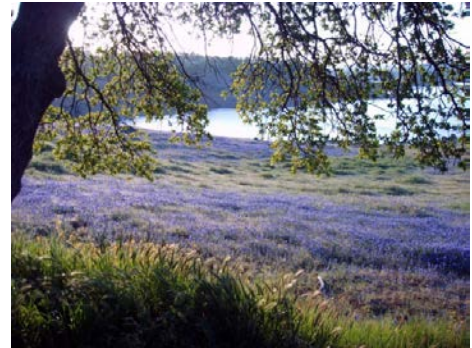


**WATER QUALITY ASSESSMENT
STUDY REPORT
DON PEDRO PROJECT
FERC NO. 2299**



Prepared for:
Turlock Irrigation District – Turlock, California
Modesto Irrigation District – Modesto, California

Prepared by:
HDR Engineering, Inc.

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Water Quality Assessment Study Report

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	Part 2: Sampling Ambient Waters For Trace Metals at EPA Water Quality Levels
	Part 3: Data Review and Verification Checklist
Attachment B	Calibration and Quality Assurance Documentation
Attachment C	Water Quality Element Data

List of Acronyms

ac	acres
ACEC	Area of Critical Environmental Concern
AF	acre-feet
ACOE	U.S. Army Corps of Engineers
ADA	Americans with Disabilities Act
ALJ	Administrative Law Judge
APE	Area of Potential Effect
ARMR	Archaeological Resource Management Report
AWQC	Ambient Water Quality Criteria
BA	Biological Assessment
BDCP	Bay-Delta Conservation Plan
BLM	U.S. Department of the Interior, Bureau of Land Management
BLM-S	Bureau of Land Management – Sensitive Species
BMI	Benthic macroinvertebrates
BMP	Best Management Practices
BO	Biological Opinion
CalEPPC	California Exotic Pest Plant Council
CalSPA	California Sports Fisherman Association
CAS	California Academy of Sciences
CCC	Criterion Continuous Concentrations
CCIC	Central California Information Center
CCSF	City and County of San Francisco
CCVHJV	California Central Valley Habitat Joint Venture
CD	Compact Disc
CDBW	California Department of Boating and Waterways
CDEC	California Data Exchange Center
CDFA	California Department of Food and Agriculture
CDFG	California Department of Fish and Wildlife (as of January 2013; previously, Department of Fish and Game)
CDMG	California Division of Mines and Geology
CDOF	California Department of Finance

CDPH.....	California Department of Public Health
CDPR.....	California Department of Parks and Recreation
CDSOD.....	California Division of Safety of Dams
CDWR.....	California Department of Water Resources
CE.....	California Endangered Species
CEII.....	Critical Energy Infrastructure Information
CEQA.....	California Environmental Quality Act
CESA.....	California Endangered Species Act
CFR.....	Code of Federal Regulations
cfs.....	cubic feet per second
CGS.....	California Geological Survey
CMAP.....	California Monitoring and Assessment Program
CMC.....	Criterion Maximum Concentrations
CNDDB.....	California Natural Diversity Database
CNPS.....	California Native Plant Society
CORP.....	California Outdoor Recreation Plan
CPUE.....	Catch Per Unit Effort
CRAM.....	California Rapid Assessment Method
CRLF.....	California Red-Legged Frog
CRRF.....	California Rivers Restoration Fund
CSAS.....	Central Sierra Audubon Society
CSBP.....	California Stream Bioassessment Procedure
CT.....	California Threatened Species
CTR.....	California Toxics Rule
CTS.....	California Tiger Salamander
CVRWQCB.....	Central Valley Regional Water Quality Control Board
CWA.....	Clean Water Act
CWHR.....	California Wildlife Habitat Relationship
Districts.....	Turlock Irrigation District and Modesto Irrigation District
DLA.....	Draft License Application
DO.....	Dissolved Oxygen
DPRA.....	Don Pedro Recreation Agency
DPS.....	Distinct Population Segment

EA	Environmental Assessment
EC	Electrical Conductivity
EFH	Essential Fish Habitat
EIR	Environmental Impact Report
EIS.....	Environmental Impact Statement
EPA	U.S. Environmental Protection Agency
ESA.....	Federal Endangered Species Act
ESRCD.....	East Stanislaus Resource Conservation District
ESU	Evolutionary Significant Unit
EWUA.....	Effective Weighted Useable Area
FERC.....	Federal Energy Regulatory Commission
FFS	Foothills Fault System
FL.....	Fork length
FMU	Fire Management Unit
FOT	Friends of the Tuolumne
FPC	Federal Power Commission
ft/mi.....	feet per mile
FWCA.....	Fish and Wildlife Coordination Act
FYLF.....	Foothill Yellow-Legged Frog
g.....	grams
GIS	Geographic Information System
GLO	General Land Office
GPS	Global Positioning System
HCP.....	Habitat Conservation Plan
HHWP.....	Hetch Hetchy Water and Power
HORB	Head of Old River Barrier
HPMP.....	Historic Properties Management Plan
ILP.....	Integrated Licensing Process
ISR	Initial Study Report
ITA.....	Indian Trust Assets
kV	kilovolt
m	meters
M&I.....	Municipal and Industrial

MCL.....	Maximum Contaminant Level
mg/kg	milligrams/kilogram
mg/L.....	milligrams per liter
mgd	million gallons per day
mi	miles
mi ²	square miles
MID.....	Modesto Irrigation District
MOU	Memorandum of Understanding
MPN.....	Most Probable Number
MSCS.....	Multi-Species Conservation Strategy
msl.....	mean sea level
MVA	Megavolt Ampere
MW	megawatt
MWh	megawatt hour
mya.....	million years ago
NAE	National Academy of Engineering
NAHC	Native American Heritage Commission
NAS.....	National Academy of Sciences
NAVD 88	North American Vertical Datum of 1988
NAWQA	National Water Quality Assessment
NCCP	Natural Community Conservation Plan
NEPA	National Environmental Policy Act
ng/g	nanograms per gram
NGOs	Non-Governmental Organizations
NHI	Natural Heritage Institute
NHPA.....	National Historic Preservation Act
NISC	National Invasive Species Council
NMFS.....	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NOI	Notice of Intent
NPS	U.S. Department of the Interior, National Park Service
NRCS	National Resource Conservation Service
NRHP	National Register of Historic Places

NRI.....	Nationwide Rivers Inventory
NTU	Nephelometric Turbidity Unit
NWI.....	National Wetland Inventory
NWIS	National Water Information System
NWR	National Wildlife Refuge
NGVD 29	National Geodetic Vertical Datum of 1929
O&M.....	operation and maintenance
OEHHA.....	Office of Environmental Health Hazard Assessment
ORV	Outstanding Remarkable Value
PAD.....	Pre-Application Document
PDO.....	Pacific Decadal Oscillation
PEIR.....	Program Environmental Impact Report
PGA.....	Peak Ground Acceleration
PHG.....	Public Health Goal
PM&E	Protection, Mitigation and Enhancement
PMF.....	Probable Maximum Flood
POAOR.....	Public Opinions and Attitudes in Outdoor Recreation
ppb.....	parts per billion
ppm	parts per million
PSP	Proposed Study Plan
QA.....	Quality Assurance
QC	Quality Control
RA	Recreation Area
RBP	Rapid Bioassessment Protocol
Reclamation	U.S. Department of the Interior, Bureau of Reclamation
RM	River Mile
RMP	Resource Management Plan
RP.....	Relicensing Participant
RSP	Revised Study Plan
RST	Rotary Screw Trap
RWF.....	Resource-Specific Work Groups
RWG	Resource Work Group
RWQCB.....	Regional Water Quality Control Board

SC.....	State candidate for listing under CESA
SCD.....	State candidate for delisting under CESA
SCE	State candidate for listing as endangered under CESA
SCT	State candidate for listing as threatened under CESA
SD1	Scoping Document 1
SD2	Scoping Document 2
SE.....	State Endangered Species under the CESA
SFP	State Fully Protected Species under CESA
SFPUC	San Francisco Public Utilities Commission
SHPO	State Historic Preservation Office
SJRA	San Joaquin River Agreement
SJRGa	San Joaquin River Group Authority
SJTA	San Joaquin River Tributaries Authority
SM.....	Standard Methods
SPD	Study Plan Determination
SRA.....	State Recreation Area
SRMA	Special Recreation Management Area or Sierra Resource Management Area (as per use)
SRMP	Sierra Resource Management Plan
SRP	Special Run Pools
SSC	State species of special concern
ST.....	California Threatened Species under the CESA
STORET	Storage and Retrieval
su	standard unit
SWAMP	Surface Water Ambient Monitoring Program
SWE	Snow-Water Equivalent
SWRCB.....	State Water Resources Control Board
TAC.....	Technical Advisory Committee
TAF	thousand acre-feet
TCP	Traditional Cultural Properties
TDS	Total Dissolved Solids
TID	Turlock Irrigation District
TMDL	Total Maximum Daily Load

TOC.....	Total Organic Carbon
TPH.....	Total Petroleum Hydrocarbon
TRT	Tuolumne River Trust
TRTAC	Tuolumne River Technical Advisory Committee
UC	University of California
USDA.....	U.S. Department of Agriculture
USDOC	U.S. Department of Commerce
USDOI	U.S. Department of the Interior
USFS	U.S. Department of Agriculture, Forest Service
USFWS	U.S. Department of the Interior, Fish and Wildlife Service
USGS	U.S. Department of the Interior, Geological Survey
USR.....	Updated Study Report
UTM.....	Universal Transverse Mercator
VAMP	Vernalis Adaptive Management Plan
VELB	Valley Elderberry Longhorn Beetle
VRM	Visual Resource Management
WPT	Western Pond Turtle
WSA.....	Wilderness Study Area
WSIP	Water System Improvement Program
WWTP	Wastewater Treatment Plant
WY	water year
µS/cm	microSeimens per centimeter

1.0 INTRODUCTION

1.1 Background

Turlock Irrigation District (TID) and Modesto Irrigation District (MID) (collectively, the Districts) are the co-licensees of the 168-megawatt (MW) Don Pedro Project (Project) located on the Tuolumne River in western Tuolumne County in the Central Valley region of California. The Don Pedro Dam is located at river mile (RM) 54.8 and the Don Pedro Reservoir has a normal maximum water surface elevation of 830 ft above mean sea level (msl; NGVD 29). At elevation 830 ft, the reservoir stores over 2,000,000 acre-feet (AF) of water and has a surface area slightly less than 13,000 acres (ac). The watershed above Don Pedro Dam is approximately 1,533 square miles (mi²). The Project is designated by the Federal Energy Regulatory Commission (FERC) as project no. 2299.

Both TID and MID are local public agencies authorized under the laws of the State of California to provide water supply for irrigation and municipal and industrial (M&I) uses and to provide retail electric service. The Project serves many purposes including providing water storage for the beneficial use of irrigation of over 200,000 ac of prime Central Valley farmland and for the use of M&I customers in the City of Modesto (population 210,000). Consistent with the requirements of the Raker Act passed by Congress in 1913 and agreements between the Districts and City and County of San Francisco (CCSF), the Project reservoir also includes a “water bank” of up to 570,000 AF of storage. CCSF may use the water bank to more efficiently manage the water supply from its Hetch Hetchy water system while meeting the senior water rights of the Districts. The “water bank” within Don Pedro Reservoir provides significant benefits for CCSF’s 2.6 million customers in the San Francisco Bay Area.

The Project also provides storage for flood management purposes in the Tuolumne and San Joaquin rivers in coordination with the U.S. Army Corps of Engineers (ACOE). Other important uses supported by the Project are recreation, protection of the anadromous fisheries in the lower Tuolumne River, and hydropower generation.

The Project Boundary extends from RM 53.2, which is one mile below the Don Pedro powerhouse, upstream to RM 80.8 at an elevation corresponding to the 845 ft contour (31 FPC 510 [1964]). The Project Boundary encompasses approximately 18,370 ac with 78 percent of the lands owned jointly by the Districts and the remaining 22 percent (approximately 4,000 ac) owned by the United States and managed as a part of the U.S. Bureau of Land Management (BLM) Sierra Resource Management Area.

The primary Project facilities include the 580-foot-high Don Pedro Dam and Reservoir completed in 1971; a four-unit powerhouse situated at the base of the dam; related facilities including the Project spillway, outlet works, and switchyard; four dikes (Gasburg Creek Dike and Dikes A, B, and C); and three developed recreational facilities (Fleming Meadows, Blue Oaks, and Moccasin Point Recreation Areas). The location of the Project and its primary facilities is shown in Figure 1.1-1.

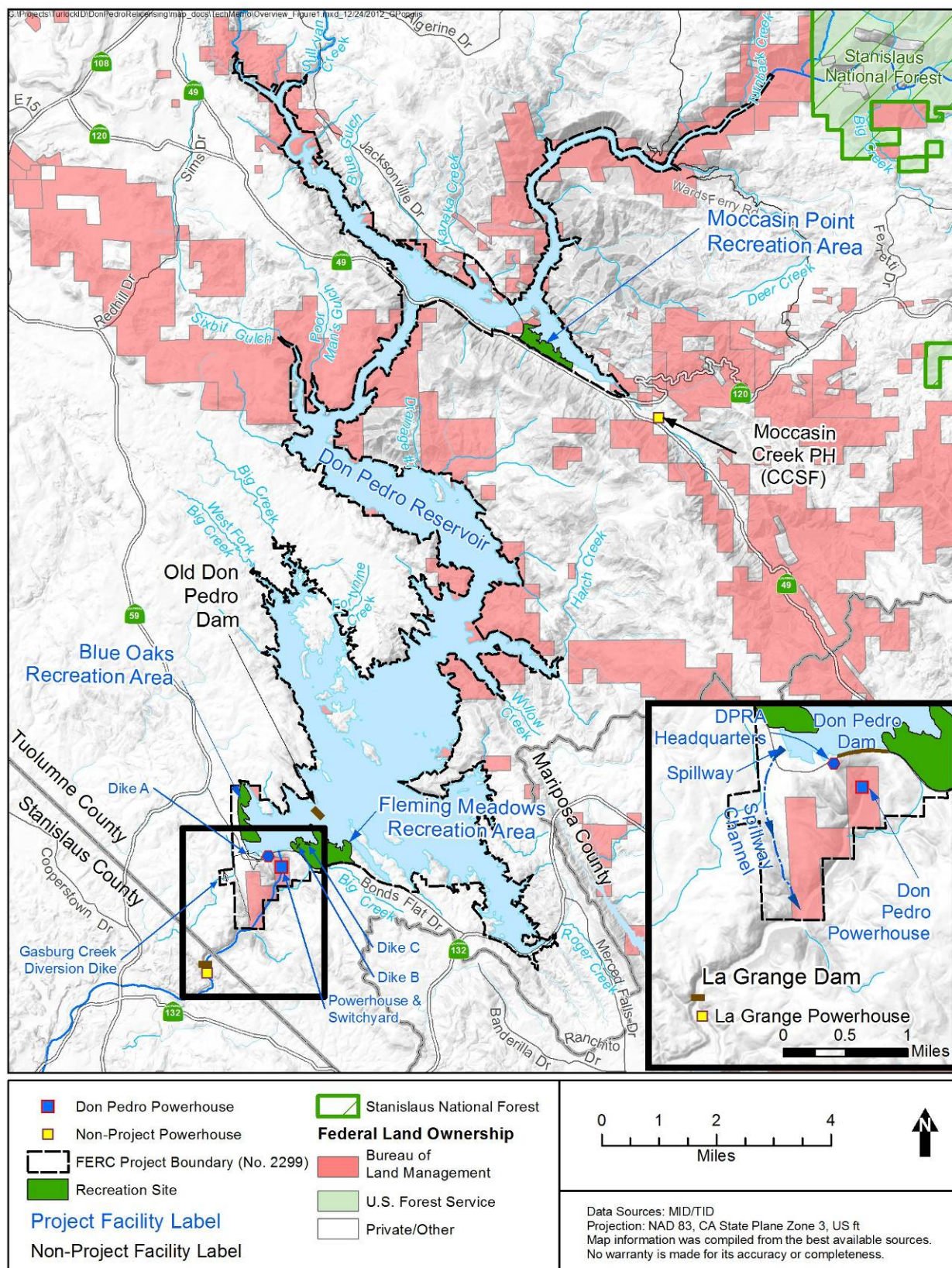


Figure 1.1-1. Don Pedro Project location.

1.2 Relicensing Process

The current FERC license for the Project expires on April 30, 2016, and the Districts will apply for a new license no later than April 30, 2014. The Districts began the relicensing process by filing a Notice of Intent and Pre-Application Document (PAD) with FERC on February 10, 2011, following the regulations governing the Integrated Licensing Process (ILP). The Districts' PAD included descriptions of the Project facilities, operations, license requirements, and Project lands as well as a summary of the extensive existing information available on Project area resources. The PAD also included ten draft study plans describing a subset of the Districts' proposed relicensing studies. The Districts then convened a series of Resource Work Group meetings, engaging agencies and other relicensing participants in a collaborative study plan development process culminating in the Districts' Proposed Study Plan (PSP) and Revised Study Plan (RSP) filings to FERC on July 25, 2011 and November 22, 2011, respectively.

On December 22, 2011, FERC issued its Study Plan Determination (SPD) for the Project, approving, or approving with modifications, 34 studies proposed in the RSP that addressed Cultural and Historical Resources, Recreational Resources, Terrestrial Resources, and Water and Aquatic Resources. In addition, as required by the SPD, the Districts filed three new study plans (W&AR-18, W&AR-19, and W&AR-20) on February 28, 2012 and one modified study plan (W&AR-12) on April 6, 2012. Prior to filing these plans with FERC, the Districts consulted with relicensing participants on drafts of the plans. FERC approved or approved with modifications these four studies on July 25, 2012.

Following the SPD, a total of seven studies (and associated study elements) that were either not adopted in the SPD, or were adopted with modifications, formed the basis of Study Dispute proceedings. In accordance with the ILP, FERC convened a Dispute Resolution Panel on April 17, 2012 and the Panel issued its findings on May 4, 2012. On May 24, 2012, the Director of FERC issued his Formal Study Dispute Determination, with additional clarifications related to the Formal Study Dispute Determination issued on August 17, 2012.

This study report describes the objectives, methods, and results of the Water Quality Assessment Study (W&AR-01) as implemented by the Districts in accordance with FERC's SPD and subsequent study modifications and clarifications. On January 17, 2013, the Districts filed the Initial Study Report for the Don Pedro Project. In response to a request made by the State Water Resources Control Board in a letter to FERC dated March 11, 2013, the Districts have edited the Water Quality Assessment Report to add a description of the Hydro Units (Hus), update the reference to the most recent Basin Plan (CVRWQCB 1998 with amendments), and remove the reference to temperature benchmark values; temperature analysis will be conducted in consultation with relicensing participants using the W&AR-03 Reservoir Temperature Model. No other comments were received. Documents relating to the Project relicensing are publicly available on the Districts' relicensing website at www.donpedro-relicensing.com.

1.3 Study Plan

The ongoing operation and maintenance (O&M) of the Project may affect water quality. The effect may be direct (e.g., release of a pollutant from a Project facility), indirect (e.g., due to

public recreation), or cumulative (i.e., combined effect of a Project-related activity with a non-Project activity).

In accordance with the FERC-approved study plan, Water Quality Assessment (W&AR-01), the Districts investigated the quality of surface water potentially affected by the Project, including water within Don Pedro Reservoir and in the Tuolumne River immediately downstream of Don Pedro Dam. A sample was collected downstream of La Grange Dam. Background conditions were also sampled, by sampling the Tuolumne River upstream of the Project. Woods Creek and Sullivan Creek, both tributaries to Don Pedro Reservoir, were dry during the sampling period and were not sampled.

The water quality investigation consisted of two elements: (1) a general water quality element and (2) a recreation-related water quality element. Each element of the study was conducted at the time and place where Project effects were expected to be most pronounced, if they occur. During the 2012 late summer season, surface water samples were collected from five locations upstream, within, and downstream of the Project and samples were analyzed for 55 general physical water quality parameters and chemical constituents. In-reservoir sites were sampled at two depths: within 1-2 meters of the reservoir's surface and within 1-2 meters of the bottom. During the 30 days surrounding and including the 2012 Independence Day holiday, five episodes of surface water samples were collected adjacent to 12 reservoir recreation sites and analyzed for bacteria and hydrocarbons.

This study addresses the following issues identified in Section 6.0 of the PAD:

- **Issue:** Effects of the Project and Project recreation on water quality (excluding water temperature) and compliance with the Central Valley Regional Water Quality Control Board's (CVRWQCB) Water Quality Control Plan for the Sacramento River and San Joaquin River Basins, fourth edition (Basin Plan).
- **Issue:** Effect of the Project on compliance with the SWRCB's CWA Section 303(d) List of TMDL Priority Schedule.
- The water quality parameter temperature was addressed through other studies. Water temperature in the reservoir is the subject of the W&AR-03 Reservoir Temperature Model Study Plan, while water temperature modeling downstream of Don Pedro Reservoir is the subject of the Lower Tuolumne River Temperature Model Study Plan (W&AR-16).

2.0 STUDY GOALS AND OBJECTIVES

This technical memorandum presents the results for the Water Quality Assessment consistent with the requirements set forth in FERC's Study Plan Determination. The goals of this study were (1) to characterize existing water quality conditions in Don Pedro Reservoir and the lower Tuolumne River, as measured at the point of discharge from the Project and (2) to determine the water's consistency with the CVRWQCB's Basin Plan Objectives (CVRWQCB 1998¹). The objective of the study was to determine whether or not Project operations and maintenance (O&M) activities are in compliance with Basin Plan objectives.

¹ With amendments through October 2011. See Section 8.0 References.

3.0 STUDY AREA

The study area includes the Project Boundary and tributaries upstream of Don Pedro Reservoir, surface waters within the Don Pedro Reservoir, and the Tuolumne River immediately below Don Pedro Dam (Figure 3.0-1). Although no point-source discharges occur in or immediately downstream of the reservoir, the study area encompasses recreation-related facilities and Project O&M activities. Water quality just downstream of La Grange Dam, was also assessed.

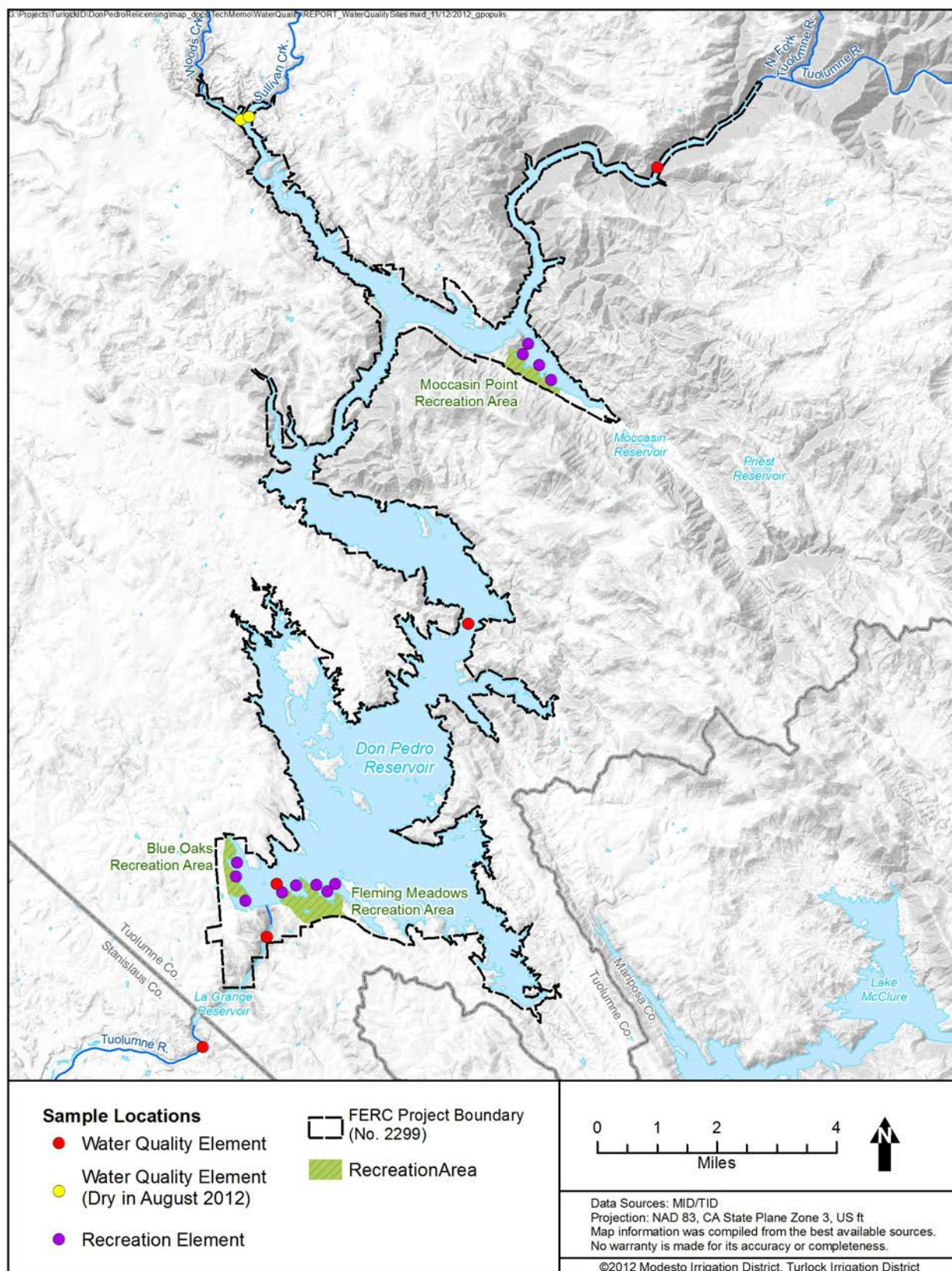


Figure 3.0-1. Study area.

4.0 METHODOLOGY

In 2012, the Districts investigated the quality of surface water potentially affected by Project O&M and recreation activities during periods when water quality effects are expected to be most pronounced, if they occur. The study consisted of two elements: a Water Chemistry Element and a Recreation Activity Element. Each is described below.

4.1 Water Chemistry Element

Water quality samples were collected between August 22 and 24, 2012, during summer low-inflow and high temperature conditions.

4.1.1 Sample Locations

The FERC-approved sampling plan called for sampling the locations listed in Table 4.1-1 and shown in Figure 3.0-1. Sampling occurred upstream, within, and downstream of Don Pedro Reservoir.

Table 4.1-1. Reservoir and stream reach sample locations.

Reservoir/Stream Reach	Sample Depth	Location
Woods Creek ¹	Just below surface	Just prior to entering Don Pedro Reservoir
Sullivan Creek ¹	Just below surface	Just prior to entering Don Pedro Reservoir
Tuolumne River above Don Pedro Reservoir	Just below surface	Upstream of Ward's Ferry Bridge at the first riffle
Don Pedro Reservoir	One meter below surface	Between Upper and Middle Bays (co-located with current CDFG temperature profile location)
	One meter above bottom	
Don Pedro Reservoir - near Dam	One meter below surface	At deepest point in the reservoir near the dam (co-located with current CDFG temperature profile location)
	One meter above bottom	
Tuolumne River just below Don Pedro Dam	Just below surface	Below Don Pedro powerhouse (co-located with current TID/MID water quality sonde)
Tuolumne River below La Grange Dam	Just below surface	Below La Grange at USGS gage USGS Gage 11289651 (about 0.5 miles below the dam)

¹ Location was either dry or had no flowing water between August 22 and 24, 2012.

Key:

CDFG = California Department of Fish and Game

USGS = U.S. Geological Survey

Of the three upstream sample locations, only the mainstem Tuolumne sample could be collected during the season investigated, as Woods and Sullivan Creeks were dry at that time. In-reservoir samples were collected at the deepest point near the dam and about 2/3 of the way upstream, between Upper Bay and Middle Bay. At each reservoir location, water quality samples were collected for laboratory analysis at two depths: within the hypolimnion and just below the surface in the epilimnion. *In situ* water quality measurements were made at the same depths using a Hydrolab DataSonde 5.

In-stream samples were taken upstream and downstream of Don Pedro Reservoir. Upstream sampling locations were limited to the Tuolumne River site, upstream of Ward's Ferry. Woods Creek and Sullivan Creek were not sampled because they either contained no flowing water or were dry during the sampling period. Water quality grab samples were collected for laboratory analysis from the moving water. *In situ* measurements were collected from the same locations using a Hydrolab Quanta or Hydrolab DataSonde 5.

4.1.2 In-Situ and Laboratory Analyses

Table 4.1-2 shows the method, target reporting limit,² method detection limit³ and hold time associated with each constituent measured for this study. Water temperature, dissolved oxygen (DO), pH, specific conductance, and turbidity were measured in the field using a Hydrolab DataSonde 5 or Quanta. Laboratory analyses were conducted using U.S. Environmental Protection Agency (EPA) Analytical Methods (EPA 2010), Standard Methods (SM, APHA et al. 2010), or an equivalent method sufficiently sensitive to detect and report levels necessary for evaluation against state and federal water quality standards.

Table 4.1-2. Water quality parameters.

Parameter		Method	Target Reporting Limit/Method Detection Limit µg/L (or other) ¹	Hold Time
Dissolved Oxygen	DO	SM 4500-O	0.1 mg/L	Field (<i>in situ</i>)
Specific conductance		SM 2510A	0.001 µmhos	Field (<i>in situ</i>)
pH		SM 4500-H	0.1 su	Field (<i>in situ</i>)
Turbidity		SM 2130 B	0.1 NTU	Field (<i>in situ</i>)
Basic Water Quality – Laboratory				
Total Organic Carbon	TOC	SM 5310	0.5/0.02 mg/L	28 d
Dissolved Organic Carbon	DOC	EPA 415.1 D	0.5/0.02 mg/L	28 d
Total Dissolved Solids	TDS	EPA 2540 C/SM 2340 C	1 mg/L	7d
Total Suspended Solids	TSS	EPA 2520 D SM 2340 D	1 mg/L	7d
Inorganic Ions				
Total Alkalinity	--	SM 2340 B	1000	14 d
Hardness (measured value)	--	EPA 2340 B/SM 2340 C	2 mg/L as CaCO ₃	14 d
Calcium	Ca	EPA 6010 B	100	180 d
Magnesium	Mg	EPA 6010 B	100	180 d
Potassium	K	EPA 6010 B	500	180 d
Sodium	Na	EPA 6010 B	500	180 d
Chloride	Cl	EPA 300.0	1000 mg/L	28 d
Nutrients				
Nitrate-Nitrite	--	EPA 300.0	100	28 d <pH 2
Total Ammonia as N	--	EPA 4500-NH ₃ /SM 4500-NH ₃	100	28 d <pH 2
Total Kjeldahl Nitrogen as N	TKN	SM 4500 N	500	28 d <pH 2
Total Phosphorous	TP	SM 4500-P	100	28 d <pH 2
Dissolved Orthophosphate	PO ₄	EPA 365.1/EPA 300.0	100	48 h at 4°C

² The reporting limit is the lowest concentration at which an analyte can be detected with a reliable precision and accuracy. At this concentration, both the identity of the analyte and its quantity are certain.

³ The method detection limit is the lowest concentration that an analyte can be detected and distinguished from other chemicals. At this concentration, the identity of the analyte is certain, but its quantity is uncertain.

Parameter		Method	Target Reporting Limit/Method Detection Limit µg/L (or other) ¹	Hold Time
Dissolved Oxygen	DO	SM 4500-O	0.1 mg/L	Field (<i>in situ</i>)
Specific conductance		SM 2510A	0.001 µmhos	Field (<i>in situ</i>)
pH		SM 4500-H	0.1 su	Field (<i>in situ</i>)
Turbidity		SM 2130 B	0.1 NTU	Field (<i>in situ</i>)
Metals (Total and Dissolved)				
Arsenic (total and dissolved)	As	EPA 200.8/1632	0.15/0.04	180 d
Cadmium (total and dissolved)	Cd	EPA 200.8/1638	0.020/0.004	180 d
Copper (total and dissolved)	Cu	EPA 200.8/1638	0.10/0.010	180 d
Iron (total and dissolved)	Fe	EPA 200.8/1638	10/3.2	180 d
Lead (total and dissolved)	Pb	EPA 1638	0.040/0.003	180 d
Mercury (total)	Hg	EPA 1631	0.0005/0.00008	28 d
Methylmercury (total and dissolved)	CH ₃ Hg	EPA 1630	0.00005/0.00002	90 d
Selenium (total)	Se	EPA 200.8/1638	0.60/0.2	180 d
Silver (total and dissolved)	Ag	EPA 200.8/1638	0.020/0.006	180 d
Zinc (total and dissolved)	Zn	EPA 200.8/1638	0.20/0.10	180 d
Herbicides and Pesticides				
Aldrin	--	EPA 8081A	3.0	7d
Alpha-BHC (=alpha-HCH)	--	EPA 8081A	0.08	7d
Beta-BHC (=beta-HCH)	--	EPA 8081A	0.08	7d
Chlordane	--	EPA 8081A	0.0043	7d
Chlorpyrifos	--	EPA 8141A	0.014	7d
Delta-BHC (=delta-HCH)	--	EPA 8081A	0.08	7d
Dieldrin	--	EPA 8081A	0.056	7d
Diazinon	--	EPA 8141A	0.05	7d
Endosulfan I	--	EPA 8081A	0.056	7d
Endosulfan II	--	EPA 8081A	0.056	7d
Endrin	--	EPA 8081A	0.036	7d
Gamma-BHC (=gamma-HCH)	--	EPA 8081A	0.08	7d
Heptachlor	--	EPA 8081A	0.0038	7d
Heptachlor Epoxide	--	EPA 8081A	0.0038	7d
Toxaphene	--	EPA 8081A	0.0002	7d

¹ When only one number is provided, it is the method detection limit.

Key:

Field = in situ

d = days

h = hours

µg/L = micrograms per liter

mg/L = milligrams per liter

SM = Standard Method

EPA= Environmental Protection Agency

California-certified laboratories analyzed the water samples for basic water chemistry, inorganic ions, metals, nutrients, herbicides, and pesticides. Frontier Geosciences, Inc., Seattle, Washington, conducted laboratory analyses for trace metals. CalScience Environmental Laboratories, Inc., Garden Grove, California, conducted all other laboratory analyses.

4.1.3 Sample Collection

Sample and data collection procedures were detailed in the Water Quality Assessment Study Plan or Quality Assurance Project Plan (QAPP) provided as Attachment A, Part 1 to this document. Hydrolab sondes were rented from Hach Hydromet in Loveland, Colorado. Calibration of each sonde was performed by Hach Hydromet prior to deployment (Attachment A Part 1). Calibration was also verified in the field using the manufacturer's recommended calibration methods. The study team noted relevant conditions during each sampling event on the field data sheet (i.e., air temperature, water flow, description of location, floating material, and evidence of oil and grease).

Each laboratory sample was collected into laboratory-supplied clean containers. Water samples to be analyzed for metals were taken using "clean hands" methods consistent with the EPA Method 1669 sampling protocol as described in *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria* (EPA 1996). Samples collected for dissolved metals analysis were filtered in the field in accordance with standard protocols.

All sample containers were labeled with the date and time that the sample was collected, assigned a sample number, and handled in a manner consistent with appropriate chain-of-custody protocols. Samples were preserved as appropriate, stored, and delivered to a California-certified water quality laboratory for analyses of the parameters listed in Table 4.1-2 in accordance with maximum holding periods for each parameter. A chain-of-custody record was maintained with the samples at all times. The sampling site location was recorded using a hand-held Global Positioning System (GPS) unit and the coordinates were recorded in a field logbook.

4.1.4 Quality Assurance

As part of the field quality assurance program defined in the Quality Assurance Project Plan (QAPP) (Attachment A, Part 1), duplicate samples, field blanks and equipment rinsate samples were collected and submitted to the laboratory for analysis (Attachment B). A duplicate sample is a sample co-located with an investigation sample and the two are sent to the laboratory together. For homogenous matrices such as water, comparing laboratory results from the duplicate and investigation samples provides a way to assess the laboratory's consistency. A field blank is a sample of analyte-free water poured into a sample container in the field, preserved, and shipped to the laboratory along with collected samples. A field blank assesses sample contamination from field methods and conditions during sampling. An equipment rinsate is a sample of analyte-free water poured over or through decontaminated field sampling equipment prior to the collection of samples. Testing of this sample assesses the adequacy of the decontamination processes. Only equipment used for reservoir sampling was used for more than one sample site; stream samples did not require sharing equipment.

All field and laboratory data were verified and/or validated as appropriate. Following field surveys and laboratory analysis, which included the laboratory's own Quality Assurance/Quality Control (QA/QC) analysis, QA/QC procedures were applied to all data, including, but not limited to: spot-checks of transcription; review of electronic data submissions for completeness; comparison of Geographic Information System maps with field notes on locations; comparison

of results to field blank and rinsate results; and, identification of any data that seemed inconsistent with expectations and requiring resolution.

All verified chemical detections, including data whose results are “J” qualified,⁴ were used for this assessment. Field-sampling conditions, as measured by the field blank and the rinsate sample results, were reviewed by the study scientist and, if appropriate, used to qualify detected concentrations.

4.2 Recreation Element

For the recreation element of the study, bacteria and total petroleum hydrocarbon (TPH) samplings were conducted at near-shore locations adjacent to recreation facilities receiving relatively lower levels of active management as identified by the recreation facility reconnaissance survey. During the survey, these locations were identified to have the potential to affect water quality. In accordance with bacteria sampling protocols (CVRWQCB 1998), bacteria samples were collected on five different days within a 30-day period including a holiday weekend. For this study, samples were collected in the 30 days surrounding and including the 2012 Independence Day holiday weekend. A single TPH sample was also collected at each location during the Independence Day holiday weekend.

4.2.1 Recreation Sample Locations

Recreation sample locations are listed in Table 4.2-1 and shown in Figure 3.0-1. At each sample location, water samples were collected from the near surface⁵ for bacteria and at the surface for TPH.

Table 4.2-1. Recreation sample locations on Don Pedro Reservoir.

Recreation Area	Bacteria and TPH Sampling Site
Fleming Meadows	Marina
	Houseboat marina
	Boat launch
	Main campground loop
	Small campground loop
Blue Oaks	Boat ramp
	Picnic area
	Loop of campground
Moccasin Point	Boat ramp
	Marina
	Main campground loop
	Picnic area

TPH = Total Petroleum Hydrocarbon

⁴ Results with a “J” qualifier are results where the chemical was detected, but there is uncertainty in the reported concentration. The quantity is above the method detection limit, but below the reporting limit.

⁵ Approximately 6 inches below the surface.

4.2.2 Laboratory Analyses

Water samples associated with recreation activities were analyzed for bacteria and TPH (Table 4.2-2). Bacteria samples were delivered to JL Analytical, Inc., Modesto, California for analysis. TPH samples were sent to CalScience Environmental Laboratories, Inc., Garden Grove, California.

Table 4.2-2. Water quality parameters addressed in the Recreation Element of the study.

Parameter	Symbol or Abbreviation	Method	Target Reporting Limit/ Method Detection Limit	Hold time
<i>Bacteria</i>				
Total coliform	--	SM 9221B	2/100 mL	24 h
Fecal coliform	--	SM 9221E	2 MPN/100 mL	24 h
<i>Escherichia coli</i>	E. coli	SM 9221F	2 MPN/100 mL	24 h
<i>Petroleum Hydrocarbons</i>				
Total Petroleum Hydrocarbon—gasoline	TPH-g	EPA 8015B(Modified)	50/48 µg/L	14 d
Oil & Grease	O&G	Visual Observation	--	--

Key:

d = days

h = hours

ml= milliliters

µg/L = micrograms per liter

MPN = Most Probable Number

SM = Standard Method

EPA= Environmental Protection Agency

At each location, visual observations of oil and grease were recorded in the field notebook, if present.

4.2.3 Sample Collection

The Recreation Element followed the same sampling protocols as the Water Quality Element (Section 4.1.3).

4.2.4 Quality Assurance

All data were verified and/or validated as defined in the Study QAPP (Attachment A, Part 1). In brief, following field surveys and laboratory analysis, which included the laboratory's own QA/QC analysis, the Districts subjected all data to QA/QC procedures including, but not limited to: spot-checks of transcription; review of electronic data submissions for completeness; comparison of Geographic Information System (GIS) maps with field notes on locations; and, identification of any inconsistent data.

4.3 Consistency with Water Quality Objectives

Beneficial uses of surface water in the vicinity of the Project are designated by the CVRWQCB and listed in the Basin Plan (CVRWQCB 1998). The designated beneficial uses for Hydro Units in the Project Boundary and vicinity consist of municipal and domestic supply (MUN);

agricultural supply (AGR); hydropower generation (POW); water contact recreation (REC-1); water non-contact recreation (REC-2); cold freshwater habitat (COLD); warm freshwater habitat (WARM); migration of aquatic organisms (MIGR), spawning, reproduction and/or early development (SPAWN), and wildlife habitat (WILD).

Specifically, the Don Pedro Project and the areas upstream and downstream of the Project fall within three Basin Plan Hydro Units: (1) Hydro Unit 536, which includes the Tuolumne River upstream of the Project; (2) Hydro Unit 536.32, which includes Don Pedro Reservoir; and (3) Hydro Unit 535, which includes the Tuolumne River from Don Pedro Dam to the San Joaquin River. Designated beneficial uses in Hydro Unit 535 consist of municipal and domestic supply, agricultural supply, industrial process supply, industrial service supply, water contact recreation, water non-contact recreation, warm freshwater habitat, cold freshwater habitat, migration of aquatic organisms, spawning habitat, and wildlife habitat.

Because most Water Quality Objectives provided in the Basin Plan are narrative, to assess the consistency of analytical data with these beneficial uses, the Districts selected numeric standards, criteria, or benchmarks correlated with each beneficial use to compare to this study's results. Provided in Table 4.3-1, selected values were primarily taken from the California Toxics Rule (CTR) (EPA 2000) and the Basin Plan itself (CVRWQCB 1998), which incorporates Title 22 drinking water standards. When a study parameter did not have a corresponding value in one of these preferred sources, values were taken from *A Compilation of Water Quality Goals* (Marshack 2008), *Water Quality Standards for Recreational Waters* (EPA 2003, another compilation with multiple regional sources), and others as cited.

Table 4.3-1. Benchmark values suggested for evaluating the protection of designated beneficial uses of Project waters.¹

Basin Plan Water Quality Objective (Potentially Affected Beneficial Uses)	Symbol or Abbreviation	Benchmark Values	Reference	Notes
<i>Bacteria (MUN, REC-1)</i>				
Total coliform	--	< 10,000 MPN per 100 mL < 240 MPN per 100 mL (geometric mean);	EPA 2003	Water contact recreation, single-day sample; Water contact recreation, 30-day geometric mean
Fecal coliform	--	< 200 MPN per 100 mL (geometric mean); < 10% of samples > 400 MPN per 100 mL	CVRWQCB 1998	Water contact recreation, 30-day geometric mean; with individual samples not > 400 MPN/100 mL
Escherichia coli	E. coli	<126 MPN per 100 mL (geometric mean) <235 MPN per 100 mL in any single sample	EPA 2003	Water contact recreation, 30-day geometric mean
<i>Biostimulatory Substances (COLD, SPAWN)</i>				
Total Kjeldahl Nitrogen	TKN	None	--	--
Total Phosphorous	TP	None	--	--
<i>Chemical Constituents (AGR, COLD, MUN)</i>				
Alkalinity	--	20 mg/L (minimum)	Marshack 2008	EPA AWQC; low alkalinity can affect water treatment

Basin Plan Water Quality Objective (Potentially Affected Beneficial Uses)	Symbol or Abbreviation	Benchmark Values	Reference	Notes
Arsenic	As	0.010 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Cadmium	Cd	5 µ/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Calcium	Ca	None	--	--
Chloride	Cl	250 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Chromium (total)	Cr (total)	50 µg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Copper	Cu	1 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Lead	Pb	15 µg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Mercury (inorganic)	Hg	0.002 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Nickel	Ni	0.1 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Nitrate	NO ₃	45 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Nitrite	NO ₂	1 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Nitrate + Nitrite	NO ₃ + NO ₂	10 mg/L (combined total)	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Potassium	K	None	--	--
Selenium	Se	0.05 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL ²
Sodium	Na	20 mg/L	Marshack 2008	Sodium Restricted Diet ³
Specific conductance	--	150 µmhos	CVRWQCB 1998	Aquatic Life Protection
Zinc	Zn	5 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
<i>Dissolved Oxygen (COLD, SPAWN)</i>				
Dissolved Oxygen	DO	7.0 mg/L (minimum)	CVRWQCB 1998	Aquatic life protection
<i>Floating Material (REC-1, REC-2)</i>				
Floating Material	--	Narrative Criteria	CVRWQCB 1998	Aesthetics - Absent by visual observation

Basin Plan Water Quality Objective (Potentially Affected Beneficial Uses)	Symbol or Abbreviation	Benchmark Values	Reference	Notes
<i>Oil and Grease (REC-1, REC-2)</i>				
Oil & Grease	--	Narrative Criteria	CVRWQCB 1998	Aesthetics - Absent by visual observation
Total Petroleum Hydrocarbons	TPH	None	--	--
<i>pH (COLD, SPAWN, WILD)</i>				
pH	--	6.5-8.5	CVRWQCB 1998	Aquatic life protection
<i>Sediment and Settleable Solids (REC-2, SPAWN, WILD)</i>				
Sediment	--	Narrative Criteria	CVRWQCB 1998	
<i>Tastes and Odors (MUN)</i>				
Aluminum	Al	0.2 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Chloride	Cl	250 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Copper	Cu	1.3 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Iron	Fe	0.3 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Silver	Ag	0.1 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Specific Conductance	--	900 umhos	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Sulfate	SO ₄	250 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Total Dissolved Solids	TDS	500 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
Zinc	Zn	5 mg/L	CDPH 2010 cited in CVRWQCB 1998	Title 22 Secondary MCL ²
<i>Toxicity (COLD, SPAWN, MUN)</i>				
<i>CTR values listed below generally assume Total Recoverable Concentrations (unfiltered)^{4,5}</i>				
Ammonia as N (pH and Temp dependent)	NH ₃ -N	24.1 mg/L (CMC); 4.1-5.9 mg/L (CCC)	EPA 2000	CTR criteria over 0-20°C assuming pH 7.0
		5.6 mg/L (CMC); 1.7-2.4 mg/L (CCC)	EPA 2000	CTR criteria over 0-20°C assuming pH 8.0
		0.9 mg/L (CMC); 0.3-0.5 mg/L (CCC)	EPA 2000	CTR criteria over 0-20°C assuming pH 9.0
Arsenic	As	0.34 mg/L (CMC); 0.15 mg/L (CCC)	EPA 2000	CTR criteria

Basin Plan Water Quality Objective (Potentially Affected Beneficial Uses)	Symbol or Abbreviation	Benchmark Values	Reference	Notes
Cadmium (hardness dependent)	Cd	0.23 µg/L (CMC); 0.15 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 5 mg/L as CaCO ₃
		0.4 µg/L (CMC); 0.34 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 10 mg/L as CaCO ₃
		0.56 µg/L (CMC); 0.53 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 15 mg/L as CaCO ₃
		0.83 µg/L (CMC); 0.95 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 25 mg/L as CaCO ₃
Copper (hardness dependent)	Cu	0.83 µg/L (CMC); 0.72 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 5 mg/L as CaCO ₃
		1.6 µg/L (CMC); 1.3 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 10 mg/L as CaCO ₃
		2.34 µg/L (CMC); 1.84 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 15 mg/L as CaCO ₃
		3.79 µg/L (CMC); 2.85 µg/L (CCC)	EPA 2000	CTR for unfiltered sample assuming hardness of 25 mg/L as CaCO ₃
Lead (hardness dependent)	Pb	0.54 µg/L (CCC) 14 µg/L (CMC)	EPA 2000	CTR for unfiltered sample assuming hardness of 25 mg/L as CaCO ₃
Mercury	Hg	0.050 µg/L	EPA 2000 40 CFR 131.38	CTR/Federal Register 5/18/00
Nitrate-Nitrite	NO ₃ -N+NO ₂ -N	10 mg/L (combined total)	CDPH 2010 cited in CVRWQCB 1998	Title 22 Primary MCL (“Blue baby Syndrome”)

Basin Plan Water Quality Objective (Potentially Affected Beneficial Uses)	Symbol or Abbreviation	Benchmark Values	Reference	Notes
Silver (hardness dependent)	Ag	0.02 µg/L (CMC) instantaneous	EPA 2000	CTR for unfiltered sample assuming hardness of 5 mg/L as CaCO ₃
		0.08 µg/L (CMC) instantaneous	EPA 2000	CTR for unfiltered sample assuming hardness of 10 mg/L as CaCO ₃
		0.16 µg/L (CMC) instantaneous	EPA 2000	CTR for unfiltered sample assuming hardness of 15 mg/L as CaCO ₃
		0.37 µg/L (CMC) instantaneous	EPA 2000	CTR for unfiltered sample assuming hardness of 25 mg/L as CaCO ₃
Zinc (hardness dependent)	Zn	9.47 µg/L	EPA 2000	CTR for unfiltered sample assuming hardness of 5 mg/L as CaCO ₃
		17.03 µg/L	EPA 2000	CTR for unfiltered sample assuming hardness of 10 mg/L as CaCO ₃
		24.01 µg/L	EPA 2000	CTR for unfiltered sample assuming hardness of 15 mg/L as CaCO ₃
		37.02 µg/L	EPA 2000	CTR for unfiltered sample assuming hardness of 25 mg/L as CaCO ₃
Aldrin	--	3.0 µg/L	Marshack 2008	AWQC
Chlordane	--	0.0043 µg/L	Marshack 2008	AWQC
Chlorpyrifos	--	0.014 µg/L	Marshack 2008	AWQC
Diazinon	--	0.05 µg/L ⁵	Marshack 2008	AWQC
Dieldrin	--	0.056 µg/L	Marshack 2008	AWQC
Endosulfan	--	0.056 µg/L	Marshack 2008	AWQC
Endrin	--	0.036 µg/L	Marshack 2008	AWQC
Heptachlor	--	0.0038 µg/L	Marshack 2008	AWQC
Heptachlor epoxide	--	0.0038 µg/L	Marshack 2008	AWQC
alpha-Hexachlorocyclohexane	--	0.08 µg/L	Marshack 2008	AWQC
beta-Hexachlorocyclohexane	--	0.08 µg/L ⁶	Marshack 2008	AWQC
delta-Hexachlorocyclohexane	--	0.08 µg/L ⁶	Marshack 2008	AWQC
gamma-Hexachlorocyclohexane	--	0.08 µg/L	Marshack 2008	AWQC
Toxaphene	--	0.0002 µg/L	Marshack 2008	AWQC

Basin Plan Water Quality Objective (Potentially Affected Beneficial Uses)	Symbol or Abbreviation	Benchmark Values	Reference	Notes
<i>Turbidity (COLD, SPAWN, WILD, MUN)</i>				
Turbidity	NTU	increase < 1 NTU for 1-5 NTU background; increase < 20% for 5-50 NTU background	CVRWQCB 1998	Aesthetics, disinfection, egg incubation

¹ Note a chemical may be listed under more than one beneficial use.

² CDPH Title 22 identified as minimum water quality thresholds, but acknowledged as insufficiently protective in some cases (CVRWQCB 1998).

³ Guidance level to protect those individuals restricted to a total sodium intake of 500 mg/day (Marshack 2008).

⁴ CMC: Criterion Maximum Concentration (one-hour acute exposure) for aquatic toxicity as defined by EPA (2000).

⁵ CCC: Criterion Continuous Concentration (four-day chronic exposure) for aquatic toxicity as defined by EPA (2000).

⁶ Value is for gama-hexachlorocyclohexane.

Key:

AGR = agricultural supply

AWQC = Ambient Water Quality Criteria

EPA = Environmental Protection Agency

CaCO₃ = Calcium carbonate

CMC = Criterion Maximum Concentration (1-hour acute exposure) for aquatic toxicity as defined by EPA (2000)

CCC = Criterion Continuous Concentration (4-day chronic exposure) for aquatic toxicity as defined by EPA (2000)

COLD = cold freshwater habitat

CTR = California Toxics Rule

MCL = Maximum Contaminant Level

MUN = municipal and domestic supply

REC-1 = water contact recreation

REC-2 = water non-contact recreation

µmhos = micromhos

µg/L = micrograms per liter

mg/L = milligrams per liter

MPN = Most Probable Number

NTU = Nephelometric turbidity units

SM = Standard Method

SPAWN = spawning, reproduction and/or early development

WILD = wildlife habitat

The CVRWQCB has adopted, by reference, California Title 22 maximum contaminant levels (MCL) for drinking water as Basin Plan objectives (CVRWQCB 1998), with the exception that more stringent criteria may apply as necessary for protection of specific beneficial uses. Hence, these values are adopted herein. It should be noted, however, that chemical concentrations that were originally intended to apply to finished tap water, rather than to untreated sources of drinking water, would be applied to the untreated reservoir or river water.

For water quality objectives related to aquatic toxicity,⁶ the CTR (EPA 2000) will be evaluated. Section 131.38 of 40 California Code of Regulations (CCR) establishes Criterion Maximum Concentrations (CMC) as the highest concentration to which aquatic life can be exposed for a short period without deleterious effects and must be based on extended sample collection and one-hour averaging. The Criterion Continuous Concentration (CCC) is defined as the highest concentration to which aquatic life can be exposed for an extended period of time (i.e., four days) without deleterious effects. When single grab samples are collected, it is assumed that constituent concentrations are representative of the continuous ambient condition, and CCC

⁶ Ammonia, nitrate, and trace metals.

values are therefore used as the appropriate criteria to compare against environmental samples. Because of differences in acute and chronic toxicity to aquatic organisms of many elements and compounds in Table 4.3-1 as well as variations with ambient water quality such as pH or hardness, several entries have multiple benchmarks to assist with their evaluation. The benchmarks for five of the metals addressed in this study plan (i.e., cadmium, copper, lead, silver and zinc) are reported for unfiltered (i.e., total metals) samples from the CTR (EPA 2000), and calculated in 5 mg/L increments of hardness since the level at which each of these metals is reportedly toxic to aquatic life is lower at lower hardness levels. In addition, the CMC and CCC levels for ammonia are a function of both pH and temperature and are presented over a range of 0 to 20°C in pH increments of 1 standard unit (su).

5.0 RESULTS

Study results are provided below by Water Quality Study Element and Recreation Water Quality Study Element. Analytical results are provided in their entirety, by reservoir and stream reach, in Attachment C.

5.1 Data Representativeness, Accuracy and Completeness

The QAPP specifies representativeness, completeness, and accuracy objectives for analytical data acquisition (Attachment A, Part 1). Representativeness was ensured via the location of sample sites as well as the season. Representative locations and measurement intervals were specified in the FERC-approved Study Plan and described above in Section 4.1 for the Water Quality Study Element and Section 4.2 for the Recreation Water Quality Study Element. The sampling design ensured representativeness of the data.

Accuracy for field and laboratory measurements is defined as the degree of conformity of a measured/calculated quantity to its actual (true) value. The accuracy objective provided in the QAPP for the study was 90 percent (Attachment A, Part 1). Calibration records for the field instruments are provided in Attachment B and show that field instruments were within acceptable limits. Though field filters and the vast majority of other sampling equipment were not shared between sites, rinsate and field blank data indicate that at the low detection and reporting limits used, some trace metals concentrations may have been introduced by the filters used for in-field filtration, field handling, or laboratory handling⁷ (Attachment B). Data were not modified to reflect this observation; however, results were used to qualify the discussion in Section 6.0. For the laboratory data, quality assurance samples (method blanks, laboratory control samples, method spikes, and others) were analyzed as appropriate for each method. All quality control analyses were within acceptable limits for the laboratory data; some data are flagged, however, to account for concentrations found below reporting limits, but above detection limits, or when method blanks had detected concentrations. All verified chemical detections, including data whose results are “J” qualified,⁸ were used in this assessment.

The completeness objective provided in the QAPP for the study was 90 percent (Attachment A, Part 1), and is defined as the number of valid measurements divided by the number of measurements collected. Though one non-conformance resulted in data loss—turbidity was not measured downstream of La Grange Dam-- the completeness objective for water quality sampling was met: valid results were obtained for > 99 percent of the data collection effort.

5.2 Water Quality Element

Analytical results and comparisons to their associated standards, criteria, and/ or benchmarks are provided in Attachment C and summarized below in Table 5.2-1. The summary consists of the parameter’s frequency of detection, range of results (minimum, maximum) and average value by

⁷ Filtering was performed in the field and not in the laboratory to address preservation and holding time concerns when sampling sites are remote from shipping sites.

⁸ Results with a “J” qualifier are results where the chemical was detected, but there is uncertainty in the quantity. The quantity is above the method detection limit, but below the reporting limit.

season. The standard, criterion, or benchmark used for the comparison (from Table 4.3-1) and the location(s) of any value above or below the standard, criterion, or benchmark (as defined) were excerpted from Attachment C and are provided in the summary tables, as well. For completeness, analytes that were not detected in any sample are also listed in Table 5.2-1.

Results that exceeded the standards, criteria, or benchmarks of Table 4.3-1 are discussed in section 6.0.

Table 5.2-1. Summer 2012 summary of water quality element results.¹

Analyte	Units	Detection Frequency ^{2,3}	Concentration Range			Standard, Criterion, or Benchmark ⁴	Location(s) of Benchmark Exceedance(s)
			min	max	average		
In Situ Measurements							
Temperature	°C	7/7	9.67	27.13	17.00	--	--
Specific Conductance	µSiemens/cm	7/7	20	44	33.7	150	None
pH	stnd units	7/7	6.40	7.95	6.94	6.5-8.5	6.40 – Tuolumne River above Don Pedro 6.47 – Mid-reservoir (Bottom) 6.42 – Near Don Pedro Dam (Bottom)
Dissolved Oxygen	mg/L	7/7	3.15	12.6	7.85	7 (minimum)	3.2 – Mid-reservoir (Bottom) 4.8 – Near Don Pedro Dam (Bottom)
Turbidity	NTU	2/6	0	282	49	--	--
Basic Water Quality, Inorganic ions and Nutrients							
Alkalinity, Total (as CaCO ₃)	mg/L	8/8	3.5	15.5	12.2	20 (minimum)	All results—upstream, downstream and within Don Pedro Reservoir
Ammonia (as N)	mg/L	0/8	0.10 ND	0.10 ND	0.10 ND	Temp & pH Dept ⁶	None
Calcium	mg/L	8/8	2.12	3.95	2.98	--	--
Carbon, Dissolved Organic	mg/L	8/8	3.1B	4.7	3.8	--	--
Carbon, Total Organic	mg/L	8/8	2.6B	4.6	3.5	--	--
Chloride	mg/L	8/8	0.58 J	0.83 J	0.70 J	230	None
Hardness, Total	mg/L	8/8	6	15	11.5	--	--
Magnesium	mg/L	8/8	0.443	1.55	1.26	--	--
Nitrate (as N)	mg/L	5/8	0.037 J	0.11	0.08	10	None
Nitrite (as N)	mg/L	0/8	0.10 ND	0.10 ND	0.10 ND	1	None
o-Phosphate (as P)	mg/L	1/8	0.051 J	0.10 ND	0.09	--	--
Phosphorus, Total	mg/L	6/8	0.025 J	0.10 ND	0.06	--	--
Potassium	mg/L	8/8	0.534	0.69	0.60	--	--
Sodium	mg/L	8/8	1.2	2.3	1.9	20	None
Solids, Total Dissolved	mg/L	8/8	20	47	29	500	None
Solids, Total Suspended	mg/L	4/8	0.10 ND	16.00	2.98	--	--
Total Kjeldahl Nitrogen	mg/L	8/8	0.50 ND	0.50 ND	0.50 ND	--	--

Analyte	Units	Detection Frequency ^{2,3}	Concentration Range			Standard, Criterion, or Benchmark ⁴	Location(s) of Benchmark Exceedance(s)
			min	max	average		
Herbicides and Pesticides							
Aldrin	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	3.0	None
Alpha-BHC	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.08	None
Beta-BHC	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.08	None
Chlordane	µg/L	0/8	0.025 ND	0.025 ND	0.025 ND	0.0043	None ⁸
Chlorpyrifos	µg/L	0/8	0.005 ND	0.010 ND	0.006 ND	0.014	None
Delta-BHC	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.08	None
Diazinon	µg/L	0/8	0.005 ND	0.010 ND	0.006 ND	0.05	None
Dieldrin	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.056	None
Endosulfan I	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.056	None
Endosulfan II	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.056	None
Endrin	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.036	None
Gamma-BHC	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.08	None
Heptachlor	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.0038	None
Heptachlor Epoxide	µg/L	0/8	0.010 ND	0.010 ND	0.010 ND	0.0038	None
Toxaphene	µg/L	0/8	0.12 ND	0.12 ND	0.12 ND	0.0002	None ⁸
Metals (Total)							
Arsenic	µg/L	8/8	0.25	0.33	0.29	10	None
Cadmium	µg/L	8/8	0.003 J	0.006 J	0.004 J	5	None
Copper	µg/L	8/8	0.48	1.18	0.71	1000	None
Iron	µg/L	8/8	18	314	72.50	300	314 – Tuolumne River above Don Pedro
Lead	µg/L	8/8	0.005 J	0.142 J	0.02 J	15	None
Mercury	ng/L	8/8	0.08 J	4.57	1.43	50	None
Methyl Mercury	ng/L	3/8	0.029 J	0.053	0.05 ND	--	--
Selenium	µg/L	0/8	0.6	0.60	0.60	50	None
Silver	µg/L	4/8	0.002 J	0.02 ND	0.01 J	100	None
Zinc	µg/L	8/8	0.14 J	6.35	1.07	5000	None
Metals (Dissolved)							
Arsenic	µg/L	8/8	0.23	0.34	0.28	--	--
Cadmium	µg/L	3/8	0.003 J	0.020 ND	0.01 J	Hardness Dep't ⁶	None

Analyte	Units	Detection Frequency ^{2,3}	Concentration Range			Standard, Criterion, or Benchmark ⁴	Location(s) of Benchmark Exceedance(s)
			min	max	average		
Copper	µg/L	8/8	0.4	8.16	2.25	Hardness Dep't ⁶	6.25 – Mid-reservoir (Bottom) 8.16 – Near Don Pedro Dam (Bottom)
Iron	µg/L	8/8	1 J	96	18	--	--
Lead	µg/L	5/8	0.008 J	0.04 ND	0.02 J	Hardness Dep't ⁶	None
Methyl Mercury	ng/L	2/8	0.05 ND	0.35	0.12	--	--
Silver	µg/L	0/8	0.02 ND	0.02 ND	0.02 ND	Hardness Dep't ⁶	None
Zinc	µg/L	8/8	0.18 J	0.90	0.46	Hardness Dep't ⁶	None

¹ All data are provided in Attachment C.

² Five locations were sampled. Two locations were sampled at two depths.

³ For duplicate sample results, the highest concentration of the two samples was used for benchmark comparisons. A duplicate sample was collected downstream of Don Pedro Dam.

⁴ The most protective standard, criterion, or benchmark of those given in Table 4.3-1 was used for this analysis. With few exceptions, aquatic life protective benchmarks were the most protective number.

⁵ Minimum concentration except where natural concentrations are less (Marshack 2008).

⁶ See Attachment C for sample specific criteria. Ammonia criteria are temperature and pH dependent. Metals Criteria are hardness dependent for cadmium, copper, lead, silver, and zinc.

⁷ The gamma-BHC benchmark was selected as the alpha-, beta-BHC, and delta-BHC benchmarks.

⁸ Benchmark is below the method detection limit for this analyte.

Key:

B = Analyte was present in the associated method blank

J = Analyte was detected at a concentration below the reporting limit and above the laboratory method detection limit. Reported value is estimated.

ND = Analyte was not detected at the reporting limit.

µg/L micrograms per Liter

mg/L milligrams per Liter

ng/L nanograms per liter

< less than the reporting limit for this analysis

-- not available or not applicable

5.3 Recreation Element

Bacteria samples were collected in surface water adjacent to 12 recreation sites five times within 30 days, including one day of the Independence Day holiday weekend (See Figure 3.0-1). The geometric mean was then calculated from the five results to allow comparison with the Water Quality Objective (fecal coliform) or benchmark (total coliform, e coli). TPH samples and visual observations for oil and grease were also recorded. Results of these comparisons are shown in Table 5.3-1.

Table 5.3-1. 2012 Independence Day bacteria sampling results and oil and grease observations.^{1,2}

Sample Date	Sample Location											
	Fleming Meadows					Blue Oaks			Moccasin Point			
	Marina	Houseboat Marina	Boat Launch	Main camp loop	Small Camp loop	Boat Launch	Picnic Area	Camp Loop	Boat Launch	Marina	Main camp loop	Picnic Area
TOTAL COLIFORM <i>< 240 MPN per 100 mL (geometric mean)</i>												
6/14/12	230	220	23	79	3500	2800	220	940	7.8	2	17	33
	--	--	--	--	--	1300	--	--	--	10	--	--
7/2/12	22	7.8	7.8	2	7.8	14	4.5	7.8	23	33	2	7.8
	--	--	--	--	--	170	--	--	4.5	--	--	--
7/4/12	49	13	46	17	33	< 1.8	< 1.8	< 1.8	11	33	4.5	13
	7.8	--	--	--	--	--	--	--	--	--	4.5	--
7/7/12	70	49	26	17	130	7.8	11	23	14	23	4.5	13
	--	--	--	9.3	--	--	--	--	--	34	--	--
7/18/12	4.5	23	4	7.8	49	33	2	4.5	4.5	2	11	< 1.8
	--	--	6.8	--	--	--	2	--	--	--	--	--
Geometric Mean¹	29	30	13	12	89	63	7	17	9	12	6	10
FECAL COLIFORM <i>< 200 MPN per 100 mL (geometric mean)</i>												
6/14/12	1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	4.5	2	6.8	6.8
	--	--	--	--	--	< 1.8	--	--	--	< 1.8	--	--
7/2/12	< 1.8	2	< 1.8	< 1.8	< 1.8	4.5	< 1.8	< 1.8	< 1.8	2	2	< 1.8
	--	--	--	--	--	170	--	--	< 1.8	--	--	--
7/4/12	< 1.8	2	4.5	4.5	7.8	< 1.8	< 1.8	< 1.8	11	4.5	2	7.8
	2	--	--	--	--	--	--	--	--	--	2	--
7/7/12	11	49	14	11	79	< 1.8	4	4.5	14	4.5	2	7.8
	--	--	--	4.5	--	--	--	--	--	15	--	--
7/18/12	4	< 1.8	4	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	2	< 1.8	4	< 1.8
	--	--	6.8	--	--	--	< 1.8	--	--	--	--	--
Geometric Mean¹	2.8	3.6	4.2	3.3	5.1	3.9	2.1	2.2	4.1	3.3	2.8	4.2

Sample Date	Sample Location											
	Fleming Meadows					Blue Oaks			Moccasin Point			
	Marina	Houseboat Marina	Boat Launch	Main camp loop	Small Camp loop	Boat Launch	Picnic Area	Camp Loop	Boat Launch	Marina	Main camp loop	Picnic Area
ESCHERICHIA COLI <i>< 126 MPN per 100 mL (geometric mean)</i>												
6/14/12	1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	4.5	< 1.8
	--	--	--	--	--	< 1.8	--	--	--	< 1.8	--	--
7/2/12	< 1.8	2	< 1.8	< 1.8	< 1.8	4.5	< 1.8	< 1.8	< 1.8	2	2	< 1.8
	--	--	--	--	--	170	--	--	< 1.8	--	--	--
7/4/12	< 1.8	< 1.8	2	4.5	< 1.8	< 1.8	< 1.8	< 1.8	2	1.8	< 1.8	< 1.8
	< 1.8	--	--	--	--	--	--	--	--	--	< 1.8	--
7/7/12	2	< 1.8	< 1.8	< 1.8	2	< 1.8	< 1.8	2	< 1.8	< 1.8	< 1.8	< 1.8
	--	--	--	< 1.8	--	--	--	--	--	< 1.8	--	--
7/18/12	< 1.8	< 1.8	4	< 1.8	< 1.8	< 1.8	< 1.8	< 1.8	2	< 1.8	4	< 1.8
	--	--	< 1.8	--	--	--	< 1.8	--	--	--	--	--
Geometric Mean¹	1.8	1.8	2.1	2.1	1.8	3.9	1.8	1.8	1.9	1.8	2.4	1.8
OIL AND GREASE <i>Aesthetics – Present or absent by visual observation</i>												
6/14/12	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
7/2/12	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
7/4/12	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
7/7/12	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
7/18/12	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
Total Petroleum Hydrocarbons (µ/L) <i>Reporting Limit = 50 µ/L (micrograms per Liter)</i>												
7/4/12	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50

¹ Geometric mean values in bold were greater than the water quality objective or benchmark.

² Duplicate sample results are provided below original sample results.

Key:

-- = No count performed for this location and time

MPN – Most Probable Number.

6.0 DISCUSSION AND FINDINGS

When developing the Pre-Application Document, the Districts found that limited analyses had been performed on water samples collected in the Project Area, but those existing data indicated that surface water is of low specific conductivity and hardness, prone to acidification, and with limited potential sources of local contamination. This study confirms those results. Water quality in the Project Area is very good, i.e., most analytes were reported from non-detectable to just above reporting limit concentrations. Further, there does not appear to be a pattern of increasing chemical concentrations from upstream to downstream of Don Pedro Dam.

Beneficial uses of surface water in the vicinity of the Project are designated by the CVRWQCB and listed in the Basin Plan (CVRWQCB 1998). The designated beneficial uses for the Project Area were introduced above Section 4.3 and consist of municipal and domestic supply; agricultural supply; hydropower generation; water contact recreation; water non-contact recreation; cold freshwater habitat; warm freshwater habitat; migration of aquatic organisms; spawning; reproduction and/or early development; and wildlife habitat.

To assess the consistency of analytical data with these beneficial uses, the Basin Plan's Water Quality Objectives were compared to the results of the study. Basin Plan Water Quality Objectives and beneficial uses were linked to each other above in Table 4.3-1 where, for situations where the Basin Plan does not provide a numeric Water Quality Objective, a pertinent regulatory standard, criteria or benchmark was selected for this evaluation. Results of these comparisons are provided in Attachment C, summarized in Section 5, and discussed below.

6.1 Biostimulatory Substances

The Basin Plan requires that water shall not contain biostimulatory substances which promote aquatic growth in concentrations that cause nuisance or adversely affect designated beneficial uses.

In August 2012, nitrate concentrations ranged between 0.037 mg/L (estimated) and 0.11 mg/L, while nitrite concentrations and Total Kjeldahl Nitrogen were not detectable. Total phosphorous levels were similarly low, ranging between 0.025 mg/L (estimated) and the reporting limit of 0.10 mg/L. Orthophosphate concentrations were only detected in one sample at 0.051 mg/L (estimated). These low nutrient levels suggest that biostimulatory substances are not currently present in sufficient quantities to cause nuisance conditions related to algal blooms or decreased water clarity. The Districts are unaware of any instances where algal bloom or decreased water clarity has been reported as a nuisance.

6.2 Chemical Constituents

The Basin Plan requires that water shall not contain chemical constituents in concentrations that adversely affect designated beneficial uses. The Basin Plan requires that water designated for use as domestic or municipal supply shall not contain concentrations of chemical constituents in excess of the MCLs specified in the provisions of Title 22 of the CCR (CDPH 2010).

MCLs are intended to be applied to finished tap water, but were applied to untreated water in this study. Samples collected in August 2012 had concentrations less than the primary MCLs for all analytes; water quality was found to be consistent with drinking water standards (See Attachment C). Analytes with secondary MCLs for tastes and odors are addressed below under “Taste & Odor.” Aquatic toxicity is discussed below under “Toxicity.”

6.3 Color

The Basin Plan includes a narrative Water Quality Objective regarding color.

The FERC-approved study did not require sampling for color. The Districts are unaware of any instances where the color of the water in the vicinity of the Project has been reported as a nuisance or has adversely affected designated beneficial uses.

6.4 pH

The Basin Plan requires that pH shall not be depressed below 6.5 nor raised above 8.5.

During August 2012 sampling, three locations had a pH value outside of these limits: the inflow sample of the Tuolumne River above Don Pedro Reservoir (6.40 su), the mid-reservoir hypolimnion of Don Pedro Reservoir (6.47 su), and the near-dam hypolimnion of Don Pedro Reservoir (6.43 su). Not unexpected for a low nutrient snow-melt derived reservoir, these values are within the sonde’s measurement error of ± 0.1 mg/L and are considered consistent with the objective.

6.5 Pesticides

The Basin Plan includes extensive discussions related to Water Quality Objectives for pesticides. Significant pesticide use does not occur within the study area, or in association with Project O&M activities. Further, the Districts are unaware of any instances where pesticide use in the vicinity of the Project has been reported to cause a nuisance or adversely affect designated beneficial uses.

Downstream of the Project, the section of the Tuolumne River from Don Pedro Reservoir to the San Joaquin River is included in the State of California’s CWA § 303(d) list regarding the non-point discharge of some agricultural pesticides (SWRCB 2010). Agricultural chemicals on the 303(d) list are chlorpyrifos, diazinon, and the Group A Pesticides—aldrin, dieldrin, chlordane, endrin, heptachlor, heptachlor epoxide, hexachlorocyclohexanes (including lindane), endosulfan, and toxaphene.

Pesticides on the 303(d) list for the lower Tuolumne River were not detected in any of the August 2012 samples analyzed at the commercially available reporting limits. However, because the detection limits for chlordane and toxaphene exceeded the reporting limits for those analytes (See Attachment C), consistency with benchmarks could not be determined. However, as stated above, since significant pesticide use does not occur in association with the Project, these non-detects are considered applicable—chlordane and toxaphene are not present in Project waters.

6.6 Sediment and Settleable Solids

The Basin Plan requires that suspended sediment load and suspended sediment discharge to surface waters shall not alter surface waters in such a manner as to cause a nuisance or adversely affect beneficial uses of Project or other water.

Total dissolved solids and total suspended solids were low in August 2012 (10 to 38 mg/L and 1.0 to 3.1 mg/L, respectively). The Districts are unaware of any sediment discharges to surface water related to the Project. Additionally, the Districts are unaware of any circumstances that suspended sediment levels or discharges of such cause a nuisance or adversely affect any designated beneficial uses of Project or other water.

6.7 Tastes and Odor

The Basin Plan requires that waters shall not contain taste- or odor-producing substances in concentrations that impart undesirable tastes or odors to domestic or municipal water supplies or to fish flesh or other edible products of aquatic origin, or that cause nuisance, or otherwise adversely affect beneficial uses of Project or other water.

During the 2012 sampling, iron was measured at a level less than its secondary MCL of 0.3 mg/L for taste and odors at all locations, but one. Above Don Pedro, the inflow sample had an iron concentration of 3.14 mg/L. Secondary MCLs are routinely applied at the point of use (i.e., “at the tap”) and existing water treatment methods appear to be adequate to meet these secondary water quality criteria. The Districts are unaware of any reports that taste or odor of water or fish caught in Don Pedro Reservoir cause a nuisance or otherwise adversely affect designated beneficial uses of Project or other water.

6.8 Toxicity

The Basin Plan requires that waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life.

The FERC-approved study states that study water quality data would be compared to the aquatic life protective benchmarks from the EPA (2000) *California Toxics Rule (CTR)* or benchmarks excerpted from Marshack (2008) *A Compilation of Water Quality Goals*. The low levels of hardness found throughout the study area are expected to increase the aquatic toxicity of some metals due to the greater proportion of free ions found in many trace metals. At the low hardness levels found in the study (i.e., 6 to 15 mg/L), sample specific dissolved cadmium, copper, lead, silver, and zinc CTR criteria were calculated (see Attachment C, Table C.2). Of these five metals, only copper exhibited a concentration greater than its sample specific CTR—and only in two samples. The mid-reservoir hypolimnion of Don Pedro Reservoir had copper (dissolved) concentration of 6.25 micrograms per liter (µg/L), as compared to a CTR guideline of 1.8 µg/L, and the near-dam hypolimnion of Don Pedro Reservoir had copper (dissolved) concentration of 8.16 µg/L, as compared to a CTR guideline of 1.8 µg/L.

The Districts are unaware of any Project O&M activity that may affect levels of copper. As reported in the PAD, algacides are not used to manage algae in project waters.

6.8.1 Mercury and Methylmercury

Downstream of the Project, the section of the Tuolumne River included in the State of California's CWA Section 303(d) list regarding the non-point discharge of pollutants/stressors is the section below the outlet of Don Pedro Reservoir to the San Joaquin River. The pollutant stressors identified in the 303(d) list are primarily related to agricultural use, but the list also includes mercury, a legacy contaminant of the gold mining era (SWRCB 2010). Mercury can affect the nervous system of higher trophic organisms and is bioaccumulated and transferred to higher trophic organisms through the food-web.

In August 2012, mercury was detected at all locations at concentrations that ranged between 0.08 J and 4.57 nanograms per Liter (ng/L). These total mercury concentrations were far less than the MCL of 0.002 mg/L (2,000 ng/L) indicating that drinking water beneficial use is being met everywhere in the Project area for mercury. In addition, the samples were below the CTR benchmark of 50 ng/L.

However, even in trace quantities, mercury is bioaccumulative in its methylated form; samples were also analyzed for methylmercury (total) and methylmercury (dissolved). Methylmercury (total) was detected in three of the eight samples. Samples that contained methylmercury were collected from the Tuolumne River inflow sample, above Don Pedro Reservoir (0.029 J ng/L), the mid-reservoir hypolimnion of Don Pedro Reservoir (0.042 J ng/L), and the near-dam hypolimnion of Don Pedro Reservoir (0.053 ng/L), while methylmercury (dissolved) was detected at higher concentrations in the mid-reservoir hypolimnion of Don Pedro Reservoir (0.293 ng/L), and the near-dam hypolimnion of Don Pedro Reservoir (0.394 ng/L). These data show that methylmercury is present; however the exact concentration is uncertain. The reported dissolved concentrations are greater than total concentrations and the laboratory cannot explain why, other than the results reflecting the difficulty of measuring methylmercury near its reporting limits.

These data are consistent with reports of water quality and fish tissue data collected by Stillwater Sciences between fall 2008 and spring 2009 in which water quality samples and higher trophic level fish species were collected from nine sites within Don Pedro Reservoir and upstream and downstream of the reservoir (TID/MID 2009). Like this study, methylmercury was not detected below either the Don Pedro or La Grange dams and methylmercury was detected in hypolimnetic samples in the Moccasin Creek arm (0.15 ng/L) and Woods Creek (0.145 ng/L) arm of Don Pedro Reservoir. However, unlike this study, no mercury was detected in water samples collected from the Tuolumne River upstream of Don Pedro Reservoir.

In addition, Stillwater Sciences (TID/MID 2009) found evidence of fish mercury bioaccumulation. Concentrations in excess of the EPA (2001) fish tissue residue criterion (0.3 mg/kg⁹) were found at all sites with Don Pedro Reservoir, as well as downstream of La Grange

⁹ Since 2001, the California Office of Environmental Health Hazard Assessment (OEHHA) has issued Advisory Tissue Levels (ATLs) that are lower than the EPA (2001) mercury criterion. ATLs are screening values developed by OEHHA to help public

Dam in the lower Tuolumne River, with the highest fish tissue mercury concentrations (0.29 to 0.99 milligrams/kilogram [mg/kg]) observed in largemouth bass sampled from the shallow Moccasin Creek and Woods Creek arms of Don Pedro Reservoir. OEHHA has not issued a fish ingestion advisory for Don Pedro Reservoir (OEHHA 2009).

The Districts are unaware of any Project O&M activity that may affect mercury methylation and do not propose any activities associated with the release or mobilization of mercury.

6.9 Turbidity

The Basin Plan requires that waters be free of changes in turbidity that cause nuisance or adversely affect beneficial uses. This objective is expressed in terms of changes in turbidity (NTU) in the receiving water body: where natural turbidity is 0 to 5 NTUs, increases shall not exceed 1 NTU; where natural turbidity is 5 to 50 NTUs, increases shall not exceed 20 percent; where natural turbidity is 50 to 100 NTUs, increases shall not exceed 10 NTUs; and where natural turbidity is greater than 100 NTUs, increase shall not exceed 10 percent.

Spatial upstream-to-downstream turbidity trends are best seen in the data as it is presented in Attachment C, which provides sample results by location. In August 2012, turbidity was 8.6 NTU upstream of the Project (Tuolumne River above Don Pedro) and 0 NTU downstream of the Project (Below Don Pedro Dam). Three of the four intermediate locations also exhibited no turbidity. The Mid-reservoir (surface) sample had a turbidity reading of 283 NTU; review of temperature profiles indicated that this reading was near the thermocline, a location where plankton reportedly accumulate. Downstream of the La Grange Dam, turbidity data were not recorded when the sonde's probe did not properly record).

The Districts are unaware of any reports that turbidity causes a nuisance or adversely affects beneficial uses in the study area or immediately downstream of the Project.

6.10 Bacteria

The Basin Plan includes a Water Quality Objective (< 200 MPN per 100 mL) for fecal coliform in waters designated for contact recreation (Table 5.3-1), but does not provide a Water Quality Objective for total coliform or *Escherichia coli* (*E. coli*).

In 2012, all twelve recreation sites sampled had fecal coliform counts below the Water Quality Objective for the time surrounding and including Independence Day. Likewise, all total coliform counts and *E. coli* levels were below their respective benchmarks. *E. coli* counts are thought to be better indicators of human impacts (EPA 2003).

6.11 Floating Material

The Basin Plan includes a narrative Water Quality Objective regarding floating material that states water shall be free of floating material in amounts that cause nuisance or adversely affect

health managers decide whether or not to ask OEHHA to evaluate the need for a fish ingestion advisory for water bodies under the manager's jurisdiction (Klasing and Brodberg 2008).

beneficial uses. The FERC-approved study did not include a provision for measuring floating material. The Districts are unaware of any instances where floating material in Project waters has been reported as a potential problem.

6.12 Oil and Grease

The Basin Plan requires that the water not contain oils, greases, waxes or other material in concentrations that cause nuisance, result in visible film or coating on the surface of the water or on objects in the water, or otherwise adversely affect beneficial uses. In 2012, the Districts looked for and did not observe any oil and grease in Don Pedro Reservoir. Samples collected adjacent to 12 recreation sites on and around the Independence Day holiday and analyzed for TPH. TPH was not detected at any of the sites.

6.13 Dissolved Oxygen

The general DO Water Quality Objective of 7.0 mg/L applies to the Tuolumne River and its tributaries (CVRWQCB 1998).

Synoptic measurements of DO in August 2012 samples were all above Basin Plan numerical limits except the mid-reservoir hypolimnion of Don Pedro Reservoir (3.2 mg/L), and the near-dam hypolimnion of Don Pedro Reservoir (4.8 mg/L). These results were expected, since large, deep reservoirs/lakes generally form strong thermoclines with oxygen poor hypolimnions in the late summer/fall period and Don Pedro Reservoir is no exception to this rule (See PAD Section 5.2.1.5, Water Temperature). DO values were above the Basin Plan Objective in all surface samples.

7.0 STUDY VARIANCES AND MODIFICATIONS

The study was conducted in conformance to the FERC-approved Water Quality Assessment Study Plan (W&AR-01), with one variance. The FERC-approved study required collection of single samples at nine sites. During the sampling period, two of the three sites upstream of Don Pedro, Woods Creek and Sullivan Creek (Figure 3.0-1), contained no flowing water. However, the Tuolumne River above Don Pedro sample was collected and reflected inflow water quality conditions.

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**STUDY REPORT W&AR-01
WATER QUALITY ASSESSMENT**

ATTACHMENT A

QUALITY ASSURANCE PROJECT PLAN

PART 1

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**GROUP A ELEMENTS:
PROJECT MANAGEMENT**

1.0 TITLE AND APPROVAL SHEET

This Quality Assurance Program Plan (QAPP) is to be used by HDR, Inc. when implementing Water Quality Assessment stud(ies) in support of the Federal Energy Regulatory Commission (FERC) approved Water Quality Assessment study developed to support the relicensing of Turlock Irrigation District's (TID) and Modesto Irrigation District's (MID) (collectively, the Districts), Don Pedro Project (Project), FERC Project No. 2299.

This document is a supporting document to:

- Study W&AR-01 Water Quality Assessment (TID and MID 2011)

Prepared by:	_____	_____
	(Name)	(Date)
Approved by:	_____	_____
	(Name)	(Date)

2.0 DISTRIBUTION LIST

This document will be distributed to the key personnel listed in Table 2.0-1 and will be provided as an attachment to relevant reports and upon request.

Table 2.0-1. Personnel Responsibilities.

Name	Affiliation	Title	Contact Information
John Devine	HDR	Project Manager	970 Baxter Boulevard Suite 301 Portland, ME 04103 207.775.4495
Carin Loy	HDR	Study Lead	2379 Gateway Oaks, Suite 200 Sacramento, CA 95833 916-564-4214
Fred Holzmer	HDR	QA Officer	379 Gateway Oaks, Suite 200 Sacramento, CA 95833 916-564-4214
Chuck Vertucci	HDR	Field Coordinator	379 Gateway Oaks, Suite 200 Sacramento, CA 95833 916-564-4214
Don Burley	CalScience	Laboratory Project Manager	7440 Lincoln Way Garden Grove, CA 92841-1427 (714) 895-5494
Kate Haney	Frontier Global Sciences Inc	Laboratory Project Manager	11720 North Creek Parkway N. Suite 400 Bothell, WA 98011 425-686-1996, ext. 1526
TBD	IEH JL Analytical Services	Laboratory Project Manager	217 Primo Way Modesto, CA 95358 Phone: (209) 538-8111

3.0 PROJECT/TASK ORGANIZATION

3.1 Involved Parties and Roles

This QAPP has been prepared for the Water Quality Assessment investigation component(s) of the Project's relicensing. Within this QAPP are descriptions of methods, procedures, and practices that will be used to assure and control the quality of chemical data.

Key personnel who will be involved in the project are listed above in Table 3.0-1. Under contract to the TID and MID, HDR will be responsible for all aspects of the Water Quality Assessment study(ies) including the organization of field staff, scheduling of sampling days, field quality assurance/quality control (QA/QC), coordination with the off-site laboratory, and reporting. Laboratory analytical services will be provided by a California certified laboratory.

The Study Lead is responsible for monitoring and verifying implementation of the QA/QC procedures found in this QAPP. Key personnel assigned to the project will have reviewed the QAPP and will be instructed by Study Lead regarding the requirements of the QA/QC program. The Study Lead will work directly with the Field Coordinator or other designee and Laboratory Project Managers to ensure that QAPP objectives are being met. All members of the team will continually assess the effectiveness of the QA/QC program and recommend modifications, as needed.

3.2 Quality Assurance Officer Role

The QA Officer is familiar with the study, but not involved in day-to-day implementation. The QA officer is versed in HDR policies, Water Quality Assessment field sampling, and laboratory procedures. The QA officer will review the study's intermediate and final products, and work with the Study Lead to ensure they are of high quality when complete.

3.3 Persons Responsible for QAPP Update and Maintenance

The Study Lead is responsible for keeping the QAPP up-to-date. Modifications may be instigated by any member of the study team—the Study Lead, the Field Coordinator, the QA Officer, the laboratory project manager, or others. Exceptions to the content of this document will be formalized in the table following the title page. New versions of the QAPP will be available to project personnel and attached to subsequent reports. Variances and non-conformances with the QAPP will be documented in applicable project reports.

3.4 Organizational Chart and Responsibilities

The organizational chart for implementation of the Water Quality Assessment investigation component of the Project relicensing is presented in Figure 3.4-1.

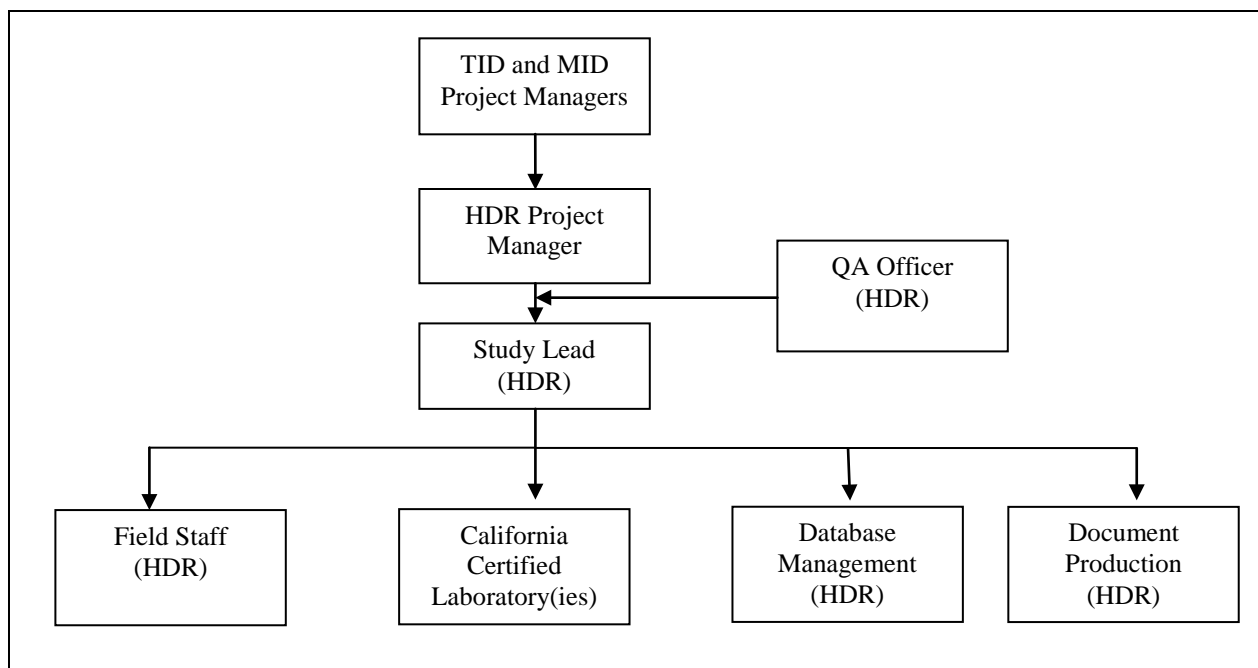


Figure 3.4-1. Organizational Chart

4.0 PROBLEM DEFINITION/BACKGROUND

4.1 Problem Statement

This QAPP has been developed to provide guidance and quality assurance for Water Quality Assessment sampling and analyses conducted to implement the FERC-approved Water Quality Assessment study plan(s) developed to support the Project's FERC relicensing.

4.2 Decisions or Outcomes

The collected data will provide one or more “snap-shots” of the physical and/or chemical state of surface water in the study area, defined in the study plan. The data will be filed with FERC in the Initial Study Report and in other relicensing documents, as needed, and will be suitable to compare to applicable regulatory standards and criteria. The data may be integrated with other information or data and used for trend analyses or for modeling. Additional information and detail can be found in the FERC-approved study plan(s).

4.3 Water Quality Assessment Regulatory Criteria

Water Quality Assessment objectives for Project reservoirs and Project affected stream reaches are established in Central Valley Regional Water Quality Assessment Control Board's (CVRWQCB) Water Quality Assessment Control Plan (Basin Plan) for the Sacramento and San Joaquin Rivers, the fourth edition of which was initially adopted in 1998 and most recently revised in 2011 (CVRWQCB 1998). The standards are composed of designated existing and potential beneficial uses and Water Quality Assessment objectives to protect the beneficial uses. Additional information and detail can be found in the FERC-approved study plan(s).

5.0 PROJECT/TASK DESCRIPTION

5.1 General Work Statement

Each FERC-approved study plan details the scope of the Water Quality Assessment investigation. Chemical constituents and characteristics of surface water will be measured both in the field and through collection of Water Quality Assessment samples for off-site analyses by a California certified laboratory. Examples of in situ water field measurements that may be performed include pH, specific conductivity, instantaneous water temperature, dissolved oxygen (DO), DO percent saturation, turbidity, and Secchi disk. Examples of analyses that may be performed on samples sent to an off-site California certified laboratory are trace metals, hardness, bacteria, sediment, nutrients, minerals, chlorophyll, pesticides, total petroleum hydrocarbons or other organics.

Refer to the “Group B Element: Data Generation and Acquisition” section of this QAPP for quality assurance practices associated with sample collection, instrument calibration, and so forth.

5.2 Project Schedule

The study schedule is specified in the FERC-approved study plan.

5.3 Geographical Setting

The Project is located in Tuolumne County, California, on the Tuolumne River, in the foothills of the Sierra Nevada.

5.4 Constraints

Water Quality Assessment sample collection will occur at elevations ranging from 44.4 to 2238.5 feet above sea level and may occur over a wide range of weather conditions (rain, snow, sun, wind, high heat, and cold weather). Stream flows may be high or low. Lake and reservoir sampling may require the use of a boat and occur at different stages of lake or reservoir surface elevation. Remote sites may require 4-wheel driving or long hikes carrying heavy bottles and equipment. Permission may need to be received from landowners prior to any work on private lands. Due to the distances covered, only five to nine locations may be visited in a single day and still meet the laboratory’s hours of operation or shipping deadlines.

Many of the watersheds where HDR works have extremely low naturally occurring levels of trace metals and waters are free or nearly free of contaminants. Hence, samples are highly susceptible to contamination during sampling and handling activities by both the field personnel and the analytical laboratory and the lowest possible method detection limits and reporting limits are required.

6.0 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Data quality objectives (DQOs) are a set of performance or acceptance criteria that the collected data should achieve in order to minimize the possibility of either making a decision error or failing to keep uncertainty in estimates to within acceptable levels. DQOs are defined in terms of five parameters: precision, accuracy, representativeness, completeness, and comparability (PARCC) and differ with different measurement techniques.

DQOs for relicensing Water Quality Assessment studies are presented in Table 6.0-1.

Table 6.0-1. Data Quality Objectives, by Measurement Type and Sampling Event

Precision	Accuracy	Representativeness	Completeness	Comparability
FIELD MEASUREMENTS (e.g. pH, specific conductivity, temperature, dissolved oxygen)				
--	Instrument calibration meets manufacturers' requirements	Sample locations, sampling frequency and analytical methods follow study plan.	90%	Meets Target Reporting Limits provided in the study plan.
ANALYTICAL LABORATORY ANALYSES (e.g. metals, nutrients)				
Field duplicates within 10%; Laboratory QA/QC meet method requirements.	Laboratory QA/QC meets method requirements.	Sample locations, sampling frequency and analytical methods follow study plan.	90%	Meets Target Reporting Limits provided in the study plan.
BACTERIA ANALYSES (e.g. fecal coliform, total coliform, e. coli)				
Field duplicates within 10%; Laboratory QA/QC meet method requirements.	Laboratory QA/QC meets method requirements.	Sample locations, sampling frequency and analytical methods follow study plan.	100%	Meets Target Reporting Limits provided in the study plan.

-- not applicable

Precision is a measure of the reproducibility of analyses under a given set of conditions. In other words, precision describes how well repeated measurements agree. Precision is typically evaluated by comparing analytical results from duplicate samples and calculating the relative percent difference (RPD), where RPD is defined as:

$$RPD = \left(\frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2} \right)} \right) \times 100, \text{ where } C_1 \text{ and } C_2 \text{ are the analyte's concentrations in each duplicate}$$

Precision will be determined through the use of field duplicates, laboratory matrix spike/matrix spike duplicates and laboratory duplicate quality control samples.

Accuracy is a measure of the bias that exists in a measurement system. In other words, accuracy describes how close an analytical measurement is to its “true” value. For analytical samples, accuracy is typically measured by analyzing a sample of known concentration (prepared using analytical-grade standards) and comparing the analytical result with the known concentration. For bacteria samples, accuracy is evaluated by comparing results to a laboratory reference sample.

Representativeness is the degree sampling data accurately and precisely depict selected characteristics. The representativeness of the data is mainly dependent on the sample design, such as locations (spatial), sampling frequency (temporal), and sample collection procedures, as well as analytical constituents and methods. The FERC-approved study plan presents the study design.

Completeness, which is expressed as a percentage, is calculated by subtracting the number of rejected and unreported results from the total planned results and dividing by the total number of planned results. Estimated results do not count against completeness because they are considered usable as long as any limitations are identified. Results rejected because of out-of-control analytical conditions, severe matrix effects, broken or spilled samples, or samples that could not be analyzed for any other reason are subtracted from the total planned number of results to calculate completeness. Though regulations currently do not require a specific percentage of data completeness, it is expected that the measurement techniques selected for use in this project are capable of generating data that is of 90% or more completeness for field and laboratory analyses.

Comparability is the degree of confidence with which one data set can be compared to another. A broad spectrum of analytical constituents has been selected to characterize Water Quality Assessment and the use of approved/documented analytical methods will ensure that analytical results adequately represent the true concentrations of constituents within these samples. In addition, Target Reporting Limits (TRLs) have been selected for each analyte, where appropriate, to ensure that the analytical methods used are of adequate sensitivity to generate useful data for the purposes of this project. Presented in the FERC-approved study plan, selection of appropriate TRLs was based on a review the CVWRCB’s numeric and narrative Water Quality Assessment objectives and other regulatory standards, criteria and benchmarks, as well as the capabilities of commercial laboratories.

7.0 SPECIAL TRAINING NEEDS/CERTIFICATION

Proper training of field and laboratory personnel represents a critical aspect of quality control.

All field personnel that participate in Water Quality Assessment monitoring will have reviewed this QAPP. Field personnel will have also been trained in Water Quality Assessment sample collection (including QA/QC, grab sampling techniques, flow measurement techniques, completing laboratory chain-of-custody forms, ordering correct laboratory analyses, and proper handling of water samples), field analysis (including instrument calibration, data recording procedures, and interpretation of collected data), and GPS use. All samplers will be provided hands-on training in the “clean hands-dirty hands” technique by the QA Officer or his designee when trace metals are constituents of interest (See Section 11). The QA Officer or his designee will provide training to field personnel. Documentation of training will be maintained in the project file.

All laboratories utilized to perform analytical services will be certified by the State of California. The certification includes requirements that laboratory personnel will be certified and trained. Certification and training is documented in the laboratory’s quality assurance manual and verified during the State audit¹.

¹ <http://www.cdph.ca.gov/certlic/labs/Pages/default.aspx>

8.0 DOCUMENTS AND RECORDS

8.1 Project Documents, Records, and Electronic Files

The documents and records that will be used or generated during this project include the following:

Study Plan. The FERC-approved study plan contains information regarding sampling locations, frequencies, sample collection methods, analytical methods, target reporting limits, and Water Quality Assessment objectives.

Quality Assurance Project Plan. The QAPP (this document) contains details on the quality assurance and quality control procedures that will be implemented throughout the Water Quality Assessment study(ies).

Field records. The Study Lead or designee will maintain all field records, including field data sheets documenting results of field analyses and QC samples, equipment maintenance and calibration documentation, and sample collection and handling documentation (copies of chain-of-custody forms, shipping receipts, etc.).

Laboratory records. The analytical laboratory will generate records for sample receipt and storage, instrument calibration, analytical QC, and reporting. Lab reports summarizing analytical results and QC results will be provided to HDR both in hard-copy and electronic formats. The information contained within and the format of the data report package will include at a minimum the sample identification number (ID), sampling date/time, test method, extraction date/time, analysis date/time, analytical result, QA sample results, instrument and equipment calibration information, and a description of any corrective action taken to resolve data quality issues.

Data verification records. Field data sheets, field QC results, chain-of-custody forms, and lab reports from each sampling event will be reviewed by the Study Lead and documented for the project file.

Project database. Microsoft Excel spreadsheets will be used to store all Water Quality Assessment data gathered during this project.

8.2 Retention of Project Documentation

Throughout the relicensing, the original field notebooks and forms, equipment maintenance and calibration documentation, chain-of-custody forms, laboratory reports, and data verification records will be stored at the HDR office at 2379 Gateway Oaks Drive, Suite 200, Sacramento, CA 95833. Records will be transferred to the Districts upon license receipt or earlier, at the Districts's discretion.

8.3 Electronic File Back-up

All electronic files will be stored on HDR network servers and will be backed-up on a regular basis by the HDR information technology staff

8.4 Distribution of QAPP Revisions

Revisions that occur after the original QAPP is approved will be indicated on the QAPP title page and will be distributed in subsequent deliverables and upon request.

**GROUP B ELEMENTS:
DATA GENERATION AND ACQUISITION**

9.0 SAMPLING PROCESS DESIGN

The FERC-approved study plan presents the study design, including sample locations, frequency of sample collection, analytical parameters, and laboratory methods.

10.0 SAMPLING METHODS

Data will be obtained in the field and in the laboratory.

The field sampler will maintain a field notebook and will note relevant conditions during each sampling event on the field data sheet. At a minimum, the following information pertaining to each sample will be recorded: date, time, weather conditions, name(s) of people collecting samples, units of measurements, depth, GPS coordinates for sample site, and river flow or reservoir water level.

Gloves and other appropriate personal protective equipment will be worn during sample and data collection activities. Observations of any field conditions that could affect sample results will be recorded in the field notebook, such as the concentrated presence of domestic animals or wildlife. Digital photo documentation of sampling conditions may also be performed. All field notes will be clearly written in a format that can be reproduced (i.e. scanned (pdf)) and entered into electronic format (Word or Excel).

10.1 Field Data Collection

The field measurement equipment that may be used during this project includes the following:

- Handheld multi-parameter meter (HydrolabTM DataSonde 5) or equivalent. A sonde will be used to measure water temperature ($\pm 0.1^{\circ}\text{C}$), dissolved oxygen (± 0.2 mg/L), pH (± 0.2 standard unit, or su), specific conductance (± 0.001 $\mu\text{mhos/cm}$), and turbidity (± 1 NTU) and depth.

Prior to each use, the instrument will be calibrated using manufacturer's recommended calibration methods (See Section 16). Any variances will be noted on the field data sheet and final report. If necessary to obtain a complete dataset, re-sampling within the FERC-approved study window will be performed. Non-disposable sampling equipment will be thoroughly cleaned between sampling sites.

Any field collected data that are not already in electronic format (Excel) will be hand entered into an electronic format and checked by a second-party.

10.2 Analytical Sample Collection

Surface samples will be collected using a grab sampling technique. Hypolimnetic samples will be collected using a Kemmerer bottle or equivalent. Each laboratory sample will be collected using laboratory-supplied clean containers, certified to meet the reporting limits specified in the study plan. Water samples to be analyzed for metals will be collected using "clean hands-dirty hands" method² consistent with the EPA Method 1669 sampling protocol as described in

² One member of a two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is all other activities that do not involve direct contact with the sample.

Sampling Ambient Water for Trace Metals at EPA Water Quality Assessment Criteria Levels (EPA 1996; Appendix A).

Samples requiring filtration before metals analysis will be filtered in accordance with standard protocols. Whether filtering is done in the field or the laboratory, samples will be filtered with a 0.45 micro millimeter (μm) diameter pore-membrane filter, prior to preservation. Filters used in the field will be disposable and certified clean at the desired reporting limits, specified in the study plan.

As part of the field quality assurance program, field blanks and equipment rinsates will also be collected and submitted to the laboratory for analysis (See Section 13). While still in the field, full sample containers will be labeled, placed in re-sealable plastic bags (e.g. Ziploc[®]), and stored in a cooler on ice to maintain a temperature of approximately 4° C.

11.0 SAMPLE HANDLING AND CUSTODY

A chain-of-custody record will be maintained with the laboratory samples at all times.

A chain-of-custody form that identifies the sample bottles, date and time of sample collection, and analyses requested will be initiated at the time of sample collection and prior to sample shipment or release. Identification information for each sample will be consistent with the information entered in the field notebook. The samples will be transported or shipped to the analytical lab in insulated containers within the appropriate holding time and will be accompanied by the chain-of-custody form. If shipment is needed, the samples will be packaged and shipped in accordance with U.S. Department of Transportation standards. The original chain-of-custody will be given to the lab with the samples and HDR will retain a copy for their records.

Once received by the laboratory, a sample receipt and storage record will be generated. The laboratory will perform all analyses within the constituent- or method- specific holding times.

After analyses, all samples will be disposed of in accordance with federal, state, and local requirements.

12.0 ANALYTICAL METHODS

The FERC-approved study plan presents the laboratory methods that will be employed. Containers, preservatives, holding times, and QA/QC requirements are specified in the analytical methods and/or in the laboratory's own standard operating procedures. Analytical methods are preferentially U.S. Environmental Protection Agency (EPA) or American Society for Testing and Materials (ASTM) methods and are detailed in the laboratory's own quality assurance manual.

For each analyte, the laboratory must be able to achieve target reporting limits and method detection limits that will allow consistency with the Basin Plan's Water Quality Assessment Objectives to be assessed. Because many of the watersheds where HDR works are free or nearly free of contaminants, low method detection limits and reporting limits are often required. Though not preferred, it may be necessary for the commercial laboratory to report estimated or "J-flagged" data to meet target reporting limits for some analytes.

13.0 QUALITY CONTROL

13.1 In Situ Data Collection

Projects that require pH and DO sampling also require a method of back-up or corrective action for inconsistent or questionable measurements collected in the field. For example, if pH is measured at less than 6 or greater than 8.5 in the field, a second measurement must be taken to verify the value. The second measurement could consist of ensuring that pH is included in the analyses of grab samples submitted to the California-certified laboratory, recalibrating the probe and re-measuring in the field, or returning to the site with a calibrated probe within the study window specified within the FERC-approved study plan. This information must be recorded in the field notes as well with explanations for the activity.

Projects that require DO sampling also require methods for back-up or corrective action measurements. For example, if a DO reading of less than 7 mg/L, for waters designated as COLD in the Basin Plan, is measured; then the instrument should be recalibrated and the sample collected again. If the reading is still questionable, then a sample must be collected for Winkler titration to verify the DO content of the water. Accurate field notes must be kept for any additional or back-up monitoring required in the field.

13.2 Sample Collection

QA/QC activities for sampling processes include the collection of field duplicates for bacterial and chemical testing, and the preparation of field blanks and/or equipment blanks as necessary. The number of duplicates should be one per every ten stations sampled or one per field visit.

Blanks will be prepared by pouring water known to be free of the substance of interest into a sample collection container then subsampling into the appropriate number of replicate sample containers. Ultrapure certified metals-free water will be used for hardness and metals.

13.3 Analytical Laboratory

All laboratories providing analytical support for this project will have the appropriate facilities to store, prepare, and process samples and appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. The California certified laboratory will have a quality assurance plan in place and will adhere to standard protocols for accuracy, precision, instrument bias, and analytical bias.

The laboratory's deliverable (i.e. data package) will include information documenting their ability to conduct the analyses with the required level of data quality. Such information may include results from inter-laboratory calibration studies, control charts, and summary data from internal QA/QC checks, and results from analyses of certified reference materials. Additionally, the laboratory will report any inconsistencies or problems associated with any sample run(s) to HDR, who will document the situation as a variance or non-conformance, as appropriate (e.g., contaminated reagents, equipment malfunction, lost or broken sample bottles upon receipt, etc.).

14.0 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

14.1 Field Equipment

The field measurement equipment that may be used during this project includes the following:

- Handheld multi-parameter meter (Hydrolab DataSonde 5). This sonde will be used to measure dissolved oxygen, temperature, pH, and conductivity in the field.

Prior to each field visit, the sonde will be rented from and calibrated by the manufacturer. Upon receipt of the Hydrolab and prior to leaving for the field, the Field Lead or his designee will confirm the probe is working. Written documentation of calibration will be maintained in the project file, attached to relevant reports, and provided upon request.

In the event that the sonde shows signs of malfunction or drift in readings during fieldwork, basic diagnostics will be performed. At a minimum, the following will be checked: batteries, computer connection, and software. The probes will be examined for obstructions, such as algae, or physical damage. The Hydrolab user manual will be taken into the field that includes some basic trouble shooting. If basic trouble shooting is not successful, the sampling team will order a replacement rental unit and return to sample the site in a few days and within the sample period specified in the FERC-approved Study Plan.

14.2 Laboratory Equipment

All laboratories utilized to perform analytical services will be certified by the State of California. The certification includes requirements that the laboratory maintain their analytical equipment in accordance with manufactures instructions and analytical method requirements. Instrument testing, inspection and maintenance procedures are documented in the laboratory's quality assurance manual and verified during the State's audit.³ Records will be kept at the laboratory and available upon request.

³ <http://www.cdph.ca.gov/certlic/labs/Pages/default.aspx>

15.0 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Field instruments will be calibrated according to manufacturer's instructions immediately before use in the field. Sondes will be rented from and calibrated by the manufacturer immediately before use in the field. Documentation of calibration prior to each field visit will be maintained in the project file.

16.0 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Project supplies and consumables that may directly or indirectly affect the quality of results include filters, samplers, gloves, bottles and more. To avoid contaminating samples through supplies, supply selection will be made to meet the needs of the study plan. Supplies will be examined for damage as they are received and consumables will be replaced no later than the date recommended in the manufacturer's instructions.

The California-certified laboratory will provide all bottles used for sample collection and cleanliness certification will be provided. Specifically, all equipment used for trace metals sample collection will be certified clean and double-bagged, allowing for the measurement at the concentrations required for the study plan using the clean hands-dirty hands technique described in EPA Method 1669 (Appendix A).

A small inventory of critical spare parts for field equipment (DO membranes, o-rings, and temperature and conductivity probes) will be kept by HDR and brought in the field if needed; however, perishable supplies or expensive parts may not be kept on hand, and will need to be ordered when needed. All spare parts and supplies will be obtained through the equipment manufacturer or other reputable sources.

17.0 NON-DIRECT MEASUREMENTS (EXISTING DATA)

Water Quality Assessment data has been previously collected in the study area. Though it is unknown at this time what existing data may be incorporated into relicensing documents, if any, the level of review of all incorporated existing data will be disclosed.

18.0 DATA MANAGEMENT

Field and laboratory data will be entered and maintained in Excel spreadsheets. The contract laboratory will provide an electronic data deliverable and an electronic narrative that includes, at a minimum, Level II documentation.

Throughout the relicensing, the original field notebooks and forms, equipment maintenance and calibration documentation, chain-of-custody forms, laboratory reports, and data verification records will be stored at the HDR office at 2379 Gateway Oaks Drive, Suite 200, Sacramento, CA 95833. Records will be transferred to the Districts upon license receipt or earlier, at the Districts' discretion.

**GROUP C ELEMENTS:
ASSESSMENT AND OVERSIGHT**

19.0 ASSESSMENTS AND RESPONSE ACTIONS

Periodic assessments will be conducted to ensure that data collection is conducted according to requirements presented in this QAPP. The Study Lead will have the primary responsibility for assessing compliance with the QAPP requirements pertaining to sample collection and handling procedures, field analytical procedures, laboratory analytical procedures, and communicating project status to the QA Officer and Project Manager. The QA Officer or his designee will conduct reviews of field sampling and analysis procedures at the beginning of each field season. The reviews may be performed at a demonstration site or involve accompanying sampling personnel to determine whether sampling activities are being conducted in accordance with the QAPP and Study Plan. Laboratory analyses will be assessed through evaluating results of QC samples and compliance with DQOs.

If a non-conformance is identified, the QA Officer and/or Study Lead, will notify the Project Manager immediately. The Project Manager, QA Office, and Study Lead will discuss the observed discrepancy with the appropriate person responsible for the activity to determine whether the information collected can still be considered accurate, what the cause(s) were leading to the deviation, how the deviation might impact data quality, and what corrective actions might be considered. The QA Officer and Study Lead will then follow up to ensure that corrective actions have been implemented.

20.0 REPORTS TO MANAGEMENT

The study schedule is specified in the FERC-approved study plan. As described in the study plan, the primary deliverable will be a technical memorandum, transmitting the data collected.

**GROUP D ELEMENTS:
DATA VALIDATION AND USABILITY**

21.0 DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

Data review, verification and validation are steps in the transition between data collection via sampling and analysis and data use and interpretation. Although data review, verification and data validation are commonly used terms, they are defined and applied differently in various organizations and quality systems. For the purposes of relicensing, the terms will be generally defined as follows:

- Data review ensures the data have been recorded, transmitted, and processed correctly. That includes, ensuring the data are sensible and checking for data entry, transcription, calculation, reduction, and transformation errors.
- Data verification is the process for evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual specifications (EPA 2002).
- Data validation is an analyte and sample specific process that extends the evaluation of data beyond method, procedure, or contractual compliance to determine the quality of a specific data set relative to the end use (EPA 2002). Data validation begins with the output from data verification.

22.0 VERIFICATION AND VALIDATION METHODS

Documentation of review, verification, and/or validation will be maintained in the project file.

For the relicensing, all data will be reviewed and verified. In brief, following the field sampling and laboratory analyses, which includes the laboratories' own QA/QC analyses, HDR will subject all data to QA/QC procedures including, but not limited to: spot-checks of transcription; review of electronic data submissions for completeness; comparison of results to field blank and rinsate results; and, identification of any data that seem inconsistent. If any inconsistencies are found, HDR will consult with the laboratory to identify any potential sources of error before concluding that the data is correct.

All verified chemical detections, including data whose results are "J" qualified, will be used for this assessment. Should the laboratory need to re-extract samples and re-run the sample under different calibration conditions, the data identified by the laboratory, as the most certain, will be used. If field-sampling conditions, as measured by the field blank and the rinsate sample results, indicate that samples have been corrupted, HDR will identify the data accordingly.

23.0 RECONCILIATION WITH USER REQUIREMENTS

To fulfill the Districts' data needs, it is important that the data collected during this project are accurate, precise, representative, and complete, and can therefore be used to characterize Water Quality Assessment within the the Districts Project area. These data requirements will be assessed by ensuring that DQOs are met throughout the project.

After each discrete sampling event, the Study Lead will evaluate if the data quality objectives (DQOs) of Table 7.0-1 have been met. Results of the evaluation will be documented on the Data Review and Verification Form provided in Appendix B. If the impact of the QC failure on data quality is minimal, the data will be flagged and included with in the database. If a greater impact is found, the Study Lead will work with the QA Officer to determine the next steps. Data that does not meet the DQOs listed in Section 7 will be evaluated to 1) determine the cause of the problem; 2) determine whether corrective actions can be implemented so that DQOs are met in the future; and/or 3) determine if re-sampling is necessary to meet completeness or other PARCC objectives.

At the end of the monitoring program, the data generated under this project will be given to the Districts.

24.0 REFERENCES

- Central Valley Regional Water Quality Control Board (CVRWQCB). 1998. The Water Quality Control Plan (Basin Plan) for the Sacramento River Basin and the San Joaquin River Basin. 4th ed. California Regional Water Quality Control Board, Central Valley Region. Revised in September 2009 with the Approved Amendments.
- EPA 2002. United States Environmental Protection Agency. 2002. Guidance on Environmental Data Verification and Data Validation (EPA QA/G-8), November 2002.

QUALITY ASSURANCE PROJECT PLAN

APPENDIX A

**SAMPLING AMBIENT WATERS FOR TRACE METALS AT EPA
WATER QUALITY LEVELS**

Method 1669

**Sampling Ambient Water for Trace Metals at EPA Water Quality
Criteria Levels**

July 1996

**U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460**

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Disclaimer

This sampling method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Further Information

For further information, contact:

W.A. Telliard
Engineering and Analysis Division (4303)
U.S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460
Phone: 202/260-7134
Fax: 202/260-7185

Introduction

This sampling method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, this sampling method, and the analytical methods referenced in Table 1 of this document, were developed by EPA to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which this sampling method and the referenced analytical methods are based.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance-based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this method should be directed to:

U.S. EPA NCEPI
11029 Kenwood Road
Cincinnati, OH 45242
513/489-8190

Note: This document is intended as guidance only. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected.

Method 1669

Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels

1.0 Scope and Application

- 1.1 This method is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals at the levels listed in Table 1. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act.
- 1.2 This method is applicable to the metals listed below and other metals, metals species, and elements amenable to determination at trace levels.

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium (III)	Cr ⁺³	16065-83-1
Chromium (VI)	Cr ⁺⁶	18540-29-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

- 1.3 This method is accompanied by the 1600 series methods listed in Table 1. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples.
- 1.4 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400-500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range. This guidance is therefore directed at the collection of samples to be measured at or near the levels listed in Table 1. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions.
- 1.5 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination. These techniques are given in Section 8.0 and are based on findings of researchers performing trace metals analyses (References 1-9).

- 1.6 Clean and Ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance to describe the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this sampling method due to a lack of exact definitions. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques (Reference 10).
- 1.7 This sampling method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 11).
- 1.8 Method 1669 is "performance-based"; i.e., an alternate sampling procedure or technique may be used, so long as neither samples nor blanks are contaminated when following the alternate procedures. Because the only way to measure the performance of the alternate procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the methods referenced in Table 1, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected. Section 9.2 provides additional details on the tests and documentation required to support equivalent performance.
- 1.9 For dissolved metal determinations, samples must be filtered through a 0.45 µm capsule filter at the field site. The filtering procedures are described in this method. The filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in this sampling method; procedures for laboratory preservation are provided in the methods referenced in Table 1. Preservation requirements are summarized in Table 2.
- 1.10 The procedures in this method are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality control levels.

2.0 Summary of Method

- 2.1 Before samples are collected, all sampling equipment and sample containers are cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water as described in the methods referenced in Table 1. The laboratory or cleaning facility is responsible for generating an acceptable equipment blank to demonstrate that the sampling equipment and containers are free from trace metals contamination before they are shipped to the field sampling team. An acceptable blank is one that is free from contamination below the minimum level (ML) specified in the referenced analytical method (Section 9.3).
- 2.2 After cleaning, sample containers are filled with weak acid solution, individually double-bagged, and shipped to the sampling site. All sampling equipment is also bagged for storage or shipment.

NOTE: EPA has found that, in some cases, it may be possible to empty the weak acid solution from the bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).

- 2.3 The laboratory or cleaning facility must prepare a large carboy or other appropriate clean container filled with reagent water (Section 7.1) for use with collection of field blanks during sampling activities. The reagent-water-filled container should be shipped to the field site and handled as all other sample containers and sampling equipment. At least

one field blank should be processed per site, or one per every ten samples, whichever is more frequent (Section 9.4). If samples are to be collected for determination of trivalent chromium, the sampling team processes additional QC aliquots as described in Section 9.6.

- 2.4 Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.
- 2.5 All sampling equipment and sample containers used for metals determinations at or near the levels listed in Table 1 must be nonmetallic and free from any material that may contain metals.
- 2.6 Sampling personnel are required to wear clean, nontalc gloves at all times when handling sampling equipment and sample containers.
- 2.7 In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site, or one field duplicate per every 10 samples, whichever is more frequent (Section 9.5). Section 9.0 gives a complete description of quality control requirements.
- 2.8 Sampling
 - 2.8.1 Whenever possible, samples are collected facing upstream and upwind to minimize introduction of contamination.
 - 2.8.2 Samples may be collected while working from a boat or while on land.
 - 2.8.3 Surface samples are collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter.
 - 2.8.4 Subsurface samples are collected by suction of the sample into an immersed sample bottle or by pumping the sample to the surface.
- 2.9 Samples for dissolved metals are filtered through a 0.45 μm capsule filter at the field site. After filtering, the samples are double-bagged and iced immediately. Sample containers are shipped to the analytical laboratory. The sampling equipment is shipped to the laboratory or cleaning facility for recleaning.
- 2.10 Acid preservation of samples is performed in the field or in the laboratory. Field preservation is necessary for determinations of trivalent chromium. It has also been shown that field preservation can increase sample holding times for hexavalent chromium to 30 days; therefore it is recommended that preservation of samples for hexavalent chromium be performed in the field. For other metals, however, the sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination.

- 2.11 Sampling activities must be documented through paper or computerized sample tracking systems.

3.0 Definitions

- 3.1 Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.
- 3.2 Definitions of other terms are given in the Glossary (Section 15.0) at the end of this method.

4.0 Contamination and Interferences

4.1 Contamination Problems in Trace Metals Analysis

- 4.1.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels (Reference 12). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.
- 4.1.2 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 3).

4.2 Contamination Control

- 4.2.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern.
- 4.2.1.1 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for controlling sample contamination are given in this sampling method and in the analytical methods referenced in Table 1.
- 4.2.1.2 Substances in a sample or in the surrounding environment cannot be allowed to contaminate the Apparatus used to collect samples for trace metals measurements. Requirements and suggestions for protecting the

Apparatus are given in this sampling method and in the methods referenced in Table 1.

4.2.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this sampling method and in the methods referenced in Table 1.

4.2.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample and Apparatus to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being performed. Therefore, it is imperative that the procedures described in this method be carried out by well trained, experienced personnel. Documentation of training should be kept on file and readily available for review.

4.2.2.1 Minimize exposure—The Apparatus that will contact samples or blanks should only be opened or exposed in a clean room, clean bench, glove box, or clean plastic bag, so that exposure to atmospheric inputs is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean, colorless zip-type bags. Minimizing the time between cleaning and use will also reduce contamination.

4.2.2.2 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.7) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.2.2.3 Use metal-free Apparatus—All Apparatus used for metals determinations at the levels listed in Table 1 must be nonmetallic and free of material that may contain metals. When it is not possible to obtain equipment that is completely free of the metal(s) of interest, the sample should not come into direct contact with the equipment.

4.2.2.3.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse

in or out of other materials, resulting either in contamination or low-biased results (Reference 3). Metal must not be used under any circumstance. Regardless of construction, all materials that will directly or indirectly contact the sample must be cleaned using the procedures described in the referenced analytical methods (see Table 1) and must be known to be clean and metal-free before proceeding.

4.2.2.3.2 The following materials have been found to contain trace metals and must not be used to hold liquids that come in contact with the sample or must not contact the sample, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 13).

4.2.2.3.3 Serialization—Serial numbers should be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the sampling process to shipment to the laboratory. Chain-of-custody procedures may also be used if warranted so that contamination can be traced to particular handling procedures or lab personnel.

4.2.2.3.4 The Apparatus should be clean when the sampling team receives it. If there are any indications that the Apparatus is not clean (e.g., a ripped storage bag), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.2.2.3.5 Details for recleaning the Apparatus between collection of individual samples are provided in Section 10.0.

4.2.2.4 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.2.2.4.1 Contamination by carryover—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. At sites where more than one sample will be collected, the sample known or expected to contain the lowest concentration of metals should be collected first with the sample containing the

highest levels collected last (Section 8.1.4). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. If the sampling team does not have prior knowledge of the waterbody, or when necessary, the sample collection system should be rinsed with dilute acid and reagent water between samples and followed by collection of a field blank (Section 10.3).

4.2.2.4.2 Contamination by samples—Significant contamination of the Apparatus may result when untreated effluents, in-process waters, landfill leachates, and other samples containing mid- to high-level concentrations of inorganic substances are processed. As stated in Section 1.0, this sampling method is not intended for application to these samples, and samples containing high concentrations of metals must not be collected, processed, or shipped at the same time as samples being collected for trace metals determinations.

4.2.2.4.3 Contamination by indirect contact—Apparatus that may not directly contact samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

4.2.2.4.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or wires; nearby roads; and even human breath (Section 4.1.2). Whenever possible, the sampling activity should occur as far as possible from sources of airborne contamination (Section 8.1.3). Areas where nearby soil is bare and subject to wind erosion should be avoided.

4.3 Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

5.0 Safety

5.1 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely determined; however, these chemicals should be treated as a potential health

hazard. Exposure should be reduced to the lowest possible level. Sampling teams are responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should also be made available to all personnel involved in sampling. It is also suggested that the organization responsible perform personal hygiene monitoring of each sampling team member who uses this method and that the results of this monitoring be made available to the member.

- 5.2 Operating in and around waterbodies carries the inherent risk of drowning. Life jackets must be worn when operating from a boat, when sampling in more than a few feet of water, or when sampling in swift currents.
- 5.3 Collecting samples in cold weather, especially around cold water bodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

6.0 Apparatus and Materials

NOTE: Brand names, suppliers, and part numbers are for illustration only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the sampling team and laboratory.

- 6.1 All sampling equipment and sample containers must be precleaned in a laboratory or cleaning facility, as described in the methods referenced in Table 1, before they are shipped to the field site. Performance criteria for equipment cleaning is described in the referenced methods. To minimize difficulties in sampling, the equipment should be packaged and arranged to minimize field preparation.
- 6.2 Materials such as gloves (Section 6.7), storage bags (Section 6.8), and plastic wrap (Section 6.9), may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either a different supplier must be obtained or the materials must be cleaned.
- 6.3 Sample Bottles—Fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL or 1 L with lids. If mercury is a target analyte, fluoropolymer or glass bottles should be used. Refer to the methods referenced in Table 1 for bottle cleaning procedures.
 - 6.3.1 Cleaned sample bottles should be filled with 0.1% HCl (v/v). In some cases, it may be possible to empty the weak acid solution from the sample bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).
 - 6.3.2 Whenever possible, sampling devices should be cleaned and prepared for field use in a class 100 clean room. Preparation of the devices in the field should be done within the glove bag (Section 6.6). Regardless of design, sampling devices must be constructed of nonmetallic material (Section 4.2.2.3.1) and free from material that contains metals. Fluoropolymer or other material shown not to

adsorb or contribute mercury must be used if mercury is a target analyte; otherwise, polyethylene, polycarbonate, or polypropylene are acceptable. Commercially available sampling devices may be used provided that any metallic or metal-containing parts are replaced with parts constructed of nonmetallic material.

6.4 Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.

6.4.1 The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 14). Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte. Assembly of the cleaned sampling device is as follows (refer to Figure 1):

6.4.1.1 Thread the pull cord (with the closing mechanism attached) through the guides and secure the pull ring with a simple knot. Screw a sample bottle onto the closing device and insert the bottle into the collar. Cock the closing plate so that the plate is pushed away from the operator.

6.4.1.2 The cleaned and assembled sampling device should be stored in a double layer of large, clean zip-type polyethylene bags or wrapped in two layers of clean polyethylene wrap if it will not be used immediately.

6.4.2 An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated (Reference 15).

6.5 Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by pumping the sample into a sample bottle. Examples of subsurface collection systems include the jar system device shown in Figure 3 and described in Section 6.5.1 or the continuous-flow apparatus shown in Figure 4 and described in Section 6.5.2.

6.5.1 Jar sampler (Reference 14)—The jar sampler (Figure 3) is comprised of a heavy fluoropolymer 1-L jar with a fluoropolymer lid equipped with two 1/4 in. fluoropolymer fittings. Sample enters the jar through a short length of fluoropolymer tubing inserted into one fitting. Sample is pulled into the jar by pumping on fluoropolymer tubing attached to the other fitting. A thick

fluoropolymer plate supports the jar and provides attachment points for a fluoropolymer safety line and fluoropolymer torpedo counterweight.

6.5.1.1 Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump, Section 6.15) is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean (Reference 14). In addition, the device is designed to eliminate atmospheric contact with the sample during collection.

6.5.1.2 To assemble the cleaned jar sampler, screw the torpedo weight onto the machined bolt attached to the support plate of the jar sampler. Attach a section of the 1/4 in. o.d. tubing to the jar by inserting the tubing into the fitting on the lid and pushing down into the jar until approximately 8 cm from the bottom. Tighten the fitting nut securely. Attach the solid safety line to the jar sampler using a bowline knot to the loop affixed to the support plate.

6.5.1.3 For the tubing connecting the pump to the sampler, tubing lengths of up to 12 m have been used successfully (Reference 14).

6.5.2 Continuous-flow sampler (References 16-17)—This sampling system, shown in Figure 4, consists of a peristaltic or submersible pump and one or more lengths of precleaned fluoropolymer or styrene/ethylene/butylene/ silicone (SEBS) tubing. A filter is added to the sampling train when sampling for dissolved metals.

6.5.2.1 Advantages of this sampling system include (1) all wetted surfaces are fluoropolymer or SEBS and can be readily cleaned; (2) the suction device is located in the boat, isolated from the sample bottle; (3) the sample does not travel through long lengths of tubing that are difficult to clean and keep clean; and (4) in-line filtration is possible, minimizing field handling requirements for dissolved metals samples.

6.5.2.2 The sampling team assembles the system in the field as described in Section 8.2.8. System components include an optional polyethylene pole to remove sampling personnel from the immediate vicinity of the sampling point and the pump, tubing, filter, and filter holder listed in Sections 6.14 and 6.15.

6.6 Field-Portable Glove Bag—I2R, Model R-37-37H (nontalc), or equivalent. Alternately, a portable glove box may be constructed with a nonmetallic (PVC pipe or other suitable material) frame and a frame cover made of an inexpensive, disposable, nonmetallic material (e.g., a thin-walled polyethylene bag) (Reference 7).

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- 6.7 Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; various lengths. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle into the water or when sampling for mercury.
- 6.7.1 Gloves, shoulder-length polyethylene—Associated Bag Co., Milwaukee, WI, 66-3-301, or equivalent.
- 6.7.2 Gloves, PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.
- 6.8 Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes).
- 6.9 Plastic Wrap—Clean, colorless polyethylene.
- 6.10 Cooler—Clean, nonmetallic, with white interior for shipping samples.
- 6.11 Ice or Chemical Refrigerant Packs—To keep samples chilled in the cooler during shipment.
- 6.12 Wind Suit—Pamida, or equivalent.
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NOTE: *This equipment is necessary only for collection of metals, such as mercury, that are known to have elevated atmospheric concentrations.*

- 6.12.1 An unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber is worn when sampling for mercury to prevent mercury adsorbed onto cotton or other clothing materials from contaminating samples.
- 6.12.2 Washing and drying—The wind suit is washed by itself or with other wind suits only in a home or commercial washing machine and dried in a clothes dryer. The clothes dryer must be thoroughly vacuumed, including the lint filter, to remove all traces of lint before drying. After drying, the wind suit is folded and stored in a clean polyethylene bag for shipment to the sample site.
- 6.13 Boat
- 6.13.1 For most situations (e.g., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping.
- 6.13.1.1 Immediately before use, the boat should be washed with water from the sampling site away from any sampling points to remove any dust or dirt accumulation.
- 6.13.1.2 Samples should be collected upstream of boat movement.
- 6.13.2 For mercury, and for situations in which the presence of contaminants cannot otherwise be controlled below detectable levels, the following equipment and precautions may be necessary:

- 6.13.2.1 A metal-free (e.g., fiberglass) boat, along with wooden or fiberglass oars. Gasoline- or diesel-fueled boat motors should be avoided when possible because the exhaust can be a source of contamination. If the body of water is large enough to require use of a boat motor, the engine should be shut off at a distance far enough from the sampling point to avoid contamination, and the sampling team should manually propel the boat to the sampling point. Samples should be collected upstream of boat movement.
 - 6.13.2.2 Before first use, the boat should be cleaned and stored in an area that minimizes exposure to dust and atmospheric particles. For example, cleaned boats should not be stored in an area that would allow exposure to automobile exhaust or industrial pollution.
 - 6.13.2.3 The boat should be frequently visually inspected for possible contamination.
 - 6.13.2.4 After sampling, the boat should be returned to the laboratory or cleaning facility, cleaned as necessary, and stored away from any sources of contamination until next use.
- 6.14 Filtration Apparatus—Required when collecting samples for dissolved metals determinations.
- 6.14.1 Filter—0.45 μm , 15 mm diameter or larger, tortuous-path capsule filters (Reference 18), Gelman Supor 12175, or equivalent.
 - 6.14.2 Filter holder—For mounting filter to the gunwale of the boat. Rod or pipe made from plastic material and mounted with plastic clamps.

NOTE: A filter holder may not be required if one or a few samples are to be collected. For these cases, it may only be necessary to attach the filter to the outlet of the tubing connected to the pump.

- 6.15 Pump and Pump Apparatus—Required for use with the jar sampling system (Section 6.5.1) or the continuous-flow system (Section 6.5.2). Peristaltic pump; 115 V a.c., 12 V d.c., internal battery, variable-speed, single-head, Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent.

NOTE: Equivalent pumps may include rotary vacuum, submersible, or other pumps free from metals and suitable to meet the site-specific depth sampling needs.

- 6.15.1 Cleaning—Peristaltic pump modules do not require cleaning. However, nearly all peristaltic pumps contain a metal head and metal controls. Touching the head or controls necessitates changing of gloves before touching the Apparatus. If a submersible pump is used, a large volume of sample should be pumped to clean the stainless steel shaft (hidden behind the impeller) that comes in contact with the sample. Pumps with metal impellers should not be used.

- 6.15.2 Tubing—For use with peristaltic pump. SEBS resin, approximately 3/8 in. i.d. by approximately 3 ft, Cole-Parmer size 18, Cat. No. G-06464-18, or approximately 1/4 in. i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent. Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.
- 6.15.3 Tubing—For connection to peristaltic pump tubing. Fluoropolymer, 3/8 or 1/4 in. o.d., in lengths as required to reach the point of sampling. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required. Cleaning of the fluoropolymer can be the same as cleaning the tubing for the rotary vacuum pump (Section 6.15.1.2). If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.
- 6.15.4 Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.
- 6.15.5 Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.
- 6.16 Carboy—For collection and storage of dilute waste acids used to store bottles.
- 6.17 Apparatus—For field preservation of aliquots for trivalent chromium determinations.
- 6.17.1 Fluoropolymer forceps—1 L fluoropolymer jar, and 30 mL fluoropolymer vials with screw-caps (one vial per sample and blank). It is recommended that 1 mL of ultrapure nitric acid (Section 7.3) be added to each vial prior to transport to the field to simplify field handling activities (See Section 8.4.4.6).
- 6.17.2 Filters—0.4 μm , 47 mm polycarbonate Nuclepore (or equivalent). Filters are cleaned as follows. Fill a 1 L fluoropolymer jar approximately two-thirds full with 1 N nitric acid. Using fluoropolymer forceps, place individual filters in the fluoropolymer jar. Allow the filters to soak for 48 hours. Discard the acid, and rinse five times with reagent water. Fill the jar with reagent water, and soak the filters for 24 hours. Remove the filters when ready for use, and using fluoropolymer forceps, place them on the filter apparatus (Section 6.17.3).
- 6.17.3 Vacuum filtration apparatus—Millipore 47 mm size, or equivalent, vacuum pump and power source (and extension cords, if necessary) to operate the pump.
- 6.17.4 Eppendorf auto pipet and colorless pipet tips (100-1000 μL)
- 6.17.5 Wrist-action shaker—Burrel or equivalent.

- 6.17.6 Fluoropolymer wash bottles—One filled with reagent water (Section 7.1) and one filled with high-purity 10% HCl (Section 7.4.4), for use in rinsing forceps and pipet tips.

7.0 Reagents and Standards

- 7.1 Reagent Water—Water in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method used for analysis of samples. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other techniques that remove the metal(s) and potential interferent(s). A large carboy or other appropriate container filled with reagent water must be available for the collection of field blanks.
- 7.2 Nitric Acid—Dilute, trace-metal grade, shipped with sampling kit for cleaning equipment between samples.
- 7.3 Sodium Hydroxide—Concentrated, 50% solution for use when field-preserving samples for hexavalent chromium determinations (Section 8.4.5).
- 7.4 Reagents—For field-processing aliquots for trivalent chromium determinations
- 7.4.1 Nitric Acid, Ultrapure—For use when field-preserving samples for trivalent chromium determinations (Sections 6.17 and 8.4.4).
- 7.4.2 Ammonium Iron (II) Sulfate Solution (0.01M)—Used to prepare the chromium (III) extraction solution (Section 7.4.3) necessary for field preservation of samples for trivalent chromium (Section 8.4.4). Prepare the ammonium iron (II) sulfate solution by adding 3.92 g ammonium iron (II) sulfate (ultrapure grade) to a 1 L volumetric flask. Bring to volume with reagent water. Store in a clean polyethylene bottle.
- 7.4.3 Chromium (III) extraction solution—For use when field-preserving samples for trivalent chromium determinations (Section 8.4.4). Prepare this solution by adding 100 mL of ammonium iron (II) sulfate solution (Section 7.4.2) to a 125 mL polyethylene bottle. Adjust pH to 8 with approximately 2 mL of ammonium hydroxide solution. Cap and shake on a wrist-action shaker for 24 hours. This iron (III) hydroxide solution is stable for 30 days.
- 7.4.4 Hydrochloric acid—High-purity, 10% solution, shipped with sampling kit in fluoropolymer wash bottles for cleaning trivalent chromium sample preservation equipment between samples.
- 7.4.5 Chromium stock standard solution (1000 µg/mL)—Prepared by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid. Store in polyethylene bottle. A commercially available standard solution may be substituted.
- 7.4.6 Standard chromium spike solution (1000 µg/L)—Used to spike sample aliquots for matrix spike/matrix spike duplicate (MS/MSD) analysis and to prepare ongoing precision and recovery standards. Prepared by spiking 1 mL of the

chromium stock standard solution (Section 7.4.5) into a 1 L flask. Dilute to volume with 1% HCl. Store in a polyethylene bottle.

- 7.4.7 Ongoing precision and recovery (OPR) standard (25 µg/L)—Prepared by spiking 2.5 mL of the standard chromium spike solution (Section 7.4.6) into a 100 mL flask. Dilute to volume with 1% HCl. One OPR is required for every 10 samples.

8.0 Sample Collection, Filtration, and Handling

8.1 Site Selection

- 8.1.1 Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.
- 8.1.2 Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples (Reference 19).
- 8.1.3 To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow (Reference 7).
- 8.1.4 The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.

- 8.2 Sample Collection Procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers). Sufficient sample volume

should be collected to allow for necessary quality control analyses, such as matrix spike/matrix spike duplicate analyses.

8.2.1 Four sampling procedures are described:

8.2.1.1 Section 8.2.5 describes a procedure for collecting samples directly into the sample container. This procedure is the simplest and provides the least potential for contamination because it requires the least amount of equipment and handling.

8.2.1.2 Section 8.2.6 describes a procedure for using a grab sampling device to collect samples.

8.2.1.3 Section 8.2.7 describes a procedure for depth sampling with a jar sampler. The size of sample container used is dependent on the amount of sample needed by the analytical laboratory.

8.2.1.4 Section 8.2.8 describes a procedure for continuous-flow sampling using a submersible or peristaltic pump.

8.2.2 The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the boat or equipment. If it is not possible to approach from both, the site should be approached from down current if sampling from a boat or approached from downwind if sampling on foot. When sampling from a boat, the bow of the boat should be oriented into the current (the boat will be pointed upstream). All sampling activity should occur from the bow.

If the samples are being collected from a boat, it is recommended that the sampling team create a stable workstation by arranging the cooler or shipping container as a work table on the upwind side of the boat, covering this worktable and the upwind gunnel with plastic wrap or a plastic tablecloth, and draping the wrap or cloth over the gunnel. If necessary, duct tape is used to hold the wrap or cloth in place.

8.2.3 All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (if the sample is not directly collected in the bottle) are handled by the individual designated as "clean hands." "Dirty hands" is responsible for all activities that do not involve direct contact with the sample.

Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may require a good deal of coordination and practice. For example, "dirty hands" must open the box or cooler containing the sample bottle and unzip the outer bag; clean hands must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place it in a cooler.

To minimize unnecessary confusion, it is recommended that a third team member be available to complete the necessary sample documentation (e.g., to document sampling location, time, sample number, etc). Otherwise, "dirty hands" must perform the sample documentation activity (Reference 7).

- 8.2.4 Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged.
- 8.2.5 Manual collection of surface samples directly into the sample bottle.
 - 8.2.5.1 At the site, all sampling personnel must put on clean gloves (Section 6.7) before commencing sample collection activity, with "clean hands" donning shoulder-length gloves. If samples are to be analyzed for mercury, the sampling team must also put their precleaned wind suits on at this time. Note that "clean hands" should put on the shoulder-length polyethylene gloves (Section 6.7.1) and both "clean hands" and "dirty hands" should put on the PVC gloves (Section 6.7.2).
 - 8.2.5.2 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.
 - 8.2.5.3 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.
 - 8.2.5.4 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes (Section 6.16) or discards the reagent water directly into the water body.
 - 8.2.5.5 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.
 - 8.2.5.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.
 - 8.2.5.7 "Dirty hands" zips the outer bag.
 - 8.2.5.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.5.9 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedure described in Section 8.3.

8.2.6 Sample collection with grab sampling device—The following steps detail sample collection using the grab sampling device shown in Figure 1 and described in Section 6.4.1. The procedure is indicative of the "clean hands/dirty hands" technique that must be used with alternative grab sampling devices such as that shown in Figure 2 and described in Section 6.4.2.

8.2.6.1 The sampling team puts on gloves (and wind suits, if applicable). Ideally, a sample bottle will have been preattached to the sampling device in the class 100 clean room at the laboratory. If it is necessary to attach a bottle to the device in the field, "clean hands" performs this operation, described in Section 6.4.2, inside the field-portable glove bag (Section 6.6).

8.2.6.2 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.

8.2.6.3 "Clean hands" opens the inside polyethylene bag and removes the sampling device.

8.2.6.4 "Clean hands" changes gloves.

8.2.6.5 "Dirty hands" submerges the sampling device to the desired depth and pulls the fluoropolymer pull cord to bring the seal plate into the middle position so that water can enter the bottle.

8.2.6.6 When the bottle is full (i.e., when no more bubbles appear), "dirty hands" pulls the fluoropolymer cord to the final stop position to seal off the sample and removes the sampling device from the water.

8.2.6.7 "Dirty hands" returns the sampling device to its large inner plastic bag, "clean hands" pulls the bottle out of the collar, unscrews the bottle from the sealing device, and caps the bottle. "Clean hands" and "dirty hands" then return the bottle to its double-bagged storage as described in Sections 8.2.5.6 through 8.2.5.7.

8.2.6.8 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the grab sampler, rinses the device with reagent water (Section 7.1), places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.

8.2.6.9 Sampling device—"Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.

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- 8.2.6.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.
- 8.2.6.11 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedures described in Section 8.3.
- 8.2.7 Depth sampling using a jar sampling device (Figure 3 and Section 6.5.1)
- 8.2.7.1 The sampling team puts on gloves (and wind suits, if applicable) and handles bottles as with manual collection (Sections 8.2.5.1 through 8.2.5.4 and 8.2.5.6 through 8.2.5.7).
- 8.2.7.2 "Dirty hands" removes the jar sampling device from its storage container and opens the outer polyethylene bag.
- 8.2.7.3 "Clean hands" opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally, the sampling device will have been preassembled in a class 100 clean room at the laboratory. If, however, it is necessary to assemble the device in the field, "clean hands" must perform this operation, described in Section 6.5.2, inside a field-portable glove bag (Section 6.6).
- 8.2.7.4 While "dirty hands" is holding the jar sampling apparatus, "clean hands" connects the pump to the to the 1/4 in. o.d. flush line.
- 8.2.7.5 "Dirty hands" lowers the weighted sampler to the desired depth.
- 8.2.7.6 "Dirty hands" turns on the pump allowing a large volume (>2 L) of water to pass through the system.
- 8.2.7.7 After stopping the pump, "dirty hands" pulls up the line, tubing, and device and places them into either a field-portable glove bag or a large, clean plastic bag as they emerge.
- 8.2.7.8 Both "clean hands" and "dirty hands" change gloves.
- 8.2.7.9 Using the technique described in Sections 8.2.5.2 through 8.2.5.4, the sampling team removes a sample bottle from storage, and "clean hands" places the bottle into the glove bag.
- 8.2.7.10 "Clean hands" tips the sampling jar and dispenses the sample through the short length of fluoropolymer tubing into the sample bottle.
- 8.2.7.11 Once the bottle is filled, "clean hands" replaces the cap of the bottle, returns the bottle to the inside polyethylene bag, and zips the bag. "Clean hands" returns the zipped bag to the outside polyethylene bag held by "dirty hands."
- 8.2.7.12 "Dirty hands" zips the outside bag. If the sample is to be analyzed for dissolved metals, it is filtered as described in Section 8.3.

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- 8.2.7.13 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.
- 8.2.8 Continuous-flow sampling (Figure 4 and Section 6.5.2)—The continuous-flow sampling system uses peristaltic pump (Section 6.15) to pump sample to the boat or to shore through the SEBS-resin or PTFE tubing.
- 8.2.8.1 Before putting on wind suits or gloves, the sampling team removes the bags containing the pump (Section 6.15), SEBS-resin tubing (Section 6.15.2), batteries (Section 6.15.4), gloves (Section 6.7), plastic wrap (Section 6.9), wind suits (Section 6.12), and, if samples are to be filtered, the filtration apparatus (Section 6.14) from the coolers or storage containers in which they are packed.
- 8.2.8.2 "Clean hands" and "dirty hands" put on the wind suits and PVC gloves (Section 6.7.2).
- 8.2.8.3 "Dirty hands" removes the pump from its storage bag, and opens the bag containing the SEBS-resin tubing.
- 8.2.8.4 "Clean hands" installs the tubing while "dirty hands" holds the pump. "Clean hands" immerses the inlet end of the tubing in the sample stream.
- 8.2.8.5 Both "clean hands" and "dirty hands" change gloves. "Clean hands" also puts on shoulder length polyethylene gloves (Section 6.7.1).
- 8.2.8.6 "Dirty hands" turns the pump on and allows the pump to run for 5-10 minutes or longer to purge the pump and tubing.
- 8.2.8.7 If the sample is to be filtered, "clean hands" installs the filter at the end of the tubing, and "dirty hands" sets up the filter holder on the gunwale as shown in Figure 4.
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- NOTE:** *The filtration apparatus is not attached until immediately before sampling to prevent buildup of particulates from clogging the filter.*
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- 8.2.8.8 The sample is collected by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.
- 8.2.8.9 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.
- 8.3 Sample Filtration—The filtration procedure described below is used for samples collected using the manual (Section 8.2.5), grab (Section 8.2.6), or jar (Section 8.2.7) collection systems (Reference 7). In-line filtration using the continuous-flow approach is described in Section 8.2.8.7. Because of the risk of contamination, it is recommended that samples for mercury be shipped unfiltered by overnight courier and filtered when received at the laboratory.

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- 8.3.1 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.
- 8.3.2 "Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 8.2.5.2 through 8.2.5.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.
- 8.3.3 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.
- 8.3.4 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.
- 8.3.5 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.
- 8.3.6 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.
- 8.3.7 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle. If preservation is required, the sample is acidified at this point (Section 8.4).
- 8.3.8 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."
- 8.3.9 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

NOTE: *It is not advisable to reclean and reuse filters. The difficulty and risk associated with failing to properly clean these devices far outweighs the cost of purchasing a new filter.*

8.4 Preservation

- 8.4.1 Field preservation is not necessary for dissolved metals, except for trivalent and hexavalent chromium, provided that the sample is preserved in the laboratory and allowed to stand for at least two days to allow the metals adsorbed to the container walls to redissolve. Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days. Mercury samples should be shipped by overnight courier and preserved when received at the laboratory.

- 8.4.2 If field preservation is required, preservation must be performed in the glove bag or in a designated clean area, with gloved hands, as rapidly as possible to preclude particulates from contaminating the sample. For preservation of trivalent chromium, the glove bag or designated clean area must be large enough to accommodate the vacuum filtration apparatus (Section 6.17.3), and an area should be available for setting up the wrist-action shaker (Section 6.17.5). It is also advisable to set up a work area that contains a "clean" cooler for storage of clean equipment, a "dirty" cooler for storage of "dirty" equipment, and a third cooler to store samples for shipment to the laboratory.
- 8.4.3 Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample. This will be sufficient to preserve a neutral sample to pH <2.
- 8.4.4 Preservation of aliquots for trivalent chromium (References 8-9).
- 8.4.4.1 Decant 100 mL of the sample into a clean polyethylene bottle.
- 8.4.4.2 Clean an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL of chromium (III) extraction solution (Section 7.4.3) to each sample and blank.
- 8.4.4.3 Cap each bottle tightly, place in a clean polyethylene bag, and shake on a wrist action shaker (Section 6.17.5) for one hour.
- 8.4.4.4 Vacuum-filter the precipitate through a 0.4 μ m pretreated filter membrane (Section 6.17.2), using fluoropolymer forceps (Section 6.17.1) to handle the membrane, and a 47 mm vacuum filtration apparatus with a precleaned filter holder (Section 6.17.3). After all sample has filtered, rinse the inside of the filter holder with approximately 15 mL of reagent water.
- 8.4.4.5 Using the fluoropolymer forceps, fold the membrane in half and then in quarters, taking care to avoid touching the side containing the filtrate to any surface. (Folding is done while the membrane is sitting on the filter holder and allows easy placement of the membrane into the sample vial). Transfer the filter to a 30 mL fluoropolymer vial. If the fluoropolymer vial was not pre-equipped with the ultrapure nitric acid (Section 7.4.1), rinse the pipet by drawing and discharging 1 mL of 10% HCl followed by 1 mL of reagent water into a waste container, and add 1 mL of ultrapure nitric acid to the sample vial.
- 8.4.4.6 Cap the vial and double-bag it for shipment to the laboratory.
- 8.4.4.7 Repeat Steps 8.4.4.4-8.4.4.6 for each sample, rinsing the fluoropolymer forceps and the pipet with 10% high-purity HCl followed by reagent water between samples.
- 8.4.5 Preservation of aliquots for hexavalent chromium (Reference 20).

8.4.5.1 Decant 125 mL of sample into a clean polyethylene bottle.

8.4.5.2 Prepare an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL NaOH to each 125 mL sample and blank aliquot.

8.4.5.3 Cap the vial(s) and double-bag for shipment to the laboratory.

9.0 Quality Assurance/Quality Control

9.1 The sampling team shall employ a strict quality assurance/ quality control (QA/QC) program. The minimum requirements of this program include the collection of equipment blanks, field blanks, and field replicates. It is also desirable to include blind QC samples as part of the program. If samples will be processed for trivalent chromium determinations, the sampling team shall also prepare method blank, OPR, and MS/MSD samples as described in Section 9.6.

9.2 The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks. The requirements for modification are given in Sections 9.3 and 9.4. Because the acceptability of a modification is based on the results obtained with the modification, the sampling team must work with an analytical laboratory capable of making trace metals determinations to demonstrate equivalence.

9.3 Equipment Blanks

9.3.1 Before using any sampling equipment at a given site, the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

9.3.2 Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device, then an equipment blank must be run on both pieces of equipment.

9.3.3 Equipment blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the equipment using the same procedures that are used in the field (Section 8.0). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility. In addition, training programs must require sampling personnel to collect a clean equipment blank before performing on-site field activities.

9.3.4 Detailed procedures for collecting equipment blanks are given in the analytical methods referenced in Table 1.

9.3.5 The equipment blank must be analyzed using the procedures detailed in the

referenced analytical method (see Table 1). If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank at the minimum level specified in the referenced method, the source of contamination/interference must be identified and removed. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

9.4 Field Blank

- 9.4.1 To demonstrate that sample contamination has not occurred during field sampling and sample processing, at least one field blank must be generated for every 10 samples that are collected at a given site. Field blanks are collected before sample collection.
- 9.4.2 Field blanks are generated by filling a large carboy or other appropriate container with reagent water (Section 7.1) in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis in accordance with the method(s) referenced in Table 1. For example, manual grab sampler field blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler field blanks are collected by immersing the tubing into the water and pumping water into a sample container.
- 9.4.3 Filter the field blanks using the procedures described in Section 8.3.
- 9.4.4 If it is necessary to acid clean the sampling equipment between samples (Section 10.0), a field blank should be collected after the cleaning procedures but before the next sample is collected.
- 9.4.5 If trivalent chromium aliquots are processed, a separate field blank must be collected and processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.5 Field Duplicate

- 9.5.1 To assess the precision of the field sampling and analytical processes, at least one field duplicate sample must be collected for every 10 samples that are collected at a given site.
- 9.5.2 The field duplicate is collected either by splitting a larger volume into two aliquots in the glove box, by using a sampler with dual inlets that allows simultaneous collection of two samples, or by collecting two samples in rapid succession.
- 9.5.3 Field duplicates for dissolved metals determinations must be processed using the procedures in Section 8.3. Field duplicates for trivalent chromium must be processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.6 Additional QC for Collection of Trivalent Chromium Aliquots

- 9.6.1 Method blank—The sampling team must prepare one method blank for every ten or fewer field samples. Each method blank is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on a 100 mL aliquot of reagent water (Section 7.1). Do not use the procedures in Section 8.3 to process the method blank through the 0.45 μm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.
- 9.6.2 Ongoing precision and recovery (OPR)—The sampling team must prepare one OPR for every ten or fewer field samples. The OPR is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on the OPR standard (Section 7.4.7). Do not use the procedures in Section 8.3 to process the OPR through the 0.45 μm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.
- 9.6.3 MS/MSD—The sampling team must prepare one MS and one MSD for every ten or fewer field samples.
- 9.6.3.1 If, through historical data, the background concentration of the sample can be estimated, the MS and MSD samples should be spiked at a level of one to five times the background concentration.
- 9.6.3.2 For samples in which the background concentration is unknown, the MS and MSD samples should be spiked at a concentration of 25 $\mu\text{g/L}$.
- 9.6.3.3 Prepare the matrix spike sample by spiking a 100-mL aliquot of sample with 2.5 mL of the standard chromium spike solution (Section 7.4.6), and processing the MS through the steps in Sections 8.4.4.1 through 8.4.4.6.
- 9.6.3.4 Prepare the matrix spike duplicate sample by spiking a second 100-mL aliquot of the same sample with 2.5 mL of the standard chromium spike solution, and processing the MSD through the steps in Sections 8.4.4.1 through 8.4.4.6.
- 9.6.3.5 If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 μm filter as described in Section 8.3.

10.0 Recleaning the Apparatus Between Samples

- 10.1 Sampling activity should be planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals collected last. In this manner, cleaning of the sampling equipment between samples is unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment should be provided for each sampling event.
- 10.2 If samples are collected from adjacent sites (e.g., immediately upstream or downstream), rinsing of the sampling Apparatus with water that is to be sampled should be sufficient.

- 10.3 If it is necessary to cross a gradient (i.e., going from a high-concentration sample to a low-concentration sample), such as might occur when collecting at a second site, the following procedure may be used to clean the sampling equipment between samples:
- 10.3.1 In the glove bag, and using the "clean hands/dirty hands" procedure in Section 8.2.5, process the dilute nitric acid solution (Section 7.2) through the Apparatus.
 - 10.3.2 Dump the spent dilute acid in the waste carboy or in the waterbody away from the sampling point.
 - 10.3.3 Process 1 L of reagent water through the Apparatus to rinse the equipment and discard the spent water.
 - 10.3.4 Collect a field blank as described in Section 9.4.
 - 10.3.5 Rinse the Apparatus with copious amounts of the ambient water sample and proceed with sample collection.
- 10.4 Procedures for recleaning trivalent chromium preservation equipment between samples are described in Section 8.4.4.

11.0 Method Performance

Samples were collected in the Great Lakes during September–October 1994 using the procedures in this sampling method.

12.0 Pollution Prevention

- 12.1 The only materials used in this method that could be considered pollutants are the acids used in the cleaning of the Apparatus, the boat, and related materials. These acids are used in dilute solutions in small amounts and pose little threat to the environment when managed properly.
- 12.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.
- 12.3 To the extent possible, the Apparatus used to collect samples should be cleaned and reused to minimize the generation of solid waste.

13.0 Waste Management

- 13.1 It is the sampling team's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.
- 13.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better—Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

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15.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this sampling method but have been conformed to common usage as much as possible.

- 15.1 Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.
- 15.2 Apparatus—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.
- 15.3 Equipment Blank—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before they are shipped to the field site. An acceptable equipment blank must be achieved before the sampling devices and Apparatus are used for sample collection.
- 15.4 Field Blank—An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine whether the field or sample transporting procedures and environments have contaminated the sample.
- 15.5 Field Duplicates (FD1 and FD2)—Two identical aliquots of a sample collected in separate sample bottles at the same time and place under identical circumstances using a dual

inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

- 15.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.
- 15.7 May—This action, activity, or procedural step is optional.
- 15.8 May Not—This action, activity, or procedural step is prohibited.
- 15.9 Minimum Level (ML)—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 21).
- 15.10 Must—This action, activity, or procedural step is required.
- 15.11 Reagent Water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal in the referenced method or additional method.
- 15.12 Should—This action, activity, or procedural step is suggested but not required.
- 15.13 Trace-Metal Grade—Reagents that have been demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of this metal(s).

The term "trace-metal grade" has been used in place of "reagent grade" or "reagent" because acids and other materials labeled "reagent grade" have been shown to contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

**TABLE 1. ANALYTICAL METHODS, METALS, AND CONCENTRATION LEVELS
APPLICABLE TO METHOD 1669**

Method	Technique	Metal	MDL (µg/L) ¹	ML (µg/L) ²
1631	Oxidation/Purge & Trap/CVAFS	Mercury	0.0002	0.0005
1632	Hydride AA	Arsenic	0.003	0.01
1636	Ion Chromatography	Hexavalent Chromium	0.23	0.5
1637	CC/STGFAA	Cadmium	0.0075	0.02
		Lead	0.036	0.1
1638	ICP/MS	Antimony	0.0097	0.02
		Cadmium	0.013	0.1
		Copper	0.087	0.2
		Lead	0.015	0.05
		Nickel	0.33	1
		Selenium	0.45	1
		Silver	0.029	0.1
		Thallium	0.0079	0.02
		Zinc	0.14	0.5
1639	STGFAA	Antimony	1.9	5
		Cadmium	0.023	0.05
		Trivalent Chromium	0.10	0.2
		Nickel	0.65	2
		Selenium	0.83	2
		Zinc	0.14	0.5
1640	CC/ICP/MS	Cadmium	0.0024	0.01
		Copper	0.024	0.1
		Lead	0.0081	0.02
		Nickel	0.029	0.1

¹ Method Detection Limit as determined by 40 *CFR* Part 136, Appendix B.

² Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50, etc., in accordance with procedures used by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

TABLE 2. ANALYTES, PRESERVATION REQUIREMENTS, AND CONTAINERS

Metal	Preservation Requirements	Acceptable Containers
Antimony Arsenic Cadmium Copper Lead Nickel Selenium Silver Thallium Zinc	Add 5 mL of 10% HNO_3 to 1-L sample; preserve on-site or immediately upon laboratory receipt.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (III)	Add 1 mL chromium (III) extraction solution to 100 mL aliquot, vacuum filter through 0.4 μm membrane, add 1 mL 10% HNO_3 ; preserve on-site immediately after collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (IV)	Add 50% NaOH ; preserve immediately after sample collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Mercury	Total: Add 0.5% high-purity HCl or 0.5% BrCl to $\text{pH} < 2$; Total & Methyl: Add 0.5% high-purity HCl ; preserve on-site or immediately upon laboratory receipt	Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps

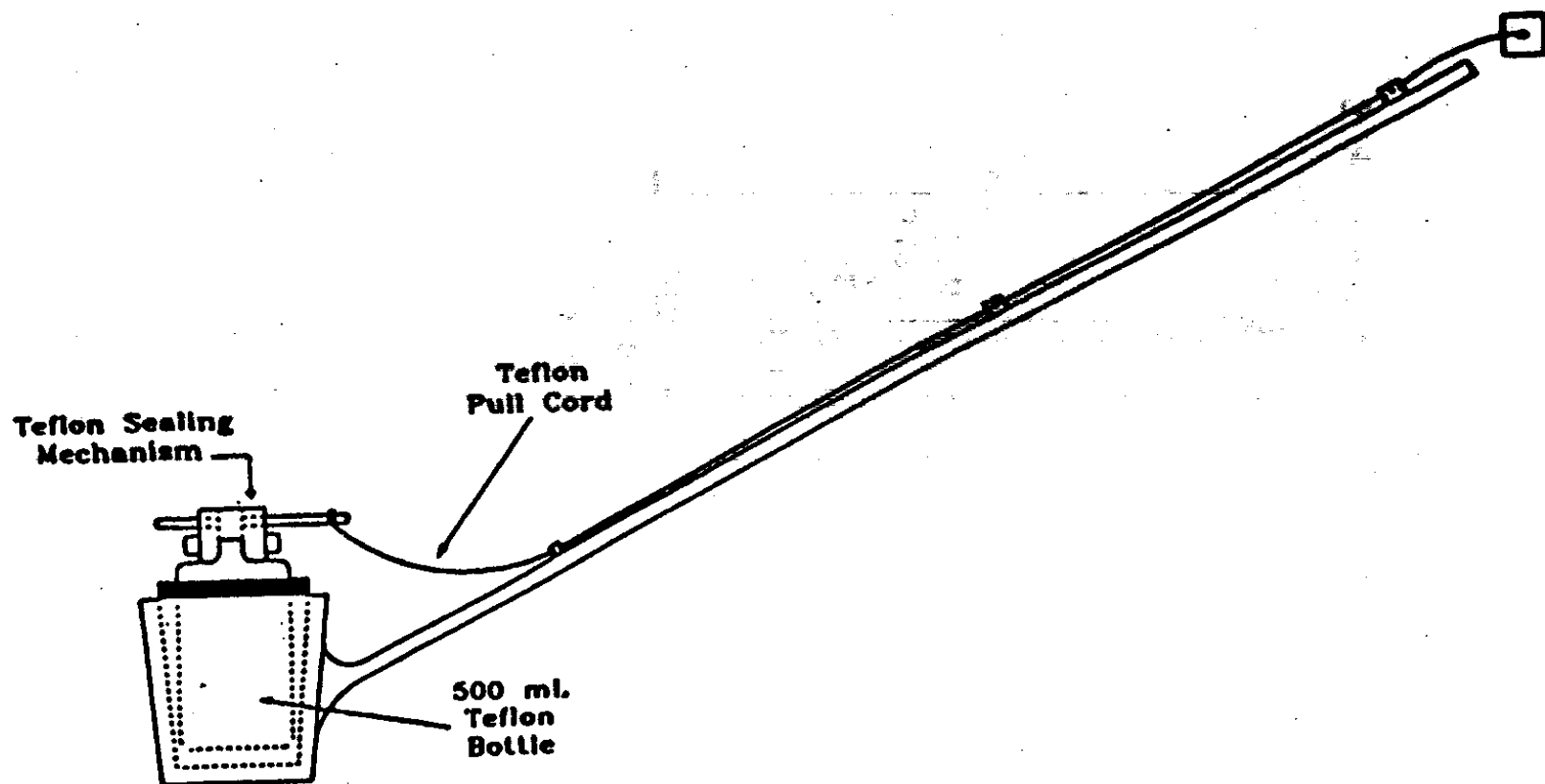
Figure 1 - Grab Sampling Device

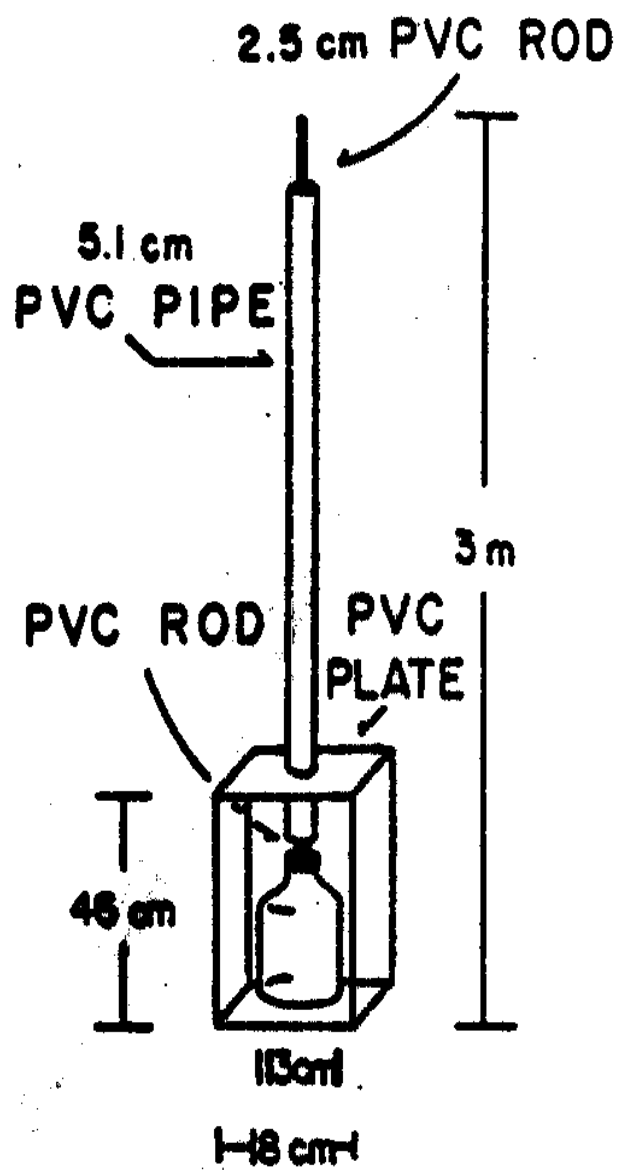
Figure 2 - Grab Sampling Device

Figure 3 - Jar Sampling Device

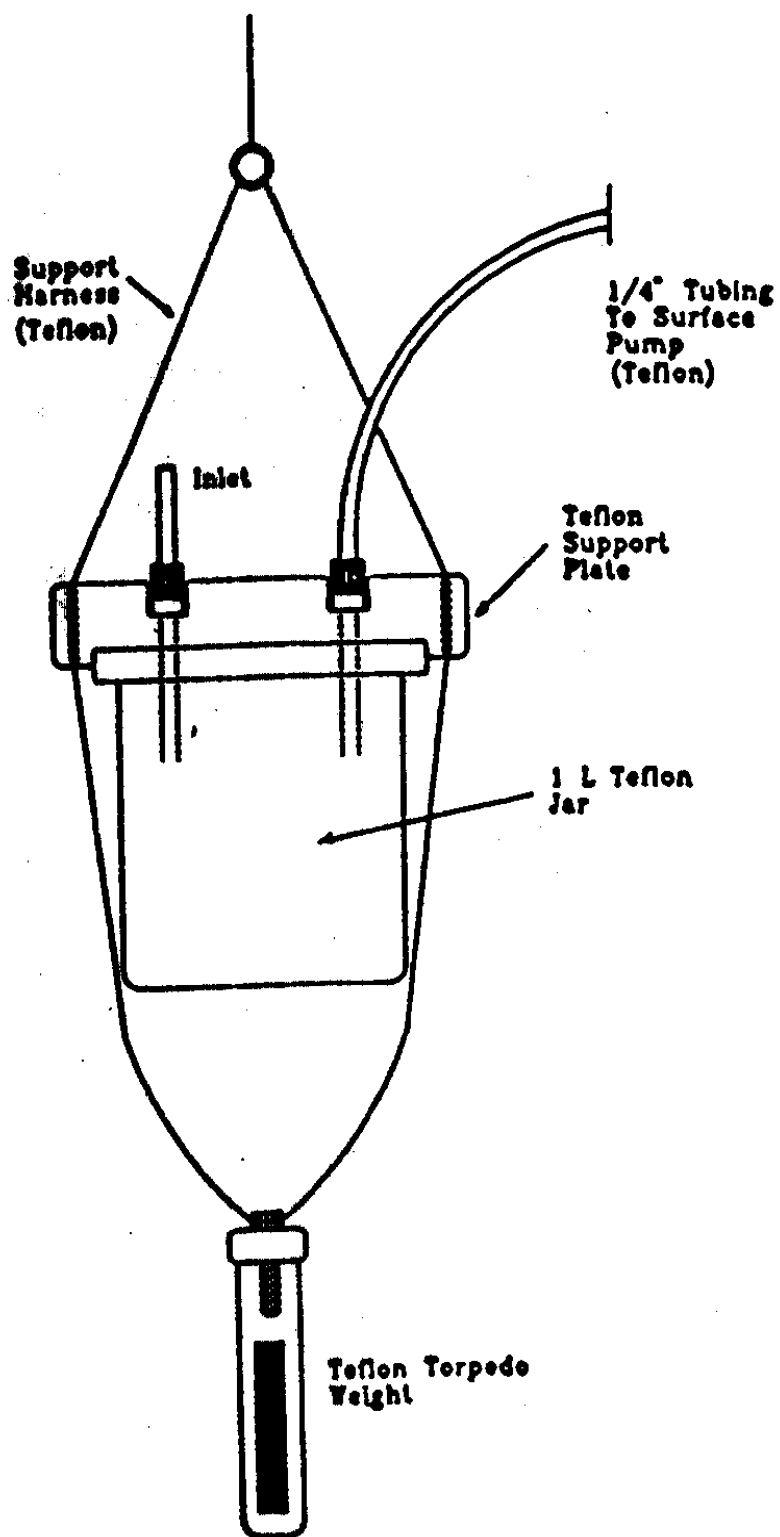
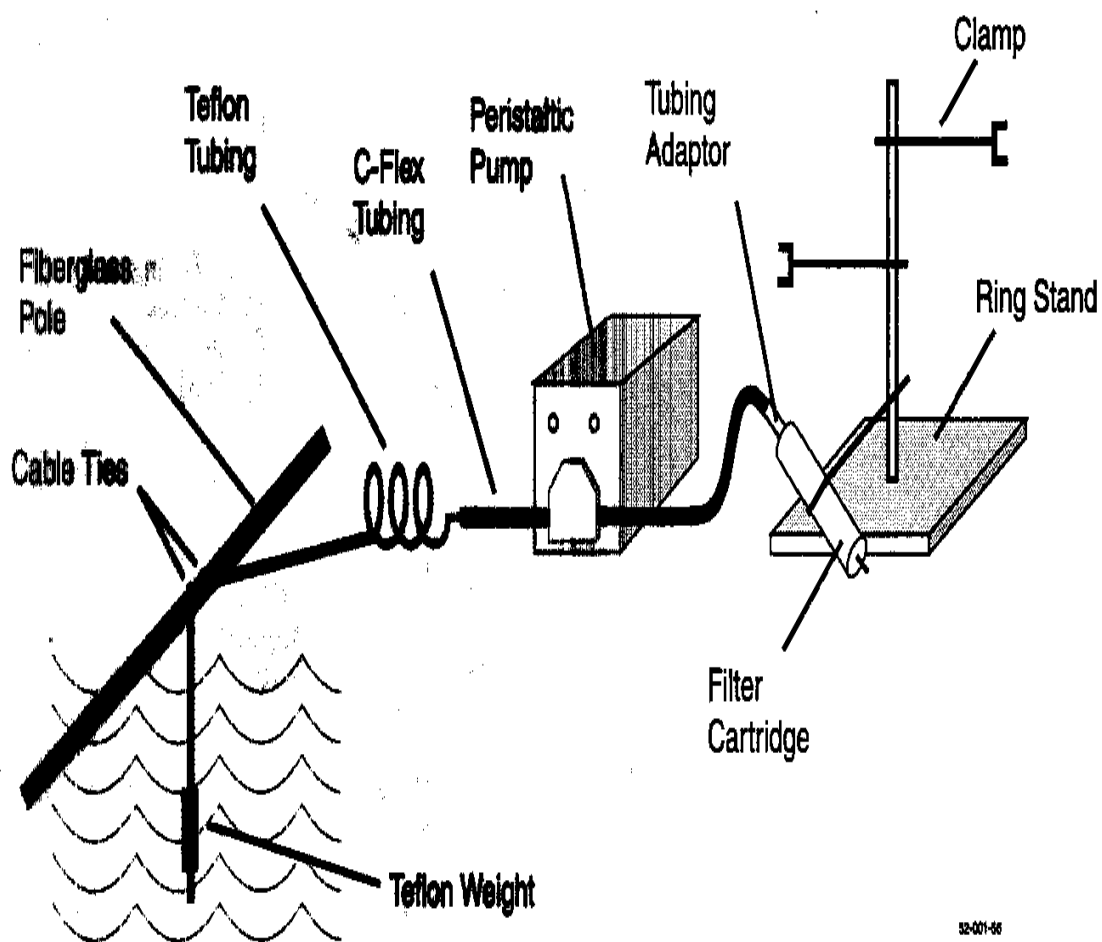


Figure 4 - Sample Pumping System

52-001-56

QUALITY ASSURANCE PROJECT PLAN

APPENDIX B

DATA REVIEW AND VERIFICATION CHECKLIST

DATA REVIEW AND VERIFICATION CHECKLIST

This checklist should be used to document data review verification of data generated through implementation of the FERC-approved study plan.

GENERAL

- ☐ For each sample event, samples have been collected and analyzed at all locations and for all analyses specified in the study plan.
- ☐ For each sample and analyses, the project file contains records field notes, chain-of-custody, and analytical results, including quality assurance documentation (hardcopy and electronic)

FIELD DATA

- ☐ Field notes and/or data sheets include date, time of sample collection, field sampling staff, time arrived at site, time left site, site identification, description of site conditions (weather), field parameters, reservoir level or flow information (measured or estimated), sample collection procedures, and call-out quality assurance samples collected. If mistakes are found on the field data sheet, changes can be made by crossing out the mistake and marking the change with a date of change, initials, and reason for change.
- ☐ Documentation of field equipment calibration is in the fieldnotes and/or project records.
- ☐ Field data entered into Excel, have been checked by a second-party.

LABORATORY REPORT

- ☐ Field duplicates, blanks, and rinsates were submitted to the laboratory at the frequency specified in the study plan.
- ☐ Any constituents found in blanks or rinsates are discussed in the final report.
- ☐ Any duplicate concentrations that differ by more than 10% are discussed in the final report.
- ☐ Samples were received by the laboratory intact and analyzed within method and/or study specified holding times.
- ☐ On laboratory reports, sample IDs, analyses, reporting/detection limits, units, column labels, footnotes, and titles are accurate. Have lab re-issue report with corrections if there are inconsistencies.
- ☐ Check that non-detects are always reported in the same manner using consistent notation. For example, either “ND” or “<.” Have lab re-issue report with corrections if there are inconsistencies.
- ☐ If observed, “J” qualified data and/or elevated detection limits are discussed in the final report.

**STUDY REPORT W&AR-01
WATER QUALITY ASSESSMENT**

ATTACHMENT B

FIELD QUALITY ASSURANCE DOCUMENTATION

DATE 10-24-08	DOCUMENT#: 19002-00-Series5Sonde
PAGE	REVISION 3

3.0 Series 5, and 5X Sonde Functional Test Data Sheet

Section A:

Service Request # <u>312222835</u>	Customer <u>Rental</u>	Date Started <u>07-25-12</u>
Housing Serial # <u>R49422</u>	Embedded Serial# <u>R49422</u>	Additional Driver Firmware:
Technician <u>HL</u>	Model: <u>Datasonde</u> <u>Minisonde</u> <u>Pipesonde</u> <u>5</u> <u>5X</u>	

Customer Display Information

ID	DOM	Baud Rate	Security	SDI	TTY
Parameter	<u>Time</u>	<u>Temp</u>	<u>pH</u>	<u>Speed</u>	<u>Sal</u>
Units		<u>°C</u>	<u>units</u>	<u>km/h</u>	<u>ppm</u>
Parameter	<u>Turb</u>	<u>DO%</u>	<u>DO</u>	<u>Depth</u>	<u>Temp</u>
Units	<u>SC</u>	<u>sat</u>	<u>mg/l</u>	<u>meters</u>	<u>Volts</u>

For Sonde with Depth - Coefficients

A:	B:	C:	D:
E:	F:	G:	H:
I:	J:	SER:	

FLUOROMETER OFFSETS

1 ST	X10:	X1:
2 ND	X10:	X1:

For Sonde with TDG or PAR - Coefficients

A:	B:	C:	D:
Local:	Ref:		

Performance, Test and Evaluation

Current MPL Rev-- <u>543</u>	pH Electrolyte & Teflon Junction Replaced-	DO membrane Replaced
Upgrade to MPL Rev-- <u>543</u>	Yes <u>No</u> NA	Yes <u>No</u> NA
Lenses cleaned -Yes <u>No</u> NA	RTC Battery Replaced <u>Yes</u> No	Desiccant Replaced <u>Yes</u>

Section B:

	Submission Day	Submission Day	Submission Day
	/ Y / N / PT&E / Upgrade	/ Y / N / PT&E / Upgrade	/ Y / N / PT&E / Upgrade
Customer Observations Verified	<u>✓</u>		
Set Time and Date	<u>✓</u>		
Verified all hardware updates as current	<u>✓</u>		
Total current draw. (Circle all that apply)			
MPL PCB 40mA			
SC Turbidity 20mA			
DO 70mA			
4Beam Turbidity 10mA			
Fluorimeters:			
1st 30mA			
2nd 30mA			
3rd 30mA			
PAR 10mA (Optimal Values not to exceed +20mA overall.)			
Current draw of circulator. (20 mA max. beyond previous values.)	<u>NA</u>		
Operation of self cleaning motor verified—	P F <u>NA</u>	P F NA	P F NA
Audio functions correctly	<u>P</u> F	P F	P F
RTC sleep/wake-up test.	<u>P</u> F	P F	P F
Temp probe test at room temperature. <u>24.35</u> °C	<u>24.34</u>		
DO 100% sat integrity window verified at +50 mHg over current bp. (Clark Cell only)	P F <u>NA</u>	P F NA	P F NA

DO 100% saturation calibration verified- local - (+/- 0.2 mg/l Clark Cell) (+/- 0.1 mg/l LDO) Scale Factor. (1.5 to 0.5) (LDO only)		15/A							
Conductivity zero (air) calibration verified - (+/- .005mS)		0.0							
Conductivity calibration verified - (+/- .2 mS) 12.856 mS/cm / 47.6 mS/cm		12.86							
Conductivity 1.412mS linearity verified - (+/- .15 mS)		1.3.96							
Conductivity .100mS verified - (+/- .005 mS)		10.2							
pH 7 buffer calibration verified- (+/- .2 pH)		N							
pH slope calibration verified at _____ units.		N							
ORP calibration verified at _____ °C (+/- 20 mV)									
Turbidity - Calibration accepted & verified with DI Water (0.0 +/-0.7 NTU)		A							
Turbidity - Calibration accepted & verified at (100.0 +/- 1 NTU) with Hach StablCal									
Turbidity - Linearity verified with 40 NTU Hach StablCal - (+/- 4 NTU)									
Depth zero calibration verified - (.02 meters)		0.0							
Depth Check verified - (+/- 0.03 meters)- Tank depth		pass							
<div style="display: flex; justify-content: space-between;"> <div>Specific Ion Low C mV</div> <div>High C mV</div> </div>		<div style="display: flex; justify-content: space-between;"> <div>Specific Ion Low C mV</div> <div>High C mV</div> </div>		<div style="display: flex; justify-content: space-between;"> <div>Specific Ion Low C mV</div> <div>High C mV</div> </div>					
N03- calibration verified		P	F	NA	P	F	NA	P	F
NH4+ calibration verified		P	F	NA	P	F	NA	P	F
Cl- calibration verified		P	F	NA	P	F	NA	P	F
Chlorophyll 'a' calibration verified		P	F	NA	P	F	NA	P	F
Rhodamine 'wt' calibration verified		P	F	NA	P	F	NA	P	F
Blue-green Algae calibration verified		P	F	NA	P	F	NA	P	F
PAR calibration verified		P	F	NA	P	F	NA	P	F
TDG calibration verified (+/- 2 mmHg)		P	F	NA	P	F	NA	P	F
Logging/Sensor Stability Test		P	F		P	F		P	F
pH linearity verified at _____ units: (+/- 0.20 units)									
Battery pack setup and checked		P	F	NA	P	F	NA	P	F
Hydras3 LT Communications verified, unused slots deactivated.									
Display, Baud Rate, Communications mode settings returned as received.		Yes	No		Yes	No		Yes	No

Calibrated Test Equipment Used -	
Description	X-number
Power Supply	X- 7208
DVM Digital Multimeter	X- 7200
Section C. Final Check-off Prior to Submitting for Estimate --	

Exterior is clean ✓ Storage cup filled with pH 4. buffer ✓	Hach Business System updated ✓ Date Completed 07-26-12
---	---

DATE: 10-23-08	DOCUMENT#: 19002-00-QUANTA
Page 3 of 4	REVISION: 2

3.0
Section A: **Quanta and Quanta G Functional Test Sheet**

Service Request # 312222835	Customer Rental	Serial # QT 5747
Technician HL	Model Type Quanta Quanta G	Date Started 07-25-12
Performance, Test and Evaluation		
Current MPL Rev. Upgrade to MPL Rev 3.1	DO membrane installed Yes No NA	PH Electrolyte and Teflon Junction installed - Yes No NA
Lenses cleaned Yes No NA	Desiccant installed Yes No NA	Turbidity Firmware Rev.

Section B:

	Submission Day <u>✓</u>	Submission Day <u> </u>	Submission Day <u> </u>
Verified customer's observations	Y / N PT&E / Upgrade	Y / N PT&E / Upgrade	Y / N PT&E / Upgrade
Verified proper operation of circulator	Y / N / NA	Y / N / NA	Y / N / NA
Temp probe test at room temperature 21.35 °C	21.34		
pH 7 Buffer calibration verified (+/- .2 pH)	7.0		
pH slope calibration verified at <u> </u> units.	18.02		
Conductivity calibration verified (+/- .2mS/cm)	12.86		
12.856 mS/cm / 47.6 mS/cm	N/A		
ORP calibration verified at <u> </u> degrees C (+/-20 mV)	102		
Conductivity .100 mS linearity verified- (+/- .005 mS)	1.413		
Conductivity 1.412 mS linearity verified - (+/- .15 mS)	P / F / NA	P / F / NA	P / F / NA
DO 100% sat integrity window verified at +50 mmHg above current bp.			
DO 100% saturation calibration verified - local (+/- .5%)	034		
Turbidity calibration verified in DI water 0.0-(+/- .5NTU)	0.0		
4 Beam Turbidity calibrated at 102 NTU (+/- 1 NTU) Dilute Formazin verified against "in-house" 2100P	99.8		
4 Beam Turbidity linearity verified at 40 NTU with Dilute Formazin verified against "in-house" 2100P (+/- 10% of reading.)	40.2		
Depth calibration verified - (+/- .02 meters)	N/A		
Depth check - (+/- .1 meters)			
Logging/Sensor Stability Test	P / F / NA	P / F / NA	P / F / NA
pH linearity verified at <u> </u> units. (+/- 0.20 units)			

Calibrated Test Equipment Used -

Description	X-number
DVM Multimeter	N/A

Section C. Final Check-off Prior to Submitting for Estimate -

Exterior is clean <u>✓</u>	Hach Business System updated <u>02P</u>
Storage cup filled with pH 4 buffer <u>✓</u>	Date Completed <u>07-26-12</u>

*Don Pedro
2012 Sampling and
Analysis*

DATA REVIEW AND VERIFICATION CHECKLIST

This checklist should be used to document data review verification of data generated through implementation of the FERC-approved study plan.

GENERAL

- ☒ For each sample event, samples have been collected and analyzed at all locations and for all analyses specified in the study plan. *Two dry sites*
- ☒ For each sample and analyses, the project file contains records field notes, chain-of-custody, and analytical results, including quality assurance documentation (hardcopy and electronic)

FIELD DATA

- ☒ Field notes and/or data sheets include date, time of sample collection, field sampling staff, time arrived at site, time left site, site identification, description of site conditions (weather), field parameters, ~~reservoir level or flow information (measured or estimated)~~, sample collection procedures, and call-out quality assurance samples collected. If mistakes are found on the field data sheet, changes can be made by crossing out the mistake and marking the change with a date of change, initials, and reason for change. *N/A not in study plan*
- ☒ Documentation of field equipment calibration is in the fieldnotes and/or project records.
- ☒ Field data entered into Excel, have been checked by a second-party. *S. Bunge*

LABORATORY REPORT

- ☒ Field duplicates, blanks, and rinsates were submitted to the laboratory at the frequency specified in the study plan.
- ☒ Any constituents found in blanks or rinsates are discussed in the final report.
- ☒ Any duplicate concentrations that differ by more than 10% are discussed in the final report.
- ☒ Samples were received by the laboratory intact and analyzed within method and/or study specified holding times.
- ☒ On laboratory reports, sample IDs, analyses, reporting/detection limits, units, column labels, footnotes, and titles are accurate. Have lab re-issue report with corrections if there are inconsistencies.
- ☒ Check that non-detects are always reported in the same manner using consistent notation. For example, either "ND" or "<." Have lab re-issue report with corrections if there are inconsistencies.
- ☒ If observed, "J" qualified data and/or elevated detection limits are discussed in the final report.

Table B-1. Rinstate and Trip Blank Water Quality Data--Summer 2012

Analyte	Sample ID	Method Detection Limit	Reporting Limit	FIELD BLANK-1		METHOD BLANK-1		FIELD BLANK-3		METHOD BLANK-3		RINSATE-1		FIELD BLANK-2		METHOD BLANK-2		177261-8		177261-8	
	Date			8/21/2012		--		8/22/2012		--		8/22/2012		8/23/2012		--		8/23/2012		8/23/2012	
	Sample Type			Field Blank		Method Blank		Field Blank		Method Blank		Rinsate		Field Blank		Method Blank		Original		Duplicate	
	latitude/longitude			Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes
	Units	--	--	737842	4195595	--		--		732763	4183297	732763	4183297	727608	4176308	727608	4176308	727341	4174879	727341	4174879
Basic Water Quality, Inorganic Ions, and Nutrients																					
Alkalinity, Total (as CaCO ₃)	mg/L	0.85	1.0	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	12.5		12.5	
Ammonia (as N)	mg/L	0.094	0.10	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.10	ND	0.10	ND
Calcium	mg/L	0.0118	0.10	0.0286	J	0.1	ND	0.038	J	0.1	ND	0.0466	J	0.0819	J	0.1	ND	2.83		2.74	
Carbon, Dissolved Organic	mg/L	0.021	0.50	0.78	B	0.18	J	0.45	B,J	0.19	J	0.47	B,J	0.29	J	0.5	ND	3.6		3.6	
Carbon, Total Organic	mg/L	0.026	0.50	0.34	B,J	0.12	J	0.42	B,J	0.17	J	0.39	B,J	0.28	J	0.5	ND	3.4		3.4	
Chloride	mg/L	0.24	1.0	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	0.74	J	0.71	J
Hardness, Total	mg/L	0.99	2.0	2	ND	2	ND	2	ND	2	ND	2	ND	2	ND	2	ND	11		11	
Magnesium	mg/L	0.00336	0.10	0.00543	J	0.1	ND	0.00483	J	0.1	ND	0.00361	J	0.0123	J	0.1	ND	1.25		1.25	
Nitrate (as N)	mg/L	0.037	0.10	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.047	J	0.063	J
Nitrite (as N)	mg/L	0.016	0.10	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.10	ND	0.10	ND
o-Phosphate (as P)	mg/L	0.031	0.10	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.1	ND	0.10	ND	0.10	ND
Phosphorus, Total	mg/L	0.022	0.10	0.037	J	0.1	ND	0.027	J	0.1	ND	0.052	J	0.1	ND	0.1	ND	0.1	ND	0.1	ND
Potassium	mg/L	0.103	0.50	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.535		0.534	
Sodium	mg/L	0.103	0.50	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.398	J	0.5	ND	1.93		1.81	
Solids, Total Dissolved	mg/L	0.82	1.0	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	30		27	
Solids, Total Suspended	mg/L	0.95	1.0	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	1	ND	1.0	ND	1.0	ND
Total Kjeldahl Nitrogen	mg/L	0.46	0.50	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.5	ND	0.50	ND	0.50	ND
Pesticides																					
Aldrin	µg/L	0.0016	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Alpha-BHC	µg/L	0.0017	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Beta-BHC	µg/L	0.0039	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Chlordane	µg/L	0.0052	0.025	0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND
Chlorpyrifos	µg/L	0.0024	0.005	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND
Delta-BHC	µg/L	0.0016	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Diazinon	µg/L	0.0029	0.0050	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND
Dieldrin	µg/L	0.0016	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Endosulfan I	µg/L	0.0015	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Endosulfan II	µg/L	0.0016	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Endrin	µg/L	0.0016	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Gamma-BHC	µg/L	0.0023	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Heptachlor	µg/L	0.0018	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Heptachlor Epoxide	µg/L	0.0017	0.010	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Toxaphene	µg/L	0.023	0.12	0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND
Total Metals Concentrations																					
Arsenic	µg/L	0.04	0.15	0.15	ND	--		0.05	J	--		0.06	J	0.05	J	--		0.26		0.27	
Cadmium	µg/L	0.003	0.02	0.02	ND	--		0.02	ND	--		0.003	J	0.02	ND	--		0.004	J	0.003	J
Copper	µg/L	0.01	0.1	0.02	J	--		0.02	J	--		0.87		0.02	J	--		0.49		0.48	
Iron	µg/L	0.6	10	0.8	J	--		10	ND	--		2	J	10	ND	--		19		18	
Lead	µg/L	0.003	0.04	0.04	ND	--		0.04	ND	--		0.010	J	0.04	ND	--		0.005	J	0.006	J
Mercury	ng/L	0.08	0.5	0.5	ND	--		0.16	J	--		27.4		0.08	ND	--		0.34	J	0.28	J
Methyl Mercury	ng/L	0.026	0.05	0.05	ND	--		0.05	ND	--		0.436		0.05	ND	--		0.05	ND	0.05	ND
Selenium	µg/L	0.31	0.6	0.6	ND	--		0.6	ND	--		0.6	ND	0.6	ND	--		0.6	ND	0.6	ND
Silver	µg/L	0.002	0.02	0.02	ND	--		0.02	ND	--		0.02	ND	0.02	ND	--		0.002	J	0.02	ND
Zinc	µg/L	0.03	0.2	0.13	J	--		0.19	J	--		1.07		0.08	J	--		0.19	J	0.18	J
Dissolved Metals Concentrations																					
Arsenic	µg/L	0.04	0.15	0.4	J	--		0.06	J	--		0.04	J	0.05	J	--		0.27		0.24	
Cadmium	µg/L	0.003	0.02	0.02	ND	--		0.02	ND	--		0.02	ND	0.02	ND	--		0.02	ND	0.02	ND
Copper	µg/L	0.01	0.1	0.04	J	--		0.06	J	--		0.45		0.05	J	--		0.47		0.46	
Iron	µg/L	0.6	10	10	ND	--		10	ND	--		0.6	J	10	ND	--		4	J	3	J
Lead	µg/L	0.003	0.04	0.04	ND	--		0.04	ND	--		0.04	ND	0.04	ND	--		0.04	ND	0.04	ND
Methyl Mercury	ng/L	0.026	0.05	0.05	ND	--		0.05	ND	--		0.26		0.5	ND	--		0.05	ND	0.05	ND
Silver	µg/L	0.002	0.02	0.02	ND	--		0.02	ND	--		0.02	ND	0.05	ND	--		0.02	ND	0.02	ND
Zinc	µg/L	0.03	0.2	0.11	J	--		0.20		--		0.91		0.09	J	--		0.29		0.27	

- Laboratory methods do not include method blanks specific to water quality study metals analyses.
- BAnalyte was present in the associated method blank.
- FBField Blank
- JAnalyte was detected at a concentration below the reporting limit and above the laboratory method detection limit. Reported value is estimated.
- NDAnalyte included in the analysis, but not detected at the reporting limit.

**STUDY REPORT W&AR-01
WATER QUALITY ASSESSMENT**

ATTACHMENT C

WATER QUALITY ELEMENT DATA

Table C-1. Water Quality Data--Summer 2012

Analyte	Benchmark	River Name	Method Detection Limit	Reporting Limit	Tuolumne River		Woods Creek		Sullivan Creek		Don Pedro Reservoir		Don Pedro Reservoir		Don Pedro Reservoir		Don Pedro Reservoir		Tuolumne River		Tuolumne River		Tuolumne River	
		Sample Location			Above Don Pedro Reservoir		Above Don Pedro Reservoir		Above Don Pedro Reservoir		Between Upper and Middle Bays		Between Upper and Middle Bays		Near Don Pedro Dam		Near Don Pedro Dam		Below Don Pedro Dam		Below Don Pedro Dam		Below La Grange Dam	
		Sample ID			177261-3		177261-1		177261-2		177261-4		177261-5		177261-6		177261-7		177261-8		177261-8		177261-9	
		Sample Depth			Surface		Surface		Surface		Surface		Bottom		Surface		Bottom		Surface		Surface		Surface	
		Date			8/21/2012		8/22/2012		8/22/2012		8/22/2012		8/22/2012		8/23/2012		8/23/2012		8/23/2012		8/23/2012		8/22/2012	
		Sample Type			Original		Original		Original		Original		Original		Original		Original		Original		Duplicate		Original	
		latitude/longitude			Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes	Result	Notes
In Situ Measurements		Units	--	--	737842	4195595	--		--		732763	4183297	732763	4183297	727608	4176308	727608	4176308	727341	4174879	727341	4174879	725619	4171913
Basic Water Quality, Inorganic Ions, and Nutrients																								
Alkalinity, Total (as CaCO ₃)	< 20 or > 500	mg/L	0.85	1.0	3.5		--		--		13.8		15.5		12.6		15		12.5		12.5		12.2	
Ammonia (as N)	Temp & pH Dep't	mg/L	0.094	0.10	0.10	ND	--		--		0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND
Calcium	--	mg/L	0.0118	0.10	2.12		--		--		2.9		3.95		2.73		3.77		2.83		2.74		2.79	
Carbon, Dissolved Organic	--	mg/L	0.021	0.50	3.1	B	--		--		3.3	B	4.7		3.7		4.6		3.6		3.6		3.4	
Carbon, Total Organic	--	mg/L	0.026	0.50	2.6	B	--		--		3.3	B	4.6		3.4		4		3.4		3.4		3.2	
Chloride	230	mg/L	0.24	1.0	0.58	J	--		--		0.64	J	0.72	J	0.75	J	0.83	J	0.74	J	0.71	J	0.6	J
Hardness, Total	--	mg/L	0.99	2.0	6		--		--		11		15		12		15		11		11		11	
Magnesium	--	mg/L	0.00336	0.10	0.443		--		--		1.52		1.46		1.38		1.55		1.25		1.25		1.25	
Nitrate (as N)	45	mg/L	0.037	0.10	0.10	ND	--		--		0.10	ND	0.10		0.10	ND	0.11		0.047	J	0.063	J	0.037	J
Nitrite (as N)	1	mg/L	0.016	0.10	0.10	ND	--		--		0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND
o-Phosphate (as P)	--	mg/L	0.031	0.10	0.10	ND	--		--		0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.10	ND	0.051	J
Phosphorus, Total	--	mg/L	0.022	0.10	0.055	J	--		--		0.057	J	0.076	J	0.025	J	0.034	J	0.1	ND	0.1	ND	0.046	J
Potassium	--	mg/L	0.103	0.50	0.647		--		--		0.547		0.662		0.61		0.693		0.535		0.534		0.546	
Sodium	> 20	mg/L	0.103	0.50	1.2		--		--		1.96		1.86		2.3		2.31		1.93		1.81		1.49	
Solids, Total Dissolved	500	mg/L	0.82	1.0	20		--		--		27		30		27		47		30		27		23	
Solids, Total Suspended	--	mg/L	0.95	1.0	16		--		--		1.1		1.0	ND	1.0	ND	1.0	ND	1.0	ND	1.0	ND	1.7	
Total Kjeldahl Nitrogen	--	mg/L	0.46	0.50	0.50	ND	--		--		0.50	ND	0.50	ND	0.50	ND	0.50	ND	0.50	ND	0.50	ND	0.50	ND
Pesticides																								
Aldrin	3.0	µg/L	0.0016	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Alpha-BHC	0.08	µg/L	0.0017	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Beta-BHC	0.08	µg/L	0.0039	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Chlordane	0.0043	µg/L	0.0052	0.025	0.025	ND	--		--		0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND	0.025	ND
Chlorpyrifos	0.014	µg/L	0.0024	0.005	0.0050	ND	--		--		0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND
Delta-BHC	0.08	µg/L	0.0016	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Diazinon	0.05	µg/L	0.0029	0.0050	0.0050	ND	--		--		0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND	0.0050	ND
Dieldrin	0.056	µg/L	0.0016	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Endosulfan I	0.056	µg/L	0.0015	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Endosulfan II	0.056	µg/L	0.0016	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Endrin	0.036	µg/L	0.0016	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Gamma-BHC	0.08	µg/L	0.0023	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Heptachlor	0.0038	µg/L	0.0018	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Heptachlor Epoxide	0.0038	µg/L	0.0017	0.010	0.010	ND	--		--		0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND	0.010	ND
Toxaphene	0.0002	µg/L	0.023	0.12	0.12	ND	--		--		0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND	0.12	ND
Total Metals Concentrations																								
Arsenic	10	µg/L	0.04	0.15	0.28		--		--		0.25		0.32		0.28		0.33		0.26		0.27		0.3	
Cadmium	5	µg/L	0.003	0.006	J		--		--		0.004	J	0.003		0.004	J	0.004	J	0.004	J	0.003	J	0.003	J
Copper	1000	µg/L	0.01	0.1	0.69		--		--		0.98		0.65		0.62		1.18		0.49		0.48		0.58	
Iron	300	µg/L	0.6	10	314		--		--		105		38		32		33		19		18		21	
Lead	15	µg/L	0.003	0.04	0.142		--		--		0.008	J	0.007	J	0.008	J	0.008	J	0.005	J	0.006	J	0.008	J
Mercury	50	ng/L	0.08	0.5	1.08		--		--		0.62		4.07		0.08	J	4.57		0.34	J	0.28	J	0.43	J
Methyl Mercury	--	ng/L	0.026	0.05	0.029	J	--		--		0.05	ND	0.042	J	0.05	ND	0.053		0.05	ND	0.05	ND	0.05	ND
Selenium	50	µg/L	0.31	0.6	0.6	ND	--		--		0.6	ND	0.6	ND	0.6	ND	0.6	ND	0.6	ND	0.6	ND	0.6	ND
Silver	100	µg/L	0.002	0.02	0.002	J	--		--		0.002	J	0.003	J	0.02	ND	0.02	ND	0.002	ND	0.02	ND	0.02	ND
Zinc	5000	µg/L	0.03	0.2	1.03		--		--		0.2		6.35		0.14	J	0.3		0.19	J	0.18	J	0.18	J
Dissolved Metals Concentrations																								
Arsenic	--	µg/L	0.04	0.15	0.23		--		--		0.28		0.29		0.29		0.34		0.27		0.24		0.27	
Cadmium	Hardness Dep't	µg/L	0.003	0.02	0.003	J	--		--		0.02	ND	0.004	J	0.003	J	0.02	ND	0.02	ND	0.02	ND	0.02	ND
Copper	Hardness Dep't	µg/L	0.01	0.1	0.4		--		--		0.96		6.25		0.7		8.16		0.47		0.46		0.63	
Iron	Hardness Dep't	µg/L	0.6	10	18		--		--		96		8	J	1	J	7	J	4	J	3	J	5	J
Lead	Hardness Dep't	µg/L	0.003	0.04	0.01	J	--		--		0.008	J	0.01	J	0.04	ND	0.008	J	0.04	ND	0.04	ND	0.009	J
Methyl Mercury	--	ng/L	0.026	0.05	0.05	ND	--		--		0.05	ND	0.293		0.05	ND	0.349		0.05	ND	0.05	ND	0.05	ND
Silver	Hardness Dep't	µg/L	0.002	0.02	0.02	ND	--		--		0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND	0.02	ND
Zinc	Hardness Dep't	µg/L	0.03	0.2	0.36		--		--		0.18	J	0.90		0.20		0.88		0.29		0.27		0.61	

Table C-1. Water Quality Data--Summer 2012: Notes and Footnotes

NOTES

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Table C-2. Ammonia Criteria

pH	USEPA National Recommended Water Quality Criteria to Protect Freshwater Aquatic Life										Maximum Concentration	
	Total Ammonia Nitrogen Continuous Concentration, 30-day Average (mg N/L)											
	Fish Early Life Stages Present Temperature, degrees C										1-hour Average (mg N/L)	
											Salmonids	
	6.5 -14	15.8	16.6 - 16.8	17.1	17.6	17.9	20.0	20.7	20.9	21.3	Present	Absent
6.6	6.6	6.0	5.7	5.6	5.4	5.3	4.6	4.4	4.3	4.2	31.3	46.8
6.7	6.4	5.9	5.6	5.5	5.3	5.2	4.5	4.3	4.3	4.2	29.8	44.6
6.8	6.3	5.8	5.5	5.3	5.1	5.1	4.4	4.2	4.2	4.1	28.0	42.0
6.9	6.1	5.6	5.3	5.2	5.0	4.9	4.3	4.1	4.0	4.0	26.2	39.2
7.0	5.9	5.4	5.2	5.0	4.8	4.8	4.1	4.0	3.9	3.8	24.1	36.1
7.1	5.7	5.2	5.0	4.8	4.6	4.6	4.0	3.8	3.7	3.7	21.9	32.9
7.2	5.4	5.0	4.7	4.6	4.4	4.3	3.8	3.6	3.6	3.5	19.7	29.5
7.3	5.1	4.7	4.4	4.3	4.2	4.1	3.6	3.4	3.4	3.3	17.5	26.2
7.4	4.7	4.4	4.1	4.0	3.9	3.8	3.3	3.2	3.1	3.1	15.3	23.0
7.5	4.4	4.0	3.8	3.7	3.6	3.5	3.1	2.9	2.9	2.8	13.3	19.9
7.6	4.0	3.7	3.5	3.4	3.3	3.2	2.8	2.7	2.6	2.6	11.4	17.0
7.7	3.6	3.3	3.1	3.0	2.9	2.9	2.5	2.4	2.4	2.3	9.6	14.4
7.8	3.2	2.9	2.8	2.7	2.6	2.6	2.2	2.1	2.1	2.1	8.1	12.1
7.9	2.8	2.6	2.4	2.4	2.3	2.3	2.0	1.9	1.8	1.8	6.8	10.1
8.0	2.4	2.2	2.1	2.1	2.0	2.0	1.7	1.6	1.6	1.6	5.6	8.4
8.1	2.1	1.9	1.8	1.8	1.7	1.7	1.5	1.4	1.4	1.4	4.6	6.9
8.2	1.8	1.7	1.6	1.5	1.5	1.4	1.3	1.2	1.2	1.2	3.8	5.7
8.3	1.5	1.4	1.3	1.3	1.2	1.2	1.1	1.0	1.0	1.0	3.1	4.7

Source: Marshack 2008

Notes:

mg N/L = milligrams Nitrogen per Liter

Table C-3. Hardness-dependent Metals (dissolved) Criteria

California Toxics Rule

Continuous Concentration, 4 day average (dissolved)

Hardness	Cadmium	Copper	Lead	Silver	Zinc
mg/L as CaCO ₃	µg/L	µg/L	µg/L	µg/L	µg/L
5	0.24	0.7	0.09	0.020	9
6	0.28	0.8	0.11	0.027	11
7	0.31	0.9	0.13	0.036	12
8	0.34	1.0	0.15	0.045	14
9	0.38	1.1	0.17	0.055	15
10	0.41	1.3	0.19	0.066	17
11	0.44	1.4	0.21	0.077	18
12	0.46	1.5	0.24	0.090	20
13	0.49	1.6	0.26	0.103	21
14	0.52	1.7	0.28	0.117	22
15	0.55	1.8	0.30	0.132	24