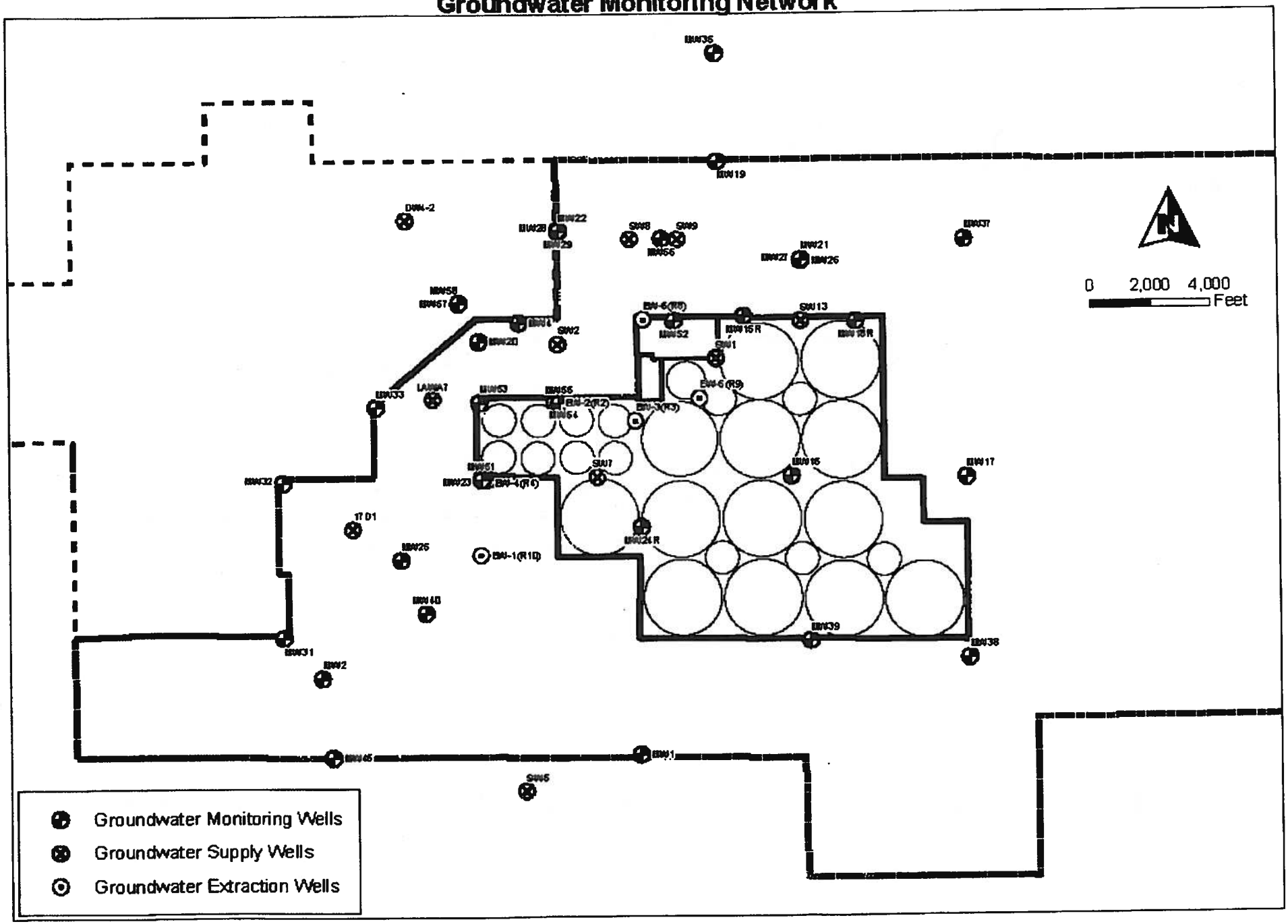
Palmdale Water Reclamation Plant Upgraded Facilities and Sampling Locations



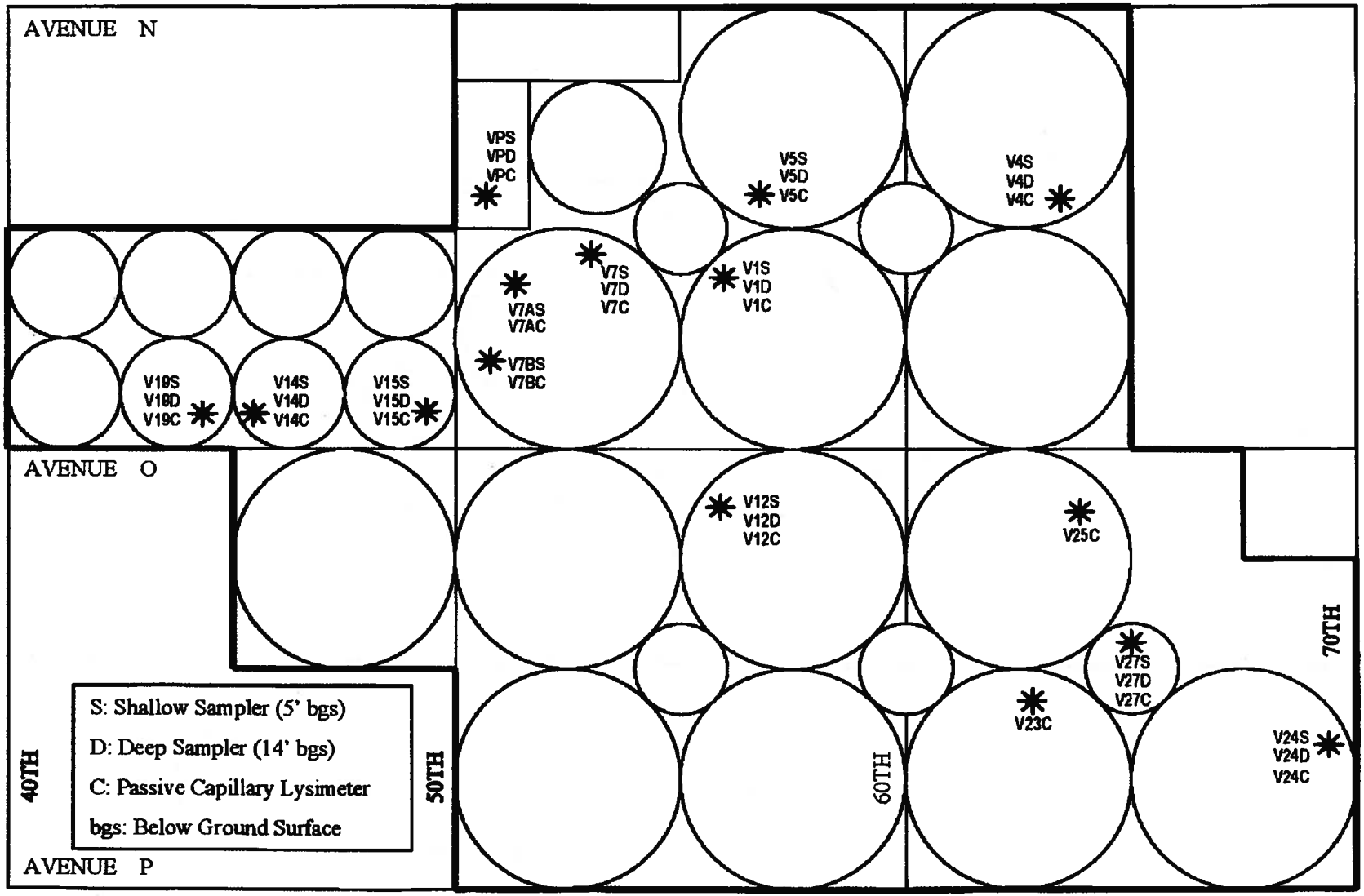
Tertiary Treatment Facilities Process Schematic



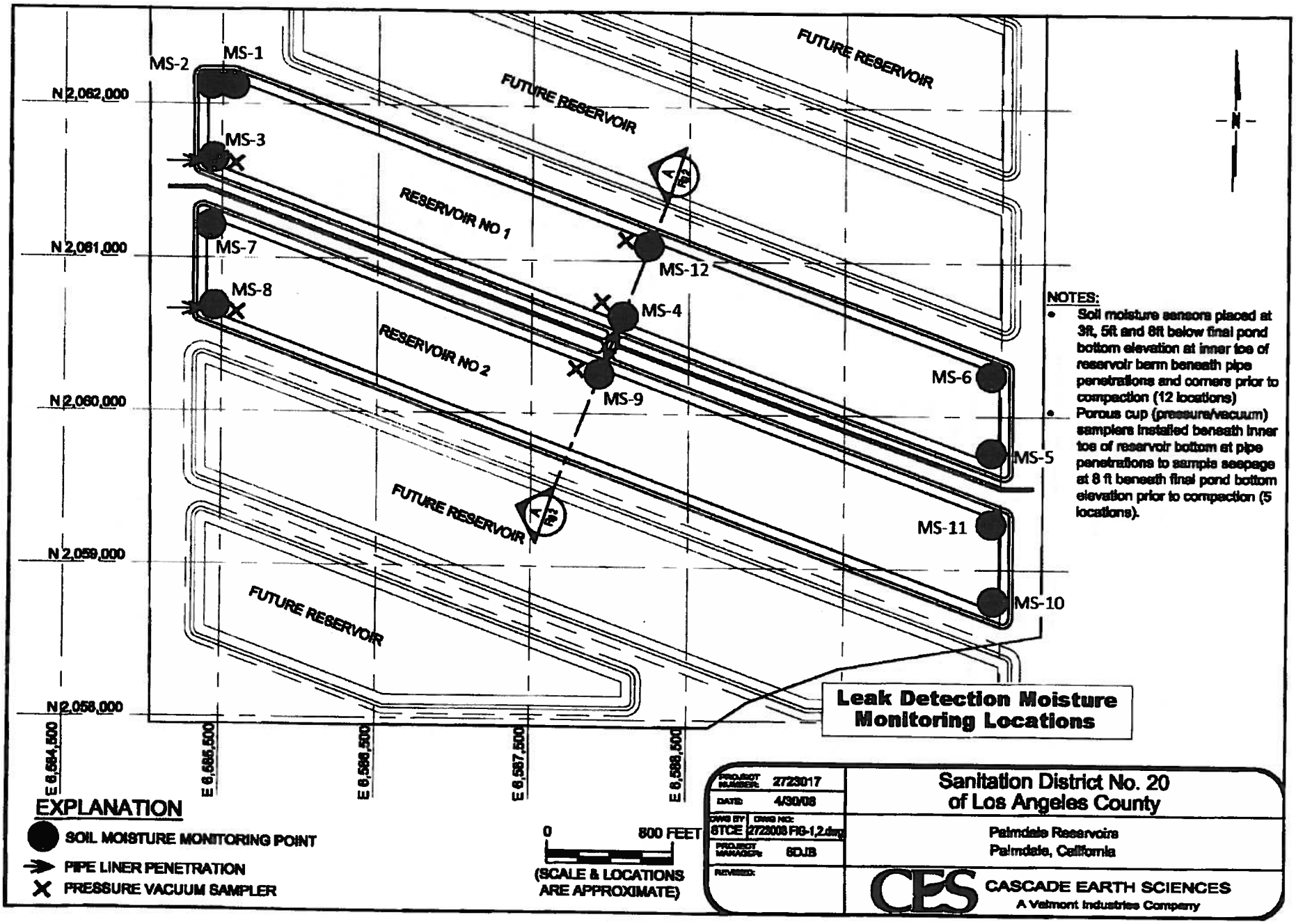
Groundwater Monitoring Network



Palmdale Agricultural Site Vadose Zone Monitoring Locations



Palmdale Storage Reservoir Soil Moisture and Lysimeter Locations



Monitoring Well Survey Data & Specifications

Palmdale Water Reclamation Plant
Palmdale, California

Well Name	Total Depth	Northing	Easting	Ground Surface Elevation	Well Screen Interval
MW-1	400	2037502.70	6549335.03	2590.70	360-400
MW-2	540	2040118.68	6538766.67	2560.61	480-540
MW-4	334	2052029.08	6545407.39	2500.78	292-336
MW-15R	373	2052219.40	6552858.10	2507.92	333-363
MW-16	333	2046854.80	6554373.48	2540.62	281-315
MW-17	290	2046767.52	6560141.64	2545.70	245-290
MW-18R	363	2052021.13	6556537.67	2515.04	326-356
MW-19	337	2057425.72	6552019.87	2488.75	290-335
MW-20	296	2051414.25	6544089.47	2501.66	257-295
MW-21	340	2054123.00	6554750.62	2506.27	300-340
MW-22	322	2055081.45	6546743.43	2487.28	282-320
MW-23	398	2046777.79	6544147.63	2525.42	369-397
MW-24R	358	2045155.50	6549411.66	2541.24	325-350
MW-25	350	2044080.79	6541437.49	2541.10	321-349
MW-26	373	2054081.84	6554746.34	2506.14	361-370
MW-27	401	2054101.23	6554747.28	2506.34	390-399
MW-28	436	2055132.47	6546744.10	2487.85	421-431
MW-29	510	2055109.47	6546744.01	2487.59	491-500
MW-31	520	2041476.81	6537512.68	2557.89	484-518
MW-32	403	2046690.83	6537504.06	2533.85	372-395
MW-33	379	2049208.24	6540626.73	2514.33	363-377
MW-37	359	2054760.76	6560134.16	2508.82	318-353
MW-38	320	2040685.28	6560198.38	2575.19	281-316
MW-39	350	2041306.44	6554954.21	2570.70	307-346
MW-40	364	2042274.80	6542261.12	2551.64	330-360
MW-46	551	2037457.67	6539111.68	2574.42	511-550
MW-51	458	2046787.89	6544376.40	2525.47	331-340
MW-52	353	2052075.29	6550543.03	2506.05	317-347
MW-53	340	2049363.46	6544090.92	2511.59	295-330
MW-54	364	2049395.84	6546871.91	2513.66	331-356
MW-55	483	2049332.46	6546718.30	2513.89	465-475
MW-56	500	2054844.72	6550164.18	2493.86	325-365
MW-57	359	2052690.05	6543446.04	2495.47	339-349
MW-58	440	2052709.35	6543438.26	2495.20	375-390

Appendix B

Sample Collection Standard Operating Procedures

Standard Operating Procedure
Palmdale Water Reclamation Plant
Daily Sample Collection
(Without Custody Transfer)

Introduction

This procedure is to be used when there is no custody transfer and the analyses are performed by the same person(s) responsible for collection of the sample(s). Typically, this type of operation is associated with laboratories located at the water reclamation plant (WRP) site and defined as Treatment Plant Laboratories. Samples collected in this manner are securely maintained on site until analyses have been completed, after which the same person(s) discard the sample(s).

Equipment, Materials and Supplies

- Automated samplers with programmable controls to allow for flow weighted compositing. (SIGMA 900 Max or similar samplers)
- Paddle made of polypropylene for mixing collected sample.
- Large mouth glass sample container for sampler
- Sample bottles which have been pre-cleaned and are compatible with constituents to be analyzed.
- Ice to be used in sampler if it is not refrigerated.
- Sample log book.

Setting & Initiating Sampling

1. Position the sampler at a location representative of effluent being discharged from the WRP after completion of all treatment processes or before treatment processes, if influent untreated wastewater is desired.
2. Obtain typical plant flow data for influent or effluent streams covering a 24-hour period.
3. Establish numerical values that correspond to sample volumes to be collected at intervals that result in a flow weighted composite sample.
4. Enter sampling parameters along with numerical values into the sampler programming unit using the manufacturer's guidelines.
5. Install a clean sample collection container in the sampler and ice if it is not refrigerated.
6. Initiate the start of the sampler program (and confirm the first sample in the sequence is collected).
7. Let it run.

Retrieval & Collection

- At the end of the sample collection period check the sampler to confirm that there was no malfunction and that the appropriate volume of sample was collected.

- Visually inspect the area around the sample collection point to determine if any conditions exist that may lead to unusual analytical results. If the sampler malfunctioned or other conditions prevail that may contribute to unusual results, then record these observations in the sample log book.
- Pre-label clean bottles designated for specific constituent analyses. Sample dates, times, location & type are to be recorded along with the name of the individual collecting the sample.
- Take out sample container from sampler, and in a mix-pour manner, pour aliquots of the sample into pre-labeled bottles that are compatible with constituents to be analyzed.
- Bottles are to be iced from this point till arrival at the laboratory.
- Upon return to the laboratory, immediately commence with analysis of the samples or proper preservation if the sample is to be held.

Sampler Maintenance

- The sampler and its container are to be cleaned with water, detergent, acid, and a solvent as necessary for its next use.
- If batteries are used, they are to be re-charged.

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	Not Applicable
Method Name	Sigma Composite Sampling
Version	10.1.0
Method Date	February 18, 2010
Reasons for Method Revision	Annual Review; no revisions were made

Reviewed by:

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Laboratory Technician II
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Signature

3/24/10
Date

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Lavern Tamoria
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Signature

3/24/10
Date

Final Approval:

Maria Pang
Assistant Manager of
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Signature

4/22/10
Date

SIGMA COMPOSITE SAMPLING PROCEDURE

INTRODUCTION

The Sample Receiving group collects influent and effluent samples for priority pollutants and other regulated constituents. The dedicated stationary samplers used by this group are Sigma 900 MAX All Weather Refrigerated Sampler manufactured by the HACH Company and we, therefore, refer to our samplers as Sigmas. Because it is impractical to study the entire body of water treated by a water reclamation plant, a sample is taken that represents the entire body. The Sigma sampler achieves this by collecting either a flow-weighted composite over a 24 hr period for the constantly fluctuating Raw Influent or a time-weighted composite for the Secondary Final Effluent due to its static flow rate. Sample Receiving field crews program the Sigma to collect fixed volumes at designated times based on the average daily flow of the reclamation plant being sampled. The aliquots are combined into a single container during sampling. Once sampling has been completed, the single large volume is divided into smaller containers for transport back to the lab for analysis.

The flow-weighted sample times are created using a flow calculation spreadsheet specific to each plant. The calculations are based on the average daily flow per hour of the reclamation plant's raw influent over a period of 3 days. The days used are typically weekdays which do not immediately follow weekends or holidays. These days are selected to record data that will be most representative of a typical day's influent into the plant. The hourly flows are then averaged into 2 hr increments and entered into a spreadsheet to generate 12 sample times for collection over a 24 hr period. Calculations are updated on a semi-annual basis following the time change for Daylight Savings Time. Time-weighted samples times are programmed into the Sigma at 2 hr intervals based on the start time, usually from 6:00 am to 6:00 am, in a 24 hr period.

Some samples require low-level analysis (e.g., Hg and NDMA). In these cases it is necessary to take further steps in preparing the Sigma sampler prior to sampling to insure no contaminants are introduced from the Sigma sampler or associated tubing. (See 9.)

1. Scope and Application

1.1 The Sigma composite sampler is used to collect a representative sample of the water reclamation plant's activity over a period of 24 hrs.

1.2 Raw influent and final effluent are collected by this method as required by Wastewater Discharge Requirements (WDR) permits.

2. Summary of Method

2.1 Composite samples are collected over a 24 hr period using calculated time intervals.

2.2 Typically 12 collection times for Raw Influent are calculated based on the flow into the particular reclamation plant.

2.3 Typically 12 collection times for the Secondary Final Effluent are set for every two hours from the time the Sigma is programmed.

3. Sample Handling and Preservation

3.1 Water Reclamation Plants (WRP) samples are collected using appropriate containers and preservation methods as directed in Standard Methods for the Examination of Water and Wastewater.

3.2 After collection, and as soon as possible, place samples into an ice chest with ice to keep their temperature at 0-6°C during transport from the sample collection site to Sample Receiving Control (SRC).

3.3 Once removed from the ice chest the samples are placed into a refrigerator or walk-in cooler to maintain the cold temperature for storage.

4. Interferences

4.1 If a reclamation plant is not operating normally, an extreme drop in water level below the strainer may interrupt sampling.

4.2 Interruption in power to the Sigma may cause failure to complete sampling.

4.3 During excessive rainfall, it may not be possible to collect a representative sample.

4.4 During excessive cold weather, sample line to the Sigma may freeze.

5. Apparatus

5.1 Sigma 900 MAX All Weather Refrigerated Sampler (Figure 1)

5.2 10, 12, or 25 ft, 3/8" ID -- Teflon lined suction tubing with stainless steel strainer

5.3 3 ft Silastic medical grade silicon tubing

5.4 1 to 4 10 L glass jars depending on amount to be collected

5.5 Teflon stir bar

5.6 Stainless steel funnel

6. Reagents

6.1 ACS Grade Sodium Thiosulfate crystals

7. Procedure

7.1 Sigma Setup

7.1.1 Open the top cover from the Sigma sampler unit (Figure 1).

7.1.2 Remove cover plates from the pump case and liquid detector.

7.1.3 Thread the silicon tubing through the pump tube port and the center section tube guide.

7.1.4 Thread the other end of the silicon tubing through the pump case and the liquid detector.

7.1.5 Replace pump and liquid detector covers. When complete, the setup should look like Figure 2.

7.1.6 Place the 10 L glass jars into the refrigerated section.

7.1.7 If a dechlorinated sample is required, add 0.5 g of Sodium Thiosulfate crystals per 1 L of sample to the 10 L jar (approximately 4.5 g for a full sampling event).

7.1.8 Close the sampler.

7.2 Programming the Sigma

7.2.1 Basic set up is performed at initial equipment installation (see catalog #8854 Sigma 900 MAX All Weather Refrigerator user manual for instructions) operator must use the "Modify" option when programming the Sigma for sampling.

7.2.2 Figure 3 shows the programming tree of the programming options.

7.2.3 The first display should be MAIN MENU as seen in Figure 4. From the Main Menu select SETUP>MODIFY ALL ITEMS. Press ACCEPT.

7.2.4 Enter the number of sample bottles and the bottle volume. Select gallons or milliliters using the CHANGE UNIT key. Press ACCEPT and continue to Intake Tubing.

7.2.5 Enter the intake tube length of the intake tubing attached to the sampler. Length values from 100 to 3000cm (3 to 99ft) are valid. Change measurement unit using the CHANGE UNITS key. Press ACCEPT to move to the Intake Tubing Type

7.2.6 Select the type of intake tube (3/8 in. Teflon). Press ACCEPT pass PROGRAM LOCK and PROGRAM DELAY to continue with Sample Collection.

7.2.7 Select the type of sample collection; Time Proportional or Flow-Proportional Constant Volume, Variable Time (CVVT)

7.2.7.1 For **Time Proportional sampling** (time-weighted) go to Sample Collection menu, press CHANGE CHOICE until Timed Proportional is displayed, press ACCEPT and enter the interval between samples (normally two hours) and press ACCEPT. Select TAKE FIRST SAMPLE IMMEDIATELY or AFTER FIRST INTERVAL, press ACCEPT to start sampling program.

7.2.7.2 For **Flow Proportional Constant Volume, Variable Time (CVVT)**

(flow-weighted) go to Sample Collection menu and press CHANGE CHOICE until Flow Proportional is displayed, press ACCEPT. In the Flow Proportional menu press CHANGE until CVVT is displayed. Press ACCEPT. Select either Internal or External flow meter and press ACCEPT. Enter the flow volume between samples and select a unit of measure using the CHANGE UNITS key. Enable or Disable the Timed Over-Ride using the CHANGE CHOICE key. Press ACCEPT, then enter a time period using numeric key. Select Take First Sample Immediately or After First Interval, press ACCEPT to start sampling program.

7.3 Setting up Sampler at the Reclamation Plant

7.3.1 Prior to departing for the sample location, contact the operations group of the reclamation plant to ensure the plant is operating normally.

7.3.2 Upon arrival to the sample location observe the surrounding area for normal sampling conditions. Note any unusual events if any are observed.

7.3.3 Open the cover of the top section.

7.3.4 Insert the Teflon lined suction tube into the loose end of the silicon pump tubing about 1 to 1.5 cm.

7.3.5 Lower the stainless steel strainer into the sample source. The strainer should be about 2 ft below the surface of the sample source. This depth can vary depending on the conditions of the source; however, 2 ft should be sufficient for most conditions.

7.3.6 Proceed with Programming the Sigma.

7.3.7 Replace the top cover.

7.4 Sigma Sampler Collection

7.4.1 Remove top cover.

7.4.2 Check display, it will indicate if any problem occurred while sampling

7.4.3 Remove suction tubing from pump tubing. If sample remains in the tubing, press REVERSE PUMP to purge the line.

7.4.4 Open refrigerated section of the sampler and remove sample jars.

7.4.5 Gently stir sample with Teflon bar.

7.4.6 Carefully pour sample into appropriate sample containers. If necessary, use a stainless steel funnel to aid in pouring.

7.4.7 Dump any remaining sample back into the sample source.

7.4.8 Collect all materials (tubing, cones, etc.) and store them securely in the vehicle.

7.4.9 Preserve samples as necessary and place all samples in an ice chest for transport. Take the necessary precautions in loading the cooler to prevent breakage during transport.

7.5 Cleaning the Sampler

7.5.1 Wash all equipment with Liquinox and water.

7.5.2 Run Liquinox through suction tubing using an Isco portable sampler pump.

7.5.3 Flush suction tubing thoroughly with tap water to remove all soap.

7.5.4 Rinse the inner surface of the 10L glass jar with a 1:1 nitric acid solution. Carefully move the acid solution around inside the jar to sufficiently coat the inner surface of the jar.

7.5.5 Dump excess acid into a sink under a fume hood and rinse the jar with copious volumes of DI water.

7.5.6 Rinse all equipment with methanol. Add a small amount into the tubing and jars. Move the methanol around in the equipment to sufficiently rinse the inner surface.

7.5.7 Rinse all equipment several times with DI water.

7.5.8 Set equipment out to air dry.

8. Calculations

8.1 Table 1 shows an example of the average daily flow measurements over a period of 3 days. The 2 hr averages are used in Table 1 to calculate sample collection times.

8.2 The calculations take into account the total average daily flow, the ratio of the 2 hr average flow, and the cumulative ratio of total flow to derive sample times which would be the most representative for the given 2 hr time interval.

9. Quality Assurance Guidelines

9.1 Equipment Blank

9.1.1 Fill a 10 L glass jar with reagent-grade water.

9.1.2 Place the stainless steel strainer into the 10L glass jar filled with reagent-grade water.

9.1.3 Press MANUAL SAMPLE or PUMP FORWARD to run the reagent-grade water through the sampling equipment and into the sample collection jar.

9.1.4 Pour off the collected water into appropriate containers for analysis.

9.2 NDMA Equipment Blank

9.2.1 Sampling the equipment blank and bottle blank for NDMA follows the same procedure as listed in 9.1 with a few additions.

9.2.3 The sample containers must be rinsed three times with laboratory's reagent-grade water before filling for the equipment blank or bottle blank.

10. Method Performance

10.1 Not Applicable.

11. References

11.1 User Manual Sigma 900 MAX All Weather Refrigerated Sampler, Copyright 2006.

11.2 Laboratory Section Procedures for the Characterization of Water and Wastewater, Fourth Edition, 1989, p. II-1 to II-14 – Sampling.

11.3 Sampling Receiving Control – Field Sampling Protocol, Section 1.

Figure 1.

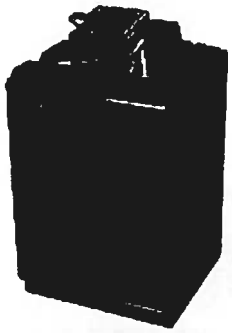

Figure 2.

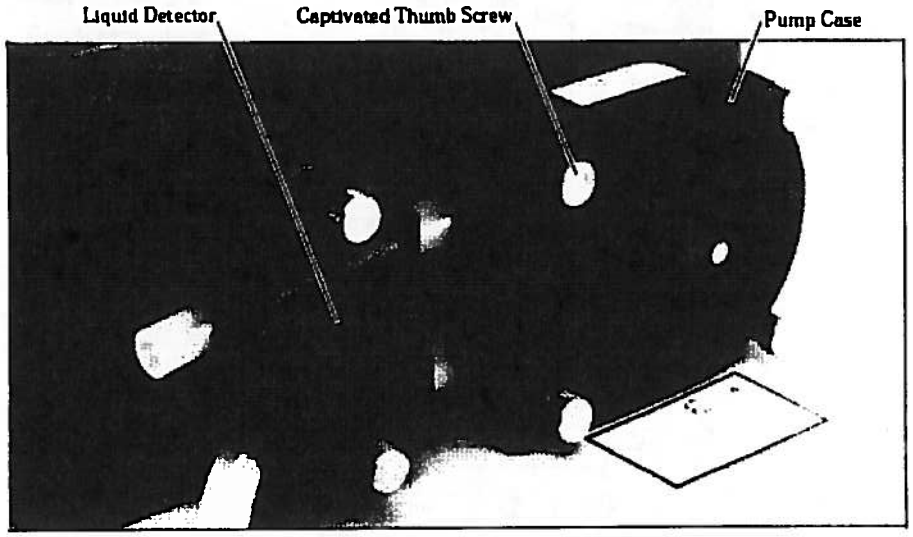

Figure 3.

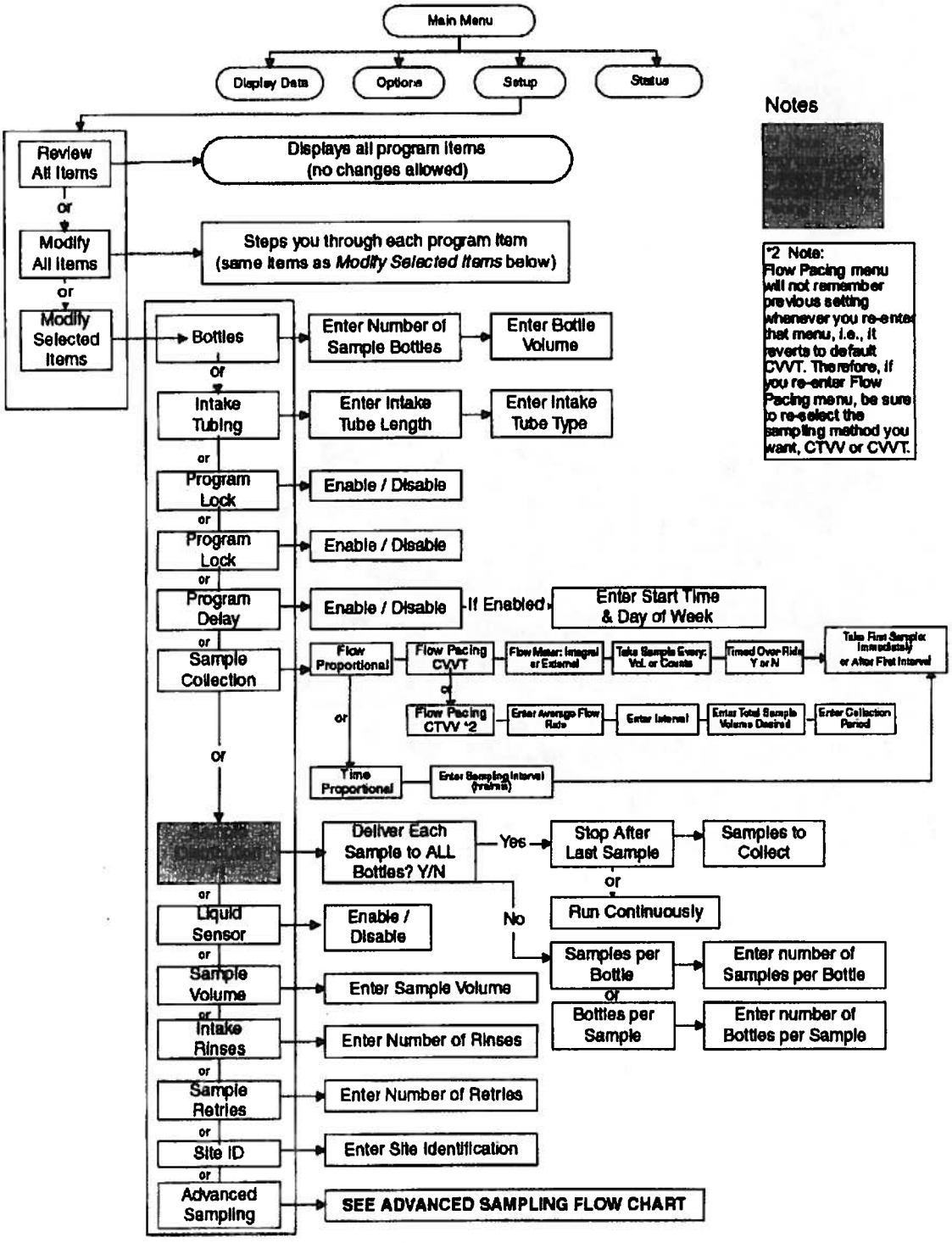
Main Menu
Display Data
Options
Setup
Status
Review All Items
or
Modify All Items
or
Modify Selected Items
Displays all program items (no changes allowed)
Steps you through each program item (same items as Modify Selected Items below)
Bottles
Enter Number of Sample Bottles
Enter Bottle Volume
or
Intake Tubing
Enter Intake Tube Length
Enter Intake Tube Type
or
Program Lock
Enable / Disable
or
Program Lock
Enable / Disable
or
Program Delay
Enable / Disable
If Enabled
Enter Start Time & Day of Week
or
Sample Collection
Flow Proportional
Flow Pacing CVVT
Flow Meter: Integral or External
Take Sample Every: Vol. or Counts
Timed Over-Ride Y or N
Take First Sample Immediately or After First Interval
or
Flow Pacing CTVV *2
Enter Average Flow Rate
Enter Interval
Enter Total Sample Volume Desired
Enter Collection Period
or
Time Proportional
Enter Sampling Interval (minutes)
Deliver Each Sample to ALL Bottles? Y/N
Yes
Stop After Last Sample
Samples to Collect
or
Run Continuously
No
Samples per Bottle
Enter number of Samples per Bottle
or
Bottles per Sample
Enter number of Bottles per Sample
or
Liquid Sensor
Enable / Disable
or
Sample Volume
Enter Sample Volume
or
Intake Rinses
Enter Number of Rinses
or
Sample Retries
Enter Number of Retries
or
Site ID
Enter Site Identification
or
Advanced Sampling
SEE ADVANCED SAMPLING FLOW CHART
Notes
*2 Note:
Flow Pacing menu will not remember previous setting whenever you re-enter that menu, i.e., it reverts to default CVVT. Therefore, if you re-enter Flow Pacing menu, be sure to re-select the sampling method you want, CTVV or CVVT.

Table 1.

FLOW WEIGHTED COMPOSITE CALCULATIONS:

TIME	AVERAGE FLOW (MGD)	RATIO OF TOTAL FLOW	CUMULATIVE FLOW	SAMPLING TIMES	
2.00	5.55	0.0667	0.066693	2.4632	2.28
4.00	5.97	0.0717	0.138394	4.7325	4.44
6.00	6.50	0.0781	0.216503	6.7637	6.46
8.00	7.30	0.0877	0.304226	8.6486	8.39
10.00	7.38	0.0887	0.39295	10.515	10.31
12.00	7.77	0.0933	0.486281	12.288	12.17
14.00	7.92	0.0951	0.581414	14.034	14.02
16.00	7.85	0.0943	0.675746	15.815	15.49
18.00	7.68	0.0923	0.768075	16.246	16.15
20.00	7.75	0.0931	0.861206	19.394	19.24
22.00	6.03	0.0725	0.933707	21.539	21.32
24.00	5.52	0.0663	1	24	24.00
TOTAL FLOW =	83.22 MGD				

Example Flow Calculation (first 2hr time interval):

$$\frac{(2/24) * 2}{0.563} + 4 - \frac{2}{0.0563} * 0.135428 = 2.14 \text{ (sample collection time in decimal form)}$$

$(2.14 - 2) * 0.6 + 2 = 2.09$ (sample collection time)

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	Not Applicable
Method Name	ISCO Composite Sampling Procedure
Version	10.1.0
Method Date	February 09, 2010
Reasons for Method Revision	Annual review; no modifications were made

Written by:

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Laboratory Technician II
QA/Sample Receiving

Jessica Pacheco
Signature

2/10/10
Date

Approved by:

Lavern Tamoria
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Lavern Tamoria
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3/10/2010
Date

Final Approval:

Maria Pang
Assistant Manager of
the Laboratories

M. Pang
Signature

3/15/10
Date

ISCO COMPOSITE SAMPLING

INTRODUCTION

The Sample Receiving group collects influent and effluent samples for priority pollutants and other regulated constituents. The portable samplers used by this group are manufactured by the ISCO Company and we, therefore, refer to our samplers as ISCOs. Because it is impractical to study the entire body of water treated by a water reclamation plant, a sample is taken that represents the entire body. The ISCO sampler achieves this by collecting a flow-weighted composite over a 24 hr period. Sample Receiving field crews set up ISCOs to collect fixed volumes at designated times based on the average daily flow of the reclamation plant being sampled. The aliquots are combined into a single container during sampling. Once sampling has been completed, the single large volume is divided into smaller containers for transport back to the lab for analysis.

The flow-weighted sample times are created using a flow calculation spreadsheet specific to each plant. The calculations are based on the average daily flow per hour of the reclamation plant's final effluent discharge over a period of 3 days. The days used are typically weekdays which do not immediately follow weekends or holidays. These days are selected to record data that will be most representative of a typical day of discharge from the plant. The hourly flows are then averaged into 2 hr increments and entered into a spreadsheet to generate 12 sample times for collection over a 24 hr period. Calculations are updated on a semi-annual basis following the time change for Daylight Savings Time.

Some samples require low-level analysis (e.g., Hg and NDMA). In these cases it is necessary to take further steps in preparing the ISCO sampler prior to sampling to insure no contaminants are introduced to the sample from the sampler (see 9.).

1. Scope and Application

   1.1 The ISCO composite sampler is used to collect a representative sample of the water reclamation plant's activity over a period of 24 hrs.

   1.2 Raw influent and final effluent are collected by this method as required by National Pollution Discharge Elimination System (NPDES) permits.

2. Summary

   2.1 Composite samples are collected over a 24 hr period using calculated time intervals.

   2.2 Typically 12 collection times are calculated based on the flow discharged from the particular reclamation plant.

3. Sample Handling and Preservation

3.1 Water Reclamation Plants (WRP) samples are collected using appropriate containers and preservation methods as directed in Standard Methods for the Examination of Water and Wastewater.

3.2 After collection, and as soon as possible, place samples into an ice chest with ice to keep their temperature at 0-6°C during transport from the sample collection site to Sample Receiving Control (SRC).

3.3 Once removed from the ice chest the samples are placed into a refrigerator or walk-in cooler to maintain the cold temperature for storage.

4. Interferences

4.1 If a reclamation plant is not operating normally, an extreme drop in water level below the stainless steal strainer may interrupt sampling.

4.2 Insufficiently charged batteries may cause failure to complete sampling.

4.3 During excessive rainfall, it may not be possible to collect a representative sample.

5. Apparatus

5.1 ISCO 3710 Compact portable sampler (Figure 1)

5.2 10, 12, or 25 ft, 3/8" ID – Teflon lined suction tubing with stainless steel strainer

5.3 3 ft Silastic medical grade silicon tubing

5.4 10 L glass jar

5.5 Charged rechargeable Ni/Cd or lead/acid battery

5.6 Teflon stir bar

5.7 Stainless steel funnel

5.8 Orange safety cones

6. Reagents

6.1 Sodium Thiosulfate crystals

7. Procedure

7.1 ISCO Setup

7.1.1 Remove the top cover from the ISCO sampler unit (Figure 1).

7.1.2 Remove cover plates from the pump case and liquid detector (Figure1).

7.1.3 Thread the silicon tubing through the pump tube port and the center section tube guide (Figure 2).

7.1.4 Thread the other end of the silicon tubing through the pump case and the liquid detector as shown in Figure 3.

7.1.5 Replace pump and liquid detector covers.

7.1.6 Place the 10 L glass jar into the base section.

7.1.7 Fill the remaining space of the base section around the 10 L jar with ice.

7.1.8 If a dechlorinated sample is required, add 0.5 g of Sodium Thiosulfate crystals per 1 L of sample to the 10 L jar (approximately 4.5 g for a full sampling event).

7.1.9 Reassemble the sampler.

7.2 Programming the ISCO

7.2.1 Press the ON/OFF button to turn the sampler ON.

7.2.2 Figure 4 shows the programming tree of the programming options.

7.2.3 The first display should be STANDBY as seen in Figure 4. Anything other than STANDBY indicates the sampler encountered a problem during its last use. If this has happened the screen may read PROGRAM HALTED and should be treated the same as if it read STANDBY for initial programming. Press the ENTER/PROGRAM button to begin programming.

7.2.4 Figure 4 - Display #1, will appear as the next screen. Use the Left or Right Arrow keys to highlight PROGRAM, the selected item should flash when highlighted, and press ENTER.

7.2.5 Table 1 shows the series of steps to follow and the appropriate selection for each.

7.2.6 Next enter the appropriate collection times. Use Flow Calculations for the specific reclamation plant being sampled (Table 3).

7.2.7 Enter hours HH, minutes MM, day DD, and month MM pressing ENTER after each to proceed to the next. By default the day and month displayed will be the current day and month, where as the times will be the times previously programmed.

7.2.8 At 2400 hours enter 00:00 for the time value and advance the day to the next day.

7.2.9 Enter 750 mL for the sample volume; press ENTER.

7.2.10 This should complete programming and PROGRAMMING SEQUENCE COMPLETED should appear briefly before returning to the initial STANDBY screen.

7.2.11 Occasionally after entering the volume other options may appear on the display screen depending on the configuration of the sampler. Typically these two options will appear: SUCTION HEAD OF: 12 FEET (1 – 12) and CALIBRATE SAMPLE VOLUME [YES, NO]. If this does occur, enter the length of suction line being used for the first option and select NO for the second.

7.3 Setting up Sampler at the Reclamation Plant

7.3.1 Prior to departing for the sample location, contact the operations group of the reclamation plant to ensure the plant is operating normally.

7.3.2 Upon arrival to the sample location observe the surrounding area for normal sampling conditions. Note any unusual events if any are observed.

7.3.3 Place sampler at the appropriate sample location.

7.3.4 Remove the cover of the top section.

7.3.5 Insert the Teflon lined suction tube into the loose end of the silicon pump tubing about 1.5 to 2 cm.

7.3.6 Lower the stainless steel strainer into the sample source. The strainer should be about 2 ft below the surface of the sample source. This depth can vary depending on the conditions of the source; however, 2 ft should be sufficient for most conditions.

7.3.7 Wrap excess suction tubing around the base of the sampler. Be sure not to allow the tubing to become kinked or crushed under the weight of the sampler.

7.3.8 Press START SAMPLING, the display should read: SAMPLE 1 of 12, at HH:MM

7.3.9 Replace the top cover.

7.3.10 Place a safety cone near the sampler so that the equipment is clearly visible.

7.4 ISCO Sampler Pick-Up

7.4.1 Remove top cover.

7.4.2 Check display, it should read: DONE 12 SAMPLES

7.4.3 Remove suction tubing from pump tubing. If sample remains in the tubing, press REVERSE PUMP to purge the line.

7.4.4 Remove the center section from the base section.

7.4.5 Gently stir sample with a clean Teflon bar.

7.4.6 Carefully remove jar from base section. Avoid putting fingers inside the sample jar to remove it from the base.

7.4.7 Carefully pour sample into appropriate sample containers. If necessary, use a clean stainless steel funnel to aid in pouring.

7.4.8 Return any remaining sample back into the sample source.

7.4.9 Replace the jar into the base section and reassemble the sampler for transport back to SRC.

7.4.10 Collect all materials (tubing, cones, etc.) and store them securely in the vehicle.

7.4.11 Preserve samples as necessary and place all samples in an ice chest for transport. Take the necessary precautions in loading the cooler to prevent breakage during transport.

7.5 Cleaning the Sampler

7.5.1 Wash all equipment with Liquinox and water.

7.5.2 Run Liquinox through pump and suction tubing.

7.5.3 Flush pump and suction tubing thoroughly with tap water to remove all soap.

7.5.4 Rinse the inner surface of the 10 L ISCO jar with a 1:1 nitric acid solution. Carefully swirl the acid solution around the inside the jar to sufficiently coat the inner surface of the jar.

7.5.5 Dispose excess acid into a sink under a fume hood and rinse the jar with copious volumes of DI water.

7.5.6 Rinse all equipment with methanol. Add a small amount into the tubing and jars. Swirl the methanol around in the equipment to sufficiently rinse the inner surface.

7.5.7 Rinse all equipment several times with DI water.

7.5.8 For the final rinse use reagent-grade water from the SJC MRQA laboratory. Put the water into a carboy to be used at the cleaning station in SRC. Water should be renewed per each cleaning event.

7.5.9 Set equipment out to air dry.

8. Calculations

8.1 Table 2 shows an example of the average daily flow measurements over a period of 3 days. The 2 hr averages are used in Table 2 to calculate sample collection times.

8.2 The calculations take into account the total average daily flow, the ratio of the 2 hr average flow, and the cumulative ratio of total flow to derive sample times which would be the most representative for the given 2 hr time interval.

9. Quality Assurance Guidelines

9.1 Equipment Blank

9.1.1 Fill a 10 L glass jar with reagent-grade water.

9.1.2 Setup an ISCO sampler for normal sampling.

9.1.3 Place the stainless steel strainer into the 10 L ISCO jar filled with reagent-grade water.

9.1.4 Press MANUAL SAMPLE or PUMP FORWARD to run the reagent-grade water through the sampling equipment and into the sample collection jar.

9.1.5 Pour off the collected water into appropriate containers for analysis.

9.2 NDMA Equipment Blank

9.2.1 Sampling the equipment blank and bottle blank for NDMA follows the same procedure as listed in 9.1 with a few additions.

9.2.2 The source for the reagent-grade water is the SJC MRQA Laboratory; the laboratory where the sample will be analyzed.

9.2.3 Sample containers (4 L amber jugs) must be thoroughly rinsed with the laboratory's reagent-grade water. Rinse the containers several times before filling for the equipment blank or bottle blank.

10. Method Performance

10.1 Not Applicable

11. References

11.1 Instruction Manual 3710 Standard and Compact Sampler, Copyright 1996, Issued: July 12, 1996, Revision: D, January 1998.

11.2 Laboratory Section Procedures for the Characterization of Water and Wastewater, Fourth Edition, 1989, p. II-1 to II-14 – Sampling.

11.3 Sample Receiving Control – Field Sampling Protocol, Section 1.

FIGURE 1

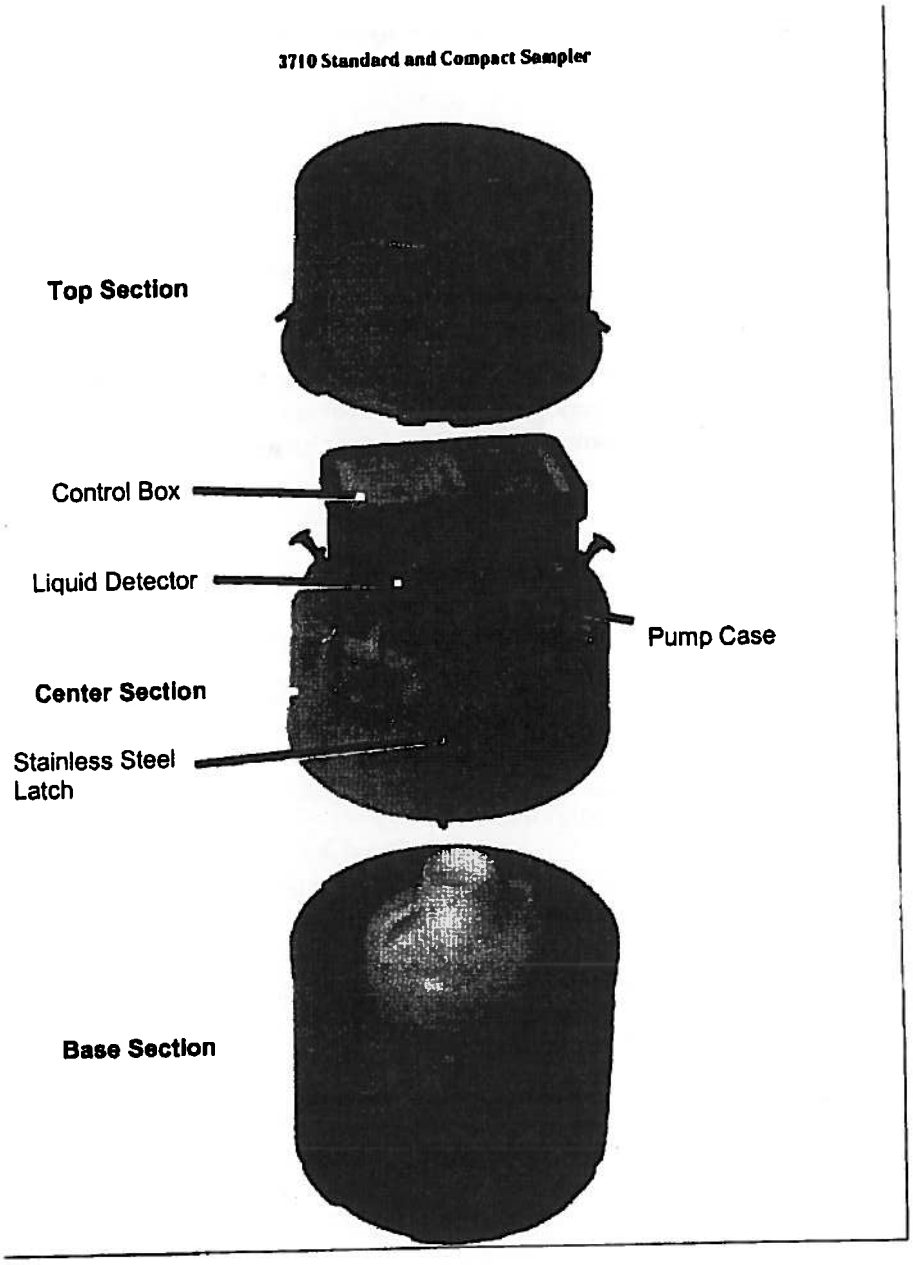
3710 Standard and Compact Sampler
Top Section
Control Box
Liquid Detector
Pump Case
Center Section
Stainless Steel Latch
Base Section

FIGURE 2

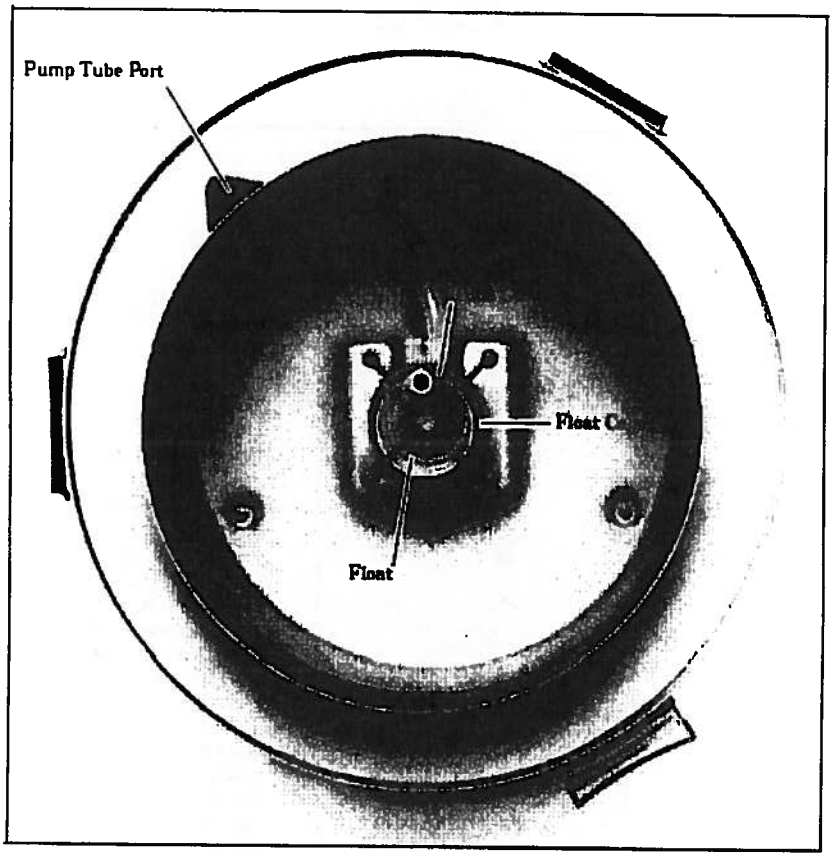

FIGURE 3

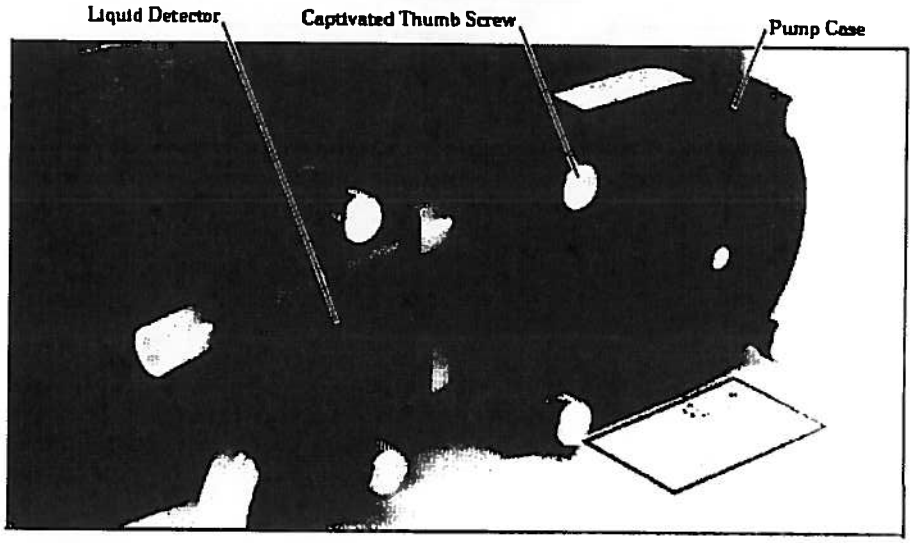

FIGURE 4

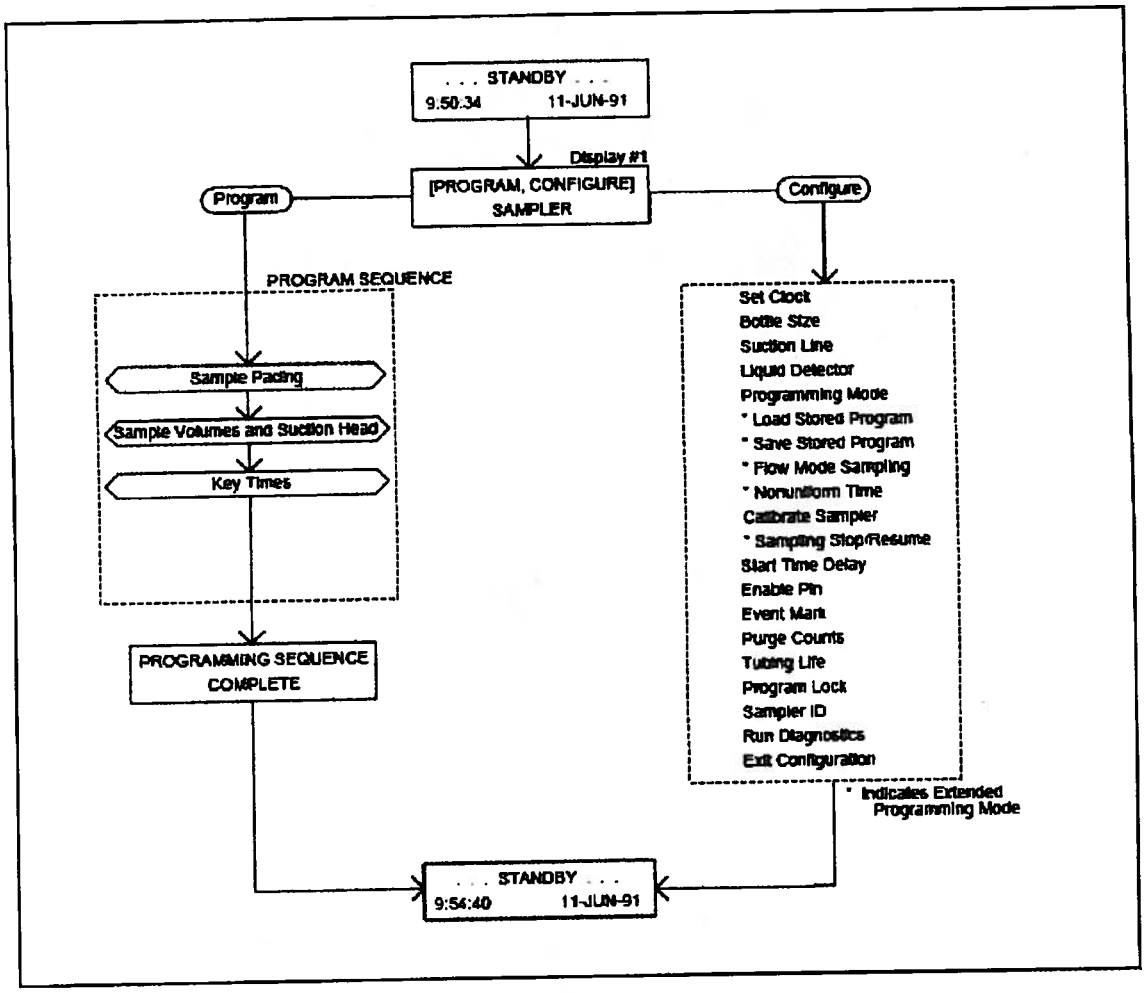
. . . STANDBY . . .
9:50:34 11-JUN-91
Display #1
[PROGRAM, CONFIGURE]
SAMPLER
Program
Configure
PROGRAM SEQUENCE
Sample Pacing
Sample Volumes and Suction Head
Key Times
PROGRAMMING SEQUENCE
COMPLETE
Set Clock
Bottle Size
Suction Line
Liquid Detector
Programming Mode
* Load Stored Program
* Save Stored Program
* Flow Mode Sampling
* Nonuniform Time
Calibrate Sampler
* Sampling Stop/Resume
Start Time Delay
Enable Pin
Event Mark
Purge Counts
Tubing Life
Program Lock
Sampler ID
Run Diagnostics
Exit Configuration
* Indicates Extended Programming Mode
. . . STANDBY . . .
9:54:40 11-JUN-91

TABLE 1

SECTION	CHOICES	SELECTION
SAMPLER	PROGRAM, CONFIGURE	PROGRAM
PACED SAMPLING	TIME, FLOW	TIME
TIME INTERVALS	UNIFORM, NONUNIFORM	NONUNIFORM
MODIFY SEQUENCE	YES, NO	YES

TABLE 2

	FLOW	FLOW	FLOW	AVERAGE	2-HOUR AVE
TIME	11/13/07	11/14/07	11/15/07	FLOW	FLOW
1:00	5.30	5.40	5.80	5.50	
2:00	5.20	5.50	6.10	5.60	5.55
3:00	5.50	6.10	6.00	5.87	
4:00	6.00	6.10	6.10	6.07	5.97
5:00	5.80	6.40	6.70	6.30	
6:00	6.50	6.90	6.70	6.70	6.50
7:00	7.00	7.20	7.50	7.23	
8:00	6.90	7.50	7.70	7.37	7.30
9:00	6.90	7.50	7.70	7.37	
10:00	6.90	8.20	7.10	7.40	7.38
11:00	7.60	8.70	7.70	8.00	
12:00	7.60	7.00	8.00	7.53	7.77
13:00	7.80	7.90	8.10	7.93	
14:00	7.50	8.20	8.00	7.90	7.92
15:00	7.50	8.30	7.80	7.87	
16:00	7.20	8.30	8.00	7.83	7.85
17:00	7.30	7.90	8.00	7.73	
18:00	7.30	7.80	7.80	7.63	7.68
19:00	7.40	8.10	8.10	7.87	
20:00	7.50	7.80	7.60	7.63	7.75
21:00	7.30	5.70	6.60	6.53	
22:00	5.50	5.90	5.20	5.53	6.03
23:00	5.60	5.90	5.00	5.50	
0:00	5.50	6.50	4.60	5.53	5.52

TABLE 3

FLOW WEIGHTED COMPOSITE CALCULATIONS

TIME	AVERAGE FLOW (MGD)	RATIO OF TOTAL FLOW	CUMULATIVE FLOW	SAMPLING TIMES	
2.00	5.55	0.0667	0.066693	2.4632	2.28
4.00	5.97	0.0717	0.138394	4.7325	4.44
6.00	6.50	0.0781	0.216503	6.7637	6.46
8.00	7.30	0.0877	0.304226	8.6486	8.39
10.00	7.38	0.0887	0.392950	10.515	10.31
12.00	7.77	0.0933	0.486281	12.288	12.17
14.00	7.92	0.0951	0.581414	14.034	14.02
16.00	7.85	0.0943	0.675746	15.815	15.49
18.00	7.68	0.0923	0.768075	16.246	16.15
20.00	7.75	0.0931	0.861206	19.394	19.24
22.00	6.03	0.0725	0.933707	21.539	21.32
24.00	5.52	0.0663	1	24	24.00
TOTAL FLOW =	83.22 MGD				

Example Flow Calculation (first 2hr time interval):

$$\frac{(2/24) * 2}{0.563} + 4 - \frac{2}{0.0563} * 0.135428 = 2.14 \text{ (sample collection time in decimal form)}$$

$(2.14 - 2) * 0.6 + 2 = 2.09$ (sample collection time)

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	Not Applicable
Method Name	Volatile Organic Compound Sampling
Version	09.1.0
Method Date	November 19, 2009
Reasons for Method Revision	First formal written procedure

Written or revised by:

Andre Dubois
Laboratory Technician
QA/Sample Receiving

Signature _____ Date 1/14/10

Approved by:

Lavern Tamoria
Supervising Chemist
QA/Sample Receiving

Signature _____ Date 1/14/2010

Final Approval:

Maria Pang
Assistant Manager of
the Laboratories Section

Signature _____ Date 3/17/2010

VOLATILE ORGANIC COMPOUND SAMPLING

INTRODUCTION

Volatile Organic Compounds (VOCs) are organic chemical compounds that have high enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere. The Sample Receiving Group frequently samples for these compounds at several well locations, and at all of the Los Angeles County Sanitation Districts water reclamation plants, for both raw influent and final effluent. This standard operating procedure (SOP) states the responsibilities and describes the process of sampling volatile organic compounds, including the selection of equipment and materials used in the sampling process.

1. Scope and Application

   1.1 Raw influent and final effluent are collected by this method as required by National Pollution Discharge Elimination System (NPDES) permits.

   1.2 A grab sample is collected to provide a snapshot of the current state of the reclamation plant's activity.

   1.3 A grab sample is collected to minimize loss of constituents through volatilization.

2. Summary

   2.1 Obtain a grab sample in a 1 L wide-mouth amber glass jar.

   2.2 If the sample is chlorinated, de-chlorinate the sample with sodium thiosulfate (see §7.2).

   2.3 Fill 3-6 septum vials (40 mL) with no headspace.

3. Sample Handling and Preservation

   3.1 Water Reclamation Plants (WRP) samples are collected using appropriate containers and preservation methods as directed in Standard Methods for the Examination of Water and Wastewater.

   3.2 After collection, and as soon as possible, place samples into an ice chest with ice to keep their temperature at 0-6°C during transport from the sample collection site to Sample Receiving Control (SRC). This will minimize volatilization of target analytes.

3.3 Once removed from the ice chest, the samples are placed into a refrigerator or walk-in cooler to maintain the cold temperature for storage.

4. Interferences

4.1 Several common office products can easily contaminate septum vials with VOCs including; cleaning solvents, paints, adhesives, markers, solvents and some strong odors. Storage of the septum vials nearby these products should be avoided.

4.2 Septum vials should not be stored near products that can potentially off-gas VOCs into the air (i.e. photocopy machines).

4.3 Burning biomass (including cigarette smoke) can emit VOCs into the air, contaminating samples, or sample containers.

4.4 The kit used by Sample Receiving personnel for field chlorine residual analysis has been linked to possible VOC contamination. This kit should not be used for storage of VOC vials at any time.

5. Apparatus

5.1 1 L wide-mouth amber glass jar

5.2 100 mL graduated cylinder

5.3 250 mL Nalgene cup

5.4 VOC vials. There are two types of vials typically used for VOC sampling including: 40 mL amber glass vials with a septum cap (Scientific Specialties Service, Inc. product number: 376840-VAC), and 40 mL clear glass vials with a septum cap, pre-preserved with Hydrochloric Acid(Scientific Specialties Service, Inc. product number: 376740-1/2HCL-V).

6. Reagents

6.1 Acetate Buffer Solution, pH 4

6.2 Potassium Iodide (KI)

6.3 Soluble Starch Solution

6.4 Deionized Water

6.5 1% Sodium Thiosulfate Solution. Dissolve 1 g of sodium thiosulfate in 1 L of deionized water, and pour an aliquot into a dropper bottle. This solution should be made on the day of sampling, and discarded at the end of the day.

7. Procedure

7.1 Collect the Grab Sample

7.1.1 Using white masking tape, securely attach the 1 L wide-mouth amber glass jar to the end of a grab pole, and collect the grab water sample by submerging the bottle 1 foot below the surface.

7.1.2 If the sample is chlorinated, de-chlorinate using §7.2 of this SOP.

7.1.3 Fill each septum vial with the sample. If the vial is pre-acidified, avoid any overflow of sample. To prevent volatilization of the compounds in the sample, minimize turbulence of the sample.

7.1.4 Pour a small amount of sample into the cap, and use the cap to top off the vial. The vial should be filled enough so that the surface tension holds the water in a "convex meniscus", and then apply the cap. Some overflow is lost using this method, but air space in the vial is eliminated.

7.1.5 After capping, turn the vial over and gently tap it to check for gas bubbles. If gas bubbles can be seen in any vials, those vials should be re-opened in order to repeat the procedure, until all samples are free of gas bubbles.

7.2 De-chlorinate the Sample

7.2.1 Rinse both the 100 mL graduated cylinder and the 250 mL Nalgene cup three times with deionized water, and then three times with a small portion (about 20 mL) of sample from the 1 L wide-mouth amber glass jar .

7.2.2 Fill the graduated cylinder with 100mL of sample from the 1 L wide-mouth amber glass jar. Transfer the 100mL of sample into the 250 mL Nalgene cup.

7.2.3 Add approximately 0.5 – 1 g KI crystals to the sample. Avoid a gross excess of KI. Add approximately 4 mL of acetate buffer solution.

7.2.4 Swirl to mix.

7.2.5 Add 1 mL starch solution. If a blue color is apparent, the sample must be de-chlorinated using the following steps. If the solution is clear, continue to §7.1.3

7.2.6 Drop-wise, add the 1% Sodium Thiosulfate Solution to the sample. Swirl to mix after each drop. When the sample is completely clear again, record the number of drops used.

7.2.7 Use Section 8 (Calculations) to determine how many drops of 1% Sodium Thiosulfate Solution to use to de-chlorinate the sample left in the 1 L wide-mouth amber glass jar.

7.2.8 Replace the lid to the 1 L wide-mouth amber glass jar, and gently swirl to mix. Do not shake the sample, as it can cause the volatilization of target compounds.

8. Calculations

8.1 Determine the approximate volume remaining in the 1 L wide-mouth amber glass jar. This volume would typically be between 800 and 900 mL.

8.2 Divide this volume by 100 mL (the volume of sample that was de-chlorinated in §7.2.2).

8.3 Multiply the result by the number of drops recorded in §7.2.6. The result is the number of drops of Sodium Thiosulfate Solution to add to the remaining sample in the 1 L wide-mouth amber glass jar.

9. Quality Assurance Guidelines

9.1 Trip Blanks must be made for each VOC constituent being analyzed. If VOCs are to be collected using both the clear and amber septum vials, then trip blanks must be made using both clear and amber vials.

9.1.1 Use water from the "double" deionized water system, located on the south wall of the Instrumentation Lab. Allow the water system to run for one full minute before filling the trip blank vials. Assure there is no headspace left in the vials, as in §7.1.5. If this water system cannot be accessed, or it is non-functional, use Arrowhead water from the tap in the Laboratories section break room.

9.2 The Trip Blanks must be kept alongside the sample vials until the sampling is complete, and samples have been delivered to SRC.

10. Method Performance

10.1 To verify the chlorine residual analysis method, sample collectors participate in quarterly quantitative chlorine residual analyses as part of the QA Check Sample program.

11. References

11.1 Standard Methods For The Examination Of Water And Wastewater, 21st Edition, 2005, pp. 6-1 to 6-3.

11.2 U.S. Environmental Protection Agency, 2004, 5.B. Sampling Procedures And Techniques, Office of Enforcement and Compliance Assurance, Washington, D.C.

11.3 U.S. Environmental Protection Agency, Methods For Organic Chemical Analysis Of Municipal And Industrial Wastewater, Method 624: Purgeables, 1996, Office of Science and Technology, Washington, D.C.

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	1S3
Method Name	Dissolved Oxygen Field Measurements
Version	10.1.0
Method Date	February 24, 2010
Reasons for Method Revision	Annual review; no revisions were made

Written by:

Julie Randol
Laboratory Technician I
Lancaster Sample Receiving

Julie Randol
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02-24-10
Date

Approved by:

Lavern Tamoria
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Lavern Tamoria
Signature

3/10/2010
Date

Final Approval:

Maria Pang
Assistant Manager of
Laboratories

Signature

3/15/2010
Date

1S3. OXYGEN, DISSOLVED - FIELD MEASUREMENT

INTRODUCTION

The concentration of dissolved oxygen (DO) in a water source depends on the prevailing physical, chemical and biological activities. An electrometric method, using a dissolved oxygen meter, is based on the rate of diffusion of molecular oxygen across a membrane. As part of the "Receiving Water Limitations" in NPDES permits, the dissolved oxygen in receiving waters shall not be depressed below 5 mg/L as a result of the wastes discharged.

1. Scope and Application

   1.1 The membrane electrode provides an excellent method for DO analysis in polluted waters, highly colored waters, and strong waste effluents as well as drinking, surface, and saline waters.

   1.2 This method is recommended for use under conditions that are unfavorable for use of the Winkler method, or when that test and its modifications are subject to serious errors caused by interferences.

   1.3 The meter for the dissolved oxygen probe is calibrated in a convenient range (e.g., 0 to 5, 0 to 10, or 0 to 20 mg/L).

2. Summary of Method

   2.1 The dissolved oxygen probe functions on a polarographic principle, measuring the partial pressure of oxygen in a gas or dissolved in a liquid. The sensor consists of two electrodes, a silver anode and a gold cathode, in an electrolyte gel or solution. This system is separated from the sample by a gas permeable membrane. A polarizing voltage, supplied by the instrument, causes oxygen to diffuse across the membrane and be reduced at the gold cathode. This reduction causes a current to flow. This current is linearly proportional to the partial pressure of oxygen present. The current is amplified and monitored by the instrument. The instrument must be standardized regularly against known conditions.

3. Sample Handling and Preservation

   3.1 The probe may be used in the field in tanks, ponds, streams, etc. Where there is not rapid natural movement of the water, artificial agitation must be provided.

4. Interferences

4.1 Plastic films used with the membrane electrode systems are permeable to a variety of gases other than oxygen, none of which is easily depolarized at the indicator electrode.

4.2 Prolonged use of membrane electrode in water solutions containing gases such as H_2S tends to lower the cell sensitivity. This is eliminated by frequent changing of the membrane and calibration of the membrane electrode.

4.3 Dissolved oxygen probes are temperature-sensitive, and the manufacturer typically provides automatic temperature compensation.

4.4 Organic materials may coat the membrane, reducing sensitivity. Clean with detergent or HCl as directed by the manufacturer.

5. Apparatus

5.1 YSI 550 Handheld Dissolved Oxygen meter, or equivalent

5.2 300 mL glass BOD bottle with air-tight glass stopper

6. Reagents

6.1 Filling solutions, electrolytes, spare membranes; handle as directed in the manufacturer's manual.

6.2 Deionized water

7. Procedure

7.1 Use and Care of the Probe

7.1.1 The probe is kept in the transport chamber attached to the back of the instrument between measurements. A small sponge is kept moistened inside the chamber to provide a water saturated air environment, which is ideal for air calibration.

7.1.2 The probe is also stored in the transport chamber; the moist environment will prolong effective membrane performance and probe life.

7.1.3 Maintain sponge moistness with tap water only.

7.2 Dissolved Oxygen Meter Air Calibration

7.2.1 The DO meter must be calibrated before making DO measurements.

7.2.2 Turn the instrument on by pressing the **ON/OFF** key. Allow 15 minutes for warm-up.

7.2.3 Fill a BOD bottle to about half with fresh DI water. Remove the probe from the storage chamber and unscrew the probe guard.

7.2.4 Press the **MODE** key until mg/L appears on the right side of the screen prior to calibration.

7.2.5 Place the probe in the bottle. Let the temperature acclimate for a couple of minutes. Record current temperature value as it will disappear once in calibration mode.

7.2.6 Enter the calibration menu by pressing and releasing both the **UP ARROW** and **DOWN ARROW** keys at the same time.

7.2.7 The meter should now display CAL on the lower left of the screen as well as the current DO reading.

7.2.8 Obtain the solubility of oxygen in mg/L by using a corresponding temperature displayed by the meter. Review the temperature you recorded and use it with the solubility chart (see Figure 1). Use this value as your adjusted calibration value. Record both the value you started with and the calibrated value you adjusted to in the calibration log.

7.2.9 Using the **UP ARROW** and **DOWN ARROW** keys, adjust the DO reading to the value found in the chart and press **ENTER**. The meter will now prompt you for a salinity value of the water that will be analyzed. Enter "0" and press the **ENTER** key.

7.2.10 The meter should now return to normal operation and is ready for use in the field. Screw the probe guard back on and place the probe back into the storage chamber for transport to the field.

7.3 DO Measurement of Aqueous Samples

7.3.1 Immerse the probe into a flowing water source assuring that it is kept below the surface. Keep all sediment and algae away from the tip of the probe.

7.3.2 Measure the DO of the sample. Record the value after the DO stabilizes.

7.3.3 If the value is out of acceptable range (exceedence is < 5 mg/L), check the DO of upstream receiving water station or outfall of the upstream water reclamation plant, whichever is closer. Record the upstream values to report with the exceedence. DO exceedences are reported by email to the appropriate laboratory and monitoring staff within a day or two of their discovery.

7.3.4 Rinse probe with deionized water after measurement and return to the transport chamber.

8. Calculations

8.1 Not Applicable

9. Quality Assurance Guidelines

9.1 Duplicate every tenth sample.

9.2 It is imperative that the DO meter be calibrated prior to use.

9.3 Rinse the probe with deionized water between measurements in the field.

9.4 Note correction value for temperature. Adjust value if applicable.

9.5 Check calibrated DO meter at least every 4th calibration by comparison with BOD dilution water obtained from the Treatment Plant laboratory. The Treatment Plant Laboratory determines the DO of the BOD dilution water by the Winkler method. Note the difference in the calibration log.

10. Method Performance

10.1 The thermometer of the meter is calibrated once a year by the QA group at SJCWQL by comparison to an NIST certified thermometer in a water bath.

11. References

11.1 Sanitation Districts of Los Angeles County, Laboratory Section: Procedures for the Characterization of Water and Wastes, 4th Edition, 1989, James D. Lehner, "Method 115B, Dissolved Oxygen".

11.2 YSI Incorporated Dissolved Oxygen Meter Model 550 Manual, September 2000.

Figure 1. Solubility of Oxygen in mg/L in Water Exposed to Water-Saturated Air at 760 mm Hg Pressure

Temp°C	Chlorinity: 0 Salinity: 0	5.0 ppt 9.0 ppt	10.0 ppt 18.1 ppt	15.0 ppt 27.1 ppt	20.0 ppt 36.1 ppt	25.0 ppt 45.2 ppt
0.0	14.62	13.73	12.89	12.10	11.36	10.66
1.0	14.22	13.36	12.550	11.78	11.07	10.39
2.0	13.83	13.00	12.22	11.48	10.79	10.14
3.0	13.46	12.66	11.91	11.20	10.53	9.90
4.0	13.11	12.34	11.61	10.92	10.27	9.66
5.0	12.77	12.02	11.32	10.66	10.03	9.44
6.0	12.45	11.73	11.05	10.40	9.80	9.23
7.0	12.14	11.44	10.78	10.16	9.58	9.02
8.0	11.84	11.17	10.53	9.93	9.36	8.83
9.0	11.56	10.91	10.29	9.71	9.16	8.64
10.0	11.29	10.66	10.06	9.49	8.96	8.45
11.0	11.03	10.42	9.84	9.29	8.77	8.28
12.0	10.78	10.18	9.62	9.09	8.59	8.11
13.0	10.54	9.96	9.42	8.90	8.41	7.95
14.0	10.31	9.75	9.22	8.72	8.24	7.79
15.0	10.08	9.54	9.03	8.54	8.08	7.64
16.0	9.87	9.34	8.84	8.37	7.92	7.50
17.0	9.67	9.15	8.67	8.21	7.77	7.36
18.0	9.47	8.97	8.50	8.05	7.62	7.22
19.0	9.28	8.79	8.33	7.90	7.48	7.09

Temp ₀C	Chlorinity: 0 Salinity: 0	5.0 ppt 9.0 ppt	10.0 ppt 18.1 ppt	15.0 ppt 27.1 ppt	20.0 ppt 36.1 ppt	25.0 ppt 45.2 ppt
20.0	9.09	8.62	8.17	7.75	7.35	6.96
21.0	8.92	8.46	8.02	7.61	7.21	6.84
22.0	8.74	8.30	7.87	7.47	7.09	6.72
23.0	8.58	8.14	7.73	7.34	6.96	6.61
24.0	8.42	7.99	7.59	7.21	6.84	6.50
25.0	8.26	7.85	7.46	7.08	6.72	6.39
26.0	8.11	7.71	7.33	6.96	6.62	6.28
27.0	7.97	7.58	7.20	6.85	6.51	6.18
28.0	7.83	7.44	7.08	6.73	6.40	6.09
29.0	7.69	7.32	6.96	6.62	6.30	5.99
30.0	7.56	7.19	6.85	6.51	6.20	5.90
31.0	7.43	7.07	6.73	6.41	6.10	5.81
32.0	7.31	6.96	6.62	6.31	6.01	5.72
33.0	7.18	6.84	6.52	6.21	5.91	5.63
34.0	7.07	6.73	6.42	6.11	5.82	5.550
35.0	6.95	6.62	6.31	6.02	5.73	5.46
36.0	6.84	3.52	6.22	5.93	5.65	5.38
37.0	6.73	6.42	6.12	5.84	5.56	5.31
38.0	6.62	6.32	6.03	5.75	5.48	5.23
39.0	6.52	6.22	5.98	5.66	5.40	5.15
40.0	6.41	6.12	5.84	5.58	5.32	5.08
41.0	6.31	6.03	5.75	5.49	5.24	5.01
42.0	6.21	5.93	5.67	5.41	5.17	4.93
43.0	6.12	5.84	5.58	5.33	5.09	4.86
44.0	6.02	5.75	5.50	5.25	5.02	4.79
45.0	5.93	5.67	5.41	5.17	4.94	4.72

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	1S1
Method Name	Field pH Measurements
Version	10.1.0
Method Date	February 24, 2010
Reasons for Method Revision	Amended to include Extech ExStik EC500 meter

Written by:

Julie Randol
Laboratory Technician I
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Julie Randol
Signature

02-24-10
Date

Approved by:

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3/10/2010
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Final Approval:

Maria Pang
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3/15/2010
Date

1S1. pH (HYDROGEN ION CONCENTRATION) - FIELD

INTRODUCTION

Measurement of pH is one of the most important and frequently used tests in water chemistry. At a given temperature the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. pH as defined by Sorenson as – log (H+); it is the intensity factor of acidity.

The pH value of a highly dilute solution is approximately the same as the negative common logarithm of the hydrogen ion concentration. Natural waters usually have pH values in the range of 4 to 9, and most are slightly basic because of the bicarbonates and carbonates of the alkali and alkaline earth metals. As part of the "Receiving Water Limitations" in the Joint Outfall System NPDES permits, the pH of inland surface waters shall not be depressed below 6.5 or raised above 8.5 as a result of the wastes discharged. For the Antelope Valley, the WDR limitations are 6.0 and 9.0 pH units as set forth by the Lahontan RWQCB.

1. Scope and Application

   1.1 This procedure is applicable to all waters and wastewaters.

2. Summary of Procedure

   2.1 The pH meter is standardized with the appropriate buffer solutions taking into account the solution temperature.

   2.2 For receiving water stations, the pH is measured by immersing the electrode directly in the stream with flow continuously running over the probe.

   2.3 For groundwater locations, the pH is measured using electrodes enclosed in a flow-through cell. The probe has a stirring apparatus attached to provide continuous mixing of the water sample.

3. Sample Handling and Preservation

   3.1 No sample is collected; this procedure is specific to field measurements.

4. Interferences

4.1 High sodium concentrations at a high pH will cause an error. This sodium error can be reduced by either using "low sodium error electrodes" or by making approximate corrections in accordance with information supplied by the manufacturer.

4.2 Temperature affects pH in two ways. First, the pH potential, i.e., the change in potential per pH unit, varies with temperature. Second, the ionization in the sample varies with temperature.

5. Apparatus

5.1 YSI 60 handheld pH meter, VWR Model SP20 portable pH meter, QED MicroPurge Basics Flow Cell MP20, Extech ExStik EC500, or equivalent

5.2 3-100 mL plastic graduated cylinders

5.3 Rinse container (for waste water used in calibration)

6. Reagents

6.1 Buffer solutions. Buffer solutions of various concentrations are prepared as indicated from commercially obtained reagents.

6.2 Deionized water

7. Procedure

7.1 Use and Care of the Electrode

7.1.1 For short term storage between measurements in the field (up to one week)

7.1.1.1 YSI. Place the probe in the transport chamber in the side of the instrument case. Make sure that the sponge inside the chamber is wet (tap water).

7.1.1.2 VWR. This probe does not require any special storage procedures. After being cleaned and dried, place the storage cap over the end of the probe to prevent any possible damage during storage or transport.

7.1.1.3 QED. Place approximately 1 cm of tap (**not distilled or deionized**) water in the transport storage container and insert probe.

7.1.1.4 ExTech: Place the probe in the wetting cap, ensuring that the sponge is moistened with pH 4 buffer solution.

7.1.2 For long term storage (over one week)

7.1.2.1 YSI: Place the probe in the storage bottle containing a mixture of 50 % pH 4 buffer and 50 % 1.5 M KCl. This will assure the fastest possible pH response. If this mixture is not available, storage in tap water is the next best choice. **Do NOT store the probe dry or in distilled or deionized water.**

7.1.2.2 VWR, QED, and Extech: Use the same procedures as for short-term storage.

7.1.3 The electrode should never be used in organic solvents.

7.1.4 The electrode should be rinsed and blotted dry with a Kimwipe. Do not wipe the surface, as it will damage the membrane (in the case of the YSI model). Do not use paper towels.

7.1.5 Cleaning and Maintenance

7.1.5.1 All meters and connectors should be wiped down after use to prevent any possible contamination and as part of maintaining a clean work environment.

7.1.5.2 The pH probes should be cleaned both prior to and after sampling, and may occasionally require other maintenance.

7.1.5.3 The glass bulbs may become coated with oil or other substances as a result of the samples being analyzed. If this occurs, remove the bulb cover (if present) and use a cotton swab and rubbing alcohol to carefully clean the probe of all residues. Should the above procedure prove insufficient to clean the sensor, use a cotton swab and 1 M HCl to gently clean the glass bulb.

7.1.5.4 The probe can also be soaked in a 1:1 dilution of chlorine bleach for up to an hour to remove any possible contaminants. **(NOTE: the probe should in turn be rinsed and soaked in deionized water for an additional hour to remove any remaining bleach.)**

7.1.5.5 Rinse and swab the probe with deionized water and replace the cover (if applicable).

7.1.5.6 Make sure that all probes are properly rinsed with deionized water and recalibrated prior to use.

7.2 Calibration of the pH Meter

7.2.1 YSI 60 Handheld pH meter

7.2.1.1 The pH meter must be calibrated before making pH measurements.

7.2.1.2 Turn the instrument on by pressing the **ON/OFF** key.

7.2.1.3 Remove the probe from the transport chamber and rinse with deionized water.

7.2.1.4 Place 25 to 30 mL of pH 7 buffer into a clean 100 mL graduated cylinder. **CAUTION:** Skin irritant; use safety goggles, gloves and lab coat for protection.

7.2.1.5 Immerse the probe into the cylinder being sure to immerse both the pH and temperature sensors.

7.2.1.6 Allow the probe to acclimate the pH 7 buffer before calibrating; this should take about 5 to 10 minutes.

7.2.1.7 Set the meter to calibrate by pressing and releasing the **UP ARROW** and **DOWN ARROW** keys at the same time. You should see CAL and STAND appear at the bottom of your screen if you are in calibration mode. STAND will be flashing, and the display should show a pH value of 7.

7.2.1.8 Press the **ENTER** key. STAND will stop flashing and the pH calibration value will be shown with middle decimal point flashing. When the reading is stable, the decimal point will stop flashing. Press and hold the **ENTER** key to save the calibration point. SAVE and OFS will flash on the display screen to indicate the value has been saved.

7.2.1.9 SLOPE will appear flashing. This indicates the meter is ready to be calibrated with a second point.

7.2.1.10 Rinse the probe with DI water and place into a clean 100 mL graduated cylinder with either pH 4 or pH 10 buffer solutions. If the pH is 4, a decimal point will flash to the left of the middle point and if it is pH 10, the decimal will flash to the right of the middle point.

7.2.1.11 Press the **ENTER** key. When the reading is stable the decimal point will stop flashing. Press and hold the **ENTER** key to save the first SLOPE. SAVE and SLP will flash on the screen to indicate the SLOPE has been saved. SLOPE will again flash on the screen to indicate the meter is ready for the third pH buffer.

7.2.1.12 Rinse and place the probe into the third clean 100 mL graduated cylinder with the pH buffer not yet chosen, either the pH 4 or pH 10. Press **ENTER**. Once again, depending on the value of the third pH buffer the decimal point will flash to the right or the left of the middle point. When the decimal stops flashing, press and hold the **ENTER** key to save the second slope value. Again the meter will flash SAVE and SLP to indicate the second slope has been saved.

7.2.1.13 The meter is now calibrated at three points and will now return to normal operation.

7.2.1.14 Rinse the probe and take a reading of pH 7 buffer solution from a 2nd lot and let acclimate for a few minutes. The reading should be within $\pm$ 0.2 pH units from 7.0.

7.2.1.15 Document the calibration, recording the calibrated values at each point in the calibration log.

7.2.2 VWR Model SP20 portable pH meter

7.2.2.1 The pH meter must be calibrated before making pH measurements.

7.2.2.2 Attach the electrode and ATC probes to meter

7.2.2.3 Press the power button to turn on the meter.

7.2.2.4 Rinse the probe with deionized (DI) water and then with pH 7.00 buffer solution.

7.2.2.5 Place 25 to 30 mL of pH 7 buffer into a clean 100 mL graduated cylinder. **CAUTION:** Skin irritant; use safety goggles, gloves and lab coat for protection.

7.2.2.6 Immerse the probe into the cylinder being sure to immerse both the pH and temperature sensors.

7.2.2.7 Allow the probe to acclimate the pH 7 buffer before calibrating; this should take about 5 to 10 minutes.

7.2.2.8 Set the meter to calibrate by pressing and releasing the **CAL** key. It will indicate that the probe is calibrating by displaying a slope graphic in the lower field of the screen.

7.2.2.9 P1 will be displayed in the temperature area as the first calibration measurement is being made.

7.2.2.10 When the **READY** light appears, press **OK**; this will accept the initial pH value.

7.2.2.11 When **P2** is displayed and flashing, the probe is ready to be calibrated with the second buffer.

7.2.2.12 Rinse the probe with DI water and place into a clean 100 mL graduated cylinder with either pH 4 or pH 10 buffer solutions.

7.2.2.13 The second calibration will begin as soon as the probe is immersed in the new solution. When the reading is stable the **READY** light will appear. Press the **OK** key to save the second calibration buffer data. The meter is ready for the third pH buffer.

7.2.2.14 Rinse and place the probe into the third clean 100 mL graduated cylinder with the pH buffer not yet chosen, either the pH 4 or pH 10. The third calibration will begin, and the **READY** light will appear when the reading is stable. Save the third calibration data by pressing the **OK** button to accept. The main field will display the slope obtained by the three-point calibration.

7.2.2.15 The meter is now calibrated at three points and will now return to normal operation.

7.2.2.16 Rinse the probe and take a reading of pH 7 buffer solution from a 2nd lot and let acclimate for a few minutes. The reading should b within $\pm$ 0.2 pH units from 7.0.

7.2.2.17 Document the calibration, recording the calibrated values at each point in the calibration log.

7.2.3 QED MicroPurge Basics Flow Cell MP20

7.2.3.1 The pH meter must be calibrated before making pH measurements.

7.2.3.2 Turn on the meter and allow to boot up. When the meter is prepared to receive data, all applicable measuring criteria will be displayed.

7.2.3.3 Set the circulator to **OFF** if necessary by pressing the **ESC/Circulator** key. This will prevent any calibration standards used from being splashed.

7.2.3.4 Set the screen page to **CALIB**, and then scroll down using the arrow keys to pH, which is the value to be calibrated. The **7.00 Indicator Light** will flash in the corner of the display screen to show that this is the parameter being calibrated.

7.2.3.5 Attach the calibration cup; rinse the probe with deionized (DI) water and then with pH 7.00 buffer solution.

7.2.3.6 Fill the calibration cup to within 1cm of the top with pH 7.00 buffer solution. The pH probe should be fully immersed. **CAUTION:** Skin irritant; use safety goggles, gloves and lab coat for protection.

7.2.3.7 Press and release the **ARROW** (Enter) key to calibrate for the initial buffer solution.

7.2.3.8 The main display will show the value of the first buffer solution. Use the **UP** and/or **DOWN** arrows to change the display until the true value of the calibration solution is shown.

7.2.3.9 Press and release the **ARROW** key; this will accept the initial pH value. If the value is accepted for calibration, the display will return to the **CALIB** screen. Should the value not fall within the sensors parameters, the screen will read **FAIL** before returning to the **CALIB** screen.

7.2.3.10 Should such failure occur, replace the buffer solution and recalibrate. The probe may also require cleaning. If this is the case proceed with the proper procedures as listed in section 7.1.3.

7.2.3.11 When the initial calibration value has been accepted, the probe is ready to be calibrated with the second buffer. Press **ESC** to move to the second value for calibration.

7.2.3.12 Rinse the probe with DI water and fill the calibration cup with either pH 4 or pH 10 buffer solutions.

7.2.3.13 Press and release the **ARROW** key to begin calibrating for the second buffer. Use the **UP** and/or **DOWN** arrows until the display shows the true numeric value of the buffer solution. Press the **ARROW** key to accept the second calibration buffer data. The meter is ready for the third pH buffer.

7.2.3.14 Rinse the probe again, and fill the calibration cup with the pH buffer not yet chosen, either the pH 4 or pH 10. Use the **ARROW** key and **UP** and/or **DOWN** arrows to set the numeric value of the buffer solution. Save the third calibration data by pressing the **ARROW** button to accept. Use the **ESC** key to return to the main display page.

7.2.3.15 The meter is now calibrated at three points and ready to return to normal operation.

7.2.3.16 Rinse the probe and take a reading of pH 7 buffer solution from a 2^{nd} lot and let acclimate for a few minutes. The reading should be within $\pm$ 0.2 pH units from 7.0.

7.2.3.17 Document the calibration, recording the calibrated values at each point in the calibration log.

7.2.4 Extech

7.2.4.1 The pH meter must be calibrated before making pH measurements.

7.2.4.2 Turn the instrument on by pressing the **ON/OFF** key.

7.2.4.3 Remove the probe from the transport chamber and rinse with deionized water.

7.2.4.4 Place approximately 4 mL of pH 7 buffer into the corresponding calibration tube. Insert the probe into the tube, ensuring that enough buffer is present to contact the tip of the electrode. **CAUTION:** Skin irritant; use safety goggles, gloves and lab coat for protection.

7.2.4.5 Allow the probe to acclimate the pH 7 buffer before calibrating; this should take about 5 to 10 minutes.

7.2.4.6 Set the meter to calibrate by pressing and holding the **CAL/RECALL** key. It will indicate that the probe is calibrating by displaying "CAL" in the lower field of the screen.

7.2.4.7 The pH reading will flash as the first calibration measurement is being made.

7.2.4.8 The meter automatically recognizes the solution, and calibrates to the corresponding value, as indicated by the circled letter on the LCD screen. These are indicated as **L** (4), **M** (7), and **H** (10).

7.2.4.9 The meter will display **SA**, then **END** when calibration is complete. It will then return to normal operation mode.

7.2.4.10 The unit is ready for the second calibration. Remove the probe from the solution, rinse with DI water, and fill the calibration cup with the second buffer solution, either pH 4 or 10.

7.2.4.11 Press and hold **CAL/RECALL** until "CAL" is displayed. The unit will now calibrate to the second buffer, again displaying the value (L, M, H) circled on the screen.

7.2.4.12 Calibration has been achieved when the unit displays **SA**, then **END**, and returns to normal operation mode.

7.2.4.13 Prepare the probe for the third calibration. Remove the probe from the solution, rinse with DI water, and fill the calibration cup with the third buffer solution, either pH 4 or 10 (whichever was not yet used).

7.2.4.14 Press and hold **CAL/RECALL** until "CAL" is displayed. The unit will now calibrate to the third buffer, again displaying the value (L, M, H) circled on the screen.

7.2.4.15 When the unit displays **SA**, then **END**, the third calibration has been completed, and the probe is ready for analysis. Remove from solution and rinse with DI water.

7.2.4.16 Rinse the probe and take a reading of pH 7 buffer solution from a 2^{nd} lot and let acclimate for a few minutes. The reading should b within $\pm$ 0.2 pH units from 7.0.

7.2.4.17 Document the calibration, recording the calibrated values at each point in the calibration log.

7.2.5 Troubleshooting Procedures

7.2.5.1 pH Out of Range

7.2.5.1.1 Ensure that the probe is properly submerged in the solution to be measured, and that the electrodes are firmly connected to the meter.

7.2.5.1.2 Recalibrate using fresh buffer solutions. Make sure to check that the correct buffers are being used, and that they are not past their expiration dates.

7.2.5.1.3 Sample may indeed be out of range.

7.2.5.2 pH Auto-Calibration Errors. This can occur when the user is attempting to accept values that are outside the range or when calibrating buffers out of sequence.

7.2.5.3 Verify buffers being used, and recalibrate using fresh buffer samples.

7.2.5.4 Clean electrodes if necessary.

7.2.6 Calibration Standard Errors. Same pH values are recorded for two different buffers.

7.2.6.1 Check that different buffers are in fact being used, and that the correct buffer is being measured.

7.2.6.2 Recalibrate using fresh buffer solutions.

7.2.7 Bad Slope. pH slope is not inside the accepted value of 80-120%.

7.2.7.1 Recalibrate using fresh buffers.

7.2.7.2 Clean electrodes if necessary.

7.2.8 No Display

7.2.8.1 Press the power button to ensure that the meter did not utilize its auto shut-off function.

7.2.8.2 Check that batteries are properly aligned, and replace if necessary.

7.3 pH Measurement

7.3.1 Receiving Water Stations

7.3.1.1 Immerse the probe upstream of your position into the flow making sure to keep both temperature and pH sensors under the surface. Keep all sediment and algae away from the tip of the probe.

7.3.1.2 Let sit for a few minutes until pH stabilizes. Record value.

7.3.1.3 If value is out of acceptable range (6.5 – 8.5), check pH of upstream receiving water station or outfall of upstream water reclamation plant, whichever is closer. Record the upstream values to report with the exceedence to monitoring. pH exceedences are reported by e-mail to appropriate laboratory and monitoring staff within a day or two of their discovery.

7.3.1.4 Rinse probe with deionized water after measurement and return to transport chamber.

7.3.2 Groundwater Monitoring

7.3.2.1 Replace the storage cap with the flow-through cell, and attach the unit to the groundwater well using the enclosed tubing and corresponding connectors.

7.3.2.2 Press and release the **ESC** key while on the main screen to turn on the circulator (if necessary).

7.3.2.3 Use the **LEFT/RIGHT ARROW** keys to toggle the unit to **STORE** mode and select **ENTER** using the main arrow key.

7.3.2.4 The flow cell will now record field measurements at three0minute intervals until all corresponding parameters have stabilized. Field pH will show as stable when it maintains a range of $\pm$0.2 units.

7.3.2.5 The meter will beep and flash a slope icon when the sample is stable and ready for collection. Note the pH and other applicable data on the appropriate field sheet.

8. Calculations

8.1 Not applicable

9. Quality Assurance Guidelines

9.1 Duplicate every tenth sample or fraction thereof.

9.2 It is imperative that the pH meter be calibrated prior to use.

9.3 Rinse the probe with deionized water between changes of calibration buffer solutions and measurements in the field.

9.4 To test for drift during the day, rinse the probe and place in pH 7 buffer solution. Record the reading and repeat this step after returning back to SRC from the field using a different pH 7 standard. The reading should be $\pm$ 0.2 pH units.

9.5 Note correction factor for temperature. Adjust value if applicable.

10. Method Performance

10.1 The thermometer of the meter is calibrated once a year by the QA group at SJCWQL by comparison to a NIST certified thermometer in a water bath.

11. References

11.1 Laboratory Section: Procedures for the Characterization of Water and Wastes, 4th Edition, 1989, James D. Lehner, pp. 101-1 through 101-3.

11.2 YSI Incorporated Model 60 Manual, July 2001, pp. 6-16.

11.3 VWR Portable pH/ISE Meters Instruction Manual, April 2001, pp. 12, 24-25.

11.4 QED Flow Cell User's Guide, March 2004, pp. 9-11, 19-20.

11.5 Extech ExStik EC500 User's Guide, March 2008, pp. 8-9.

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	302 (field measurement)
Method Name	Chlorine Residual Field Measurement
Version	10.1.0
Method Date	February 09, 2010
Reasons for Method Revision	Annual review; no modifications were made

Reviewed by:

Jessica Pacheco
Laboratory Technician II
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Signature: Jessica Pacheco Date: 2/10/10

Approved by:

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Signature: Lavern Tamoria Date: 3/10/2010

Final Approval:

Maria Pang
Assistant Manager of
the Laboratories

Signature: Date: 3/15/2010

302. FIELD CHLORINE RESIDUAL QUALITATIVE ANALYSIS

INTRODUCTION

Chlorination is one way to disinfect or kill microorganisms during the final stages of wastewater treatment. The amount of the chlorine that can be discharged out of a treatment plant after the dechlorination stage must be less than 0.05 mg/L. High levels of chlorine are toxic to fish and other organisms. The field chlorine residual qualitative analysis is used to determine the presence or absence of chlorine in a sample. When chlorine levels exceed 0.05 mg/L a blue coloration will form and further quantitative measurements are necessary. The sample will be taken to one of the local treatment plant laboratories for quantitative analysis. Field chlorine residual is an NPDES permit requirement for the Saugus and Valencia Water Reclamation Plants operated by the Sanitation Districts of Los Angeles County, applicable to receiving water stations RA, RB, RC, RD, and RE.

1. Scope and Application

   1.1 The field chlorine Residual qualitative analysis detects the presence or absence of chlorine.

   1.2 The field chlorine residual qualitative analysis is conducted along receiving water sites covered in the NPDES permits for Saugus and Valencia Water Reclamation Plants.

2. Summary of Method

   2.1 Obtain sample and add KI, acetate buffer solution, and soluble starch solution. Swirl to mix.

   2.2 If the mixture appears clear, the level of chlorine present in the sample is less than 0.05 mg/L. If the mixture forms a blue color, the level of chlorine is greater than 0.05 mg/L.

3. Sample Handling and Preservation

   3.1 This procedure is performed in the field.

   3.2 The sample is observed for blue color immediately and discarded as prolonged exposure to sunlight may generate a false positive.

   3.3 When a sample exceeds 0.05mg/L, a sample is collected in a 1 liter Nalgene bottle with no headspace, and taken to a local treatment plant laboratory for a

quantitative chlorine residual analysis. The sample should be analyzed immediately after collection and should not be stored or exposed to excessive light or agitation during transit.

4. Interferences

4.1 Manganese, iron, and nitrite interfere, but buffering to pH 4 before the addition of KI may minimize their effect.

4.2 An unusually high concentration of organic matter may cause some uncertainty in the endpoint. This uncertainty can be reduced by lowering the pH to 1.0 in the absence of manganese, iron, and nitrate.

5. Apparatus

5.1 250 mL Nalgene Cup

6. Reagents

6.1 Acetate Buffer Solution, pH 4

6.2 Potassium Iodide (KI)

6.3 Soluble Starch Solution

6.4 Deionized Water

7. Procedure

7.1 Rinse the 250 mL Nalgene cup three times with deionized water and then rinse three times with sample.

7.2 Collect 200 mL of sample in a 250 mL Nalgene cup.

7.3 Add approximately 0.5 – 1 g KI crystals to the sample. Avoid a gross excess of KI. Add approximately 4 mL of acetate buffer solution.

7.4 Swirl to mix.

7.5 Add 1 mL starch solution. If a blue color is apparent, a quantitative chlorine residual determination must be determined. If the solution is clear, record the chlorine residual as < 0.05 mg/L and disregard the rest of this procedure.

7.6 Upon completion of the qualitative measurement, collect waste in a 1 liter plastic Nalgene bottle for proper disposal in the laboratory. Rinse the 250 mL plastic cup three times with deionized water.

7.7 If chlorine is detected in the qualitative test, a sample is collected in a 1 liter Nalgene bottle with no headspace, and taken to a local treatment plant laboratory for a quantitative chlorine residual analysis. The sample must be analyzed as soon as possible after collection.

7.8 Notify Operations if chlorine is detected from the quantitative analysis, so treatment plant personnel are aware. Also, notify a supervisor or a chemist in the Sample Receiving Section to allow the result to be reported immediately to the Water Quality Control Board. An email notification of exceedence is sent to the applicable operations, monitoring and laboratory staff as soon as possible.

8. Calculations

8.1 Not applicable.

9. Quality Assurance Guidelines

9.1 All reagents must be replaced when the expiration date is exceeded.

9.2 Keep all reagents out of sunlight and tightly sealed when not in use.

9.3 Potassium iodide has a white color; a purple color indicates that it must be discarded and fresh used.

9.4 The soluble starch solution is prepared by the San Jose Creek West APL.

10. Method Performance

10.1 To verify the chlorine residual analysis method, quarterly quantitative chlorine residual analyses are performed as part of the QA Check Sample program.

11. References

11.1 Laboratory Section: Procedures for the Characterization of Water and Wastes, 4th Edition, 1989, James Lehner, Method.302A.

11.2 Sample Receiving Control - Field Sampling Protocol, Section 1.2.4, pp. 20-22.

REPRESENTATIVE SAMPLING OF GROUNDWATER FOR HAZARDOUS SUBSTANCES

Guidance Manual for Groundwater Investigations

July 1995
Revised February 2008

California Environmental Protection Agency
Department of Toxic Substances Control

FOREWORD

The California Environmental Protection Agency (Cal/EPA) was created in 1991 by Governor's Executive Order. Six Boards, Departments, and Office were placed within the Cal/EPA "umbrella" to create a cabinet level voice for the protection of human health and the environment. Cal/EPA's mission is to restore, protect, and enhance the environment, to ensure public health, environmental quality, and economic vitality. Within Cal/EPA, groundwater investigations are mainly conducted under the oversight of the Department of Toxic Substances Control (DTSC), the State Water Resources Control Board (SWRCB) and its nine Regional Water Quality Control Boards (RWQCBs). DTSC's mission is to restore, protect, and enhance the environment, to ensure public health, environmental quality, and economic vitality, by regulating hazardous waste, conducting and overseeing cleanups, and developing and promoting pollution prevention. The SWRCB's mission is to preserve and enhance the quality of California's water resources, and ensure their proper allocation and efficient use for the benefit of present and future generations. The mission of the RWQCBs is to develop and enforce water quality objectives and implementation plans which will best protect the beneficial uses of the State's waters, recognizing local differences in climate, topography, geology and hydrology.

Within DTSC's Emergency Response and Statewide Operations Division (ERSO), the Engineering and Geological Services Branch (EGSB), supports the other programs within DTSC by providing expert technical assistance. As part of the EGSB, the Geological Support Unit (GSU) provides geologic assistance, training, and guidance. This document was prepared by GSU staff and it provides guidelines for the characterization and investigation of groundwater at hazardous substance release and hazardous waste sites. It should be used in conjunction with the two-volume companion reference for hydrogeologic characterization activities:

> *Guidelines for Hydrogeologic Characterization of Hazardous Substances Release Sites* (Cal/EPA 1995a)
>
> *Volume 1: Field Investigation Manual*
> *Volume 2: Project Management Manual*

Within this document, the terms *hazardous substance release site, hazardous waste site* and *toxic waste site*, are used synonymously. However, it should be noted that any unauthorized release of a substance, hazardous or not, that degrades or threatens to degrade water quality may require corrective action to protect its beneficial use.

This document is an updated version of and supersedes the document, *Representative Sampling of Groundwater for Hazardous Substances, Guidance Manual for Groundwater Investigations* (Cal/EPA 1995c). Additional copies of this document may be obtained from DTSC's web site at www.dtsc.ca.gov.

COMMENT SHEET

As a user of this document, your comments are Important. Please use this sheet to inform us of any errors, deficiencies or suggested improvements to this document. If you identify an error or deficiency, please suggest how it can be corrected. Attach additional sheets if necessary. Send your comments to:

California Department of Toxic Substances Control
5796 Corporate Avenue
Cypress, California 90630

Attention: Theodore Johnson, C.E.G., C.Hg., Geological Services Unit

REPRESENTATIVE SAMPLING OF GROUNDWATER FOR HAZARDOUS SUBSTANCES GUIDANCE MANUAL FOR GROUNDWATER INVESTIGATIONS JUNE 2005					
Contact Information - Providing contact information is optional; however, including this information will help us follow-up and address your comments.					
Name					
Agency/Company					
Street Address					
City		**State**		**Zip Code**	
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Section Number		**Section Title**	
Comment			
Suggested Revision			

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1.0 INTRODUCTION

The goal of groundwater sampling is to generate effective, meaningful, and representative groundwater chemistry data. Samples representative of in-situ groundwater conditions are those collected by methods that minimize artifacts caused by sampling equipment or procedures. Groundwater sample collection and handling procedures can cause variability in reported water quality concentrations due to differences in personnel, sampling procedures, and equipment (U.S. EPA 1995). The goal of this document is to promote consistent sampling methods in order to minimize variability in groundwater sampling data caused by equipment or procedures.

No single sampling method is applicable for all sampling objectives. As new methods and/or equipment are developed, additional groundwater sampling protocols should be developed and incorporated into this document. This document was revised to include guidelines on low-flow (minimal drawdown) sampling procedures and the use of passive samplers. Key references are cited within this guidance. A more detailed discussion of sampling procedures, devices, techniques, etc. is provided in various publications by the United States Environmental Protection Agency (U.S. EPA) (Barcelona et al. 1985 and U.S. EPA 1993, 2002 (Yeskis and Zavala)) and the U.S. Geological Survey (Wilde et. al. 1998).

1.1 PURPOSE

This document is intended to provide guidelines for the sampling and analysis of groundwater used for the characterization of hazardous substance release and hazardous waste sites. The purpose of this document is to aid in the selection of sampling devices and analytical methods, provide recommended quality assurance and quality control (QA/QC) procedures, and to provide a standardized approach for the presentation of the resulting data. The recommendations contained herein represent minimum criteria judged necessary to obtain quality data and assure reasonable and independently verifiable interpretations.

The recommendations presented here are a subset of the larger site characterization process. Refer to the *Guidelines for Hydrogeologic Characterization for Hazardous Substance Release Sites* (Cal/EPA 1995a) for additional information on investigative tools for site characterization.

1.2 APPLICABILITY

This guidance is applicable to the characterization and investigation of groundwater associated with hazardous substance release sites, hazardous waste sites, and proposed new or expanding school sites under the oversight of DTSC pursuant to the following statutes:

- Hazardous waste sites - Health and Safety Code, division 20, chapter 6.5 – Hazardous Waste Control
- Hazardous substance release sites - Health and Safety Code, division 20, chapter 6.8 – Hazardous Substance Account
- Proposed new or expanding school sites - Education Code, sections 17210, 172101, 17213.1, and 17213.2

1.3 LIMITATIONS

The recommendations presented here represent criteria that can aid in obtaining quality data and assuring reasonable and independentiy verifiable interpretations. Some sites may require investigative efforts above and beyond the scope of this document, while at other sites a less rigorous application of this guidance may be appropriate. It is the obligation of the responsible parties and qualified professionals performing site investigations to consult with pertinent regulatory agencies, identify all requirements, and meet them appropriately.

This document discusses broad categories of methods and devices used in sampling groundwater. It does not define specific operating procedures for sampling nor propose guidelines for every available

sampling device. This guidance is not intended to exclude alternate sampling approaches; however, any alternative method should only be used with the concurrence of Department of Toxic Substances Control (DTSC). The qualified professional in charge of the field investigation should specify the sampling methods, equipment, and operating procedures in an appropriate work plan and document any significant departures from the work plan.

This document does not supersede existing statutes and regulations. Applicable or relevant and appropriate federal, state and local regulations, statutes, and ordinances should be identified, and site characterization activities should be performed in accordance with the most stringent of these requirements.

2.0 WORK PLAN

A work plan should be prepared for the investigation to be conducted. The work plan provides the purpose of the investigation, summary of site background information, and a description of the tasks to be performed and should include a sampling and analysis plan (SAP) and health and safety plan (HSP). For groundwater investigations, the SAP should specify all procedures and techniques used for groundwater sample collection, sample preservation and shipment, analytical procedures, and chain-of-custody documentation. Field personnel should follow the SAP while performing, collecting, and analyzing groundwater samples. Project tasks and time lines, dates anticipated for initiating and completing monitoring activities may be included in the SAP.

2.1 SAMPLING AND ANALYSIS PLAN

The SAP consists of a field sampling plan (FSP) and a quality assurance project plan (QAPP). The FSP describes, in detail, the sampling and data-gathering methods to be used in the field on a project. The QAPP describes the policy, organization, activities, and protocols necessary to achieve the data quality objectives dictated by the intended use of the data. The SAP should include the following information:

- Field Sampling Plan (FSP)
  - Site background
  - Sampling objectives;
  - Sample location and frequency
  - Sample designation
  - Sampling equipment and procedures
  - Sample handling and analysis
- Quality Assurance Project Plan (QAPP)
  - Project description
  - Project organization and responsibilities
  - QA objectives for measurement
  - Sampling procedures
  - Calibration procedures
  - Analytical procedures
  - Data reduction, validation, and reporting
  - Internal Quality Control
  - Performance and systems audits
  - Preventative maintenance
  - Data assessment procedures
  - Corrective actions
  - Quality assurance reports

Additional guidance on the preparation of SAPs can be found in the *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA* (U.S. EPA 1988).

During preparation, the following information specific to groundwater sampling should be considered and incorporated into the SAP:

- Sampling objectives
- Pre-sampling activities;
- Sampling method selection
- In-situ or field analyses
- Sample preservation and handling
- Chain-of-custody documentation and records management
- Analytical procedures and quantitation limits for both laboratory and field methods
- Field and laboratory quality assurance/quality control
- Evaluation of data quality

2.1.1 Sampling Objectives

The specific objectives of a sampling effort should describe the intended use of data and should include the collection of samples "representative" of the current groundwater conditions over a specific volume of aquifer (U.S. EPA 2002). In meeting this objective, sampling equipment, sampling method, monitoring well construction, monitoring well operation and maintenance, and sample handling procedures should not alter the chemistry of the sample. A sample obtained from a poorly constructed well, using improper sampling equipment, using poor sampling techniques, or improperly preserving samples, can bias the analytical results. Biased or unrepresentative samples can lead to misinterpretations of groundwater quality data (Nielson 1991and Nielsen, 2006)

The sampling program data quality objectives (DQOs) should be thoroughly developed, presented and understood by all parties involved in the sampling. The purpose of the sampling effort and data use(s) should be clearly defined when developing the DQOs. For example, DQOs for site assessment sampling to determine if a contaminant is present may differ from those for determining the nature and extent of a contaminant. Differences in the sampling objectives may dictate the type of sampling equipment used, type of information collected, sampling protocol, and analytical scheme.

A dynamic site conceptual model should be constructed to develop appropriate DQOs. The conceptual model, as it applies to the DQOs, should focus on the contaminant fate and transport processes, such as contaminant migration pathways, influence of geologic materials on contaminant migration (e.g. depositional environments, geologic structure, lithology, etc.), contaminant types (e.g., hydrophobic versus hydrophilic, dissolved verses suspended, and processes that influence concentrations of the contaminants present (e.g. dilution, biodegradation, and dispersion) (U.S. EPA 2002). The detail of the conceptual model is dependent on the information available when the plan is developed. The conceptual site model should be modified as new data becomes available. Initial investigations will have a simpler conceptual site model than previously investigated sites. Specific parameters that should be described or shown in a conceptual model that may impact the design of a groundwater-sampling program include:

- Geologic materials controlling contaminant transport to and from the site.
    - Horizontal (lateral) and vertical (thickness) , extent
    - Horizontal and vertical flow direction
    - Horizontal and vertical hydraulic conductivity and contrasts between different geologic materials
- Types of contaminants to be sampled and factors that could bias sampling results.
- Horizontal and vertical distribution of contaminants.

Prior to the completion of a groundwater monitoring well installation program, vertical aquifer characterization is strongly recommended. A detailed vertical aquifer characterization program should include field characterization of hydraulic conductivities, determination of vertical and horizontal flow directions, assessment of lithologic and geologic variations, and determination of vertical and horizontal contaminant distributions (U.S. EPA 2002).

2.1.2 Sampling Frequency

In most situations, sampling frequency should be based on the hydrogeology of the site. There is no minimum or maximum sampling frequency set by DTSC for all sites. Groundwater analytical results should be reviewed periodically, and sampling frequency modified according to data needs, historical water quality trends, and regulatory goals. To track potential seasonal changes in concentration, at least two sampling rounds should roughly coincide with maximum and minimum water table or potentiometric surface elevations. DTSC recommends sampling at least quarterly for a minimum of one year to track seasonal changes and establish water quality trends. The document *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance* (U.S. EPA 1992a) suggests a method for choosing a sampling interval that will reflect site-specific hydrogeologic conditions. The method uses the Darcy equation to determine the horizontal component of the average linear velocity of

groundwater flow for confined, semi-confined, and unconfined aquifers. This value is used to determine a sampling interval that will yield an Independent sample of groundwater. Research performed in the area of groundwater sampling frequency (Barcelona et. al. 1989) indicates that groundwater monitoring data should be carefully collected over long periods of time (i.e. greater than two years) to determine optimal sampling frequency and to delineate seasonal trends in groundwater monitoring results. In this research, groundwater samples were collected biweekly for 18 months and analyzed for 26 water quality and geochemical constituents. The researchers determined that for the study site, groundwater sampling performed four to six times per year would result in an estimated data/information loss below 20 percent and would minimize redundancy. The researchers concluded that by using careful sampling and analytical procedures, sampling and analytical errors can be controlled to approximately ±20 percent of the annual mean inorganic chemical constituent concentration in groundwater.

2.1.3 Pre-Sampling Activities

The following activities should be conducted before each sampling event.

2.1.3.1 WELL-HEAD INSPECTION

Well-head conditions (e.g., condition of well casing, well lock, marking, standing water at surface, condition of surface pad, and annular seal) and any suggested maintenance should be assessed and documented in the field notes. The SAP should describe procedures and schedules for performing routine well maintenance. Incidental maintenance should be documented and conducted in a timely manner. A well-head maintenance checklist should be included in the SAP. The well-head inspection should include gas monitoring in and around well-heads and well vaults.

2.1.3.2 STATIC WATER LEVEL ELEVATION MEASUREMENT

The SAP should include provisions for measuring the static water elevation in each well prior to each sampling event. Measurement of water level elevations on a continuing basis is important to determine whether horizontal and vertical components of the hydraulic gradient change over time. A change in groundwater flow may necessitate modification to the design of the groundwater monitoring system. The following methods for determining water level elevations are suggested:

- Electric water level sounders
- Pressure transducers

These devices and other methods are described in more detail in U.S. EPA (1987), Aller et al. (1989), Nielsen (1991), and ASTM D4750 (2001) . The SAP should specify the device to be used for water level measurements, procedure for measuring water levels, and accuracy of the measuring device.

The following criteria should be met when determining water level elevations in monitoring wells or piezometers:

- The top of the well casing should be surveyed and tied into a known vertical datum.

- Each well should have a permanent, easily identified reference point from which all depth measurements are taken. The reference point (the top of the inner casing, outer casing, or security/protective casing) should remain constant through all measurements, should be clearly marked on the casing and its description recorded. The inner casing should be used as a reference point, since the outer casing and surrounding area may be affected by other phenomena (e.g., general instability of outer casings due to frost heaving, and vehicular damage) which could cause movement of casings. The elevation of this reference point should be known and clearly marked at the well site (Nielsen, 1991 and Nielsen, 2006). This reference point should also have a known latitude and longitude consistent with the Regional and National Minimum Data Elements requirements. The elevation of the reference point should be surveyed relative to Mean Sea Level (MSL) using the NAVD 88 datum (U.S. EPA 2002).

- After well construction and development, water levels should be allowed to stabilize for a minimum of 24 hours prior to measurement. Low yield aquifers may take longer, and several water level measurements should be made over a period of several days to ensure that adequate recovery has occurred.

- Water levels (the depth to standing water) should be accurately measured with a precision of ±0.01 foot from the survey datum on the top of the well casing. The method or device used to measure water levels should be sufficiently sensitive so that a measurement to 0.01 foot can be reliably obtained.

- Water level measurements used to establish a water table (the surface of the zone of saturation) or any single potentiometric surface should be collected as soon as practicable (e.g., within less than one day). This practice is adequate if the magnitude of change is insignificant over a specific time period. In certain situations, small water level changes could be significant or site-specific variables may warrant collecting water level measurements within a short time interval. These situations may include:

    - tidally influenced aquifers
    - aquifers affected by river stage, bank storage, impoundments, and/or unlined ditches
    - aquifers stressed by intermittent pumping of production, irrigation or supply or remediation wells
    - aquifers being actively recharged because of recent precipitation
    - aquifers that demonstrate significant water level fluctuations in response to barometric pressure changes

- Water level and well depth measurement equipment should be constructed of chemically inert materials not prone to sorption or desorption.

- Water level and well depth measurement equipment should be decontaminated prior to use at each well to ensure sample integrity and prevent cross-contamination of groundwater.

- Devices used to measure water levels and well depths should be periodically calibrated.

- Total well depth measurements should be made periodically using a weighted tape measure or marked cable. The purpose of these depth-to-bottom measurements is two-fold. The first is to determine the length of the water column for purposes of well volume purging calculations. The second is to determine if the well is filling with sediment over time indicating the need for periodic removal of bottom sediments and/or well redevelopment. The weight should be heavy enough to keep the tape measure straight and it should be blunt so that it will not penetrate soft materials on the bottom of the well. The deeper the well, the heavier the weight has to be to "feel" the bottom of the well. Standing water level measuring devices may not be appropriate for making well depth measurements. For wells with dedicated equipment, the total depth should be measured anytime the pump is removed for repair or maintenance or when indicated by elevated turbidity measurements.

  Note: When using a well volume purge procedure, depth-to-bottom measurements should be made ***before*** purging and calculating the purge volume. For other sampling methods, where the well volume calculation is not critical (e.g., low-flow sampling), the depth-to-bottom measurement should be conducted ***after*** sampling to avoid generating artifact turbidity and to minimize the possibility of introducing contaminants before sampling.

2.1.3.3 DETECTION OF IMMISCIBLE LAYERS

The SAP should include provisions for detecting and measuring the thicknesses of immiscible liquid contaminants, such as light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs), if present or likely to be present each time the water level is measured. LNAPLs, also known

as "floaters", are organic liquids, less dense than water, that tend to spread across the water table (in unconfined aquifers). DNAPLs, also known as "sinkers", are relatively insoluble organic liquids that are denser than water. DNAPLs tend to migrate downward and accumulate on underlying lower impermeable intervals. The detection of immiscible layers requires specialized equipment that should be used before a well is evacuated for conventional sampling. The SAP should specify the device(s) to be used to locate and determine the thickness of LNAPLs and DNAPLs, as well as the procedures to be used for detecting and sampling these contaminants.

Extra health and safety precautions should be taken when asphyxiates, LNAPLs or DNAPLs are expected in a well, and the lead regulatory agency should be notified when they are detected.

2.1.3.3.1 LNAPL Detection/Collection

The SAP should specify the following procedures for detecting the presence of LNAPLs. These procedures should be followed before the well is purged for conventional sampling.

1. Open the well vault and sample the air in the vault for target vapors using an appropriate testing device capable of detecting the contaminant; typically, a photoionization detector or an organic vapor analyzer is used for common organic contaminants. Record the measurement results. The air above the well head should be monitored to determine the potential for fire, explosion, or health and safety hazards. Air monitoring also serves as a first indication of the presence of LNAPLs. The presence of LNAPLs precludes the exclusive use of water level sounders to make a determination of static water level.

2. Inspect the well vault and the well head to observe evidence of infiltration or danger.

3. If it is safe to do so, and the lid can be opened without introducing non-native materials into the well, remove the locking and protective caps.

4. Sample the air in the well head for target vapors using an appropriate testing device and record the measurements.

5. Two possible methods to determine the presence of LNAPL are:

    a. Gently lower a clear disposable bailer into the well to just below the fluid level and retrieve a sample. Use of a clear bailer is best for visually determining the presence of very thin or sheen-type layers.

    b. Alternatively, lower an interface gauging probe or a weighted tape coated with commercially available reactive indicator into the well to determine the depth to the air/LNAPL and the LNAPL/water interfaces. The interface probe serves two related purposes. First, as it is lowered into the well, the probe registers when it is exposed to an organic liquid and thus identifies the presence of LNAPLs. Secondly, after passing through the LNAPL layer, the probe indicates the depth to water. Careful recording of the depths of the air/LNAPL and LNAPL/water interfaces establishes a measurement of the thickness of the LNAPL in the well casing.

6. The approach to collecting LNAPL samples depends on the depth to the floating layer surface and the thickness of the layer. A sample of the LNAPL should be collected without purging the well. To collect an LNAPL sample, a bottom valve bailer is the equipment of choice. The bailer should be lowered slowly until contact is made with the surface of the LNAPL. The bailer should then be lowered to a depth less than that of the LNAPL/water interface depth, determined beforehand using the interface probe.

2.1.3.3.2 DNAPL Detection/Collection

The SAP should specify the following procedures for detecting the presence of DNAPLs. These procedures should be followed before the well is evacuated for conventional sampling:

1. Open the well vault and sample the air in the vault for target vapors using an appropriate testing device capable of detecting the contaminant; typically a photoionization detector or an organic vapor analyzer is used for common organic contaminants, but specialized equipment should be employed where potentially dangerous volatiles are suspected. Record the measurement results. The air around and below the well head should be monitored to determine the potential for the accumulation of dense gases or low oxygen conditions. Air monitoring also serves as a first indication of the presence of DNAPLs. A water interface probes may be used to locate the depth to water, but the presence of DNAPLs can not be determined through the exclusive use of water level sounder.

2. Inspect the well vault and the well head to observe evidence of infiltration or danger.

3. If it is safe to do so, and the lid can be opened without introducing non-native materials into the well, remove the locking and protective caps.

4. Sample the air in the well head for target vapors using an appropriate testing device and record the measurement results

5. Determine the static groundwater level using a water level sounder or other device listed in Section 2.1.3.2.

6. Two possible methods to determine the presence of DNAPL are:

    a. lower an interface probe (conductivity or resistivity sensor) to the well bottom to determine if an organic liquid is present; or

    b. lower a transparent, double check-valve bailer to the bottom of the well and withdraw a sample to visually check for the presence of DNAPL. DNAPLs should be collected by slowly lowering and raising the bailer within the well or leaving the bailer in the bottom of the well for an extended period (i.e., overnight).

2.1.4 Sampling Method Selection

Sampling method selection should be based on site-specific conditions and site-specific DQOs. DQOs for the data collection activity include the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability, and completeness. As described in Chapter One of SW-846, DQOs should be defined prior to the initiation of the field and laboratory work (U.S. EPA 1992b).

Field and laboratory organizations performing the work of the DQOs should be informed so their personnel may make informed decisions during the course of the project to attain those DQOs. The procedures used to characterize the hydrogeology of a site, to design and construct a monitoring network, to collect and analyze environmental samples, and to evaluate analytical results should ensure that the data are of the type and quality necessary to allow for the detection of contamination when hazardous substances have migrated from the waste management area (U.S. EPA 1992b). Please refer to Section 2.1.1, Sampling Objectives, for additional information.

Method selection refers to the type of sampling method that will be used at the site, such as low-flow, bailer, or passive samplers. Implementation of each method will differ at each site and at specific wells. Some criteria to be considered when selecting a sampling method include location of the sampling intake, purge completion measurements, the general composition of the groundwater, recharge rates, and

degree of screen submersion. Each of these and other site-specific conditions should be considered when selecting a groundwater sampling method for a site. Regardless of the sampling method used at the site, detailed step-by-step procedures and rationale for the proposed sampling method should be included in the SAP.

Sampling method selection should take into consideration that water in a well screen and surrounding filter pack is generally in a state of flux, while water in the blank casing above the screen tends to stagnate (Robin and Gillham 1987, Powell and Puls 1993, U.S. EPA 2002, and ASTM 2002). Groundwater sampling methods that purge relatively large volumes from the well to achieve a representative sample must ensure that the blank casing water is effectively removed before sample collection. Methods that do not remove multiple casing volumes must ensure the sampling location is within the screen interval to assure formation water is sampled. Non-pumping sampling methods, also known as passive sampling, relies on a constant state of flux in the screen zone and that samples are collected from the actively flushed portion of well (i.e. the screen zone).

The following sections include details of several common sampling methods. However, other methods may be applicable to a groundwater monitoring program. Methods not included here can be proposed to the regulatory agency, detailing the proposed method. Alternate methods, meeting site data quality objectives, are encouraged.

2.1.4.1 CHANGING SAMPLING METHODS

Cal-EPA recognizes sampling technologies or methods will evolve. During the site investigation or remediation, new technologies or sampling methods may be proposed. Maintaining the same sampling method throughout the life of a project, provided the method is carried out the same way every time (e.g., pump inlet depth), removes a variable that may impact sample results. However, a new method may be proposed as being more cost effective and capable of providing a representative sample. In cases where a new sampling method is proposed to replace a previous sampling method, some type of comparison evaluation is necessary. When applicable, comparisons should include conversion between volume-based purging and sampling and low flow purging and sampling.

Comparison between two sampling methods can be in the form of side-by-side evaluations (collection of water samples using the two different sampling methods over a period of time, trend evaluations (change sampling method and provide the trend plots from the previous and new sampling method on the same graph), or a combination of methods. How the method(s) will be compared and evaluated should be established prior to initiation of the new sampling method and presented in an appropriate workplan or SAP. Results of the comparison sampling can be provided in either a separate groundwater sampling report or incorporated into an existing routine groundwater report (e.g., quarterly groundwater monitoring report).

2.1.4.2 WELL PURGING METHOD SELECTION

Water standing in a monitoring well casing may not be representative of in-situ formation groundwater quality. Water in the blank (unscreened) portion of the well is generally considered "stagnant" and non-representative. Studies have shown that water within the screened section of a well can be representative of adjacent groundwater (Robin and Gillham 1987, Powell and Puls, 1993, U.S. EPA 2002, ASTM 2002). In cases where water from the "stagnant" casing cannot be separated from the screen zone water (e.g. during ball sampling, or due to drawdown during pumping), purging of well water is conducted to assure screen zone formation water is collected.

Well purging and the requirements for completion criteria were updated and revised in the groundwater literature over the last 20 years. This guidance incorporates findings of available research and field practice, as well as allowing for new findings and new technologies, and includes discussion and rationale for several well sampling procedures. No judgment is made about what purging methodology is most appropriate in every scenario because different sampling approaches may be applicable for different sampling needs. The overarching purpose of the guidance is to outline the requirements of several sampling protocols and to help the user choose a protocol appropriate for site-specific DQOs. For

methods not specifically discussed, it is recommended that the user incorporate elements of a similar method/protocol in the SAP and discuss variances with the site's lead regulator for concurrence on the sampling methodology prior to sampling.

The SAP should include detailed, step-by-step procedures for the selected purge method including the purge method rationale. Depending on the type of purge method chosen, the SAP should contain descriptions of the equipment to be used for pumping, the instrumentation used to quantitatively measure water quality indicator parameters (including calibration methods), intervals between parameter readings, well drawdown, the location of the pump in relation to the well screen and water table, and the purge pump rate.

2.1.4.3 PURGE METHODS

Well purging methods are as follows:

1. Purge a Minimum of Three to Five Well Casing Volumes. This approach is based on the removal of a sufficient volume of water from the well prior to sample collection to assure "stagnant" or non-representative water is removed and formation water is being sampled. The minimal volume is cited as three to five casing volumes (U.S. EPA 1987, Wilde et. al. 1998) reportedly based on engineering calculations used to determine effective flushing. For enforcement purposes, U.S. EPA recommends the collection of water quality stabilization parameters (U.S. EPA 1998) during purging. As technology and experience with the practice of well sampling advanced, the collection of indicator parameters to document parameter stabilization with this method became routine. In such cases, many SAPs stipulate well purging will cease when one of the two criteria first occurs, either removal of the minimal purge volume (usually three casing volumes) or the attainment of the parameter stabilization criteria.

2. Purge to Stabilization. This approach is referred to as "Purging to Stabilization" or "Well Volume Approach" (U.S. EPA 2002). This method evolved from the traditional three to five well volume/parameter stabilization approach, but without purging a fixed minimum number of well volumes. The method is based on continuously monitoring groundwater indicator parameters during purging until they have stabilized within an acceptable range, at which point stagnant water is presumed to be removed and steady-state conditions achieved. When parameter stabilization occurs, the sample is presumed to be representative. This approach became possible with the development of flow-through cell water quality indicator parameter measurement instruments with continuous data recording capability, which greatly enhanced the ability to determine parameter stabilization characteristics and assurance of steady state conditions. The critical issue with this purge method is to define the criteria for indicator parameter stabilization (e.g., the time interval between measurements, minimal purge time, purge rate, and parameter selection.) Refer to U.S EPA 2002b for an example protocol for this purge method.

3. Low-Flow Purging ("Low-Stress Approach", "Micro-Purge Method" or "Minimal Drawdown Method"). Low-flow purging practices (Puls and Barcelona 1996) were the culmination of numerous observations and studies, in the late 1980s and early 1990s, that groundwater generally flows through the monitoring well screen with sufficient velocity to maintain an exchange with formation water surrounding the screen. If water is removed from a well at rate minimizing stress to the groundwater system, as measured by drawdown in the well, then the pumped water should be representative of formation water after water level and parameter stabilization. In low-flow purging, the pump intake must be situated within the screened portion of the well, and well drawdown must be minimized (Puls and Barcelona 1996). This approach effectively isolates the screened interval from the overlying (stagnant) casing water which the more traditional methods remove by purging. Groundwater indicator parameters are measured during low-flow purging and purging is considered complete, regardless of the amount of water removed from the well, when the indicators parameters have stabilized. During purging, careful measurement and documentation of water levels and pump rate are required to assure that this

method is being effectively performed. Puls and Barcelona recommend this method not be used with well screen intakes greater than ten feet. Refer to U.S EPA 2002a for an example protocol for this purge method.

DTSC recommends the type of sampling method chosen be determined on a well-by-well basis, depending on the hydraulic properties of the monitored zone, the physical nature of the contaminants, and the hydraulic performance of the well (Barcelona et al. 1990, Barcelona, 1985). DTSC will consider the following recommendations and requirements when evaluating monitoring well purge methods:

- Some purge method strategies may be better suited to specific site conditions than others. For example, purging three to five well volumes may detect contamination, while a low-flow method, at the same well, may not. This may be due to the differing hydraulic influence (i.e. radius of influence) of each method. At sites where characterization is limited or uncertain, where well characteristics are not fully known, or where specific constituents are sensitive to certain purge methods, side-by-side comparisons between purging protocols should be considered to determine which method should be used to yield the most representative data or to meet the site-specific DQOs.

- The use of purging equipment which can excessively disrupt the well and potentially affect sample quality, such as bailers or vacuum systems, are discouraged. The use of a dedicated pump is recommended to minimize turbulence during sampling and eliminates the need for equipment decontamination.

- Pump placement within the well may be critical to effective purging. The depth of pump placement should be determined based on the selected purge method, pump design, aquifer characterization, well characteristics, and the nature of contaminants. Comparative sampling at various depths within the screen interval may be required to avoid missing zones of contamination or preferential contaminant pathways.

- Wells should be purged at rates below those used to develop the well. This is to prevent excessive stress on the well (i.e. inducing high turbidity), to prevent damage to the well, and to avoid disturbing accumulated corrosion or reaction products in the well (Puls et al. 1990; Puls and Barcelona 1989a, Puls and Barcelona 1989b, Barcelona et al. 1985). A low purge rate will also reduce the possibility of stripping volatile organic compounds (VOCs) from groundwater, and will reduce the likelihood of mobilizing solids in the subsurface that are immobile under natural flow conditions. However, purge rates should not be purposefully kept low to mask deficiencies in well design or development, as shown by excessively high turbidity. Water quality parameters should be resampled at the lower sampling rate to ensure water quality parameters are stable.

- Water levels should be monitored during purging and sampling to ensure the proper pump flow rate is used to provide minimum drawdown and/or water level stabilization.

- Water quality indicator parameters should be measured in all cases to document stabilization and steady-state conditions. Parameters should include temperature, specific conductance, pH, oxidation-reduction potential (ORP), and dissolved oxygen (Puls and Eychaner 1990, Puls et al. 1990; Puls and Barcelona 1989a, Puls and Barcelona 1989b). In general, the order of parameter stabilization is pH, temperature, specific conductance, ORP, dissolved oxygen, and turbidity. In-line flow-through cells instruments are preferred, and are considered essential for the purge to stabilization method. Turbidity measurements should be collected during purging, and should be used to evaluate the need to redevelop monitoring wells.

- Parameter stabilization should be based on the criteria shown in Table 1, at the end of this section. The intervals between parameter readings should be based on either a set time interval or a specified volume of water purged. These intervals (time or water volume) should be of

sufficient spacing and quantity to assure true stabilization trends are achieved before sampling. At a minimum, four parameter stabilization measurements should be recorded while purging.

- At a minimum, wells with screens below the water table should be purged of a volume of water equivalent to the volume of water standing in the blank casing of the well above the screened interval.

- For wells screened in media with low hydraulic conductivities, special considerations apply. If development data or pump tests show a well will either pump to dryness or that pumping will expose a significant portion of the saturated screen interval, the well recharge rate should be quantitatively determined to evaluate if water is entering the well with excessive turbulence. Turbulent flow can cause a significant loss of volatile contaminants and may affect water chemistry. Once identified and characterized, such wells should be purged at sufficiently low pump rates to avoid turbulent flow (low-flow).

- The purging/sampling method should ensure formation water does not cascade (i.e. flow vertically down the screen) down the sides of the well screen (this may occur when the water level in the well is lowered into or below the screened interval). Laboratory experiments have shown that unless cascading is prevented, up to 70 percent of the volatiles present could be lost before sampling. At no time should a well be purged to dryness if recharge causes formation water to cascade down the sides of the screen, as this may cause an accelerated loss of volatile constituents, resulting in a sample not representative of actual groundwater quality. This problem should be anticipated; water should be purged from the well at a rate that does not cause recharge water to be excessively agitated.

- Wells recharging at a slow rates should be sampled as soon as a sufficient volume of groundwater has entered the well to enable the collection of the necessary groundwater samples. Re-purging should be performed if a well is inactive for more than 24 hours after full recharge.

- Purged water should be stored in appropriate containers until analytical results are available, at which time proper arrangements for disposal or treatment should be made.

TABLE 1. Stabilization Criteria with References for Water-Quality-Indicator Parameters

Parameter	Stabilization Criteria	Reference
Temperature	± 3% of reading (minimum of ± 0.2° C	SAM 2002
pH	+/- 0.1	Puls and Barcelona, 1996; Wilde et al., 1998
specific electrical conductance (SEC)	+/- 3%	Puls and Barcelona, 1996
oxidation-reduction potential (ORP)	+/- 10 millivolts	Puls and Barcelona, 1996
dissolved oxygen (DO)	+/- 0.3 milligrams per liter	Wilde et al., 1998

2.1.4.4 *PUMP INTAKE POSITION*

There are two positions for pump intake placement, within the screened interval or the blank casing above the screen. Each of these positions has advantages and disadvantages based on the portion of the screen sampled, data reproducibility, and potential purge volumes (U.S. EPA 2002).

The vertical location within the well where the pump is placed during an assessment is of primary concern. Unless adequate precautions are taken to lower the pump into the exact position used in previous sampling rounds, or a dedicated system is used, the position of the sampling pump intake may vary between sampling rounds potentially resulting in sampling different zones within the aquifer. When the pump intake location varies along the well screen, reproducibility of the sampling results can be reduced. The variability of sample collection points along the well screen length can be reduced by using dedicated sampling pumps or a premeasured sampling pump hose.

To minimize the contact time between groundwater and the well construction materials during sampling, and ensure the evacuation of the stagnant water above the screen, Keely and Boateng (1987) suggested that the sample pump be gradually lowered through the submerged blank casing while purging. This would minimize contact time between the groundwater and the well construction materials while sampling, as well as ensure the evacuation of the stagnant water above the screen. (U.S. EPA 2002).

DTSC recommends placing the pump intake location during sampling within the well screen, instead of above it, to minimize potential mixing of stagnant water, to minimize the required purge time, and to keep the intake off the bottom of the well where accumulated sediment may be disturbed and drawn into the sample. Locating the pump intake centrally within the well screen provides the best opportunity to collect samples representative of water across the entire well screen (Varljen 2006). Shorter well screens are preferred to reduce concentration averaging across large profiles of the aquifer and to reduce time required for water to reach the pump intake from portions of the screen distant from the pump intake.

2.1.4.5 *PASSIVE METHODS*

Passive Sampling. Passive sampling approaches do not incorporate purging or pumping as part of the groundwater sampling method. These include diffusion samplers such as polyethylene diffusion bags (PDB), or rigid porous pipe samplers (RPP); *equilibrated* grab samplers such as the Snap Sampler or Hydrasleeve; and sorptive samplers such as the Gore sampler. These devices are placed in the screened section of wells for a device-specific equilibration period. Most devices can be left downhole between sampling events. Passive methods rely on ambient aquifer flow-through to deliver groundwater to the sampling device. The operation of these devices includes exposure and diffusion of contaminants of concern into the sampling device, or collection of a whole water sample at a user-identified collection event.

2.1.4.6 *GROUNDWATER SAMPLING EQUIPMENT SELECTION AND USE*

The following is a list of the most common categories and types of groundwater sampling devices (Nielsen 2006, Pohlmann and Hess 1988, ITRC 2007):

- Active
  - Grab samplers (e.g. bailers and syringe devices)
  - Positive displacement pumps (e.g. gear drive, bladder, helical rotor, piston, and centrifugal)
  - Suction lift pumps (e.g. peristaltic)
  - Gas contact pumps
- Passive
  - Polyethylene Diffusion Bags
  - Rigid Porous Pipe Samplers
  - Dialysis Membrane Sampler
  - Snap Samplers
  - Hydrasleeve

- Gore Sampler

DTSC prefers all sampling equipment be dedicated to a particular well. To encourage innovation, DTSC may allow the use of other devices that are not specifically mentioned above if it can be demonstrated that the device will yield "representative" groundwater samples.

The following criteria should be considered when selecting sampling equipment:

- Sampling equipment should be chosen based on the analytes of interest and the characteristics and depth of the saturated zone from which the sample is withdrawn. For example, the choice of sampling equipment should reflect consideration of the potential for LNAPLs and DNAPLs.

- Sample collection equipment should not alter analyte concentrations, such as by sorption or desorption, degradation, or corrosion.

- Sampling equipment should cause minimal sample agitation and should be selected to reduce/eliminate sample contact with the atmosphere during sample transfer. Sampling equipment should not allow volatilization or aeration of samples that may alter analyte concentrations.

Appendix A briefly discusses each category and various types of sampling devices, including their appropriateness for use and relative advantages and disadvantages.

2.1.4.7 DECONTAMINATING SAMPLING EQUIPMENT

When dedicated equipment is not used for sampling (or purging), or when dedicated equipment is stored outside of the well, the SAP should include procedures for disassembly and cleaning of equipment before each use at each well.

Disposable items such as rope and low-grade tubing should be properly disposed between wells. Thoroughly cleaning equipment parts that come into contact with well water is especially important. In addition, a clean plastic sheet should be placed adjacent to or around the well to prevent surface debris from coming in contact with the purging and sampling equipment. Clean sampling equipment should not be placed on the ground or on other contaminated surfaces prior to insertion in the well. The effects of cross-contamination can be minimized by sampling the least contaminated well first and progressing to more contaminated ones. Equipment blanks to document the effectiveness of the decontamination procedures should be collected on a regular basis from non-dedicated equipment. The frequency depends on the SAP and regional protocols.

The following cleaning procedure is recommended for organic constituents:

1. Wash the equipment with a non-phosphate detergent
2. Rinse with tap water
3. Rinse with organic-free reagent water or deionized water

If separate phase or hydrophobic contaminants are present (such as LNAPL, DNAPL, high levels of contaminants, etc.), additional decontamination steps may be added. For example, an organic solvent, such as reagent-grade isopropanol or acetone may be added as a first spraying/bucket prior to the soapy water/tap, water/deionized rinse procedure/buckets.

The following cleaning procedure is recommended for inorganic constituents:

1. Wash the equipment with a non-phosphate detergent/soap mixture
2. Rinse with dilute (0.1Mole) hydrochloric or nitric acid
3. Rinse with tap water

4. Rinse with reagent water. Dilute hydrochloric acid with a reagent water rinse is preferred when cleaning stainless steel because nitric acid may oxidize the steel.

The waste decontamination fluids should be containerized and characterized to determine whether they should be treated or disposed of as hazardous waste.

2.1.4.8 COLLECTING GROUNDWATER SAMPLES

Monitoring well sampling should always progress from the well expected to be least contaminated to the most contaminated, to minimize the potential for cross-contamination of samples that may result from inadequate decontamination of sampling equipment. Samples should be collected and containerized according to the volatility of the target analytes. The preferred collection order for some of the more common groundwater analytes is as follows:

- Volatile organic compounds (VOCs)
- Semivolatile organic compounds (SVOCs)
- Major water quality cations and anions
- Stable isotopes (e.g. oxygen, hydrogen, nitrogen, lead)
- Metals
- Cyanide
- Turbidity
- Radionuclides

The following guidelines should be adhered to while using and operating groundwater sampling equipment:

- Check valves should be designed and inspected to ensure that fouling problems do not reduce delivery capabilities or result in aeration of samples.

- Sampling equipment (especially bailers) should never be dropped into the well, as this will cause degassing of the water upon impact.

- Sampler contents should be transferred to sample containers in a way that will minimize sample agitation and aeration.

- Clean sampling equipment should not be allowed to come into contact with the ground or other contaminated surfaces prior to insertion into the well.

- The rate at which a well is sampled should not exceed the rate at which the well was purged. Sampling rates of less than one liter per minute are suggested for wells that have historically yielded turbid samples (Puls et al., 1990). Wells are routinely sampled at rates as low as 100 to 500 milliliter per minute (Puls, et al., 1990; Puls and Barcelona, 1989a).

- Water levels should be monitored during purging and sampling to ensure the proper pump flow rate is used to provide minimum drawdown and/or water level stabilization.

- If the rates of purging and sampling are different, the sample water should be verified as stable by collecting additional field parameters and utilizing the stabilization criteria herein.

- If a flow through cell is used, groundwater samples should be collected before the flow-through cell, between the flow-through cell and the well head. Installation of a Y-fitting approximately 1 foot from the inlet to the flow-through cell will facilitate sampling without interrupting flow.

2.1.5 In-Situ or Field Analyses

Physically or chemically unstable analytes should be measured in the field, rather than in the laboratory. Examples of unstable parameters include pH, redox potential, chlorine, dissolved oxygen, ferrous iron, alkalinity, and temperature. It is suggested that dissolved oxygen, turbidity, and specific conductance be determined in the field as soon as practicable. Although the specific conductance (i.e. electrical conductance) of a sample should be relatively stable, DTSC recommends that this analyte also be measured in the field. Most conductivity instruments require temperature compensation; therefore, the temperature of the samples should be measured at the time conductivity is determined unless the instrument automatically makes this compensation.

Three methods can be employed for measuring unstable field parameters:

- Specially designed meters with probes that may be lowered down into the well.
- In-line flow-through monitoring chamber with ports for probe attachment, allowing continuous readings during purging
- Collect a sample in a clean bottle or beaker in the same manner that a sample for laboratory analysis would be collected, and then to analyze the sample using field test kits or meters.

Unstable parameters should be measured in samples collected from the well after the well has been purged and before samples are collected for laboratory analysis. If down-hole probes (pH electrode, specific ion electrode, and thermistor) are used to measure unstable parameters, the probes should be decontaminated in a manner that prevents the probe(s) from contaminating the water in the well. In no case should field analyses be performed directly on samples that will be submitted for laboratory analysis. Monitoring probes should not be placed in shipping containers containing groundwater samples for laboratory analysis. Dissolved oxygen should only be measured with a flow-through cell or downhole instrument.

The SAP should list the specific parameters that will be measured in the field, types of instruments (e.g. downhole probes, meters) that will be used to make these measurements, and describe the procedures for operating the instruments and recording the measurements. The SAP should describe all instrument calibration procedures, including the frequency of calibration. The description of calibration procedures should include: discussion of initial calibration, multi-level calibration for determination of usable range, periodic calibration checks, conditions that warrant re-calibration of instruments, acceptable control limits, and the maintenance of calibration records in the field log book. All instruments should be calibrated with standards that have not exceeded their expiration dates. At a minimum, all field instruments should be calibrated at the beginning of each use and in accordance with the frequency suggested by the manufacturer. Field instruments should be calibrated using at least two calibration standards spanning the range of results anticipated during the sampling event. For example, the pH meter should be calibrated at 4 and 7 pH, or at 7 and 10 pH, dependent if the anticipated pH of the groundwater is either acidic or basic, respectively.

2.2 SAMPLE PRESERVATION AND HANDLING

The procedures employed for sample preservation and handling are nearly as important for ensuring the integrity of the samples as the collection device itself. Detailed procedures for containerization, preservation, packaging, and handling (e.g. shipped daily by overnight courier) should be provided in the SAP. Samples collected from a well should never be composited in a large container for subsequent transfer to the appropriate smaller bottles. Regardless of the analytes of concern, exposure of the samples to the ambient air should be minimized.

Splitting of samples is sometimes required for quality assurance/quality control purposes. When sampling for VOCs, the procedure is changed slightly. For non-VOC samples, one half of the sample is emptied from the sampling device into one container, and one half is emptied into the other, with the procedure being repeated until the containers are full. For VOCs, however, the first volatile organic analysis (VOA) container should be completely filled and sealed, and then the VOA container into which the other split sample will be placed should be completely filled and sealed.

2.2.1 Sample Containers

The SAP should identify the type of sample containers to be used to collect samples, as well as the procedures used to ensure that sample containers are free of contaminants prior to use. The SAP should refer to the specific analytical method that designates an acceptable container and sufficient sample quantity.

The most important factors to consider when choosing sample containers are compatibility with the contaminant or waste, cost, resistance to breakage, and volume. Containers must not distort, rupture, or leak as a result of chemical reactions with constituents of concern. The containers must have adequate wall thickness to withstand handling during sample collection and transport to the laboratory. Containers with wide mouths are often desirable to facilitate transfer of samples from samplers to containers.

New containers should be prepared based on the analyte of interest; used containers are to be discarded. The cleanliness of a batch of precleaned bottles should be verified in the laboratory. The residue analysis should be available prior to sampling in the field.

2.2.2 Sample Preservation

The SAP should identify the sample preservation methods that will be used. Methods of sample preservation are relatively limited, and are generally intended to 1) retard biological action, 2) retard chemical reactions such as hydrolysis or oxidation, and 3) reduce sorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and protection from light.

Most sample containers provided by a laboratory have pre-added preservative if the analyte of interest requires preservation. If these are not available, then preservatives should be added in the field. Samples should not be brought back to the laboratory for preservation. For pH control, test strips should be used to verify that samples have attained the appropriate pH range for sample preservation.

Most commercial shipping containers ("coolers") leak when the interior water level reaches the lid-body interface and may result in the carrier refusing to ship the container. For this reason, DTSC recommends using two water-tight sealable polyethylene bags for shipping. The first will contain the sample bottles, the second the ice needed to keep the samples at 4±2 °C. Glass containers should be protected from breakage using holders bubble wrap and/or vermiculite. The vermiculite will also absorb any spills or melted ice. The number of samples in the cooler should not prevent effective sample preservation (i.e. cooling). Blue ice should only be used if the samples are pre-cooled before shipping, since blue ice may not chill the samples sufficiently for the duration of the trip to the laboratory. Care should also be taken with the VOC samples to prevent freezing in transit.

As specified by U.S. EPA (1998), a temperature history of the samples should be maintained as a quality control measure. This is done by recording the temperature on the chain-of-custody record (Section 2.3.4) before the sample containers are sealed for shipment. Upon receipt of the shipment, the laboratory is required to record the temperature at receipt on the chain-of-custody record. A temperature blank should be included in the cooler (i.e. a vial or container filled with clean water and marked as such, which is measured by the laboratory upon receipt).

Holding time refers to the period that begins when the sample is collected from the well and ends with its extraction or analysis. Holding time is not measured from the time the laboratory receives the samples. Any laboratory submission to DTSC should contain the date/time sampled, the date/time received, the date/time extracted, and the date/time analyzed.

2.2.3 Special Handling Considerations

During groundwater sampling, every attempt should be made to minimize changes in the chemistry of the samples so that data representative of subsurface hydrogeochemistry are collected. DTSC agrees with the following U.S. EPA protocols that will assist in preserving the natural chemistry of groundwater samples:

- Do not routinely filter groundwater samples in the field.
- Do not transfer samples from one sample container to another.
- Do not allow headspace in the containers of samples that will be analyzed for volatile organic compounds, alkalinity, and dissolved gases.

2.2.3.1 SAMPLE FILTRATION

Decisions to filter samples should be dictated by sampling objectives rather than as a fix for poor sampling practices. Field-filtering of certain compounds should not be the default. Evaluation of what the application of field-filtration is trying to accomplish should be considered (Puls and Barcelona 1996) and included in the SAP.

Groundwater samples used to determine if there is statistically significant evidence of groundwater contamination by organic compounds should not be field-filtered. Data generated from filtered samples provide information on only the dissolved constituents that are present, as suspended materials are removed by the filtration process. The analytical results of both filtered and un-filtered groundwater samples are used to determine if hazardous constituents were released to groundwater. As discussed in greater detail below, current research in groundwater sampling protocol indicates that hazardous constituents are mobile in the subsurface in both the aqueous (dissolved) phase and the solid phase. The research of Puls and Barcelona (1989a), Puls and Barcelona (1989b), Penrose et al. (1990), Backhus et al. (1993) and West (1990) are the primary sources of the discussion of field filtration that follows.

During groundwater sampling, every attempt should be made to minimize changes in the chemistry of the sample so the data is representative of site conditions. A sample that is exposed to the atmosphere or changes in ambient conditions as a result of field filtering is very likely to undergo chemical changes (e.g. volatilization, precipitation, chemical flocculation) that alter constituent concentrations. These reactions can change the concentrations of organic compounds and metals if they are present in the sample. VOCs may to partition to the atmosphere if exposed, thereby resulting in groundwater monitoring data that are not representative of in-situ concentrations. Further, precipitated and emulsion trapped constituents migrating in the aquifer are lost through field filtering, because they are unable to pass through a standard 0.45 micron field filter.

For metals analysis of groundwater samples, however, the situation is not as clear. The argument against filtering is that it will not provide accurate information concerning the mobility of metal contaminants. Metals may move through the aquifer matrices not only as dissolved species, but also as precipitated phases, and/or polymeric species; some metals may be adsorbed to, or encapsulated in, organic or inorganic particles (e.g. colloid-size particles), that are likely to be removed by filtration. In addition, field filtration may introduce oxygen into the sample, which can oxidize dissolved ferrous iron to form a ferric hydroxide precipitate ($Fe(OH)_3$); this may enmesh other metals in the sample, removing them from solution. Precipitated and entrapped constituents would be removed by field filtration.

The argument for filtering samples prior to analysis for inorganic constituents is that small differences in sample turbidity can mean very large differences in analytical results. Sample turbidity is an indirect measurement of the amount of particulate matter suspended in a sample, and is highly dependent on the nature of the aquifer material. In aquifers containing significant silt or clay, turbidity can be reduced through proper well design, construction and development, and by use of appropriate sample collection methods. However, turbidity is rarely eliminated. Since sample turbidity is not directly related to sources of contamination, resulting values from unfiltered samples do not necessarily provide direct evidence of metals contamination, and are generally not a useful indication of contaminant load in an aquifer.

Based on these arguments, the following recommendations are provided as a guide to sampling groundwater for the analysis of trace metals:

- For risk assessment, unfiltered samples should be analyzed if the potential for colloidal transport is suspected.

- Field filtered samples may be collected at the same time for comparison purposes, but field filtering is not a substitute for properly constructed, developed and sampled wells.

- Samples should never be filtered when a water supply well is sampled.

Since significant differences in water quality may be attributed to contamination, it is critical to control other variables that may affect groundwater quality. In addition to factors already discussed in this document, these recommendations, where applicable, should also be followed:

- Monitoring wells should be designed, constructed and developed to minimize turbidity; well construction is discussed in *Monitoring Well Design and Construction for Hydrogeologic Characterization* (Cal/EPA 1995b), and in the Department of Water Resources Bulletin 74-90 (DWR 1990).

- Whenever possible, well purging and sampling should be performed with dedicated pumps at low discharge rates.

- As previously stated throughout this document, wells should be purged until measured values for the stabilization criteria in Table 1 are achieved.

- In-line, positive-pressure filters should be used at all times; vacuum filtration is not acceptable.

- Manufacturer's recommendations for the volume of water to be flushed through the filter prior to sampling should be followed; if guidelines are not available, a volume of groundwater equal to twice the capacity of the filter should be flushed through the filter and discarded before collecting samples.

- There are certain circumstances where it is necessary to filter or centrifuge the sample under controlled laboratory conditions prior to analysis to prevent instrument damage. Sample filtration in the laboratory is permissible if insoluble materials that could damage laboratory equipment (e.g., silicates) remain after acid digestion of the sample. If this step is necessary, the filter and the filtering apparatus should be thoroughly cleaned and pre-rinsed with dilute nitric acid before use. Laboratory personnel should refer to SW-846 (U.S. EPA 1998) for information concerning these procedures. The analytical reports submitted to DTSC should clearly state that groundwater samples were laboratory filtered.

- Samples should not be transferred from one sample container to another. Transferring samples between containers may result in losses of organic material onto the walls of the container or sample aeration.

- To minimize the possibility of volatilization of organics, no headspace should exist in the containers of samples containing volatile organics. Field logs and laboratory analysis reports should note the headspace, if present, in the sample container(s) at the time of receipt by the laboratory, as well as at the time the sample was first transferred to the sample container at the wellhead.

2.3 CHAIN-OF-CUSTODY AND RECORDS MANAGEMENT

A chain-of-custody procedure should be designed to allow for the reconstruction of how and under what circumstances a sample was collected, including any problems encountered. U.S. EPA (1998) provides a complete description of chain-of-custody and records management. The chain-of-custody procedure is intended to prevent misidentification of the samples, to prevent tampering with the samples during

shipping and storage, to allow easy identification of any tampering, and to allow for the easy tracking of possession. Groundwater samples should always be stored in a secure area.

To avoid water damage of the chain-of-custody form during transport in the sample cooler, the form should be placed into a water-tight sealable bag and placed on top of the cooler contents.

2.3.1 Sample Labels

To prevent sample misidentification, labels should be affixed to each sample container at the time of sampling. The labels should be sufficiently durable to remain legible even when wet and should contain, at a minimum, the following information:

- Site designation
- Sample identification number
- Name and signature of collector
- Date and time of collection
- Place of collection
- Parameters requested (if space permits)

Samples can be labeled by recording the above information directly on the sample containers. Alternatively, multiple-part labels consisting of a unique identification number that is placed on the container and at least two copies of the descriptive information for the samples (referenced to the identification number) may be used. One copy should be kept in a separate file or logbook, and a second copy is shipped inside the cooler with the samples to the laboratory.

2.3.2 Sample Custody Seal

In cases where samples leave the samplers immediate control (e.g. shipment to laboratory), a custody seal should be placed on the shipping container or on the individual sample bottles. Custody seals provide prevention or easy detection of sample tampering. The custody seal should bear the signature of the collector and the collection date. It can be placed on the front and back of a cooler, around the opening of sealable polyethylene bags or on the lid of each sample container before it is taped shut for shipping. Caution should be exercised in doing any of the above. Experience has shown that the seal may not always adhere to some plastic coolers, and the cooler may arrive at the destination without the appropriate seal. Sometimes the sample containers become wet from melting ice or condensation; thus, while their labels will stick, their custody seals may not. Taping over the seal with a transparent tape generally solves this problem and can be similarly applied to cooler lids (Note: Some tapes contain chemicals which may be chemicals of concern).

2.3.3 Field Logbook or Log Sheets

If a sample analysis produces an unexpected or unexplainable result, it will be necessary to determine if the circumstances of sample collection, rather than a change in the groundwater quality, are responsible. Examination of the field logbook or log sheets is critical in this process. The field logbook or log sheets should document the following:

- Well identification
- Condition of well and surface completion
- Top of casing surveyed elevation
- Well depth from top of casing
- Static water level depth and measurement technique
- Presence and thickness of immiscible layers and detection method
- Well purging procedure and equipment
- Purge volume and pumping rate
- Time well purged
- Well yield (high or low)

- Well recovery after purging (slow, fast)
- Collection method for immiscible layers
- Sample withdrawal procedure and equipment
- Date and time of collection
- Measurement of groundwater stabilization parameters
- Well sampling sequence
- Types of sample bottles used and sample identification numbers
- Preservatives used and pH verification
- Parameters requested for analysis
- Field observations of sampling event
- Name of collector
- Climatic conditions, including air temperature
- Internal temperature of field and shipping containers

The field logbook or log sheets for well purging and sampling should be included within reports submitted to DTSC.

2.3.4 Chain-of-Custody Record

Sample possession should be clear from the chain-of-custody record sheet. A chain-of-custody sheet should be filled out and should accompany all samples. It should also contain enough copies so that each person possessing the shipment receives his/her own copy. At a minimum, the record should contain the following information:

- Site designation
- Site address
- Sample number
- Sample description and location
- Signature of collector
- Date and time of collection
- Sample matrix (e.g. groundwater)
- Identification of sampling point (well)
- Number and types of containers
- Parameters requested for analysis
- Preservatives used
- Signature of persons involved in the chain of possession
- Inclusive dates and times of possession
- Internal temperature of shipping container when samples were sealed into the container for shipping
- Internal temperature of container when opened at the laboratory
- Remarks section to identify potential hazards or to relay other information to the laboratory

2.3.5 Sample Analysis Request Sheet

This document should accompany the sample(s) on delivery to the laboratory and clearly identify which sample containers have been designated for each requested parameter. It may be included in the chain-of-custody record. Addition of preservatives should also be noted. This document should include the following types of information:

- Name of person receiving the sample
- Name and addresses of analytical laboratory
- Laboratory sample number (if different from field number)
- Date of sample receipt
- Analyses to be performed
- Internal temperature of shipping container upon opening in the laboratory

- Preservatives added in the field

2.3.6 Laboratory Logbook

Once the sample has been received in the laboratory, the sample custodian and/or laboratory personnel should clearly document the processing steps that are applied to the sample. All sample preparation techniques and instrumental methods used should be identified in the logbook. Experimental conditions, such as the use of specific reagents, temperatures, reaction times, and instrument settings, should be noted. The results of the analyses of all laboratory quality control samples should be identified, specific to each batch of groundwater samples analyzed. The laboratory logbook should include the time, date, and name of the person who performed each processing step.

2.4 ANALYTICAL PROCEDURES

The SAP should describe in detail the analytical procedures that will be used to determine the concentrations of constituents or parameters of interest. These procedures should include suitable analytical methods, the associated analytical detection limits, as well as proper quality assurance and quality control protocols.

The SAP should identify a method that will be used for each specific parameter or target analyte that can achieve the required detection limits. The following should be addressed:

1. For SW-846 analytical methods, reference SW-846 and the analysis methods (by method number), including all sample preparation methods (U.S. EPA 1998).

2. For analysis by modified- or non-SW-846 methods, the analytical procedure and method detection limits to be used should be documented in the format of a Standard Operating Procedure (SOP).

2.5 FIELD AND LABORATORY QUALITY ASSURANCE/QUALITY CONTROL

It is important to establish programs to ensure the reliability and validity of field and analytical laboratory data, as part of the overall groundwater monitoring program. Refer to SW-846 (U.S. EPA 1998) for requirements and guidance on establishing and maintaining field and laboratory quality control programs. In general, laboratory quality assurance and quality control (QA/QC) programs should address the following areas:

- Control samples
- Acceptance criteria
- Deviations
- Corrective action for sampling and analysis procedures
- Data handling
- Laboratory control samples
- Method blanks
- Matrix-specific effects

The SAP should explicitly describe the QA/QC program that will be used in the field and laboratory in the Quality Assurance Project Plan (QAPP). The QAPP describes the quality assurance and quality control (QA/QC) protocols necessary to achieve the objectives dictated by the intended use of the data. Control protocols include the procedures for sample collection, preservation, chain-of-custody, and transport, calibration and maintenance of instruments, processing verification, storage, and reporting of data, and other relevant QA/QC procedures required to maintain precision and accuracy of the data. The DQOs of the project should be described in terms of precision, accuracy, completeness, representativeness and comparability for both field activities (sampling, measurements and screening) and laboratory analyses, including the project required acceptance limits and means to achieve these QA objectives. Refer to U.S. EPA 1992b, for a discussion of DQOs. In addition, the preventative maintenance procedures to be used for the field and laboratory instruments and the groundwater monitoring system should be described. A

table showing the type of maintenance to be performed and the frequency is appropriate. Many groundwater samples are analyzed at commercial laboratories. In these cases, the SAP should be used by the laboratory analyzing samples.

Both field and laboratory QC samples should be prepared during the sampling event. The following samples in Table 2 should be analyzed with each batch of samples (generally every 20 samples):

TABLE 2. Quality Control Samples

Type	Typical Frequency	Purpose
Field duplicate	1 per 10 samples	Evaluate precision of sampling and analysis procedures.
Matrix spike	1 per 20 samples or 1 per analytical batch	Evaluate accuracy of analytical procedures.
Matrix spike duplicate	1 per 20 samples or 1 per analytical batch	Evaluate accuracy of analytical procedures.
Equipment blank	1 per set of equipment cleaned. Collect one sample at the beginning of sampling and one each day after decontamination.	Evaluate cross-contamination caused by non-dedicated equipment.
Field blank	1 per day	Evaluate whether contaminants introduced by ambient air during sample collection.
Trip blank	1 per sample cooler containing VOCs	Evaluate whether VOC contamination introduced during sampling, storage, or shipment.
Temperature blank	1 per sample cooler	Evaluate whether sample preservation requirements are achieved.

The matrix-specific detection limit should be determined. This determination does not need to be made on a sample batch basis, but should be made whenever the matrix is suspected to have altered, or as frequently as necessary to document that the matrix has not altered. For an aquifer with relatively static hydrogeological characteristics, this may mean making a matrix-specific detection limit determination twice annually.

2.5.1 Field QA/QC Program

The SAP should provide for the routine collection and analysis of QC samples. Various types of QC samples and blanks should be used to verify that the sample collection and handling process has not affected the quality of the samples. Blanks are to be subjected to the same analysis as the groundwater. Contaminants found in the blanks may be the result of: (1) inter-action between the sample and the container, (2) contaminated rinse water, (3) contaminated preservatives, or (4) a handling procedure that alters the sample analysis results. The concentrations of any contaminants found in the blanks should not be used to correct the groundwater data. The contaminant concentrations should be noted, and if the concentrations are more than an order of magnitude greater than the field sample results, groundwater should be re-sampled. All field QC samples should be prepared exactly as regular investigation samples

with regard to sample volume, containers, and preservation. The QC samples should be prepared and analyzed for all of the required monitoring parameters.

Other QA/QC practices such as sampling equipment calibration and decontamination procedures and chain-of-custody procedures should be described in the SAP. Refer to the previous sections in this document for a discussion of these practices.

2.5.2 Laboratory QA/QC Program

The SAP should provide for the use of control samples, as defined in SW-846 (U.S. EPA 1998). Appropriate statistical procedures (U.S. EPA 1992a) should be used to monitor and document performance and to implement an effective program to resolve testing problems (e.g. instrument maintenance, operator training). Data from control samples (e.g. spiked samples, duplicates and blanks) should be used as a measure of performance or as an indicator of potential sources of cross-contamination. When contaminants are detected in QA/QC samples (field, trip, or lab blanks), the accompanying sample results should be appropriately flagged. All sample results shall be reported unadjusted for blank results or spike recoveries. All QA/QC data should be submitted to DTSC with the groundwater monitoring sample results.

2.5.3 Groundwater Data Quality Evaluation

A groundwater sampling and analysis program produces a variety of hydrogeological, geophysical, and groundwater constituent concentration (GWCC) data. This section pertains primarily to the evaluation of GWCC data. The GWCC data may be presented to the owner or operator via electronic transmittal or on reporting sheets. These data then should be compiled and statistically analyzed prior to submittal to the lead regulatory agency. If data are to be transmitted electronically, the procedures should be discussed with the lead regulatory agency staff to ensure that all software and hardware being used are compatible with the electronic data formats for integration in the agencies database.

The following guidelines should help to ensure that units of measure associated with data values are reported consistently and unambiguously:

- The units of measure should accompany each target analyte. Laboratory data sheets that include the statement "values are reported in ppm unless otherwise noted" should generally be discouraged, and at least should be examined in detail by the technical reviewer.

- The units of measure for a given target analyte should be consistent throughout the report.

- Data should be reported correctly for the results to be valid. Chemical analysis, laboratory reporting, computer automation, and report preparation data should be generated and processed to avoid mistakes and ensure completeness and full documentation.

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APPENDIX A
Sampling Devices

GRAB SAMPLERS

The four main varieties of bailers are the single check valve, double check valve, messenger, and syringe bailers. Bailers are among the simplest groundwater sampling devices. A bailer is simply a rigid tube that fills with water when lowered into the well; when raised back out of the well, it is sealed on one or both ends by some mechanism. The groundwater sample is subsequently transferred into sample containers from the bailer. Bailers are relatively inexpensive to purchase or fabricate (especially the single and double check valve bailers), easy to clean, portable, simple to operate, and require no external power source (U.S. EPA, 1983).

Disadvantages are that their use can be time consuming and labor intensive and that the transfer of water to a sample container may significantly alter the chemistry of groundwater samples due to degassing, volatilization or aeration. Use of a bailer may also result in an increase of turbidity that may affect analysis results. Bailers should not be used to sample groundwater that will be analyzed for volatile organic compounds, unless a bailer is the only available method, or the bailer is used for sampling LNAPL or DNAPL or the use of a bailer is approved by the lead regulatory agency.

Bailers used to collect groundwater samples and the cable used to raise and lower the bailer should be constructed of material (e.g., fluorocarbon resin, Teflon®, stainless steel, HDPE, or PVC) which does not cause analyte concentrations alteration or cause loss of analytes via sorption. Ideally the bailer should be easy to disassemble to facilitate cleaning and decontamination.

Bailers should never be dropped into a well and should be removed from the well in a manner that causes as little agitation to the sample as possible. For example, the bailer should not be removed in a jerky fashion or be allowed to continually bang against the well casing as it is drawn up. To ensure consistent samples, DTSC recommends that the bailer be submerged only to a depth necessary for filling, except when the bailer is being used to sample a DNAPL. When transferring the sample from a bailer to a container, a bottom emptying device with a valve to allow the water to slowly drain from the bailer should be used. The sample should be allowed to run down the sides of the collection bottle to avoid excessive agitation of the sample.

POSITIVE DISPLACEMENT (SUBMERSIBLE) MECHANISMS

Positive displacement mechanisms for groundwater sampling include gear drive electric submersible pumps, bladder pumps, helical rotor electric submersible pumps, gas-drive piston pumps, and centrifugal pumps. The following sections briefly describe each of these types of pumps and their applications and limitations with regard to collecting groundwater samples.

Bladder Pumps

Bladder pumps (also referred to as gas squeeze pumps) consist of a flexible membrane often enclosed in a rigid stainless steel housing. A strainer or screen attaches below the bladder to filter any material that could clog either of the check valves located above and below the bladder. Water enters the membrane through the lower check valve; compressed gas is injected into the cavity between the housing and bladder. The sample is transported through the upper check valve and into the discharge line. The upper check valve prevents water from reentering the bladder. The process is repeated to cycle the water to the surface. Bladder volumes (e.g., volume per cycle) and sampler geometry can be modified to increase the sampling abilities of the pump. Automated control systems are available to control gas flow rates and pressurization cycles. Bladder pumps prevent contact between the gas and water sample and can be fabricated entirely of fluorocarbon resin and stainless steel. A nearly continuous flow can be attained with

the proper cycles. Pohlmann and Hess (1988) determined that bladder pumps can be suitable for collecting groundwater samples for almost any given organic or inorganic constituent. Disadvantages of bladder pumps include the large gas volumes required to actuate the pump (especially for sampling deep groundwater), and potential bladder rupture. Hence, gas cylinders or air compressors are needed to power the pumps. If using a gasoline or diesel powered air compressor, the compressor should be placed downwind of the wellhead.

If a bladder pump has been chosen as the sampling device, it should be operated at a discharge rate of 100 ml/min or less when collecting samples for volatiles analysis. Higher flow rates can increase the loss of volatile constituents and can cause fluctuation in pH and pH-sensitive analytes. Bladder pumps should be operated in a continuous, non-pulsating manner so that they do not produce samples that are aerated in the return tube or upon discharge. Once the portions of the sample reserved for the analysis of volatile components have been collected, a higher pumping rate may be used, particularly if a large sample volume will be collected. The pump lines should be cleared at a low rate before collecting samples for volatiles analysis, or else the sample collected will be from when the pump was rapidly operating. Running the pump at a low flow rate will take time and may deter the use of a bladder pump when the wells are deep and the lines are long.

Helical Rotor Electric Submersible Pumps

The helical rotor electric submersible pump consists of a sealed electric motor that powers a helical rotor. The water sample is forced up a discharge line by an electrically driven rotor-stator assembly by centrifugal action. Submersible pumps provide relatively high discharge rates for water withdrawal at depths beyond suction lift capabilities. Pumping rates vary depending upon the size of the motor and sampling depth. Heat buildup should be monitored when low (less than 1 gpm) pump rates are used. Heat shields or pump shrouds may be used to aid in heat buildup. A submersible pump provides higher extraction rates than the majority of other methods. However, considerable sample agitation in the well results from operating at high rates, and this may cause alteration of the sample chemistry. In addition, high pumping rates can introduce sediments from the formation into the well that are immobile under ambient groundwater flow conditions, resulting in the collection of unrepresentative samples for metals due to potential partitioning upon contact with the sediment. Further, the potential exists for the introduction of trace metals into the sample from the pump materials. Steam cleaning of the unit followed by rinsing with unchlorinated, deionized water in between sampling is recommended. Where the submersible pump is used for sampling, those parts of the pump in contact with water should be constructed of stainless steel.

Gas-drive Piston Pumps

A piston pump uses compressed air to force a piston to raise the sample to the surface. A typical design consists of a stainless steel chamber between two pistons. The alternating chamber pressurization activates the piston, which allows water entry during the suction stroke of the piston, and forces the sample to the surface during the pressure stroke. Pumping rates of 500 ml/min have been reported from 30.5 meters; sampling depths of 150 meters are possible. The piston pump provides continuous sample withdrawal at depths greater than is possible with most other approaches. Nevertheless, contribution of trace elements from the stainless steel and brass fittings is a potential problem. Pumping rates at depths less than 150 meters are generally slower than with other pumps.

Centrifugal Pumps

A centrifugal (sometimes called impeller) pump is similar to the direct line pump except that a centrifugal pump is connected to the tubing at the surface rather than a vacuum pump. A foot valve is usually attached to the end of the well tubing to assist in priming the extraction tube. A centrifugal pump is capable of delivering large quantities of water, against high as well as low head conditions, with good efficiency. Under field conditions a centrifugal pump has an average suction lift capability of 20-25 feet (6.1-7.6 meters) (Driscoll, 1986). Although relatively high pumping rates can be attained, centrifugal pumps cause sample agitation.

SUCTION LIFT PUMPS

Suction lift pumps can be categorized as direct line and peristaltic. The direct line pump requires lowering one end of a plastic tube into a well or piezometer. The surface end of the tube is connected to a two-way stoppered bottle, and a manually or auxiliary powered vacuum pump is attached to a second tube that leads from the bottle. A check valve is attached between the second tube and the vacuum pump to maintain a constant vacuum control.

A peristaltic pump (also called rotary peristaltic) is a self-priming, low-volume suction pump consisting of a rotor and three ball bearing rollers. Plastic tubing inserted around the pump rotor is squeezed by the rollers as they revolve in a circle around the rotor. One end of the tubing is placed into the well while the other end is connected directly to a two-way stoppered flask. As the rotor revolves, water is drawn into the sampling tube and discharged into the collection vessel. A drive shaft connected to the rotor head can be extended so that multiple rotor heads can be attached to a single drive shaft. The withdrawal rate of peristaltic pumps can be carefully regulated by adjusting the rotor head revolution. The system can be arranged so that the sample contacts only fluorocarbon resin tubing prior to entering the sample container. A limiting factor is the depth of sampling; the depth of sample collection is limited to situations where the potentiometric level is less than 25 feet below land surface (Nielsen, 1991). The suction lift approach offers a simple retrieval method for shallow monitoring wells. However, the method can result in sample mixing and oxidation. Degassing and loss of volatiles also occur to some extent. A peristaltic pump provides a lower sampling rate and less agitation than direct line or centrifugal pumps. Hence, when sampling for VOCs, the sampling results will be biased low. Accordingly, sampling with suction lift pumps should be done for screening purposes only.

GAS CONTACT PUMPS

Gas contact sampling devices include gas-lift and gas-drive devices.

Gas-Lift Pumps

An air or gas lift pump allows collection of groundwater samples by bubbling air or gas at depth in the well. Sample transport occurs primarily as a result of the reduced specific gravity of the water being lifted to the surface. Water is forced up a discharge pipe, which may be the outer casing or a smaller diameter pipe inserted into the well. Air or gas lift methods can result in considerable sample agitation and mixing in the well, and are not permitted for collecting samples for chemical analysis. The considerable pressures required for deep sampling can result in significant redox and pH changes.

Gas-Drive Pumps

Gas drive (gas displacement) pumps are distinguished from air lift pumps by their method of sample transport. Gas displacement pumps force a column of water under linear flow conditions to the surface without extensive mixing of the pressurized gas and water. A vacuum can also be used to assist the gas. The disadvantages of a gas drive pump are that the drive gas comes into contact with the water and therefore, can be a source of contamination; also, the pump can be difficult to clean.

Gas control pumps should not be used for the collection of groundwater samples at hazardous substances release sites due to the potential for sample alteration.

PASSIVE SAMPLERS

The effectiveness of a single passive sampler in a well is dependent on groundwater flow through the well screen and whether the water quality directly adjacent to the sampler is representative of the entire screened interval. If there is intrabore flow, multiple intervals contributing to flow, or varying concentrations of contaminants vertically within the screened interval, then multiple passive samplers within a well may be more appropriate for sampling the well. (Vroblesky, D.A., 2001a, Vroblesky, D.A., 2001b).

Passive samplers are classified on the basis of sampler mechanism and nature of the collected sample. A more detailed discussion of these samplers can be found at www.ltrcweb.org/Documents/DSP_4.pdf.:

1. *Devices that recover a grab well water sample.*
Samples are an instantaneous representation of conditions at the sampling point at the moment of sample collection.
- HydraSleeve™ Samplers
- Snap Sampler™

2. *Devices that rely on diffusion of the analytes for the sampler to reach and maintain equilibrium with the sampled medium.*
Samples are time-weighted toward conditions at the sampling point during the latter portion of the deployment period. The degree of weighting depends on analyte and device-specific diffusion rates. Typically, conditions during the last few days of sampler deployment are represented.
- Regenerated-Cellulose Dialysis Membrane Samplers
- Nylon-Screen Passive Diffusion Samplers (NSPDS)
- Passive Vapor Diffusion Samplers (PVDs)
- Peeper Samplers
- Polyethylene Diffusion Bag Samplers (PDBs)
- Rigid Porous Polyethylene Samplers (RPPS)

3. *Devices that rely on diffusion and sorption to accumulate analytes in the sampler.*
Samples are a time-integrated representation of conditions at the sampling point over the entire deployment period. The accumulated mass and duration of deployment are used to calculate analyte concentrations in the sampled medium.
- Semi-Permeable Membrane Devices (SPMDs)
- GORE™ Sorber Module
- Polar Organic Chemical Integrative Samplers (POCIS)
- Passive In-Situ Concentration Extraction Sampler (PISCES)

HYDRASLEEVE™ SAMPLERS

HydraSleeve™ samplers are designed to recover groundwater from monitoring wells without purging and can be used to sample a wide spectrum of analytes (e.g., VOCs, semi-volatile organics, and metals) and can also be used to sample low-yielding wells. HydraSleeve™ samplers allow recovery of discrete samples from the screened zone where the sampler is activated, with no drawdown and minimal agitation of the water column. The reed valve design keeps the device closed except during sample collection, thereby assuring that the sample is collected from the desired interval within the screened zone.

SNAP SAMPLER™

The Snap Sampler™ is designed to collect groundwater samples in situ without purging. The Snap Sampler™ utilizes specialty double-ended bottles closed while submerged in the well. A well re-equilibration period is recommended for passive deployments. The Snap Sampler™ VOA vial can be used directly in common laboratory auto sampler equipment, so samples are not exposed to ambient air during retrieval, field preparation, or analysis at the lab unless manual dilutions or re-analyses are required. Utilizing minimum sample volume requirements, this sampler can be used for analyzing many different physical and/or chemical water quality parameters, including VOCs and metals.

REGENERATED-CELLULOSE DIALYSIS MEMBRANE SAMPLERS

Regenerated-cellulose dialysis membrane samplers collect groundwater samples for inorganic ionic constituents as well as organic constituents using a diffusion-type sampler. Dialysis membrane samplers can be used to sample a wide spectrum of water-quality parameters.

NYLON-SCREEN PASSIVE DIFFUSION SAMPLERS (NSPDS)

NSPDS are diffusion based samplers developed to sample for a broader range of analytes than can be collected by the PDB sampler. Larger volumes can be obtained by using a stack of bottles in the same mesh sleeve.

PASSIVE VAPOR DIFFUSION (PVD) SAMPLERS

Passive-vapor-diffusion (PVD) samplers have been used successfully as reconnaissance tools at many hazardous waste sites. The primary use of PVD samplers is to identify locations where VOC contaminated groundwater is discharging into surface water. PVD samplers also have been used as passive-soil-gas samplers in the unsaturated zone. USGS Water-Resources Investigations Report 02-4186 provides detailed guidance for construction and use of PVD samplers.

PEEPER SAMPLERS

Peeper samplers (a.k.a. Hesslein in-situ Pore Water Sampler) are rigid structures, which can hold volumes of water separated from the environment by porous membranes to monitor constituents in saturated environments. Peeper samplers rely on diffusion of the analytes to reach equilibrium between the sampler and the pore water. Peeper samplers (i.e., dialysis cells) have been used for in situ monitoring of dissolved constituents in saturated sediments. The Peeper sampler measures pore water analyte concentrations. Peeper samplers can be stacked in a specially designed corer so that they sample discrete near-surface depths.

POLYETHYLENE DIFFUSION BAG (PDB) SAMPLERS

The Polyethylene Diffusion Bag (PDB) sampler was developed in the late 1990's and has become a widely accepted technique for determining concentrations of VOCs in groundwater monitoring wells. PDBs are installed in groundwater monitoring wells, at one or more intervals below the water surface in the well screen, and left in place under natural flow conditions. PDBs are also used in saturated sediments in and around surface water to approximate VOC discharge to the surface.

RIGID POROUS POLYETHYLENE SAMPLERS (RPPS)

Rigid porous polyethylene samplers (RPPSs) are diffusion based samplers developed to sample for a broader range of analytes than can be collected by the PDB sampler. The RPPS is constructed from thin sheets of foam-like porous polyethylene with pore sizes of 6 to 15 microns. The sampler is filled with water free of the target analytes, capped at both ends, and placed inside a mesh liner, which is subsequently attached to a deployment rope using cable-ties and deployed in a well.

SEMI-PERMEABLE MEMBRANE DEVICES (SPMDS)

Semi-permeable Membrane Devices (SPMDs) are designed to sample chemicals dissolved in surface water, mimicking the bioconcentration of organic contaminants into the fatty tissues of organisms. The SPMD enables concentration of trace organic contaminant mixtures for analysis, toxicity assessments, and toxicity identification evaluation. It is designed to sample lipid or fat-soluble (nonpolar or hydrophobic) semi-volatile organic chemicals from water and air. The SPMD is an integrative sampler which accumulates analyte mass over a deployment period ranging from days to months. SPMDs provide a highly reproducible means for monitoring contaminant levels, and are largely unaffected by many environmental stressors affecting biomonitoring organisms.

GORE™ SORBER MODULE

The GORE™ Sorber Module relying on diffusion and sorption to accumulate analytes in the sampler. These modules yield a total mass of analytes that can be correlated with analyte concentrations in water

or air. This device can be utilized to sample soil gas in the vadose zone and dissolved organic analytes in water saturated soils or in groundwater monitoring wells. This device has been used in both fresh and saltwater environments, including sampling sediments in marshes, streams, river embankments, and coastal settings.

POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS)

The Polar Organic Chemical Integrative Sampler (POCIS) is designed to sample water-soluble (polar or hydrophilic) organic chemicals from aqueous environments. This device relies on diffusion and sorption to accumulate a total mass of analytes. The residence period ranges from weeks to months. The POCIS samples chemicals from the dissolved phase, mimicking the respiratory exposure of aquatic organisms. The POCIS also concentrates trace organic contaminants for toxicity assessments and toxicity identification evaluation (TIE) approaches.

PASSIVE IN-SITU CONCENTRATION EXTRACTION SAMPLER (PISCES)

The Passive In Situ Concentration Extraction Sampler (PISCES) is designed to sample non-polar or hydrophobic organic chemicals in surface water. This device relies on diffusion and sorption to accumulate a total mass of analytes. The residence period ranges from one day to one month. PISCES consist of a membrane, typically low-density polyethylene (LDPE), forming one end of a metal container filled with an organic solvent, typically hexane or isooctane (2,2,4- trimethylpentane). Analyte uptake is driven by the preferential partitioning of nonionic organic chemicals from water to the solvent. The membrane excludes ionic, high molecular-weight natural organic matter, and particulates.

Where site conditions are not fully characterized, side-by-side comparisons between multiple well-volume purge, low flow groundwater sampling, and diffusion bag sampling methods may be necessary to determine which method should be used to yield the most representative data. The sampling method ultimately used should be discussed with the lead agency before implementation.

Additional information on the use of these samplers can be found at www.itrcweb.org/Documents/DSP_4.pdf

PACKER ASSEMBLAGES

A packer assembly provides a means by which to isolate and sample a discrete interval in the subsurface. Hydraulic- or pneumatic-activated packers are wedged against the casing wall allowing sample collection from an isolated portion of the well. The packers deflate for vertical movement within the well and inflate when the desired depth is attained. Packers are usually constructed from some type of rubber or rubber compound and can be used with submersible, gas lift, and suction pumps.

If pumps are operated at a low rate, a packer assembly allows sampling of low-yielding wells, and wells that would otherwise produce turbid samples. A number of different samplers can be placed within the packers depending upon the analytical specifications for sample testing. One disadvantage is that vertical movement of water outside the well (e.g., if used in the screened interval) is possible with packer assemblages, depending upon the pumping rate and formation properties. Another possible disadvantage is that the packer material may contribute undesirable organic constituents to the water sample.

TABLE A1. Generalized guide for selection of groundwater sampling devices. Modified from U.S. EPA (1991).

Device Type		Device	Groundwater Parameters													
			Inorganic							Organic					Radioactive	
			EC	pH	Redox	Major ions	Trace metals	Nitrate/ Fluoride	Dissolved gases	Non-Volatile	Volatile	TOC	TOX	Coliform bacteria	Radium	Gross alpha and beta
Portable Sampling Devices	Grab	Open Bailer	!	G	G	!	!	!	G	!	G	G	G	!	!	G
		Point Source Bailer	!.	!	!	!	!	!	G	!	G	!	!	!	!	G
		Passive Diffusion Bags	G	G	G	G	G	G	G	G	Limited constituents	G	G	G	G	G
		Bat Sampler	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Hydropunch	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Geoprobe	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Syringe Sampler	!	!	!	!	!	!	G	!	!	G	G	!	!	!
	Positive Displacement (Submersible)	Gear-drive	!	!	!	!	!	!	!	!	!	!	!	G	!	!
		Bladder Pump	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Helical Rotor (electrical)	!	!	!	!	!	!	!	!	!	!	!	G	!	!
		Piston Pump (gas drive)	!	G	G	!	!	!	G	!	!	G	G	G	!	!
		Centrifugal (low-rate)	!	!	!	!	!	!	!	!	!	!	!	!	!	!
	Suction Lift	Peristaltic	!	G	G	!	!	!	G	!	G	G	G	!	!	!
		Pneumatic	!	!	!	!	!	!	G	!	G	G	G	!	!	!

Acronyms and Abbreviations

EC electroconductivity
Redox oxidation/reduction potential
TOC total organic carbon
TOX total organic halides

Symbols

! Device is generally suitable for application (assuming device is properly operated and is constructed of suitable materials).
G Device may be unsuitable or untested for application.

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	Not Applicable
Method Name	Low-flow purging for groundwater sampling
Version	10.1.0
Method Date	February 18, 2010
Reasons for Method Revision	Annual Review; no revisions were made

Reviewed by:

Kelly Lechuga
Laboratory Technician II
Lancaster Sampling Receiving

Signature _____ Date 3/24/10

Approved by:

Lavern Tamoria
Supervising Chemist
QA/Sample Receiving

Signature _____ Date 3/24/10

Final Approval:

Maria Pang
Assistant Manager of
the Laboratories

Signature _____ Date 4/22/10

LOW-FLOW PURGING AND SAMPLING FOR GROUNDWATER

INTRODUCTION

Monitoring wells in the Antelope Valley area have been used over a number of years to assess groundwater quality. The monitoring wells vary in depth from less than 15 feet (MW120 in Lancaster) to 540 feet (MW2 in Palmdale). Several wells are located in the same vicinity while others are more isolated (see Attachments 1 and 2).

1. Scope and Application

1.1 This procedure is applicable to groundwater.

1.2 This procedure explains the limiting factors involved in sampling low-flow monitoring wells, lists the hazards and appropriate safety precautions needed, and identifies what is required of personnel performing these tasks.

1.3 This procedure describes the protocol for LACSD low-flow sampling of monitoring wells in Lancaster and Palmdale. It explains the proper procedures to collect field data including depth-to-water (DTW), purge wells, and to collect samples for later analysis by both Districts' and contract laboratories.

2. Summary of Procedure

2.1 Measure the depth-to-water (DTW) of the well by lowering an engineering tape down the well casing until the probe contacts the surface of the water.

If more than one well in the local area will be sampled, take DTW measurements of the wells **before any** purging or sampling is performed. Compare the DTW measurements, and sample the shallow well first, the deeper well next and the deepest well last.

2.2 Assemble the well purging equipment. This includes connecting the hose valves to the control box and N_2/CO_2 canisters, attaching the control box to the well port, and connecting the flow cell to the discharge line on the well assembly.

2.3 Adjust the settings on the control box according to the well specifications. Purge the well line, and allow the field parameters to reach stability prior to sampling the well water.

3. Sample Handling and Preservation

3.1 Groundwater samples are collected using appropriate containers and preservation methods as directed in Standard Methods for the Examination of Water and Wastewater.

3.2 After collection, and as soon as possible, place samples into an ice chest with ice to keep their temperatures at 0-6°C during transport from the sample location to Sample Receiving (SRC).

3.3 Once removed from the ice chest, the samples are placed into a refrigerator or walk-in cooler to maintain the cold temperature for storage.

4. Interferences

4.1 A flattened well bladder, or ruptured bladders/tubing, will result in insufficient sample volumes produced.

4.2 Blowing sand can affect sampling by contaminating the samples being collected. It can also damage the equipment, as sand particles can become lodged in the pressure relief valves, preventing the required pressure from being available for sampling.

4.3 Extreme temperatures are often a deterrent to well sampling. Highs above 100°F can cause the gases in the N_2/CO_2 tanks to expand, resulting in uncontrolled pressure fluctuations. Below freezing temperatures are common in the Antelope Valley during the winter months. Since the check valve on the well pump prevents backflow of water into the well, extreme low temperatures can freeze water contained within the upper feet of the pump tubing.

4.4 Fluctuating groundwater tables within the Antelope Valley can prevent well sampling. When the water levels are within three feet of the top of the well inlet, the water pressure becomes insufficient to provide the force necessary to raise the water to ground level. Additionally, any significant drawdown will prevent the bladder from fully inflating, resulting in poor sample volumes per purge.

5. Apparatus

5.1 Compressed nitrogen gas (cylinder size T is preferable), or compressed carbon dioxide gas (for use with the backpack sampler)

5.2 Depth-to-Water Meter [Micro Purge basics (MP) 30 Drawdown Meter]

5.3 Control Boxes (MP10 Controller)

5.4 Backpack Sampler (MP15 Control & Power Pack)

5.5 Hydrolab (MP20 Flow Cell)

5.6 Tubing (Bonded 1/4" and 3/8" Teflon-lined; 1/2" Tygon)

5.7 Hoses (200' extended reach reel; various hoses with male/female quick connects)

6. Reagents

6.1 Not Applicable.

7. Procedure

7.1 Use and Care of the Equipment

7.1.1 Check all equipment connections and hoses prior to and after each use to ensure that no damage has occurred.

7.1.1.1 Examine depth-to-water meter probe and individual flow cell probes for possible fouling of membranes after each use.

7.1.2 All equipment should be stored securely in the vehicle lock boxes to prevent possible theft or damage from the elements.

7.2 Calibration

7.2.1 The flow cell is calibrated in accordance with the specifications as outlined in the QED Flow Cell User's Guide.

7.2.1.1 Calibrations are performed at the start of each sampling day.

7.3 Procedural Guidelines

7.3.1 Depth-to-Water. This instrument measures depth readings from a set point at the top of the well port to a level even with the water's surface. It is composed of a probe at the end of a graduated engineering tape. The probe sends an audible signal when it comes in contact with the water.

7.3.1.1 Test the meter prior to use to ensure that the batteries are charged, as this allows the signal to be heard.

7.3.1.2 Switch the speaker control to on, and press the I/O button (unit on/off) to test for signal strength.

7.3.1.3 Note the tubing length for the well in question as this will approximate how far the probe may need to be fed into the well.

7.3.1.4 Remove the cap from the well assembly, and slowly lower the probe into the well casing. As there is no brake provided on the handle of the DTW meter, lower the line at a controllable rate.

7.3.1.5 When the probe sounds, indicating that it has come in contact with water, slowly reel in the line until the probe is just even with the water's surface.

7.3.1.6 Measurements will be taken at a point even with the top of the well port. This number should be documented as the DTW for the appropriate well.

7.3.1.7 Allowable drawdown is equal to 1/4 the distance from DTW to the pump.

7.3.1.7.1 For example, if the DTW is 310', and the tubing length is 330', drawdown equal to 5' is allowed for that well.

7.3.1.8 Switch the drawdown control to on, and lower the probe to the depth indicated as the maximum allowable drawdown. With drawdown control on, the probe will sound when it loses contact with water.

7.3.1.9 Attach one end of the cable connection to the control port on the meter; the other end should be attached to the control box.

7.3.1.9.1 This connector signals the controller when maximum allowable drawdown is reached, causing the unit to pause pumping until the well has recovered.

7.3.1.10 The DTW meter has its own port on the well assembly, so the line should remain in place during the well purge to monitor any possible drawdown.

7.3.1.10.1 **As purging and sampling can impact nearby wells, it is important, prior to purging wells adjacent to one another, to take all applicable DTW measurements.**

7.3.1.11 If the probe loses contact with water for more than ten minutes, the unit will automatically shut off; press the I/O button to turn it on again.

7.3.2 Assembly of Well Purging Equipment - This includes the gas cylinders, control box, hydrolab, tubing, and hoses. Most of the well equipment is fitted with male/female quick connects, allowing for easy assembly.

7.3.2.1 Nitrogen gas cylinders – These will typically only be used on deep Palmdale wells, although all wells can be purged using nitrogen gas.

7.3.2.1.1 Carefully remove the cover from the top of the cylinder, and screw on the protective sampling cap.

7.3.2.1.2 Screw the regulator to the cylinder, and use a wrench to ensure a secure connection.

7.3.2.1.3 Attach the other end of the hose to the "Air In" valve of the control box.

7.3.2.2 Backpack Sampler - This is a combination of a small aluminum CO_2 canister with attached control box. The backpack sampler is used for more remote Lancaster wells when accessibility is an issue. It consists of one hose, which attaches directly to the well cap.

7.3.2.2.1 Switch the power button to "on" after connecting the hose, and then turn on the cylinder.

7.3.2.2.2 Adjust the pressure by pulling out slightly on the regulator knob and then turning it to the correct psi setting.

7.3.2.2.3 All other adjustments are made as with the other control box.

7.3.2.3 Control Box

7.3.2.3.1 Attach one end of the connector hose to the "Air Out" valve of the control box, and the other end of the hose to the appropriate connection on the well cap.

7.3.2.3.2 Make sure the nitrogen cylinder is securely attached.

7.3.2.3.3 Open the valve slightly on the top of the cylinder, allowing the pressure to equilibrate.

7.3.2.3.4 Once the pressure is stable, and it is determined that no gas is leaking through the various connections, open the valve all the way, and lock the cylinder cap.

7.3.2.4 Hydrolab

7.3.2.4.1 The probes on the hydrolab are stored in a casing containing tap water, which prevents the probes from drying out.

7.3.2.4.2 Unscrew this cover, making sure not to spill the water, and set to the side.

7.3.2.4.3 With the hydrolab equipment is a flow-thru cell that allows water to pass over the probes and escape through a short piece of tygon tubing.

7.3.2.4.4 Attach the flow-thru cell to the probe end of the hydrolab. The flow-thru cell prevents the water from contacting air directly, thereby providing representative groundwater samples.

7.3.2.4.5 The hydrolab is equipped with a circulator, which provides a continuously fresh sample to the sensors, allowing for reliable dissolved oxygen measurements.

7.3.3 Well Purging. The wells are tagged with all the necessary information to perform a successful sampling event.

7.3.3.1 The control box should be set to the predetermined ID number (the ID numbers are pre-determined based on the number of cycles per minute, as well as discharge and refill rates).

7.3.3.1.1 This is achieved by pressing the "Mode" button once to get the curser underneath the ID number, and then using the up and down arrows to make any adjustments.

7.3.3.1.2 If needed, the cursor can be moved to the next column over using the (⇔) Value button.

7.3.3.2 Once set to the given ID number, adjust the pressure throttle to reflect the maximum pressure indicated on the well tag. This will result in the flow maintaining a slow and steady rate.

7.3.3.3 Press the start button to begin sampling.

7.3.3.4 It is recommended to have a 5-gallon bucket or similar to collect any water discharged.

7.3.3.5 Use a plastic beaker to measure the amount of water released per cycle. The estimated mL/min should be indicated on the well tag, as should the minimum purge volume (a value equal to the amount of water present in the tubing).

7.3.3.6 Once this minimum volume has been purged, connect the hydrolab to the dedicated well tubing with the tygon inflow tubing on the flow cell.

7.3.3.6.1 The connector may need to be replaced, depending on the tubing diameter of the well (various connector pieces are provided with the flow cell).

7.3.3.7 The hydrolab will gradually fill with water. When the flow cell is full, tilt the hydrolab to remove any air pockets surrounding the probes.

7.3.3.8 Use the left/right arrows to move the cursor to the purge scan icon marked "Store", and press Enter. This will execute the selected icon, and begin tracking for stabilization of the selected parameters.

7.3.3.8.1 The hydrolab will automatically store data every three minutes, with back-up data every five minutes.

7.3.3.9 When at least three consecutive readings have been taken that satisfy the stabilization range, the hydrolab will sound; note the time and record temperature (T), pH, dissolved oxygen (DO), and specific conductivity (SPC) from hydrolab readout.

7.3.3.10 Any water samples to be collected should be taken through the dedicated tubing to prevent possible sample contamination, so disconnect the hydrolab, and collect the requisite samples.

7.3.3.11 When the needed samples have been collected, push the hold "][" button on the control box. This will halt any further refill/discharge cycles.

7.3.3.12 Turn the gas cylinder to off. Turn the control box throttle counter-clockwise to release any remaining pressure in the "Air Out" line, and disconnect the hose from "Air Out" to the well cap.

7.3.3.13 Turn the throttle clockwise as far as possible, and push the hold button twice.

7.3.3.13.1 This will allow any air/nitrogen remaining in the "Air In" line to escape.

7.3.3.14 When no more gas is escaping, turn the throttle back to zero and disconnect the compressor/cylinder.

7.3.3.15 **Be sure to remove the regulator from the gas cylinder prior to transport.**

7.4 Troubleshooting Procedure

7.4.1 For wells that fail to produce water or have decreasing purge rates, try the following:

7.4.1.1 Pressure may drop/be insufficient for purging; check control box.

7.4.1.2 Adjust the discharge/refill times to ensure water is still being released at the end of the discharge cycle, and that at least five seconds of refill time remain when venting ceases.

7.4.1.3 Attach control box directly to compressor/cylinder without the extension hose.

7.4.1.4 Check that all attachments are secure.

7.4.1.5 Check tubing length for well. Occasionally there is too little water present to purge and sample. The water should be at least 3 feet over the top of the pump to provide sufficient lift.

7.4.1.6 Look for possible drawdown; the well may not have enough refill time to meet demand.

7.4.1.7 Examine the tubing for kinks or tears. Depending on outside temperatures, the water may also freeze in the lines, which will prevent sampling from occurring.

7.4.2 If the hydrolab is not stabilizing:

7.4.2.1 Make sure there is no air trapped in the flow cell.

7.4.2.2 Check the previous data frames to determine which constituent is preventing stabilization from being reached (typically DO)

7.4.2.3 The hydrolab can store up to 200 data frames; make sure it has not reached this maximum. If it has, "Fail" will be displayed in the parameter readings.

7.4.2.4 Look for the circulator icon on the unit screen. If the icon is not displayed, press and hold the "Esc" button to toggle it on again.

7.5 Hazard Control Measures and Limitations

7.5.1 Take proper precautions when approaching well sites to prevent vehicles from becoming trapped in the sand. Examine the ground if necessary, and contact the project engineer if the site is inaccessible.

7.5.2 *Sampling cannot be conducted under extreme climatic conditions. Freezing temperatures prevent sampling, as the water remains in the tubing at or above ground level. In addition, sampling also cannot occur on excessively hot days (temperatures in excess of 100 °F), due to pressure gradients in the hoses and control box.*

7.5.3 When opening well covers, do so carefully and open away from you to avoid possible contact with any animals, spiders, etc, which may be present.

7.5.4 Always carry a first-aid kit, and know the protocol to follow (contact persons, location of emergency care facilities, etc) in case of emergency. Familiarizing oneself with these procedures **in advance** may aid in avoiding confusion should incidents occur.

7.5.5 Snakes, coyotes, and other animals may be encountered, and spiders (black widows in particular) are an almost certainty. Vagrants are known to occasionally frequent areas near some of the well sites, so it is advisable to be alert to one's surroundings.

7.5.6 Improper connections could result in leakage of N_2/CO_2 gas, or hoses thrashing about if they become disconnected. Ensure that all connections are secure and tightened prior to turning on gas cylinders.

8. Calculations

8.1 Not Applicable.

9. Quality Assurance Guidelines

9.1 Not Applicable.

10. Method Performance

10.1 Not Applicable.

11. References

11.1 Laboratory Section: Procedures for the Characterization of Water and Wastes, 4th Edition, 1989, James D. Lehner.

11.2 QED Flow Cell User's Guide, March 2004.

Sanitation Districts of Los Angeles County
Laboratories Section

METHOD APPROVAL FORM

Method Number	Not Applicable
Method Name	Lysimeter Sampling of Groundwater
Version	10.1.0
Method Date	April 28, 2010
Reasons for Method Revision	Annual review; no revisions were made

Written by:

Julie Randol
Laboratory Technician II
Lancaster Sample Receiving

Julie Randol
Signature

04-28-10
Date

Approved by:

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Signature

4/28/10
Date

Final Approval:

Maria Pang
Assistant Manager of
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M. Pang
Signature

4/28/10
Date

LYSIMETER SAMPLING OF GROUNDWATER

INTRODUCTION

LACSD utilizes lysimeters in Palmdale to sample vadose zone water quality in sites used for both effluent land application and water recycling through agricultural reuse. The vadose zone monitoring stations (VZ) are located within the authorized effluent management site, and consist of pressure-vacuum (p-v) samplers and passive capillary (pcap) lysimeters. Several samplers are installed at each station at depths of approximately 5 feet and 15 feet in order to provide a vertical distribution of vadose zone pore-fluid chemistry (see the District's amended Vadose Zone Monitoring Plan for lysimeter specifications and approximate locations).

1. Scope and Application

   1.1 This procedure is applicable to vadose-zone groundwater.

   1.2 This procedure explains the limiting factors involved in sampling lysimeters, lists the hazards and appropriate safety precautions needed, and identifies what is required of personnel performing these tasks.

   1.3 This procedure describes the protocol for LACSD sampling of lysimeters in Lancaster and Palmdale. It explains the proper procedures to collect samples for laboratory analysis.

2. Summary of Procedure

   2.1 Connect the sample line for the passive capillary lysimeter to the portable pump using the vacuum flask and appropriate hose.

   2.2 Turn on the portable pump, and use the vacuum flask to collect any water present in the system.

   2.3 For pressure-vacuum samplers, use the vacuum line attachment to set a vacuum, which allows the lysimeter to draw water from the surrounding area. The following day, use the pressure hose attachment to retrieve any water collected over the previous 24 hours.

3. Sample Handling and Preservation

   3.1 Lysimeter samples are collected using appropriate containers and preservation methods as directed in Standard Methods for the Examination of Water and Wastewater.

3.2 After collection, and as soon as possible, place samples into an ice chest with ice to keep the temperatures at 0-6°C during transport from the sample location to Sample Receiving.

3.3 Once removed from the ice chest, the samples are placed into a refrigerator or walk-in cooler to maintain the cold temperature for storage.

4. Interferences

4.1 The samplers are located in agricultural reuse areas, so the amount of water present is significantly affected by the amount of water being applied at that time. Fallow pivot areas may produce no moisture until crops are reintroduced.

4.2 Blowing sand can affect sampling by contaminating the samples being collected. It can also damage the equipment, as sand particles can become lodged in the pressure relief valves, preventing the required pressure from being available for sampling.

4.3 Agricultural equipment may occasionally cause damage by tearing through the sample lines during routine maintenance of the crop area.

5. Apparatus

5.1 Portable Electric P-V Pump Model 2008 (Soil Moisture Equipment Corp.)

5.2 Vacuum flask

5.3 Pressure/Vacuum Gauges

6. Reagents

6.1 Not Applicable.

7. Procedure

7.1 Use and Care of the Equipment

7.1.1 Check all equipment connections, gauges and lines prior to and after each use to ensure that no damage has occurred.

7.1.2 All equipment should be stored securely in the vehicle lock boxes to prevent possible theft or damage from the elements.

7.2 Calibration

7.2.1.1 Not applicable

7.3 Procedural Guidelines

7.3.1 Assembly of Sampling Equipment -

7.3.1.1 P-V Pump – The pump has two attachment sites, labeled "pressure port" and "vacuum port".

7.3.1.1.1 The pressure port is used exclusively for collection with the p-v samplers. It should be connected to the tubing of the lysimeter via the pressure gauge.

7.3.1.1.2 The vacuum port is used when producing a vacuum on the lysimeter sample lines. Attach the vacuum gauge to the appropriately labeled connector on the pump. Connect the gauge to the pressure-vacuum line if sampling a p-v lysimeter, or to a vacuum flask if collecting water from a pcap.

7.3.1.2 Vacuum Flask – This is only used when sampling pcap lysimeters, and allows for the collection of water samples while maintaining a vacuum on the sampling line.

7.3.1.2.1 Connect the vacuum gauge to the portable p-v pump. Attach the gauge to the flask via the short piece of black tubing attached to the hose barb.

7.3.1.2.2 Remove the o-ring from the pcap lysimeter blue sample line, and attach the sample line to the stopper of the flask via the attached green tubing.

7.3.2 Lysimeter Sampling – At the top of the lysimeter are two lines with 3/16" tubing attached to the end of each. These ends are folded over, and held in place with an o-ring that maintains the vacuum (where applicable) within the sample line. Note: the tubing may remain pinched after removing the o-rings. Roll or manipulate the tubing to allow for free flow of air/water.

7.3.2.1 Passive Capillary Lysimeters – Pcap lysimeters use a tipping spoon to collect water without applying pressure to the system.

The lysimeters contain a calibration line and a vacuum sampling line.

7.3.2.1.1 Attach the vacuum gauge to the p-v pump, and connect it to the blue sample line via the vacuum flask.

7.3.2.1.2 Turn on the pump, making sure to keep the flask in an upright position to prevent any sample from accidentally entering the pump via the gauge.

7.3.2.1.3 Any water present in the system will register on the gauge as an increase in in-Hg, and enter the vacuum flask via the sample line.

7.3.2.1.4 When all the water has been cleared from the system, turn the p-v pump off and record the amount of water collected in the flask. Remove the connections, and dispense the collected sample into the appropriate containers.

7.3.2.1.5 Replace the o-ring on the end of the sample line.

7.3.2.2 Pressure-Vacuum Sampler – P-V samplers collect water by first applying a vacuum to the line, and then using pressure to force the collected water to the surface. They consist of a p-v line and a separate sample line.

7.3.2.2.1 Connect the black p-v line to the pump via the vacuum gauge. Remove the o-ring at this time.

7.3.2.2.2 Turn on the pump, and allow it to run until the vacuum gauge reads approximately 20in-Hg.

7.3.2.2.3 Fold over the end of the p-v line to maintain the vacuum. Turn off the pump and replace the o-ring.

7.3.2.2.4 Wait 24 hours to allow the vacuum in the line to pull the interstitial moisture from the surrounding soil. This provides a sufficient period for collection without exceeding the holding time for required constituents.

7.3.2.2.5 Attach the black p-v line to the pump via the pressure gauge. Remove the o-ring from both the p-v line and the corresponding green sample line.

7.3.2.2.6 Turn on the pump, and allow it to run until no more moisture comes through the sample line.

7.3.2.2.7 Any sample present should be collected directly into the sample container(s). Debris can build up on the ends of the sample line, so allow it to run a second or two before directing the flow into the collection jar.

7.3.2.2.8 When there is no more moisture present in the system, turn off the pump. Remove the connections and replace the o-rings on the ends of the p-v and sample lines.

7.4 Troubleshooting Procedure

7.4.1 For lysimeters that fail to produce water, try the following:

7.4.1.1 Examine the tubing for kinks or tears. Depending on outside temperatures, the water may also freeze in the lines, which will prevent sampling from occurring.

7.4.1.2 Ensure that the correct gauge is being used, and that it is attached to the appropriate location on the p-v pump.

7.4.1.3 For p-v samplers, check that the vacuum has not been lost. If the vacuum was not maintained during the 24-hour period, it is possible that there may be a break in the line.

7.5 Hazard Control Measures and Limitations

7.5.1 Take proper precautions when approaching lysimeter sites to prevent vehicles from becoming trapped in the sand. Examine the ground if necessary, and contact the project engineer if the site is inaccessible.

7.5.2 ***Sampling cannot be conducted under extreme climatic conditions. Freezing temperatures prevent sampling, as the water remains in the tubing at or above ground level.***

7.5.3 When opening lysimeter covers, do so carefully and open away from you to avoid possible contact with any animals, spiders, etc, which may be present.

7.5.4 Always carry a first-aid kit, and know the protocol to follow (contact persons, location of emergency care facilities, etc) in case of emergency. Familiarizing oneself with these procedures **in advance** may aid in avoiding confusion should incidents occur.

7.5.5 Snakes, coyotes, and other animals may be encountered, and spiders (black widows in particular) are an almost certainty. Vagrants are known to occasionally frequent areas near some of the lysimeter sites, so it is advisable to be alert to one's surroundings.

8. Calculations

8.1 Not Applicable.

9. Quality Assurance Guidelines

9.1 Not Applicable.

10. Method Performance

10.1 Not Applicable.

11. References

11.1 Laboratory Section: Procedures for the Characterization of Water and Wastes, 4th Edition, 1989, James D. Lehner.

11.2 Vadose Zone Monitoring System Installation Report, October 2005, Cascade Earth Sciences.

Appendix C

Chain of Custody / Login Sheet

San Jose Creek Water Quality Laboratory
Chain of Custody/Login Sheet

162722 [redacted] Collect Date: 09/01/2010 Matrix: W

WO: PALM_WELL_Q Profile: 361-PalmWellsSR Sample ID: Palmdale Qtrly Well Template

Project Manager: Lavern Tamoria Ext: 3038 BU: 2013002 UID: B669

Collector: Julie Randol Receive Temperature: °C

Container List:

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

FLDCOLOR - Field Color
FLDDO - DissolvedOxygen(membrane) FLD
FLDDTW - Field Depth To Water
FLDPH - Field pH
FLDSM2510B - Conductivity, Field
FLDTEMP - Field Temperature (Water)
FLDTURB - Field Turbidity

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

E351.2 - Nitrogen, Kjeld,Total,FIA(TKN)
SM4500NH3G - Ammonia, FIA

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

SM2540C - Residue, Filterable (TDS)
SM4500NO3F - Nitrite-nitrate, Total, FIA

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

SM5540C - Surfactants (MBAS)

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

E200.8_W - Metals EPA 200.8 ICPMS (water)

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

SM5310C - Total Organic Carbon

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

SUB8015BDO - TPH as Diesel/TPH as Oil(Sub)

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

SUB8015GRO - TPH as Gasoline (Sub)
TOTAL_TPH - Total Petroleum Hydrocarbons

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

E625 - EPA 625 Semi-Volatiles

Work Lab	Container Type	Preservative
[redacted]	[redacted]	[redacted]

E300.0 - Anions by IC, EPA 300.0

Sample Inspection: (If "No" selected for any parameter, enter comment on sample and notify PM)

All Containers Intact?	Yes	No	N/A	NOTES:
Containers labeled correctly (match COC)?	Yes	No	N/A	
Proper containers for requested analyses?	Yes	No	N/A	
Containers preserved properly?	Yes	No	N/A	
VOA vial(s) free of headspace?	Yes	No	N/A	
Samples received on Ice?	Yes	No	N/A	If N/A, directly from:
Metals sample preserved with HNO3?	Yes	No	N/A	If No, report to bench analyst immediately
Special Handling Instructions?	Yes	No	N/A	If Yes, report to bench analyst

Relinquished by:_____ Date:_____ ___:___ Received by:_____ Date:_____ ___:___

Relinquished by: Date: : Received by: Date: :

Appendix D

Minimum Reporting Levels for Priority Pollutants

Minimum Levels for Individual Priority Pollutants As Listed in MRP, Attachment E

Inorganic Constituents

Name of Constituent	Minimum Level	Unit
Antimony	5	µg/L
Arsenic	1	µg/L
Asbestos*	0.2	MFL >10 µm
Beryllium	1	µg/L
Cadmium	0.25	µg/L
Chromium, Total	2	µg/L
Chromium, Hexavalent	5	µg/L
Copper	0.5	µg/L
Cyanide, Total	5	µg/L
Lead	0.5	µg/L
Mercury	0.0005	µg/L
Nickel	5	µg/L
Selenium	5	µg/L
Silver	1	µg/L
Thallium	1	µg/L
Zinc	10	µg/L

* Monitoring not required, according to MRP

Pesticides and PCBs

Name of Constituent	Minimum Level	Units
4,4-DDD	0.05	µg/L
4,4-DDE	0.05	µg/L
4,4-DDT	0.01	µg/L
Alpha-Endosulfan	0.02	µg/L
Alpha-BHC	0.01	µg/L
Aldrin	0.005	µg/L
Beta-Endosulfan	0.01	µg/L
Beta-BHC	0.005	µg/L
Chlordane	0.1	µg/L
Delta-BHC	0.005	µg/L
Dieldrin	0.01	µg/L
Endosulfan Sulfate	0.05	µg/L
Endrin	0.01	µg/L
Endrin Aldehyde	0.01	µg/L
Heptachlor	0.01	µg/L
Heptachlor Epoxide	0.01	µg/L
Lindane (Gamma-BHC)	0.02	µg/L
Aroclor 1016*	0.5	µg/L
Aroclor 1221*	0.5	µg/L
Aroclor 1232*	0.5	µg/L
Aroclor 1242*	0.5	µg/L
Aroclor 1248*	0.5	µg/L
Aroclor 1254*	0.5	µg/L
Aroclor 1260*	0.5	µg/L
Toxaphene	0.5	µg/L
2,3,7,8-TCDD (dioxin)*	5.00×10^{-6}	µg/L

* Monitoring not required, according to MRP

Volatile Organic Constituents

Name of Constituent	Minimum Level	Units
1,1-Dichloroethane	1	µg/L
1,1-Dichloroethene	0.5	µg/L
1,1,1-Trichloroethane	2	µg/L
1,1,2-Trichloroethane	0.5	µg/L
1,1,2,2-Tetrachloroethane	0.5	µg/L
1,2-Dichlorobenzene	2	µg/L
1,2-Dichloroethane	0.5	µg/L
1,2-Dichloropropane	0.5	µg/L
1,2,4-Trichlorbenzene	5	µg/L
1,3-Dichlorobenzene	2	µg/L
1,3-Dichloropropylene (cis & trans)	0.5	µg/L
1,4-Dichlorobenzene	2	µg/L
Acrolein	5	µg/L
Acrylonitrile	2	µg/L
Benzene	0.5	µg/L
Bromoform	2	µg/L
Bromomethane (Methyl Bromide)	2	µg/L
Carbon Tetrachloride	0.5	µg/L
Chlorobenzene (monochlorobenzene)	2	µg/L
Chloroethane	2	µg/L
2-Chloroethyl vinyl ether	1	µg/L
Chloroform	0.5	µg/L
Chloromethane (Methyl Chloride)	2.0	µg/L
Dibromochloromethane	0.5	µg/L
Dichlorobromomethane	0.5	µg/L
Dichlormethane (Methylene Chloride)	2	µg/L
Ethylbenzene	2	µg/L
Hexachlorobenzene	1	µg/L
Hexachlorobutadiene	1	µg/L
Hexachlorethane	1	µg/L
Naphthalene	10	µg/L
Tetrachloroethylene	0.5	µg/L
Toluene	2	µg/L
Trans 1,2-Dichloroethylene	1	µg/L
Trichloroethylene	2	µg/L
Vinyl Chloride	0.5	µg/L

Semi-Volatile Organic Constituents (Base/Neutral and Acid Extractable)

Name of Constituent	Minimum Level	Units
1,2-Benzanthracene (Benzo(a)Anthracene)	5	µg/L
1,2-Diphenylhydrazine	1	µg/L
2-Chlorophenol	2	µg/L
2,4-Dichlorophenol	1	µg/L
2,4-Dimethylphenol	2	µg/L
2,4-Dinitrophenol	5	µg/L
2,4 Dinitrotoluene	5	µg/L
2,4,6 Trichlorophenol	10	µg/L
2,6 Dinitrotoluene	5	µg/L
2-Nitrophenol	10	µg/L
2-Chloronaphthalene	10	µg/L
3,3-Dichlorobenzidine	5	µg/L
3,4-Benzofluoranthene (Benzo(b)fluoranthene)	10	µg/L
4-Chloro-3-Methylphenol	5	µg/L
4,6-Dinitro-2-methylphenol	10	µg/L
4-Nitrophenol	10	µg/L
4-Bromophenyl phenyl ether	10	µg/L
4-Chlorophenyl phenyl ether	5	µg/L
Acenaphthene	1	µg/L
Acenaphthylene	10	µg/L
Anthracene	10	µg/L
Benzidine	5	µg/L
Benzo(a)pyrene	2	µg/L
Benzo(g,h,i)perylene	5	µg/L
Benzo(k)fluoranthene	2	µg/L
Bis(2-chloroethoxy)methane	5	µg/L
Bis(2-chloroethyl)ether	1	µg/L
Bis(2-chloroisopropyl)ether	10	µg/L
Bis(2-ethylhexyl)phthalate	5	µg/L
Butyl benzyl phthalate	10	µg/L
Chrysene	5	µg/L
di-n-Butyl phthalate	10	µg/L
di-n-Octyl phthalate	10	µg/L
Dibenzo(a,h)-anthracene	0.1	µg/L
Diethyl phthalate	2	µg/L
Dimethyl phthalate	2	µg/L
Fluoranthene	10	µg/L
Fluorene	10	µg/L
Hexachlorocyclopentadiene	5	µg/L
Indeno(1,2,3,cd)-pyrene	0.05	µg/L
Isophorone	1	µg/L
N-Nitrosodiphenyl amine	1	µg/L
N-Nitrosodimethyl amine	5	µg/L
N-Nitroso-di-n-propyl amine	5	µg/L
Nitrobenzene	10	µg/L
Pentachlorophenol	1	µg/L
Phenanthrene	5	µg/L
Phenol	1	µg/L
Pyrene	10	µg/L