Coordinated Integrated Monitoring Program (CIMP)

For the Peninsula CIMP Group













Prepared for:

The Los Angeles Regional Water Quality Control Board

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Peninsula Outfall Screening Report

LIST OF ACRONYMS

AED Allowable Exceedance Days

ASBS Area of Special Biological Significance

BMP Best Management Practice

CEDEN California Environmental Data Exchange Network

CIMP Coordinated Integrated Monitoring Program

CML Compliance Monitoring Location

CMP Coordinated Monitoring Plan

CSMP Coordinated Shoreline Monitoring Plan

CTR California Toxic Rules

CWA Clean Water Act

DDT Dichloro-diphenyl-trichloroethane

ED Exceedance Day

EMC Event Mean Concentration

EWMP Enhanced Watershed Management Program

FIB Fecal Indicator Bacteria

GIS Geographic Information System

GM Geometric Mean

IC/ID Illicit Connection/Illicit Discharge

LACDBH Los Angeles County Department of Beaches and Harbors

LACFCD Los Angeles County Flood Control District

LID Low Impact Development

MCM Minimum Control Measure

MDL Method Detection Limit

MPN Most Probable Number

MRP Monitoring and Reporting Program

MS4 Municipal Separate Storm Sewer System

NOI Notice of Intent

NPDES National Pollutant Discharge Elimination System

OWTS Onsite Wastewater Treatment Systems

PCB Polychlorinated Biphenyl

QA/QC Quality Assurance/Quality Control

RAA Reasonable Assurance Analysis

RWL Receiving Water Limitation

SCCWRP Southern California Coastal Watershed Research Project

SMB Santa Monica Bay

SMBB Santa Monica Bay Beaches

SWRCB State Water Resources Control Board

TAC Technical Advisory Committee

TMDL Total Maximum Daily Load

TMRP Trash Monitoring and Reporting Plan

TOC Total Organic Carbon

TSS Total Suspended Solids

USEPA United States Environmental Protection Agency

WBPC Water Body-Pollutant Combination

WLA Waste Load Allocation

WMA Watershed Management Area

WQBEL Water Quality Based Effluent Limitation

1 Introduction

The 2012 Municipal Separate Storm Sewer System (MS4) Permit¹ (Permit) was adopted on November 8, 2012, by the Los Angeles Regional Water Quality Control Board (Regional Board) and became effective December 28, 2012. The Permit was created for the purpose of protecting the beneficial uses in the receiving waters in the Los Angeles region by ensuring that MS4s in the County of Los Angeles are not causing or contributing to exceedances of applicable water quality objectives. To accomplish this, the Permit allows the Permittees to coordinate stormwater planning efforts on a watershed basis, providing an opportunity for Permittees to customize their stormwater programs through the development and implementation of an Enhanced Watershed Management Program (EWMP) to achieve compliance with certain Receiving Water Limitations and Water Quality Based Effluent Limits.

Following the adoption of the Permit, the County of Los Angeles (County), Los Angeles County Flood Control District (LACFCD), and the Cities of Palos Verdes Estates, Rancho Palos Verdes, Rolling Hills, and Rolling Hills Estates (collectively the Peninsula Cities) agreed to collaborate on the development of a Coordinated Integrated Monitoring Program (CIMP) for the Palos Verdes Peninsula Group (Peninsula CIMP Group). The CIMP Group submitted a Notice of Intent to the Regional Board on June 27, 2013, stating their intent to collaborate with one another to achieve compliance with the Permit. Following initial review by the Regional Board, an amendment to the NOI was submitted by the CIMP Group on December 16, 2013.

1.1 PERMIT MONITORING AND REPORTING PROGRAM GOALS

Among other requirements established by the Permit, Attachment E of the Permit establishes the required Monitoring and Reporting Program (MRP). The MRP outlines the various monitoring, reporting, and recordkeeping requirements for the Permittees. The primary objectives of the MRP are to:

- 1. Assess the chemical, physical, and biological impacts of discharges from the MS4 on receiving waters.
- 2. Assess compliance with Receiving Water Limitations (RWLs) and Water Quality Based Effluent Limitations (WQBELs) established to implement Total Maximum Daily Load (TMDL) wet weather and dry weather waste load allocations (WLAs).

1

¹ Order No. R4-2012-0175 NPDES Permit No. CAS004001 Waste Discharge Requirements for Municipal Separate Storm Sewer System (MS4) Discharges within the Coastal Watersheds of Los Angeles County, except those Discharges Originating from the City of Long Beach MS4.

- 3. Characterize pollutant loads in MS4 discharges.
- 4. Identify source of pollutants in MS4 discharges.
- 5. Measure and improve the effectiveness of pollutant controls implemented under the Permit.

This CIMP has been developed to address the required TMDL and other MS4 monitoring elements set forth in the MRP, including receiving water monitoring, outfall based monitoring, regional monitoring, and special studies. The Peninsula CIMP Group has been coordinating with other agencies and watershed management groups in the development of this CIMP, including the City of Los Angeles, the Beach Cities CIMP Group, and in the Greater Los Angeles Harbor.

This CIMP relies on work products developed previously by the CIMP Group that detail the overall approach for the receiving water and outfall monitoring programs and the process used to select receiving water and outfall monitoring sites.

1.2 Definitions

The following definitions apply to this CIMP.

Major Outfall – An MS4 outfall pipe with an inside diameter of 36 inches or greater. ²

First Significant Rain Event – The first storm event of the storm year with a predicted rainfall of at least 0.25 inch at a seventy percent probability of rainfall at least 24 hours prior to the predicted start of rainfall.³

Storm Year – July 1 through June 30. A storm year, as used in the Permit MRP and this CIMP, is therefore consistent with the reporting period established in the Permit.

² A major outfall is defined by the Permit as a "MS4 outfall that discharges from a single pipe with an inside diameter of 36 inches or more or its equivalent (discharge from a single conveyance other than circular pipe that is associated with a drainage area of more than 50 acres); or for MS4s that receive stormwater from lands zoned for industrial activity (based on comprehensive zoning plans or the equivalent), an outfall that discharges from a single pipe with an inside diameter of 12 inches or more or from its equivalent (discharge from other than a circular pipe associated with a drainage area of 2 acres or more)." Given the lack of industrial zoning within the Peninsula Area, the definition of a major outfall is limited here to an outfall of at least 36 inches in diameter (or equivalent size).

³ Because a significant storm event is based on predicted rainfall, it is recognized that this monitoring may be triggered without 0.25 inches of rainfall actually occurring. In this case, the monitoring event will still qualify as meeting this requirement provided that sufficient sample volume is collected to do all required laboratory analysis. Documentation will be provided showing the predicted rainfall amount as well as the measured rainfall.

1.3 OVERVIEW OF PENINSULA CIMP AREA

The Peninsula CIMP Area includes the incorporated Cities of Rancho Palos Verdes, Palos Verdes Estates, Rolling Hills, Rolling Hills Estates, and unincorporated areas of the County of Los Angeles. This area is known as the Peninsula CIMP Area and encompasses 25.5 square miles, including portions of two HUC-12 watersheds – the Santa Monica Bay Watershed and the Dominguez Channel (including the Machado Lake and Los Angeles Harbor sub-watersheds) Watershed. The drainage within the Peninsula CIMP Area is conveyed via natural, soft-bottom canyons and engineered storm drain networks.

The majority of land in the Peninsula CIMP Area is residential (56.8% single family residential and 2.4% multi-family residential), with an additional 32.5% being vacant land. Land use breakdowns by HUC-12 watershed are shown in Table 1-1.

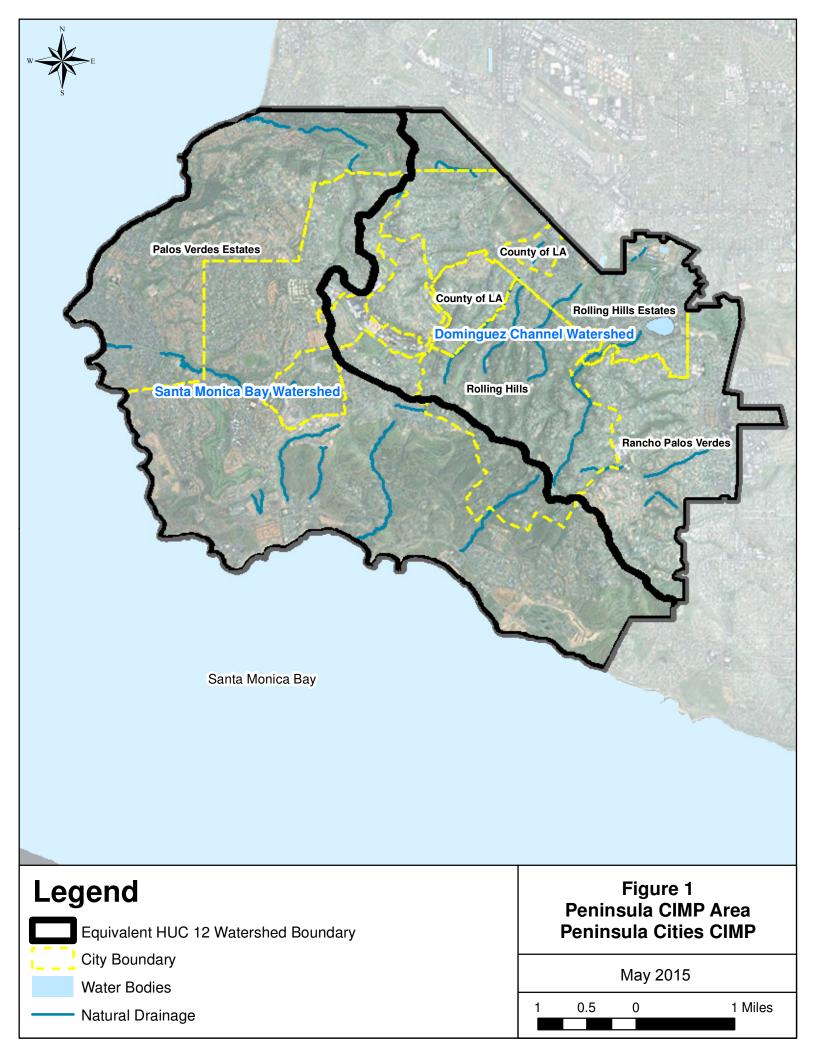
Table 1-1. Land Use Distributions Within the Peninsula CIMP Area

HUC-12 Watershed	Area (ac)	Ag (%)	Comm (%)	Edu (%)	Ind (%)	MFR ^b (%)	SFR ^b (%)	Transp (%)	Vacant (%)
Dominguez Channel	6,818	2.0%	3.5%	3.4%	4.0%	2.0%	62.8%	0.2%	22.1%
Santa Monica Bay	9,520	0.4%	1.4%	2.0%	0.4%ª	2.6%	52.5%	0.9%	39.9%
Total	16,338	1.0%	2.2%	2.6%	1.9%	2.4%	56.8%	0.6%	32.5%

^a Minor areas within the Peninsula CIMP Area are zoned for industrial use, although the actual land use is not associated with manufacturing or similar industrial activities.

The Peninsula CIMP Area is shown in Figure 1. The Peninsula CIMP Area does not include land owned by other jurisdictions, including the State of California and Federal lands.

^b MFR = Multi-Family Residential; SFR = Single Family Residential



The Los Angeles Basin Plan (Regional Board, 1995. Updated 2011) sets forth water quality regulations which are applicable to the Peninsula CIMP Agencies. These regulations are based on assigned beneficial uses to receiving water bodies. Beneficial use designations for these water bodies within the Peninsula CIMP Area include the following:

- Municipal and Domestic Supply (MUN)
- Industrial Service Supply (IND)
- Navigation (NAV)
- Commercial and Sport Fishing (COMM)
- Water Contact Recreation (REC-1)
- Non-Contact Water Recreation (REC-2)
- Warm Freshwater Habitat (WARM)
- Marine Habitat (MAR)
- Wildlife Habitat (WILD)
- Preservation of Biological Habitats (BIOL)
- Rare, Threatened, or Endangered Species (RARE)
- Migration of Aquatic Organisms (MIGR)
- Spawning, Reproduction, and/or Early Development (SPWN)
- Shellfish Harvesting (SHELL)
- Wetland Habitat (WET)

The beneficial uses of the Peninsula CIMP Area receiving waters as designated in the Basin Plan are summarized in Table 1-2. Since beneficial uses designated as "potential" are not established, these uses will not be evaluated further in the CIMP.

Table 1-2. Peninsula CIMP Area Water Bodies and Beneficial Uses
Designated in the Basin Plan

Water Body	MUN	IND	NAV	COMM	GWR	REC1	REC2	WARM	MAR	WILD	BIOL	RARE	MIGR	SPWN	SHELL	WET^a
Los Angeles Coastal																
Port Vicente			Е	Е		Е	Е		Е	Е				P	Е	
Nearshore Zone^		Е	Е	Е		Е	Е		Е	Е	Е	Ee	Ef	Ef	Е	
Los Angeles Coastal Streams	I															
Palos Verdes Coastal	P*				I	I	I	I		Е		Е				
Palos Verdes Canyon	P*				I	I	I	I		Е		Et				
Machado Lake	P*					Е	Е	Е		Е		Е				Е
Greater Los Angeles (LA) and Lo	Greater Los Angeles (LA) and Long Beach (LB) Harbor															
LA Inner Harbor		Е	Е	Е		Е	Е		Е			Ee			P	
Cabrillo Marina		Е	Е	Е		Е	Е		Е			Е			P	
Fish Harbor		Е	Е	Е		Е	Е		Е			Е			P	
LA Outer Harbor			Е	Е		Е	Е		Е			Е			P	

E = Existing beneficial use

California's 2010 list of impaired water bodies and associated pollutants within the Peninsula CIMP Area (known as the 303(d) List) are summarized in Table 1-3.

I = Intermittent beneficial use

P = Potential beneficial use

^{*}Asterisked MUN designations are designated under SB 88-63 and RB 89-03. Some designations may be considered for exemption at a later date.

^a Water bodies designated as WET may have wetlands habitat associated with only a portion of the water body. Any regulatory action would require a detailed analysis of the area.

[^] Nearshore is defined as the zone bounded by the shoreline or the 30-foot depth contours, whichever is further from the shoreline. Longshore extent is from Rincon Creek to the San Gabriel River Estuary.

e = One or more rare species utilizes all ocean, bays, estuaries, and coastal wetlands for foraging and/or nesting.

f = Aquatic organisms utilize all bays, estuaries, lagoons, and coastal wetlands, to a certain extent, for spawning and early development. This may include migration into areas which are heavily influenced by freshwater inputs.

t = Rare applies only to Agua Magna Canyon and Sepulveda Canyon areas.

Table 1-3. 2010 303(d)-Listed Water Bodies in the Peninsula CIMP Area

·		Pollutant	Notes
	Pathogens	Coliform Bacteria	Addressed by Bacteria TMDL
Santa Monica Bay Beaches	Pesticides	DDT	Addressed by PCB/DDT TMDL
Beaches	Other Organics	PCBs	Addressed by PCB/DDT TMDL
	Trash	Debris	Addressed by Debris TMDL
	Pesticides	DDT (tissue & sediment)	Addressed by PCB/DDT TMDL
Santa Monica Bay Offshore/Nearshore	Other Organics	PCBs (tissue & sediment)	Addressed by PCB/DDT TMDL
	Toxicity	Sediment Toxicity	Addressed by PCB/DDT TMDL
	Miscellaneous	Fish Consumption Advisory	Addressed by PCB/DDT TMDL
		Algae	Addressed by Nutrients TMDL
		Ammonia	Addressed by Nutrients TMDL
	NI daily and	Total Nitrogen	Addressed by Nutrients TMDL
	Nutrients	Total Phosphorus	Addressed by Nutrients TMDL
		Chlorophyll a	Addressed by Nutrients TMDL
		Dissolved Oxygen	Addressed by Nutrients TMDL
Machado Lake	Nuisance	Odor	Addressed by Nutrients TMDL
Muchado Bake		ChemA (tissue) ^a	Addressed by Pesticides and PCBs TMDL
		Chlordane (tissue)	Addressed by Pesticides and PCBs TMDL
	Pesticides	DDT (tissue)	Addressed by Pesticides and PCBs TMDL
		Dieldrin (tissue)	Addressed by Pesticides and PCBs TMDL
	Other Organics	PCBs	Addressed by Pesticides and PCBs TMDL
	Trash	Trash	Addressed by Trash TMDL
	Pathogens	Beach Closures	Addressed by Greater LA and LB Harbor Bacteria TMDL for which the Peninsula agencies are not responsible
		Benzo(a)pyrene (3,4- Benzopyrene -7-d)	Addressed by Toxic Pollutants TMDL
Greater LA and LB		Benzo[a]anthracene	Addressed by Toxic Pollutants TMDL
Harbor Waters		Chrysene (C1-C4)	Addressed by Toxic Pollutants TMDL
	Other Organics	Dibenz[a,h]anthracene	Addressed by Toxic Pollutants TMDL
		PAHs	Addressed by Toxic Pollutants TMDL
		PCBs	Addressed by Toxic Pollutants TMDL
		Phenanthrene	Addressed by Toxic Pollutants TMDL

Water Body	Pollutant Class	Pollutant	Notes	
		Pyrene	Addressed by Toxic Pollutants TMDL	
	Description	Chlordane	Addressed by Toxic Pollutants TMDL	
	Pesticides	DDT	Addressed by Toxic Pollutants TMDL	
		Copper	Addressed by Toxic Pollutants TMDL	
	Metals/Metalloids	Lead	Addressed by Toxic Pollutants TMDL	
		Mercury	Addressed by Toxic Pollutants TMDL	
		Zinc	Addressed by Toxic Pollutants TMDL	
	Toxicity	Sediment Toxicity	Addressed by Toxic Pollutants TMDL	
	Miscellaneous	Benthic Community Effects	Addressed by Toxic Pollutants TMDL	
	Pathogens	Coliform Bacteria	TMDL expected completion date of 2007	
Wilmington Drain	36.136.11.11	Copper	TMDL expected completion date of 2019	
	Metals/Metalloids ^b	Lead	TMDL expected completion date of 2019	

^a ChemA (the abbreviation for 'chemical group A') is a suite of bio-accumulative pesticides that includes chlordane and dieldrin. The 1998 303(d) listing (and subsequent listings) for ChemA was predominately based on fish tissue concentrations of chlordane and dieldrin; there was only minimal detection of other ChemA pollutants in 1983 and 1984. According to the Machado Lake Toxic Pollutants TMDL Staff Report (Regional Board, 2010), chlordane and dieldrin have been recently detected in fish tissue, while other ChemA pollutants have not been detected in 25 years. Therefore, the Machado Lake Toxic Pollutants TMDL only addresses the ChemA pollutants that are causing impairment (chlordane and dieldrin).

1.4 SUMMARY OF TMDL AND PERMIT MRP REQUIREMENTS

The Permit MRP includes requirements for receiving water monitoring, stormwater outfall-based monitoring, non-stormwater outfall-based monitoring, regional/special studies and New Development/Redevelopment Effectiveness Tracking. The general Permit requirements for each of these types of monitoring are described below, with specific details including monitoring sites, frequencies, and parameters described in subsequent sections. It is assumed that all monitoring activities will only be performed when safety permits and, as explained in the approved monitoring plan for the Machado Lake Nutrient TMDL, sampling will only be performed during business hours. Existing monitoring programs will continue to be conducted and, beginning summer of 2014, the dry weather screening of major outfalls will commence. Implementation of new monitoring programs and modifications to existing monitoring programs will be implemented beginning July 1, 2015 or 90 days after Regional Board approval of the CIMP, whichever is later.

Because the CIMP's focus is on the assessment of receiving water quality and MS4 discharge quality and quantity during both dry and wet weather, the new development and redevelopment

^b A modification to the consent decree found no impairment in Wilmington Drain for copper and lead. The Regional Board has indicated that Wilmington Drain will be delisted for copper and lead as soon as sufficient data is available to support delisting (per the Dominguez Channel and Greater LA and LB Harbor Waters Toxics TMDL).

effectiveness tracking program is not described in the CIMP. The Peninsula CIMP Agencies have developed mechanisms for tracking new development/redevelopment projects that have been conditioned for post-construction BMPs pursuant to the Permit, Part VI.D.7. Agencies also have developed mechanisms for tracking the effectiveness of these BMPs pursuant to the Permit, Attachment E, Section X.

1.4.1 RECEIVING WATER MONITORING

Receiving water monitoring is required at mass emission stations, receiving water compliance points in previously approved TMDL monitoring plans, and additional receiving water locations that are representative of the impacts from MS4 discharges from the CIMP Group. Because there are no mass emission stations within or downstream of the Peninsula CIMP Area, mass emission station monitoring is not part of this CIMP.

The objectives of the receiving water monitoring include the following:

- 1. Determine whether applicable Receiving Water Limitations are being achieved;
- 2. Assess trends in pollutant concentrations over time, or during specified conditions; and
- 3. Determine whether the designated beneficial uses are fully supported as determined by water chemistry, as well as aquatic toxicity and bioassessment monitoring.

To accomplish these objectives, TMDL receiving water monitoring as specified in approved TMDL monitoring plans will continue and additional receiving water monitoring will be conducted to meet the Permit monitoring objectives to assess the effects of MS4 discharges on receiving water quality.

1.4.1.1 <u>TMDL Receiving Water Monitoring</u>

Currently, TMDL receiving water compliance monitoring within the Peninsula CIMP Area takes place in accordance with the approved SMB Beaches Bacterial TMDL Coordinated Shoreline Monitoring Plan (CSMP) and the Coordinated Compliance Monitoring and Reporting Plan Incorporating Quality Assurance Project Plan Components for Greater Los Angeles (LA) and Long Beach (LB) Harbor Waters. Monitoring will continue as specified in these respective plans to meet the TMDL receiving water monitoring requirements of the Permit. Receiving water monitoring within Machado Lake is conducted by the City of Los Angeles and is therefore not discussed in this section, as the Peninsula CIMP Group does not play an active role in this monitoring. For the Peninsula CIMP Group's role in outfall monitoring as part of the Machado Lake Nutrient, Pesticides, and PCBs TMDL, see Section 1.4.2.1 below.

The TMDL receiving water monitoring requirements applicable to the CIMP Group are summarized below.

Santa Monica Bay Beaches Bacteria TMDL

TMDL compliance monitoring within the Peninsula CIMP Area is implemented in accordance with the SMB Beaches Bacteria TMDLs CSMP (City of Los Angeles and County of Los Angeles, 2004). The Permit MRP requires monthly data summary reports to be submitted to the Regional Board by the last day of each month for data collected during the previous month. This monthly reporting is performed by the Sanitation Districts of Los Angeles County which also conducts the shoreline monitoring for the TMDL monitoring locations within the Peninsula CIMP Area.

Currently five CSMP sites are sampled within the Peninsula CIMP Area. Historical monitoring data (2005 – 2014) at these five sampling locations acknowledges that historical average bacteria exceedance rates for each of these subwatersheds are lower than that of the reference beach for each season and there has been no increase in the historical exceedance rate trends, indicating that the high water quality of the Peninsula shoreline waters have been maintained. Nonstormwater screening has also verified that no non-stormwater discharges are reaching the wave wash on a regular occurrence except for the historical perennial stream at Malaga Cove, which is being monitored by SMB 7-1, confirming that the Peninsula MS4 is not causing or contributing to exceedances in the ocean. In addition, Heal the Bay, which comprehensively analyzes coastline water quality in California, assigning A to F grades based on bacteria-related health risks, consistently awards these beaches an "A+" ranking on its Beach Report Card (Heal the Bay, 2015). Therefore, these five CSMP sites as currently monitored are sufficient to analyze the Peninsula CIMP Group's impact on bacteria exceedances along the shoreline of the Peninsula CIMP Area.

Greater LA and LB Harbor Toxics and Metals TMDL

The Coordinated Compliance Monitoring and Reporting Plan Incorporating Quality Assurance Project Plan Components for Greater LA and LB Harbor Waters was submitted jointly in January 2014 by the California Department of Transportation, Cities of Bellflower, Lakewood, Long Beach, Los Angeles, Paramount, Rancho Palos Verdes, Rolling Hills, Rolling Hills Estates, and Signal Hill, Los Angeles County, Los Angeles County Flood Control District, Ports of Long Beach and Los Angeles. Receiving water monitoring under the Coordinated Compliance Monitoring and Reporting Plan for Greater LA and LB Harbor Waters (Plan) began in the summer of 2013 as part of the Bight Regional Monitoring Program. The Plan can be found in its entirety in Appendix G.

The Coordinated Compliance Monitoring and Reporting Plan includes sampling for both water quality and sediment quality at 22 different monitoring locations, as well as fish tissue sampling at four different locations. The Peninsula CIMP Group is tributary to nine of the 22 sediment/water quality monitoring locations (identified as Station ID's 2 through 10), and one of

the fish tissue monitoring locations (identified as Station ID 9). These sample locations are identified in Figure 3.

Water quality sampling occurs three times annually – twice during wet weather and once during dry weather – at all 22 sample sites. Measured parameters include:

- In situ water quality (temperature, dissolved oxygen, pH, salinity);
- TSS:
- Dissolved and total metals:
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene); and
- PCB congeners.

Sediment monitoring is also conducted at all 22 sites, but is performed twice every five years. Surface sediment grab samples will be collected and submitted for chemistry, toxicity, and benthic community analyses. Sediment chemistry analyses will include the following parameters:

- Total organic carbon (TOC);
- Grain size;
- Metals;
- PAHs;
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene); and
- PCB congeners.

Fish tissue samples are collected once every two years at the four specified sites. Composite samples of three fish species (white croaker [Genyonemus lineatus], California halibut [Paralichthys californicus], and shiner surfperch [Cymatogaster aggregate]) will be collected at all stations, with the exception of the Consolidate Slip location, where only white croaker will be collected. Fish tissue samples will be monitored for:

- Percent lipids;
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene); and
- PCB congeners.

As recognized by the footnote in Attachment K-4 of the Permit, the Peninsula CIMP Group has entered into an Amended Consent Decree with the United States and the State of California, including the Regional Board, pursuant to which the Regional Board has released the Peninsula CIMP Group from responsibility for toxic pollutants in the Dominguez Channel and the Greater

LA and LB Harbors. Accordingly, no inference should be drawn from the submission of this CIMP or from any action or implementation taken pursuant to it that the Peninsula CIMP Group has waived any rights under the Amended Consent Decree.

1.4.1.2 Receiving Water Monitoring

To further assess MS4 discharge effects on the receiving waters within the Peninsula CIMP Area, receiving water monitoring is required by the Permit in addition to the receiving water monitoring called for in adopted TMDLs. Although some of these receiving water monitoring locations may be located at or near existing TMDL monitoring locations, the suite of parameters sampled at these locations as well as the frequency of sampling will be different from existing TMDL monitoring (see Section 2).

Locations have been proposed considering existing TMDL monitoring locations, tributary land use, and the MS4 drainage area within each HUC-12 watershed, as well as safety and accessibility.

1.4.2 STORMWATER OUTFALL MONITORING

Stormwater outfall monitoring is required at TMDL compliance points (as specified in approved TMDL monitoring plans) and additional locations as necessary to characterize the impacts of MS4 discharges from the CIMP Group.

The objectives of the stormwater outfall monitoring include the following:

- a. Determine the quality of a Permittee's discharge relative to municipal action levels, as described in Attachment G of the Permit;
- b. Determine whether a Permittee's discharge is in compliance with applicable stormwater WQBELs derived from TMDL WLAs; and
- c. Determine whether a Permittee's discharge causes or contributes to an exceedance of Receiving Water Limitations.

1.4.2.1 <u>TMDL Outfall Monitoring</u>

Currently, TMDL stormwater outfall compliance locations have been established in the Peninsula CIMP Area by the Palos Verdes Peninsula CMP for the Machado Lake Nutrient TMDL and the Machado Lake Multipollutant TMDL MRP for the Unincorporated Areas of Los Angeles County. Additional monitoring is being facilitated or planned in accordance with requirements outlined in the Machado Lake Trash TMDL, SMB Nearshore and Offshore Debris TMDL, and the SMB TMDL for DDTs and PCBs. Monitoring will continue as specified in these respective plans to meet the TMDL outfall monitoring requirements of the Permit, as discussed below.

Machado Lake Nutrient, Pesticides and PCBs TMDL Monitoring (County and Peninsula Cities)

On May 1, 2008, the Regional Board adopted the Machado Lake Eutrophic, Algae, Ammonia and Odors (Nutrient) TMDL to protect the beneficial uses of Machado Lake. The Nutrient TMDL provides for either a concentration-based monitoring and compliance approach or a special study to establish a mass-based monitoring and compliance approach. The County elected and received approval to implement a mass-based approach, while the Peninsula Cities developed and received approval for a concentration-based monitoring program. The Peninsula CIMP Group will consolidate these two programs within the Peninsula CIMP Area.

Concentration-based monitoring for nitrogen and phosphorus began in 2011 at four locations at the termini of the Peninsula drainage system in accordance with the Palos Verdes Peninsula Coordinated Monitoring Plan. These samples, along with flow measurements, are analyzed monthly during dry weather and at least twice a year during wet weather events. The results are summarized in the yearly stormwater monitoring report by the Peninsula Cities. Within the annual report, monthly average values of total nitrogen and total phosphorus are compared with the interim waste load allocations to determine attainment. There have been two monitoring reports, encompassing the time period from 2011-2013 thus far.

Mass-based nutrient sampling is conducted by the County at two monitoring sites in the Machado Lake Subwatershed within the Peninsula CIMP Area. Both sites are monitored during wet weather and dry weather (on a quarterly basis). A third site in the Peninsula CIMP Area is monitored for flow. Wet weather monitoring is conducted for three storm events per year, including the first large storm of the season. The County's MRP states that wet weather monitoring will continue until a total of ten storm events have been collected. After four years of monitoring, nutrient sampling will be re-evaluated based on data review.

Due to redundancy in nutrient monitoring sites between the Peninsula Cites and the County, and based on results from monitoring conducted to date at these locations, the following modifications are provided for coordinated nutrient monitoring within the Peninsula CIMP Area:

• Monitoring at County sites "10-ACAD" and "10-EAST" (flow only) will cease, since these sites are immediately upstream of the monitoring at the "RHE City Hall" site. The RHE City Hall monitoring site receives runoff from County unincorporated land and all of the Peninsula Cities with the exception of Palos Verdes Estates. Additionally, tributary land uses to this site include single family residential, vacant, education, and the largest commercial area in the Peninsula Cities. Therefore, a coordinated monitoring effort will occur at this location; i.e., the County will discontinue monitoring at "10-ACAD" and "10-EAST" and collaborate on the "RHE City Hall" site.

• Monitoring at County site "20-SCGB" in the South Coast Botanical Gardens will cease, since results from initial monitoring have consistently shown that flow is not present at this site during both wet and dry weather conditions.

TMDL monitoring will continue as planned for locations not specified above. Compliance with Machado Lake Nutrient TMDL WQBELs will be evaluated based on the concentration-based monthly average calculations for Total Nitrogen and Total Phosphorus for the Peninsula CIMP group as a whole.

Wet weather sampling and analysis for Pesticides and PCBs will also be conducted at the three consolidated monitoring locations consistent with the Updated Monitoring and Reporting Plan and Quality Assurance Project Plan for Combined Machado Lake Nutrient and Toxics TMDL Sampling for the Palos Verdes Peninsula Coordinated Monitoring and Reporting Plan submitted in September 2012 ("Machado Lake Nutrient and Toxics TMDL Sampling Plan"). Additional revisions to this conditionally approved TMDL monitoring plan are being incorporated in this CIMP to address the challenges associated with collecting sufficient filtered suspended sediment samples. When insufficient filtered sediment is collected at a monitoring site to conduct the Pesticide and PCB analysis during a specific storm, the sample will be frozen and stored to be composited with samples collected at the same location during subsequent storms until sufficient sample is accumulated to conduct the analysis. Samples will only be collected and composited within a single storm-year, and will be limited to a maximum of three storm events, weather permitting.

The Machado Lake Nutrient and Toxics TMDL Sampling Plan can be found in its entirety in Appendix H.

Machado Lake Trash TMDL

The City of Rolling Hills monitors for trash to comply with the Machado Lake Trash TMDL. The City of Rolling Hills' Machado Lake Trash MRP utilizes a modified Rapid Trash Assessment Protocol from the San Francisco Bay Regional Water Quality Control Board's Surface Water Ambient Monitoring Program (SWAMP). Sampling and assessment at seven canyon outlets was conducted on a quarterly basis for the first three years of monitoring. Based

⁴ Machado Lake WLAs for DDT and PCBs are expressed as concentration-based limits on the sediment fraction (i.e., as ug/kg on a dry weight basis). The TMDL specifically requires collection and analysis of the bulk sediment from the water sample. As a result, the analysis of DDT and PCBs within the Machado Lake Subwatershed will be performed on the bulk sediment fraction of the sampled discharge.

on those results, in 2012 the Regional Board staff authorized a reduction in frequency of monitoring to twice per year and immediately following the first major storm event of the year.

The County of Los Angles, City of Rancho Palos Verdes, City of Palos Verdes Estates, and City of Rolling Hills Estates each submitted a TMRP to the Regional Board proposing compliance via the progressive installation of full capture devices throughout the Machado Lake Subwatershed. These TMRPs were approved by the Regional Board and are being implemented. Each Peninsula CIMP Agency reports its compliance individually as part of its annual report.

Santa Monica Bay Nearshore and Offshore Debris TMDL

SMB Debris TMDL does not require receiving water monitoring. Rather, Permittees may comply with trash effluent limitations using one of several compliance options broadly classified as: full capture, partial capture, institutional controls or minimum frequency of assessment and collection or any combination thereof. Permittees are to report their compliance strategy through the development of a Trash Monitoring and Reporting Plan (TMRP) and Plastic Pellets Monitoring and Reporting Plan (PMRP) or demonstrate that a PMRP is not required. Once the TMRP and PMRP are approved by the Executive Officer, an annual progress report is to be submitted to demonstrate the reduction in the amount of trash and plastic pellets, if applicable, being discharged into Santa Monica Bay. Each of the jurisdictions within SMB JG7 WMP Group will submit or have submitted a TMRP and PMRP.

The Permit states that if the TMRP is submitted by September 20, 2012, then the TMRP will be implemented 6 months from receipt of letter of approval from Regional Board Executive Officer, or the date a plan is established by the Executive Officer; or if a CIMP is submitted, then monitoring will commence within 30 days after approval of the CIMP plan by the Executive Officer.

The County of Los Angles, City of Rancho Palos Verdes, City of Palos Verdes Estates and City of Rolling Hills Estates each submitted a TMRP to the Regional Board before the TMDL-specified deadline of September 20, 2012 proposing compliance via the progressive installation of full capture devices throughout the Santa Monica Bay Watershed. The City of Rolling Hills submitted and received Executive Officer approval on September 3, 2013 to utilize an institutional control strategy consistent with the Machado Lake TMRP previously submitted and approved by the Regional Board and the resulting monitoring data to establish compliance with the Santa Monica Bay Nearshore and Offshore Debris TMDL.

The Peninsula Cities each submitted a request to the Regional Board to be exempt from the TMDL requirement to conduct monitoring for plastic pellets under the Santa Monica Bay Debris TMDL because the Peninsula has no industrial facilities or activities related to the manufacturing, handling, or transportation of plastic pellets within its jurisdiction, and has limited commercial and/or industrial transportation corridors related to such activities. Therefore,

unless the Regional Board opposes this approach, monitoring for plastic pellets within the Peninsula CIMP Area will not be conducted by the Peninsula CIMP Group.

Santa Monica Bay TMDL for DDT and PCBs

The Permit MRP requires the Permittees to develop a Monitoring and Reporting Plan for Regional Board Executive Officer approval that describes the methodologies that will be used to monitor and assess suspended sediment for DDT and PCBs. The monitoring design and assessment framework should be designed to provide credible estimates of the total DDT and PCBs mass loadings to the SMB. Monitoring should be conducted on a coordinated watershedwide basis using sufficiently sensitive analytical methods for DDT and PCBs.

Monitoring for PCBs and DDT will occur at the two MS4 outfall monitoring locations specified in Section 1.4.2.2 below (SD-1 and SD-2), and will be conducted in a manner consistent with the Machado Lake Nutrient and Toxics TMDL Sampling Plan (i.e., on the bulk sediment fraction). When insufficient filtered sediment is collected at a monitoring site to conduct the Pesticide and PCB analysis during a specific storm, the sample will be frozen and stored to be composited with samples collected at the same location during subsequent storms until sufficient sample is accumulated to conduct the analysis. Samples will only be collected and composited within a single storm-year, and will be limited to a maximum of three storm events, weather permitting.

The most sensitive EPA-approved analytical methods commercially available in the region will be used to analyze PCB congeners and DDTs in receiving water and outfall samples, as necessary (e.g., Method 1668c where feasible; otherwise, Method 8270). Monitoring for PCBs will be reported as the summation of at least 40 congeners and Aroclors, as specified in Attachment E, Table E-2 of the Permit.

1.4.2.2 MS4 Stormwater Outfall Monitoring

Stormwater outfall monitoring will be conducted at a minimum of one major outfall in each equivalent HUC-12 watershed within the Peninsula CIMP Area. A major outfall is defined by the Permit as an "MS4 outfall that discharges from a single pipe with an inside diameter of 36 inches or more or its equivalent (discharge from a single conveyance other than circular pipe that is associated with a drainage area of more than 50 acres); or for MS4s that receive stormwater from lands zoned for industrial activity (based on comprehensive zoning plans or the equivalent), an outfall that discharges from a single pipe with an inside diameter of 12 inches or more or from its equivalent (discharge from other than a circular pipe associated with a drainage area of 2 acres or more)." Given the general lack of industrial zoning within the Peninsula CIMP Area and the lack of catchment area delineation information, the definition of a major outfall is limited here to an outfall of at least 36 inches in diameter (or equivalent for a non-circular pipe).

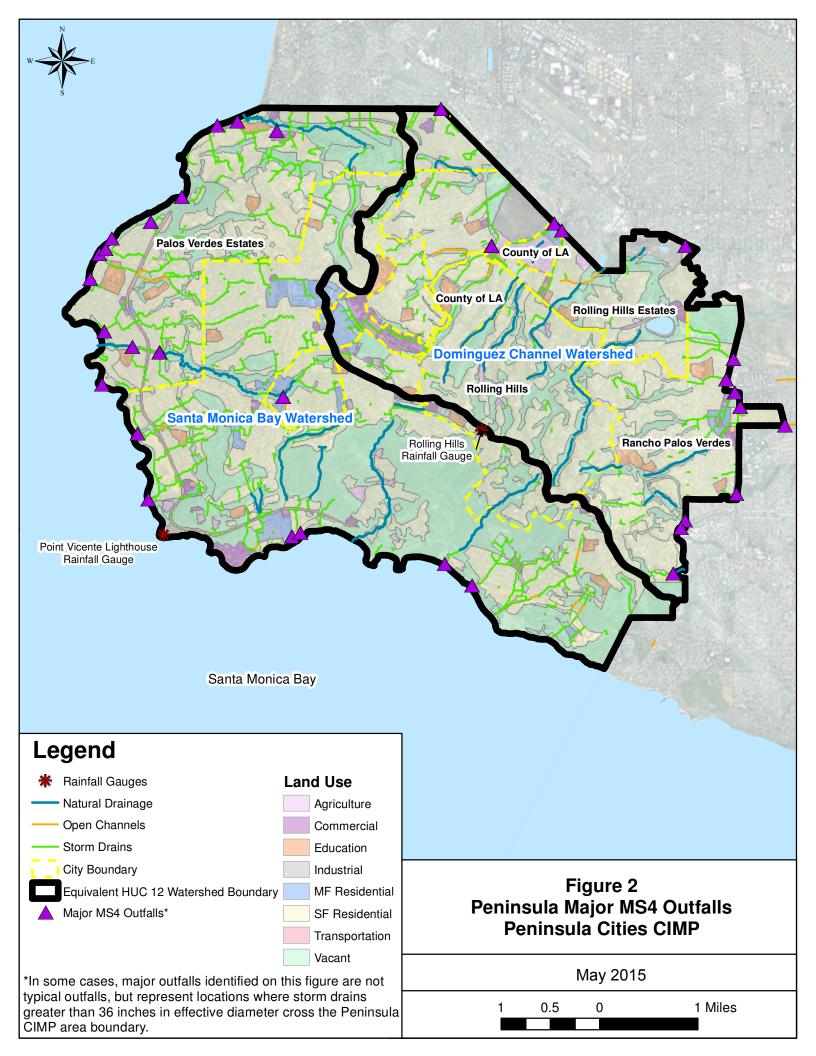
Major outfalls within the Peninsula CIMP Area that are known to exist based on current information are shown in Figure 2. No major outfalls currently exist within the City of Rolling Hills.⁵

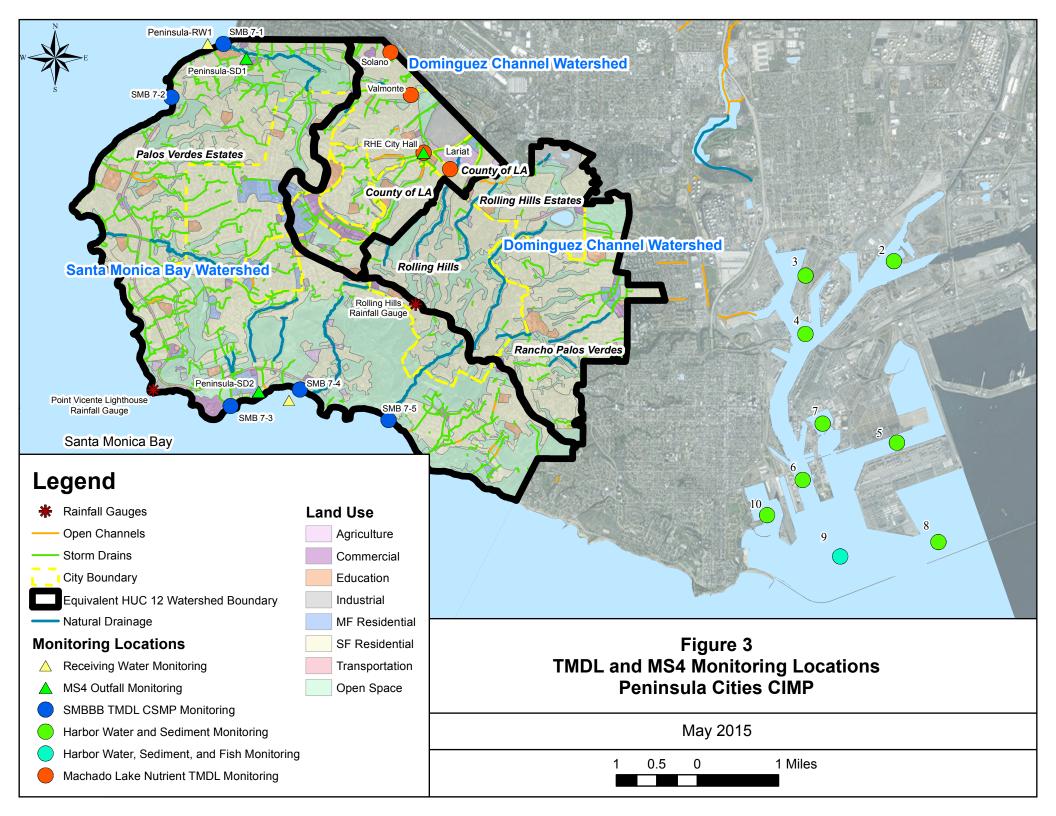
MS4 outfall monitoring locations were selected based on the following:

- 1. A desktop screening was conducted to identify major outfalls that are tributary to receiving water monitoring locations. Major outfalls were identified that discharge directly to the coast, up-current of SMB Beaches Bacteria CSMP monitoring locations, or that discharge to natural canyons that are tributary to CSMP monitoring locations.
- 2. The desktop screening was used to identify upstream land uses for the outfalls identified in Step #1. The Permit specifies that each selected outfall shall be representative of the land uses within the Permittee's jurisdiction. Due to the limited number of major outfalls in existence, this step was used to eliminate major outfalls from further screening if they reflect land uses that are unrepresentative those typical of the Peninsula CIMP Area.
- 3. The major outfalls that were not eliminated from Step #1 and #2 were then field screened to select which outfalls will be monitored. This was determined based on: a) accessibility and safety considerations for monitoring personnel; b) linkage with downstream receiving water monitoring locations; c) verification of attributes identified in the desktop screening step (e.g., outfall size, location, and tributary land use); and d) facilitation of accurate flow measurement within the outfall/storm drain. Alternative upstream monitoring locations such as manholes or channels may be proposed to facilitate access and to ensure the safety of the monitoring team.

The desktop and field screening and selection process has previously been conducted for the Machado Lake Subwatershed during development of the Machado Lake Nutrient Monitoring Plan. As a result of the previous screening effort, it is proposed that the RHE City Hall monitoring location (shown in Figure 3) serve as the representative outfall for monitoring within the Dominguez Channel Watershed. Although the RHE City Hall location is not located at the Peninsula CIMP boundary, it was previously identified as the nearest safely accessible location upstream of this boundary. This monitoring site receives runoff from County unincorporated land and all of the Peninsula Cities, with the exception of Palos Verdes Estates. Tributary land uses to this site include single family residential, vacant, education, and the largest commercial area in the Peninsula Cities.

⁵ The City of Rolling Hills received approval from the Regional Board to participate jointly in the Peninsula CIMP as a result of their lack of an MS4 network, as documented in the December 5, 2013 letter from the Regional Board to the City of Rolling Hills.





1.4.3 Non-stormwater Outfall Monitoring

Non-stormwater outfall monitoring is required at TMDL compliance points (as specified in approved TMDL monitoring plans) and major outfalls with significant non-stormwater discharges that remain unaddressed after source identification. The TMDL compliance points established in the Machado Lake Nutrient TMDL will continue to be monitored for TMDL pollutants in accordance with the approved Palos Verdes Peninsula Coordinated Monitoring Plan, with the exception of the modifications noted previously to avoid redundancy.

The objectives of the non-stormwater outfall monitoring include the following:

- a. Determine whether a Permittee's discharge is in compliance with applicable non-stormwater WQBELs derived from TMDL WLAs;
- b. Determine whether a Permittee's discharge exceeds non-stormwater action levels, as described in Attachment G of the Permit;
- c. Determine whether a Permittee's discharge causes or contributes to an exceedance of Receiving Water Limitations; and
- d. Assist a Permittee in identifying illicit discharges as described in Part VI.D.10 of the Permit.

Each identified major outfall owned by the Peninsula CIMP Group within the Peninsula CIMP Area will be screened to determine if "significant" non-stormwater discharges exist at the major outfall. Details of the approach to this screening, including follow-up actions triggered after significant non-stormwater discharges have been identified, can be found in Section 4. An initial screening has been conducted and, if necessary, a source identification investigation will be conducted. If significant non-stormwater discharges remain unaddressed after the completion of the source identification investigation, non-stormwater monitoring will be conducted at the applicable outfalls four times per year, and will be linked with downstream receiving water monitoring, where feasible.

1.4.4 REGIONAL STUDIES

The LACFCD will continue to participate in the Regional Watershed Monitoring Program (Biosassessment Program) being managed by the Southern California Stormwater Monitoring Coalition (SMC). The LACFCD will contribute necessary resources to implement the bioassement monitoring requrement of the Permit on behalf of all Permitees in Los Angeles County during the current Permit cycle. Initiated in 2008, the SMC's Regional Bioassement Program is designed to run over a five-year cycle. Monitoring under the first cycle concluded in 2013, with reporting of findings and additional special studies planned to occur in 2014. SMC, including LACFCD, is currently working on designing the bioassessment monitoring program for the next five-year cycle, which is scheduled to run from 2015 to 2019.

2 RECEIVING WATER MONITORING

Receiving water monitoring will be conducted under the CIMP in order to assess the effects of MS4 discharges on the receiving water.

The Permit MRP requirements include receiving water monitoring at previously designated mass emission stations, TMDL receiving water compliance points, and additional receiving water locations representative of the impacts from MS4 discharges, as necessary. None of the seven mass emission stations monitored by LACFCD throughout the County of Los Angeles are within or downstream of the Peninsula CIMP Area. As a result, this CIMP will not include monitoring of mass emission stations.

2.1 RECEIVING WATER MONITORING SITES

The Permit does not explicitly state how receiving water monitoring sites should be selected or the number of required receiving water monitoring sites per CIMP group or Permittee, but states that, at a minimum, mass emission station sampling and TMDL compliance sampling must continue. It does specify that receiving water monitoring must be conducted at locations that provide representative measurement of the effects of MS4 discharges on the receiving water and that the CIMP affords Permittees opportunities to increase cost efficiency and effectiveness of the monitoring program.

2.1.1 TMDL COMPLIANCE MONITORING

Currently, TMDL receiving water compliance monitoring within the Peninsula CIMP Area takes place in accordance with the SMB Beaches Bacteria TMDL CSMP. Although the Permit MRP allows for modifications to be proposed in the CIMP for TMDL monitoring programs, at this time no such changes to TMDL receiving water monitoring locations are proposed.

Table 2-1 summarizes the SMBB Bacteria TMDL-related receiving water monitoring sites within the Peninsula CIMP Area which are proposed to continue to be sampled as part of the CIMP.

Table 2-1. TMDL Compliance Monitoring Locations within the Peninsula CIMP Area

Station ID	Type ^a	Description (including historical site ID, if any)
SMB Beaches Bacterial TMDLs CSMP		
SMB 7-1	Open Beach	Malaga Cove: 300 Paseo Del Mar, Palos Verdes Estates (LACSDM)
SMB 7-2	Open Beach	Bluff Cove: 600 Paseo del Mar, Palos Verdes Estates (LACSDB)
SMB 7-3	Open Beach	Long Point: 7200 Palos Verdes Drive South, Rancho Palos Verdes (LACSD1)
SMB 7-4	Open Beach	Abalone Cove: 6000 Palos Verdes Drive South, Rancho Palos Verdes (LACSD2)
SMB 7-5 Open Beach		Portuguese Bend Cove: 4100 Palos Verdes Drive South, Rancho Palos Verdes (LACSD3)

^a Open Beach sites are not associated with freshwater outlets (storm drains or coastal creeks).

Monitoring at all TMDL-specific monitoring locations will continue for TMDL compliance purposes as specified in the SMB Beaches Bacteria TMDLs CSMP. TMDL compliance monitoring includes weekly sampling for fecal indicator bacteria (FIB) at the five SMB Beaches Bacteria TMDL receiving water locations within the Peninsula CIMP Area.

2.1.2 RECEIVING WATER MONITORING SITES

To assess MS4 discharge effects on the receiving waters within the Peninsula CIMP Area, receiving water monitoring is required by the Permit in addition to the receiving water monitoring called for in adopted TMDLs. This monitoring will be conducted in SMB at selected offshore locations.

Receiving water monitoring will be performed from a boat in Santa Monica Bay. Per Los Angeles County ordinance, no hard bottom boats can be operated within 300 yards (900 feet) of the beach due to safety concerns. Therefore, the sampling will be conducted 1,000 feet away from the shoreline (approximately the 30 foot bathometric contour), and will be conducted using manual grab sampling methods.

Proposed receiving water monitoring locations are summarized in Table 2-2.

Table 2-2. Receiving Water Monitoring Locations within Peninsula CIMP Area

Station ID	Longitude/ Latitude	Justification of Selection
Peninsula-RW1	33.80339 N 118.39919 W	1,000 ft offshore (due west) of SMB 7-1. A paired MS4 outfall is tributary to this site via Malaga Creek, and other major outfalls discharge in this vicinity. Tributary land uses are reflective of Palos Verdes Estates land uses as well as Peninsula land uses as a whole, primarily consisting of single family residential and open space, but also including multi-family residential, commercial, and education land uses.
Peninsula-RW2 33.73965 N 1,000 ft offsho located approx Cove. Tributar well as Peninsular well as Peninsular and single fam		1,000 ft offshore (due southwest) of SMB 7-4. A paired MS4 outfall is located approximately 1,000 yards west of this location, within Abalone Cove. Tributary land uses are reflective of Rancho Palos Verdes land uses as well as Peninsula land uses as a whole, primarily consisting of open space and single family residential, but also including multi-family residential, commercial, and transportation.

Although accessibility was considered when selecting these monitoring sites, it is the responsibility of the water quality monitoring personnel to take all appropriate measures with respect to health and safety considerations and private property access conditions.

2.1.3 RECEIVING WATER MONITORING FREQUENCY

Both wet and dry weather monitoring at receiving water monitoring sites will be conducted. Mobilization for wet weather monitoring will be triggered when forecasts predict a 24-hour rainfall depth of at least 0.25 inches at a 70% probability the day before the start of the storm event⁶. Using a forecast of 0.25 inches as the field mobilization criteria for monitoring will increase the likelihood that sufficient wet weather runoff will occur such that the impact of MS4 discharges on the receiving water can be assessed. Since mobilization to monitor is often required prior to the initiation of rainfall, wet weather monitoring will be based on forecasted rainfall. Storm event predictions will be taken from the National Oceanic and Atmospheric Administration (NOAA) at the location of each County rain gauge located in the Peninsula CIMP Area. Rain forecasts for each location can be found at the following links:

⁶ Because a significant storm event is based on predicted rainfall, it is recognized that this monitoring may be triggered without 0.25 inches of rainfall actually occurring. In this case, the monitoring event will still qualify as meeting this requirement. Documentation will be provided showing the predicted rainfall depth.

- Point Vicente Lighthouse (LA321) (http://www.wrh.noaa.gov/forecast/wxtables/index.php?lat=33.741304&lon=118.41121240000001&clrindex=0&table=custom&duration=7&interval=6)
- Rolling Hills FS 56 (LA376) (http://www.wrh.noaa.gov/forecast/wxtables/index.php?lat=33.7566748&lon=-118.3549980000002&clrindex=0&table=custom&duration=7&interval=6)

The forecast at one of these two locations must meet this specified criterion to initiate monitoring. If wet weather monitoring is initiated and samples are collected, these samples will be considered wet weather samples regardless of the total depth of rainfall that is recorded for the storm. If mobilization occurs but no MS4 outfall samples are collected due to a lack of flow, this event will not be considered a wet weather monitoring event.

Wet weather monitoring will occur three times per year for the parameters specified herein, with the exception of aquatic toxicity, which will be monitored twice per year. Wet weather monitoring, including toxicity, will also include the first significant rain event of the storm year⁷.

If precipitation patterns during a given storm year dictate that these triggers cannot be met, documentation will be provided by the Peninsula CIMP Group in its annual report.

Wet weather sampling events will be separated by at least three days of dry conditions (less than 0.1 inches of rainfall each day). Receiving water monitoring will begin as soon as possible after stormwater outfall monitoring in order to be reflective of potential MS4 impacts.

Dry weather monitoring will be conducted as required in Attachment E, Part VI.D of the Permit. Dry weather monitoring will occur twice per year at receiving water monitoring sites for all specified parameters except toxicity. One of the two dry weather monitoring events will occur during the month of June, which is historically the driest month in the Peninsula CIMP Area according to rain gauge records. Dry weather toxicity monitoring will occur once per year, during the month of June.

A summary of the receiving water monitoring requirements is provided in Table 2-3.

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⁷ The term "storm year" is defined as the period spanning from July 1 to June 30.

Table 2-3. Receiving Water Monitoring Requirements

Wet V	Veather	Dry	y Weather	Manitanina Danamatana
Frequency	Requirements	Frequency	Requirements	Monitoring Parameters
Three times per year (all parameters except aquatic toxicity) Two times per year (aquatic toxicity)	Sample storm events when forecasts predict a 24-hour rainfall depth of at least 0.25 inches at a 70% probability the day before the start of the storm event. Sampling events must be separated by a minimum of three dry days (less than 0.1 inch precipitation) Must sample the first significant storm event (greater than 0.25 inch precipitation, based on forecasts)	Two times per year (all parameters except aquatic toxicity) One time per year, during the month of June (aquatic toxicity)	Precipitation less than 0.1 inch and not less than 3 days after a day with 0.1 inch precipitation. Determination will be made based on measurements from 50% or more of the rain gauges in the Peninsula Area. One of the sampling events must be during the month of June, which is historically the driest month in the Peninsula Area	Pollutants with TMDLs: o Fecal coliform, total coliform, and enterococcus o PCBs/DDT Additional constituents per Permit MRP Table E-2. ^a Aquatic marine water chronic toxicity (see Appendix C, SOP for details)

^a Parameters in Permit MRP Table E-2 are to be monitored during the first significant storm of the year and during the first year of the monitoring program in June (critical dry month for dry weather receiving water sampling). If any parameter is not detected above the method detection limit (MDL) or the result is below the lowest applicable water quality objective, and is not otherwise required due to a TMDL or being on the 303(d) list, the parameter need not be further analyzed for the remainder of the Permit term.

2.2 RECEIVING WATER MONITORING PARAMETERS

At SMB TMDL monitoring sites, monitoring is limited to FIB per the SMB Beaches TMDLs CSMP. Parameters to be monitored at receiving water monitoring sites are summarized in Appendix C and will include:

- Pollutants for which a receiving water limit exists derived from TMDL WLAs.
- Chronic aquatic toxicity. A toxicity test sample is also immediately subject to toxicity identification evaluation (TIE) procedures if either the survival or sublethal endpoint

demonstrates a Percent Effect⁸ value equal to or greater than 50% of the instream waste concentration (IWC). See Appendix C for further specifications on conducting a TIE.

• Additional screening parameters listed in the Permit MRP (Table E-2), as required per Section 2.2.

Parameters required to be sampled at each receiving water monitoring site are summarized in Table 2-4.

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Parameter	Peninsula-RW1	Peninsula-RW2
Indicator Bacteria	X	X
PCBs/DDT	X	X
Table E-2 Screening Parameters ^a	X	X
Aquatic Toxicity ^b	X	X

Table 2-4. Receiving Water Monitoring Parameters

A detailed summary of the parameters that will be sampled at the receiving water monitoring locations is provided in Appendix B. Appendix B includes acceptable analytical methods for laboratory analyses, Permit-specified minimum detection levels, laboratory QA/QC requirements, holding time requirements and applicable water quality objectives for each parameter.

2.3 RECEIVING WATER MONITORING PROTOCOL

TMDL receiving water monitoring will continue to be conducted in accordance with the SMB Beaches Bacteria TMDL CSMP.

Receiving water sampling will be conducted from a boat in accordance with City of Los Angeles Environmental Monitoring Division (EMD) standard operating procedures. All monitoring protocols, including sample collection procedures, field measurement procedures, and required

^a Screening parameters can be found in Permit MRP Table E-2, and are also found in Appendix B.

^b Toxicity is required to be monitored in the receiving water twice per year during wet weather and once per year during dry weather in the month of June. Screening for toxicity test parameters will occur once during the first three years of the Permit term. Rescreening will occur in the fourth year of the Permit term.

⁸ Percent Effect is defined as the effect value—denoted as the difference between the mean control response and the mean IWC response, divided by the mean control response—multiplied by 100.

quality assurance/quality control procedures are detailed in the Standard Operating Procedures (SOP) provided as Appendix C. Details for toxicity monitoring are also provided in Appendix C.

3 STORMWATER OUTFALL MONITORING

Stormwater outfall monitoring will be conducted under the CIMP in order to characterize the impacts of MS4 discharges from the CIMP Group.

Stormwater discharges from the MS4 are required to be monitored at outfalls with drainage areas that are representative of the land uses within the Peninsula CIMP Area. The objectives of the stormwater outfall based monitoring program set forth in Part II.E.2 of the Permit MRP include the following:

- Determine the quality of a Permittee's discharge relative to municipal action levels, as described in Attachment G of the Permit;
- Determine whether a Permittee's discharge is in compliance with applicable stormwater WQBELs derived from TMDL WLAs; and
- Determine whether a Permittee's discharge causes or contributes to an exceedance of Receiving Water Limitations.

3.1 STORMWATER OUTFALL MONITORING SITES

The Permit does not explicitly state how stormwater outfall monitoring sites should be selected or the number of required stormwater outfall monitoring sites per EWMP group or Permittee. It does specify that stormwater outfall monitoring must be conducted at locations that provide representative measurement of the effects of MS4 discharges on the receiving water.

Major outfalls within the Peninsula CIMP Area identified based on current information are shown on Figure 2. No major outfalls currently exist within the City of Rolling Hills.⁹

MS4 stormwater outfall monitoring locations were selected based on the following:

1. A desktop screening was conducted to identify major outfalls that are tributary to receiving water monitoring locations. Major outfalls were identified that discharge

⁹ The City of Rolling Hills received approval from the Regional Board to participate jointly in the Peninsula CIMP as a result of their lack of an MS4 network, as documented in the December 5, 2013 letter from the Regional Board to the City of Rolling Hills.

- directly to the coast, up-current of SMB Bacteria TMDL CSMP monitoring locations, or that discharge to natural canyons that are tributary to CSMP monitoring locations.
- 2. The desktop screening was used to identify upstream land uses for the outfalls identified in Step #1. The Permit specifies that each selected outfall shall be representative of the land uses within the Permittee's jurisdiction. Due to the limited number of major outfalls in existence, this step was used to eliminate major outfalls from further screening if they drained land uses that were determined to have land use distribution unrepresentative of the Peninsula CIMP Area.
- 3. The major outfalls that were not eliminated from Step #1 and #2 were then field screened to select outfalls that will be monitored. This was determined based on: a) accessibility and safety considerations for monitoring personnel; b) linkage with downstream receiving water monitoring locations; c) verification of attributes identified in the desktop screening step (e.g., outfall size, location, and tributary land use); and d) facilitation of accurate flow measurement within the outfall/storm drain. Alternative upstream monitoring locations such as manholes or channels were considered to facilitate access and to ensure the safety of the monitoring team.

The desktop and field screening and selection process has previously been conducted for the Machado Lake Subwatershed during development of the Machado Lake Nutrient Monitoring Plan. As a result of the previous screening effort, it is proposed that the RHE City Hall monitoring location serve as the representative "outfall" for monitoring within the Dominguez Channel Watershed. Although the RHE City Hall location is not located at the Peninsula CIMP boundary, it was previously identified as the nearest safely accessible location upstream of this boundary.

3.1.1 TMDL STORMWATER OUTFALL MONITORING LOCATIONS

Currently, TMDL monitoring within the Peninsula CIMP Area is conducted by the Peninsula Cities and the County of Los Angeles in accordance with their respective Machado Lake Nutrient TMDL monitoring plans. Modifications to these TMDL monitoring locations are proposed based on monitoring results to-date and noted redundancies in monitoring locations among the two monitoring plans. Table 3-1 summarizes the Machado Lake TMDL-related monitoring sites within the Peninsula CIMP Area which are proposed to continue to be sampled as part of the CIMP.

¹⁰ Although the RHE City Hall monitoring location is technically not an outfall in a strict sense, it is the nearest accessible upstream location from the Peninsula CIMP Area boundary, and will therefore serve as the representative monitoring location for the CIMP. The term "outfall" is used for this location for simplicity.

Table 3-1. TMDL Stormwater Outfall Monitoring Locations within Peninsula CIMP Area

Station ID	Туре	Description (including historical site ID, if any)					
Machado Lake Nutrien	Machado Lake Nutrient TMDL CMP						
Rolling Hills Estates (RHE) City Hall	Manhole	RDD275, a major storm drain which drains the central commercial area as well as significant residential areas, merges with storm drains collecting wet weather flow from Ranchview and Chadwick Canyons.					
Valmonte	Open Channel	Valmonte and Ferncreek subdrainage					
Lariat	Grate Opening	Agua Magna, Sepulveda, and Blackwater Canyon subdrainages					
Solano Manhole		PVP subdrainage to Walteria Lake					

3.1.2 MS4 STORMWATER OUTFALL MONITORING LOCATIONS

To assess MS4 discharge effects on the receiving waters within the Peninsula CIMP Area, MS4 stormwater outfall monitoring is required by the Permit in conjunction with receiving water monitoring. Stormwater outfall monitoring requirements as specified in the Permit MRP (e.g., monitoring at specified intervals during wet and dry weather, screening for additional parameters, etc.) will be conducted at selected outfall locations. Locations were confirmed with a field investigation to assess each site for accessibility, monitoring feasibility, and additional physical characteristics.

Selected stormwater outfall monitoring sites are summarized in Table 3-2 below. Each monitoring site is shown in Figure 3.

Table 3-2. Locations for MS4 Outfall Monitoring within Peninsula CIMP Area

Station ID	Tributary Area (Acres)	Land Use Breakdown (Acres)	Site Description and Justification of Selection
Santa Monica Bay HUC-12			
Peninsula-SD1	47	SFR = 16.4 (34.7%) MFR = 0.8 (1.7%) Comm = 5.0 (10.6%) Vac = 25.0 (53.0%)	Located in the parkway adjacent to the intersection of Via Corta and Via del Puente, this monitoring location is accessed via a manhole upstream of Malaga Creek. Tributary land uses are reflective of Peninsula land uses as a whole, primarily consisting of single family residential and open space, but also including multifamily residential and commercial land uses. Access at this location appears safe and easy and does not require traffic control.
Peninsula-SD2	496	SFR = 251.4 (50.7%) MFR = 22.0 (4.4%) Comm = 3.4 (0.7%) Ind = 7.5 (1.5%) Edu = 14.3 (2.9%) Transp = 3.4 (0.7%) Vac = 194.2 (39.1%)	Located in the parkway adjacent to 32861 Seagate Drive, this monitoring location is accessed via a manhole upstream of the outfall at the SMB shoreline. Tributary land uses are reflective of Peninsula land uses as a whole, primarily consisting of open space and single family residential, but also including multi- family residential, commercial, and transportation. A small Southern California Edison electrical substation is tributary to this location. Access at this location appears safe and relatively easy and does not require traffic control.
Dominguez Channel HUC-12			
RHE City Hall	1,096	SFR = 603.9 (55.1%) MFR = 81.7 (7.4%) Comm = 136.6 (12.5%) Ind = 4.9 (0.4%) Edu = 75.4 (6.9%) Vac = 193.8 (17.7%)	Located in the parking lot behind Rolling Hills Estates City Hall (4045 Palos Verdes Drive N.), this monitoring location is accessed via a manhole upstream of the Rolling Hills Estates city boundary. This monitoring location receives runoff from County unincorporated land and all of the Peninsula Cities with the exception of Palos Verdes Estates. It is representative of Peninsula land uses as a whole since tributary land uses to this site include single family residential, vacant, education, and the largest commercial area in the Peninsula Cities.

SFR = Single Family Residential

MFR = Multi Family Residential

Comm = Commercial

Ind = Industrial

Edu = Educational

Transp = Transportation

Vac = Vacant/open space

Photos, figures, and site descriptions for each stormwater outfall monitoring site are provided in Appendix A. Although accessibility was considered when selecting these monitoring sites, it is the responsibility of the water quality monitoring personnel to take all appropriate measures with respect to health and safety considerations and private property access conditions.

3.2 STORMWATER OUTFALL MONITORING FREQUENCY

Stormwater discharges at selected outfalls will be monitored three times a year during wet weather. Monitoring will be initiated based on forecasted wet weather events. As is the case with receiving water monitoring during wet weather, stormwater outfall based monitoring will target the first significant rain event of the storm year.

Stormwater outfall sampling events will be separated by at least three days of dry conditions (less than 0.1 inches of rainfall each day). Stormwater outfall monitoring will be coordinated with receiving water monitoring to the maximum extent practicable, such that downstream receiving water monitoring begins as soon as possible after stormwater outfall monitoring. In cases where this is not feasible, appropriate notification will be made for inclusion in the annual report. A summary of stormwater outfall monitoring requirements is provided in Table 3-3.

Table 3-3. Stormwater Outfall Monitoring Requirements

Wet Weather									
Frequency	Requirements	Monitoring Parameters							
3 times per year	Sample storm events when forecasts predict a 24-hour rainfall depth of at least 0.25 inches at a 70% probability the day before the start of the storm event Sampling events must be separated by a minimum of 3 dry days (less than 0.1 inch precipitation) Must sample the first significant storm event (greater than 0.25 inch precipitation)	Flow Pollutants with TMDLs:							

^a Additional screening parameters identified in Permit MRP Table E-2 (see Appendix B) are required to be analyzed if and when monitoring at the nearest downstream receiving water monitoring station triggers such sampling. This occurs if a parameter in the receiving water is found to exceed the lowest applicable water quality objective.

^b Hardness will be analyzed in the lab, as there is currently no EPA-approved field testing method, and it is not economically or technically feasible to do testing in the field for hardness.

^c Aquatic toxicity monitoring is only required when triggered by downstream receiving water toxicity monitoring from the previous sampling event where a toxicity identification evaluation (TIE) is carried out and inconclusive. If a TIE is conducted at the downstream receiving water and results in the identification of pollutants, then those pollutants must also be monitored at the upstream outfall during the next monitoring event.

3.3 STORMWATER OUTFALL MONITORING PARAMETERS

Parameters monitored at selected outfalls during stormwater monitoring will include:

- Flow. Outfall flow will be monitored based on the appropriate field methodology that corresponds to site conditions. If not practical to monitor with an appropriate field methodology (e.g., automated flow meter or manual measuring device), the flow will be estimated for each outfall based on drainage area, impervious cover, and precipitation data from the nearest LA County rain gauge (refer to the SOP in Appendix C).
- Pollutants assigned a WQBEL derived from TMDL WLAs. These include FIB for SMB outfalls, PCBs/DDT at all outfalls, plus benzo(a)pyrene, chlordane, PAHs, copper, dieldrin, lead, mercury, and zinc at RHE City Hall only.
- Pollutants identified on the 303(d) list for the receiving water or downstream receiving water. This includes coliform bacteria, copper, and lead at RHE City Hall only, but copper and lead will be monitored per downstream TMDL requirements already.
- Field measurements, including: pH, dissolved oxygen, temperature, and specific conductivity. Hardness will be analyzed by the selected analytical lab, as there is currently no EPA-approved field testing method and it is not economically or technically feasible to do testing in the field for hardness.
- Aquatic toxicity monitoring is only required when triggered by downstream wet weather receiving water toxicity monitoring from the previous sampling event where a TIE is carried out and inconclusive. If a TIE is conducted at the downstream receiving water and results in the identification of pollutants, then those pollutants must also be monitored at the upstream outfall during the next monitoring event. If the pollutant is present in the discharge at levels above the applicable receiving water limits, a Toxicity Reduction Evaluation (TRE) will be performed for that pollutant.
- Additional screening parameters (see Appendix B) will be analyzed if and when an exceedance of a parameter's lowest applicable water quality objective is found at the paired downstream receiving water monitoring site. Monitoring for these identified parameters will occur at the next wet weather monitoring event at both the receiving water monitoring site and stormwater outfall monitoring site. Monitoring for these parameters will continue until the linked receiving water monitoring result is below the applicable criteria or when the monitoring data analysis is sufficient to show that the outfall discharge is not contributing to the receiving water exceedance.

Parameters required to be sampled at each stormwater outfall monitoring site are summarized in Table 3-4.

Table E-2 Screening Parameters^b

Aquatic Toxicity^c

Flow

RHE City Hall Parameter Peninsula-SD1 Peninsula-SD2 Indicator Bacteria X X X PCBs/DDT X X X Nutrients (NO3+NO2, TN, and TP) X X Metals (copper, lead, mercury, zinc) X Pesticides (dieldrin, chlordane) X PAHs, benzo(a)pyrene TSS X X X Field Measurements^a X X X

Table 3-4. Stormwater Outfall Monitoring Parameters

As Necessary

As Necessary

X

As Necessary

As Necessary

As Necessary

As Necessary

The parameters to be sampled at the various stormwater outfall monitoring locations are summarized in Appendix B. Appendix B includes acceptable analytical methods for laboratory analyses, Permit-specified minimum detection levels, laboratory QA/QC requirements, holding time requirements, and applicable water quality objectives for each parameter.

3.4 STORMWATER OUTFALL MONITORING PROTOCOL

Monitoring protocols including sample collection procedures, field measurement procedures, and flow monitoring and estimation methods, are detailed in the SOP provided as Appendix C. Sample procedures entail the collection of manual composite samples via direct manual sampling or using a swing sampler device (or similar apparatus) with an intermediate container.

4 Non-stormwater Outfall Monitoring

The Non-Stormwater (NSW) Outfall Screening Program is a multi-step process to identify and address non-stormwater discharges to the receiving waters. The outfall screening and monitoring process is intended to meet the following objectives (Part IX.A of the MRP):

^a Field measurements include pH, dissolved oxygen, temperature, and specific conductivity. Hardness will be measured in the lab as part of the screening parameter suite, as there is currently no EPA-approved field testing method for hardness.

^b Screening parameters can be found in Permit MRP Table E-2, and are also found in Appendix B. Screening parameters are required to be monitored based on downstream receiving water monitoring results.

^c Toxicity is required to be monitored based on downstream receiving water monitoring results.

- 1. Develop criteria or other means to ensure that all outfalls with significant non-stormwater discharges are identified and assessed during the term of the Permit.
- 2. For outfalls determined to have significant non-stormwater flow, determine whether flows are the result of IC/IDs, authorized or conditionally exempt non-stormwater flows, natural flows, or from unknown sources.
- 3. Refer information related to identified IC/IDs to the IC/ID Elimination Program (Part VI.D.10 of the Permit) for appropriate action.
- 4. Based on existing screening or monitoring data or other institutional knowledge, assess the impact of non-stormwater discharges (other than identified IC/IDs) on the receiving water.
- 5. Prioritize monitoring of outfalls considering the potential threat to the receiving water and applicable TMDL compliance schedules.
- 6. Conduct monitoring or assess existing monitoring data to determine the impact of non-stormwater discharges on the receiving water.
- 7. Conduct monitoring or other investigations to identify the source of pollutants in non-stormwater discharges.
- 8. Use results of the screening process to evaluate the conditionally exempt non-stormwater discharges identified in Parts III.A.2 and III.A.3 of the Permit and take appropriate actions pursuant to Part III.A.4.d of the Permit for those discharges that have been found to be a source of pollutants. Any future reclassification shall occur per the conditions in Parts III.A.2 or III.A.6 of the Permit.
- 9. Maximize the use of resources by integrating the screening and monitoring process into existing or planned IMP and/or CIMP efforts.

The non-stormwater screening process consists of the steps outlined in Table 4-1.

Table 4-1. Non-Stormwater Outfall Screening and Monitoring Program Summary

Element	Description	Implementation Dates			
Develop MS4 outfall database	Develop a database of all major outfalls with descriptive information, linked to GIS.	Ongoing			
Outfall Screening	A screening process will be implemented to collect data for determining which outfalls exhibit significant NSW discharges.				
Inventory and Identification of outfalls with NSW discharge	Based on data collected during the Outfall Screening process, identify NSW discharges.	The screening process will begin			
Inventory of outfalls with NSW discharge	Develop an inventory of major MS4 outfalls with known significant NSW discharges and those requiring no further assessment.	summer 2014			
Prioritized source investigation	Use the data collected during the screening process to determine significant discharges and prioritize outfalls for source investigations.				
Identify sources of significant NSW discharges	Perform source investigations per the prioritization schedule. If not exempt or unknown, determine abatement process.	Source investigations will be conducted for at least 25% of the significant NSW discharges by the end of December 28, 2015, and 100% by December 28, 2017.			
Monitoring NSW discharges exceeding criteria	Monitor outfalls that have been determined to convey significant NSW discharges comprised of either unknown or non-essential conditionally exempt NSW discharges, or continuing discharges attributed to illicit discharges.	Monitoring to begin within 90 days of completing the source investigation or after the CIMP has been approved by the EO, whichever is later.			

Each of these steps is discussed in more detail in the following subsections and a flow chart of the process is shown in Figure 4.

The City of Rolling Hills, due to the lack of MS4 outfalls within the city, has developed a separate Non-Stormwater Screening and Monitoring Program and submitted this program to the Regional Board for approval. A copy of this plan can be found in Appendix E.

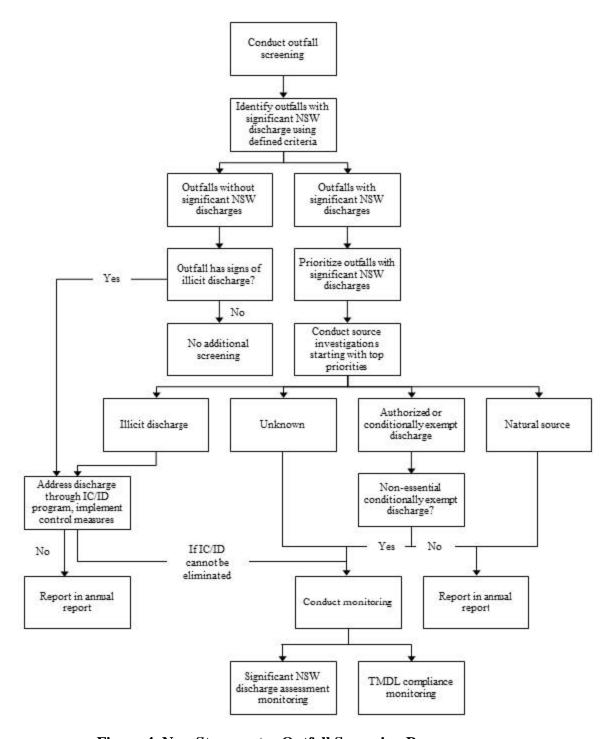


Figure 4. Non-Stormwater Outfall Screening Program

4.1 OUTFALL DATABASE

The non stormwater outfall screening program requires the development of an MS4 outfall database by the time that the CIMP is submitted. The objective of the MS4 database is to geographically link the characteristics of the outfalls within the Peninsula CIMP Area with watershed characteristics including: subwatershed, waterbody, land use, and effective impervious area. The database must contain the elements described in Table 4-2. The information will be compiled into geographic information systems (GIS) layers.

Sources GIS data used to date include:

- Los Angeles County Department of Public Works, Spatial Information Library and the Los Angeles County GIS Data Portal (jurisdictional boundaries, land use, MS4 systems, surface water bodies, existing monitoring locations).
- United States Geological Survey (USGS) National Hydrograph Dataset (HUC-12 watershed boundaries).
- Data provided directly by Peninsula Agencies (MS4 systems)
- Data created as part of the CIMP, based on gathered information (monitoring locations, non-stormwater screening results, etc.)

GIS data will be provided to the Regional Board in electronic format, concurrent with this CIMP.

Table 4-2. MS4 Database Elements

Database Element	Submitted	To Be Developed
Surface water bodies within the Peninsula CIMP Area.	X	
Watershed (HUC-12) boundaries.	X	
Land use overlay.	X	
Effective Impervious Area (EIA) overlay (if available).		X
Jurisdictional boundaries.	X	
The location and length of all open channel and underground pipes 18 inches in diameter or greater (with the exception of catch basin connector pipes).	X	
The location of all dry weather diversions.	X	
The location of all major MS4 outfalls within the Permittee's jurisdictional boundary. Each major outfall shall be assigned an alphanumeric identifier, which must be noted on the map.	X a	
Notation of outfalls with significant non-stormwater discharges (to be updated annually).	Х ь	
Storm drain outfall catchment areas for each major outfall within the Permittee(s) jurisdiction.		X c
Each mapped MS4 outfall shall be linked to a database containing descriptive and monitoring data associated with the outfall. The data shall include:		
Ownership	X	
Coordinates	X	
Physical description	X	
Photographs of the outfall, where possible, to provide baseline information to track operation and maintenance needs over time		X ^d
Determination of whether the outfall conveys significant non- stormwater discharges.	X b	
Stormwater and non-stormwater monitoring data		X d

^a All outfalls greater than 36 inches have been defined, based on known available data. The database will be updated as information is developed, and alphanumeric identifiers will be assigned following the field screening.

As shown in the table, not all information was available at this time for submittal as part of the CIMP. Most items currently not available will be collected through implementation of the Non-Stormwater Outfall Screening Program as noted in the table footnotes. As the data becomes available, it will be entered into the database. Each year, the storm drains, channels, outfalls, and

^b These are included in the non-stormwater screening results, provided as Attachment I.

^c The storm drain system is available in GIS, and identification of the catchment areas for the outfalls is being done as needed. The catchment area will be defined for all outfalls identified as significant and any outfalls selected as stormwater or NSW outfall monitoring locations.

^d This data will be gathered as part of the screening and monitoring program and will be added to the database as it is gathered.

associated database will be updated to incorporate the most recent characterization data for outfalls with significant non-stormwater discharge. The updates will be included as part of the annual reporting to the Regional Board.

4.2 Initial NSW Outfall Screening Process

The NSW outfall screening program began with a field check of all major outfalls as defined in the Permit in the database to gather the necessary field information to populate the database. During the initial field screening, which occurred in September 2014, outfalls were observed during dry weather, defined as days when precipitation is less than 0.1 inch of rain not less than 3 days (72 hours) after a rain event of 0.1 inch or greater. During the initial field screening, the following information was gathered using the field inspection form in Attachment C.3 of Appendix C, or equivalent.

- a. Date, Time, Weather
- b. Photos of outfall and receiving water using a GPS-enabled camera
- c. Coordinates of outfall
- d. Physical descriptions of outfall, site condition, and accessibility (see Section 4.4)
- e. Discharge characteristics, such as odor and color
- f. Presence of flow greater than trickle or no flow
- g. Receiving water characteristics (see Section 4.4)

After the initial event, outfalls where flow greater than a trickle was observed during the initial screening event were revisited for two more screening events. During the second and third screening events, all of the information listed above was gathered again. In addition, visual field estimates of flow were gathered, where applicable. These additional screening events occurred between October and December 2014, in order to ensure the source investigation schedule (which requires 25% of source investigations to be completed by December 2015). Results from these screenings are provided in Appendix I.

The non-stormwater outfall screening and monitoring plan will be reassessed by the end of the 4th year of the Permit term, based on screening results and other gathered information (e.g., data from an agencies illicit connection/illicit discharge program), to determine if changes or updates are needed. Any changes that are made will be described in the Peninsula CIMP Group's Annual Report.

4.3 IDENTIFICATION OF OUTFALLS WITH SIGNIFICANT NON-STORMWATER DISCHARGES

The three initial outfall screening events will be used to define the outfalls that require no further assessment and outfalls with significant non-stormwater discharges. Outfalls will be noted as requiring "No Further Assessment" in the outfall database if:

- a. No flow is observed from the outfall.
- b. The source is confirmed to be from NPDES permitted, categorically exempt essential flow or natural flow, or
- c. Flow is categorized as not significant.

The MRP (Part IX.C.1) states that one or more of the following characteristics may determine significant non-stormwater discharges:

- Discharges from major outfalls subject to dry weather TMDLs.
- Discharges for which monitoring data exceeds non-stormwater action levels (NALs).
- Discharges that have caused or may cause overtopping of downstream diversions.
- Discharges exceeding a proposed threshold discharge rate as determined by the Group Members.
- Other characteristics as determined by the CIMP Group and incorporated within the screening program.

The data collected during the outfall screening process, along with other information about the outfall catchment area, will be utilized to determine which outfalls observed to be flowing during the screening process will be categorized as having "significant discharge." Many factors will be taken into consideration when determining significant outfall discharges and may include the following criteria:

- Proximity of the outfall to the nearest downstream receiving water body where TMDLs apply.
- The discharges have caused or have the potential to cause overtopping of downstream diversions.
- Field measurements and any other available water quality data for the outfall.
- Outfall has persistent flows, meaning flow was observed on two or more of the three screenings.
- Characteristics of the catchment area, including but not limited to, presence of permitted discharges in the area, land use characteristics, and previous IC/ID results.

Outfalls with significant non-stormwater discharge will also be designated in an inventory to be included in the MS4 outfall database.

4.4 INVENTORY OF MS4 OUTFALLS WITH SIGNIFICANT NON-STORMWATER DISCHARGES

An inventory of MS4 outfalls must be developed identifying those outfalls with known significant non-stormwater discharges and those requiring no further assessment (Part IX.D of the MRP). If the MS4 outfall requires no further assessment, the inventory must include the rationale for the determination of no further action required. The inventory will be included in

the outfall database. Each year, the inventory will be updated to incorporate the most recent characterization data for outfalls with significant non-stormwater discharges.

The following physical attributes of outfalls with significant non-stormwater discharges will be included in the inventory. These characteristics will be collected as part of the screening process described in Section 4.3:

- a. Date and time of last visual observation or inspection
- b. Outfall alpha-numeric identifier
- c. Description of outfall structure including size (e.g., diameter and shape)
- d. Description of receiving water at the point of discharge (e.g., natural, soft-bottom with armored sides, trapezoidal, concrete channel)
- e. Latitude/longitude coordinates
- f. Nearest street address
- g. Parking, access, and safety considerations
- h. Photographs of outfall condition
- i. Photographs of significant NSW discharge or indicators of discharge unless safety considerations preclude obtaining photographs
- j. Estimation of discharge rate
- k. All diversions either upstream or downstream of the outfall
- l. Observations regarding discharge characteristics such as odor, color, presence of debris, floatables, or characteristics that could aid in pollutant source identification.

4.5 Prioritized Source Identification

Once the major outfalls exhibiting significant non-stormwater discharges have been identified through the screening process and incorporated in the inventory, Part IX.E of the MRP requires that the Peninsula CIMP Group prioritize the outfalls for further source investigations. The MRP identifies the following prioritization criteria for outfalls with significant non-stormwater discharges:

- Outfalls discharging directly to receiving waters with WQBELs or receiving water limitations in the TMDL provisions for which final compliance deadlines have passed.
- All major outfalls and other outfalls that discharge to a receiving water subject to a TMDL shall be prioritized according to TMDL compliance schedules.
- Outfalls for which monitoring data exist and indicate recurring exceedances of one or more of the Action Levels identified in Attachment G of the Permit.
- All other major outfalls identified to have significant non-stormwater discharges.

In addition to the Permit requirements, the following criteria will be considered when developing the prioritization schedule:

- Rate of discharge based on visual flow observations
- Size of outfall
- Odor, color and clarity of discharge
- Results of the field measurements of pH, temperature, DO, and EC
- Presence of flow in the receiving water

Once the prioritization is complete, a source identification schedule will be developed. The scheduling will focus on the outfalls with the highest priorities first. Unless the results of the field screening justify a modification to the schedule in the MRP, the schedule will ensure that source investigations are completed on no less than 25% of the outfalls with significant non-stormwater discharges by December 28, 2015 and 100% by December 28, 2017.

4.6 SIGNIFICANT NON-STORMWATER DISCHARGE SOURCE IDENTIFICATION

The screening and source identification component of the program is used to identify the source(s) and point(s) of origin of the non-stormwater discharge. Based on the prioritized list of major outfalls with significant non-stormwater discharges, investigations will be conducted to identify the source(s) or potential source(s) of non-stormwater flows.

Part IX.A.2 of the MRP requires Permittees to classify the source investigation results into one of four endpoints outlined as follows and summarized in Table 4-3:

- A. <u>Illicit connections or illicit discharges (IC/IDs)</u>: If the source is determined to be an illicit discharge, the Permittee must implement procedures to eliminate the discharge consistent with IC/ID requirements (Permit Part VI.D.10) and document actions.
- B. <u>Authorized or conditionally exempt NSW discharges</u>: If the source is determined to be an NPDES permitted discharge, a discharge subject to Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or a conditionally exempt essential discharge, the appropriate agency must document the source and report to the Regional Water Board in the next annual report. For non-essential conditionally exempt discharges, the appropriate agency must conduct monitoring consistent with Part IX.G of the MRP to determine whether the discharge should remain conditionally exempt or be prohibited.
- C. <u>Natural flows</u>: If the source is determined to be natural flows, the Permittee must document the source.
- D. <u>Unknown sources</u>: If the source is unknown, the Permittee must conduct monitoring consistent with Part IX.G of the MRP.

Table 4-3. Summary of Endpoints for Source Identification

Endpoint	Follow-up	Action Required by Permit
A. Illicit Discharge or Connection	Refer to IC/ID program	Implement control measures and report in annual report. Monitor if cannot be eliminated.
B. Authorized or Conditionally Exempt Discharges ^{a,b}	Document and identify if essential or non-essential	Monitor non-essential discharges ^c
C. Natural Flows	End investigation	Document and report in annual report
D. Unknown	Refer to IC/ID program	Monitor

^a Discharges authorized by a separate NPDES permit, a discharge subject to a Record of Decision approved by USEPA pursuant to section 121 of CERCLA, or is a conditionally exempt NSW discharge addressed by other requirements. Conditionally exempt NSW discharges addressed by other requirements are described in detail in Part III.A. Prohibitions – Non-Stormwater Discharges of the Permit.

Source investigations will be conducted using site-specific procedures based on the characteristics of the NSW discharge. Investigations could include:

- Identifying permitted discharges within the catchment area.
- Identifying if the flow is from a channelized stream or creek.
- Following dry weather flows from the location where they are first observed in an upstream direction along the conveyance system.
- Compiling and reviewing available resources including past monitoring and investigation data, land use/MS4 maps, aerial photography, and property ownership information.
- Gathering field measurements to characterize the discharge.

Based on the results of the source assessment, outfalls may be reclassified as requiring no further assessment and the inventory will be updated to reflect the information and justification for the reclassification.

Where investigations determine the non-stormwater source to be authorized, natural, or essential conditionally exempt flows, the CIMP Group will conclude the investigation, categorize the outfall as requiring no further assessment in the inventory, and move to the next highest priority

^b Per Section III.A.4 of the Permit, if the Permittee determines that an authorized or conditionally exempt essential non-stormwater discharge is a source of pollutants that causes or contributes to an exceedance of applicable RWL and/or water quality-based effluent limitations, the Regional Board will be notified within 30 days.

^c If monitoring data demonstrates that conditionally exempt non-stormwater discharges are a source of pollutants that causes or contributes to an exceedance of applicable RWL and/or water quality-based effluent limitations, the findings will be reported to the Regional Board in the annual report. Additionally, per Section III.A.4 of the Permit, the Permittee will either effectively prohibit the NSW discharge; impose conditions in addition to those in Table 8 of the Permit, subject to approval by the EO, such that the NSW discharge will not be a source of pollutants; require diversion of the NSW discharge to the sanitary sewer; or require treatment of the NSW discharge prior to discharge to the receiving water.

outfall for investigation. Where investigations determine that the source of the discharge is non-essential conditionally exempt, an illicit discharge, or is unknown – further investigation may be conducted to eliminate the discharge or demonstrate that it is not causing or contributing to receiving water problems. In some cases, source investigations may ultimately lead to prioritized programmatic or structural BMPs. Where Permittees determine that they will address the non-stormwater discharge through modifications to programs or by structural BMP implementation, the CIMP Group will incorporate the approach into the implementation schedule developed for the CIMP Group and the outfall can be lowered in priority for investigation, such that the next highest priority outfall can be addressed.

4.7 Non-Stormwater Discharge Monitoring

As outlined in the Permit MRP, outfalls with significant NSW discharges that remain unaddressed after source investigation will be monitored for water quality to meet the following objectives:

- a. Determine whether a discharge is in compliance with applicable NSW WQBELs derived from TMDL WLAs;
- b. Determine if the quality of a discharge exceeds applicable NALs, as described in Attachment G of the Permit; and
- c. Determine whether a discharge causes or contributes to an exceedance of applicable RWLs.

As identified in Table 4-3, outfalls that have been determined to convey significant non-stormwater discharges where the source investigations concluded that the source is attributable to a continued illicit discharge (Endpoint A), non-essential conditionally exempt (Endpoint B), or unknown (Endpoint D) must be monitored. Monitoring will begin within 90 days of completing a source investigation or after the EO approves the CIMP, whichever is later in time.

4.7.1 Non-Stormwater Outfall-Based Monitoring Sites

The NSW outfall monitoring sites will be determined after source investigation of significant NSW discharges is concluded.

4.7.2 MONITORED PARAMETERS, FREQUENCY, AND DURATION OF MONITORING

The requirements for constituents to be monitored are outlined in the Part VIII.G.1.a-e of the MRP. Outfalls will be monitored for all required constituents except toxicity. Toxicity monitoring is only required when triggered by recent receiving water toxicity monitoring where a TIE on the observed receiving water toxicity test was inconclusive. An overview of the constituents required to be monitored in the MRP at each NSW outfall monitoring site is listed in Table 4-4.

Table 4-4. Summary of Non-Stormwater Outfall Monitoring Parameters

Classification Identified in Permit	Preliminary List of Parameter(s)
General	Flow, hardness, pH, DO, temperature, and TSS
Pollutants assigned TMDL WLAs	Dependent on receiving water TMDLs (FIB for SMB outfalls; nitrogen and phosphorus at Machado Lake outfalls; copper, lead, mercury, and zinc at LA Harbor outfalls).
Pollutants identified for 303(d)-Listed receiving waters	Dependent on receiving water 303(d) listing (FIB, copper, and lead at Wilmington Drain outfalls)
Toxicity	To be determined
Parameters in Table E-2 of the MRP if they are identified as exceeding applicable water quality objectives in the receiving water during dry weather	To be determined

The Peninsula CIMP Group will conduct required NSW outfall monitoring four times per year. To the extent feasible, the NSW outfall monitoring events will be coordinated with the dry weather receiving water monitoring events to allow for an evaluation of whether the NSW discharges are causing or contributing to an observed exceedance of water quality objectives in the receiving water.

4.7.3 ADAPTIVE MONITORING

Monitoring for non-stormwater discharges will be more dynamic than either the receiving water or stormwater outfall monitoring. As non-stormwater discharges are addressed, monitoring at the outfall will cease. Additionally, if after one year of monitoring, results demonstrate that discharges do not exceed any WQBELs, non-stormwater action levels, or water quality standards for pollutants identified on the 303(d) list, monitoring will cease at a given outfall pending written approval from the Executive Officer of the Regional Board. Thus, the number and location of outfalls monitored has the potential to change on an annual basis.

5 TMDL SPECIAL STUDIES

The Permit MRP states that Permittees are responsible for conducting special studies required in an effective TMDL or an approved TMDL monitoring plan within their watershed area. Presently, no special studies are required by the Peninsula-applicable TMDLs or their monitoring plans. The CIMP Group will consider what, if any, special studies may be designed and implemented as more data become available about the receiving waters, land use runoff characterizations, and MS4 potential impacts. Per the Machado Lake Nutrients TMDL, the County has completed a Special Study to characterize the ambient water quality conditions of the unincorporated County islands in the Peninsula.

6 REGIONAL MONITORING

The LACFCD will continue to participate in the Regional Watershed Monitoring Program (Biosassessment Program) being managed by the Southern California Stormwater Monitoring Coalition (SMC). The LACFCD will contribute necessary resources to implement the bioassement monitoring requrement of the Permit on behalf of all Permitees in Los Angeles County during the current Permit cycle. More details are provided in Section 1.4.4.

7 DATA MANAGEMENT AND REPORTING REQUIREMENTS

7.1 MONITORING RECORDS

In accordance with the Permit requirements, the CIMP Group will retain records of monitoring information, including calibration and maintenance records, copies of reports required by the Permit for a period of at least three (3) years from the date of the sample, measurement, or report. Records of monitoring information will include:

- 1. The date, time of sampling or measurements, exact place, weather conditions, and rain fall amount.
- 2. The individual(s) who performed the sampling or measurements.
- 3. The date(s) analyses were performed.
- 4. The individual(s) who performed the analyses.
- 5. The analytical techniques or methods used.
- 6. The results of such analyses.
- 7. The data sheets showing toxicity test results.

Refer to the SOP in Appendix C for more information about how these data should be documented.

7.2 ELECTRONIC DATA MANAGEMENT AND SUBMITTAL REQUIREMENTS

The Permit requires that all stormwater quality monitoring data be reported semi-annually to the Regional Board's Stormwater website in an electronic format. An example of such an electronic format is the most recent Standardized Data Transfer Format as prescribed by the Southern California Municipal SMC, which uses the California Environmental Data Exchange Network

(CEDEN).¹¹ CEDEN is the data system managed by the State Water Board and is a repository for water quality-related data collected in California by the Regional Boards, municipalities, and research and volunteer organizations, which are made accessible to environmental managers and the public. CEDEN was originally created to support the Surface Water Ambient Monitoring Program.

If the CIMP Group elects to use the CEDEN format, monitoring data will be submitted using the appropriate template(s) to a CEDEN Regional Data Center where the data will be reviewed for compliance and entered into the centralized CEDEN database. There are four Regional Data Centers and the CIMP Group will submit data to the Southern California Regional Data Center located in Costa Mesa, which is managed by the Southern California Coastal Water Research Project (SCCWRP).

Before monitoring data can be uploaded to CEDEN through the Regional Data Center, the CIMP Group must convert or create its data in the proper CEDEN template (in Microsoft Excel format). To facilitate uploading the data to CEDEN, analytical chemistry and toxicity data collected by the CIMP Group will be requested from the laboratories in the CEDEN electronic data deliverable (EDD) format. For field measurement data (i.e., pH, temperature, dissolved oxygen, and conductivity), the CIMP Group will need to input the field data into the CEDEN field data template. Examples of the chemistry, toxicity, and field data CEDEN templates are included in Appendix D. If used, the CIMP Group will submit the data spreadsheets to the Regional Data Center and make any necessary revisions. Once approved by the Regional Data Center, the monitoring data will be uploaded into the centralized CEDEN online database where that data will be publically available for download.

7.3 STORMWATER CONTROL MEASURES

The CIMP Group will make all reasonable efforts to determine, compile, analyze, and summarize the following information in the Annual Report:

- 1. Estimated cumulative change in percent effective impervious area (EIA) since December 28, 2012 and, if possible, the estimated change in the stormwater runoff volume during the 85th percentile storm event.
- 2. Summary of new development/redevelopment projects constructed within each Peninsula Agency's jurisdictional area during the reporting year.

¹¹ CEDEN is the State Water Board's data system for surface water bodies in California (http://www.ceden.org/site_map.shtml).

- 3. Summary of retrofit projects that reduced or disconnected impervious area from the MS4 during the reporting year.
- 4. Summary of other projects designed to intercept stormwater runoff prior to discharge to the MS4 during the reporting year.
- 5. For the projects summarized above in #2 through #4, estimate the total runoff volume retained onsite by the implemented projects.
- 6. Summary of actions taken in compliance with TMDL implementation plans or approved Watershed Management Programs to implement TMDL provisions applicable to the Peninsula CIMP Group.
- 7. Summary of riparian buffer/wetland restoration projects completed during the reporting year. For riparian buffers include width, length and vegetation type; for wetland include acres restored, enhanced, or created.
- 8. Summary of other Minimum Control Measures implemented during the reporting year, as the appropriate Agency deems relevant.
- 9. Status of all multi-year efforts that were not completed in the current year and will therefore continue into the subsequent year(s). Additionally, if any of the requested information cannot be obtained, the appropriate Agency will provide a discussion of the factor(s) limiting its acquisition and steps that will be taken to improve future data collection efforts.

Based on this information and other available data, an effectiveness assessment of stormwater control measures will also be included in the Annual Report, and will include, where feasible, the information presented in Section XVIII.A.2 of the Permit MRP.

7.4 Non-Stormwater Control Measures

The CIMP Group will report on the non-stormwater outfall monitoring program in the Annual Report. In accordance with the Permit, the CIMP Group will:

- 1. List the number of identified major outfalls within the Permittee's jurisdiction in the subwatershed.
- 2. Provide the number of outfalls that were screened for significant non-stormwater discharges during the reporting year.
- 3. Provide the cumulative number of outfalls that have been screened for significant non-stormwater discharges since the date the Permit was adopted through the reporting year.
- 4. Provide the number of outfalls with confirmed significant non-stormwater discharge.

- 5. Provide the number of outfalls where significant non-stormwater discharge was attributed to other NPDES permitted discharges; other authorized non-stormwater discharges; or conditionally exempt discharges.
- 6. Provide the number of outfalls where significant non-stormwater discharges were abated as a result of the CIMP Group's actions.
- 7. Provide the number of outfalls where non-stormwater discharges was monitored.
- 8. If any of the above information cannot be obtained, the CIMP Group will provide a discussion of the factor(s) limiting its acquisition and steps that will be taken to improve future data collection efforts.

7.5 Integrated Monitoring Compliance Report

The CIMP Group will submit an Annual Report to the Regional Board Executive Officer in electronic format by December 15th of each year following Executive Officer approval of the CIMP. Each Annual Report will include the monitoring period of July 1 through June 30. When monitoring cannot be performed to comply with the Permit requirements due to circumstances beyond the CIMP Group's control, the following will be submitted to the Regional Board Executive Officer within two working days, when feasible:

- 1. Statement of situation.
- 2. Explanation of circumstance(s) with documentation.
- 3. Statement of corrective action for the future.

As part of the Annual Report, the CIMP Group will submit an Integrated Monitoring Compliance Report. The Integrated Monitoring Compliance Report will be submitted using templates developed by the Regional Board.

Monitoring results from monitoring conducted under this CIMP will be sent electronically on a semi-annual frequency to the Regional Board in the selected (e.g., CEDEN) format. ¹² These results will include the exceedances of applicable WQBELs, RWLS, action levels, and/or aquatic toxicity thresholds for all test results, with corresponding sampling dates for each monitored station. The mid-year data report will cover monitoring from July 1 – December 31, and submitted by June 15. The year-end data report will cover monitoring periods January 1 – June 30, and be submitted by December 15.

¹² Currently, as specified in the Permit MRP, MS4stormwaterRB4@waterboards.ca.gov is the preferred email address to which monitoring data will be sent.

8 Adaptive Management

The adaptive management process will be utilized on an annual basis to evaluate the CIMP and update the monitoring requirements as necessary. Several monitoring elements are dynamic and may require modifications to the monitoring sites, schedule, frequency or parameters. In particular, the non-stormwater screening program and the toxicity monitoring will likely generate changes that need to be incorporated. The CIMP will be evaluated on an annual basis and updated accordingly based on the monitoring data analysis or other monitoring developments. These may include:

- Receiving water or outfall monitoring locations could be revised due to logistical/access/safety issues and/or inability to obtain representative samples.
- Non-stormwater outfall sampling and analysis will be added to the monitoring program if through the screening process major outfalls with significant non-stormwater discharges are identified and the discharge source is unknown, determined to be conditionally exempt but non-essential, or determined to result from continuing illicit discharges. Additional outfalls may be subsequently identified for sampling based on the reassessment of major outfalls which will occur once during the Permit term.
- Toxicity Identification Evaluations (TIEs) result in the identification of additional constituents that need to be monitored.
- Modifications to sampling and/or analysis protocols could occur resulting from knowledge gained through coordination with other watershed monitoring programs. An example is a change in sampling and analysis procedures to obtain sufficient "stormborne sediment" for analysis of PCBs and DDTs.
- Monitoring procedures could be modified in the future to include use of automated flow
 measurement and sampling equipment in lieu of the current manual composite sampling
 and flow measurement methods for receiving waters, and flow estimation methods for
 outfalls.
- Analytical methods could be revised for consistency with EPA method requirements or to achieve lower detection and practical quantitation limits.
- One of the primary objectives of the CIMP is to identify water quality priorities in the Peninsula CIMP Area which would then be the focus of BMP implementation, as discussed in the applicable EWMP Work Plan. If the CIMP monitoring data identify additional constituents as being associated with MS4 discharges and demonstrate that

additional water body-pollutant combination (WBPCs) should be identified as Category 2 (High Priority) or Category 3 (Medium Priority), the Reasonable Assurance Analysis (RAA)¹³ outlined in the EWMP Work Plan will be updated accordingly to include these WBPCs. Conversely, if the monitoring data indicate that certain current Category 2 or 3 designations are not linked to MS4 discharges, these designations will be removed and further action for the particular WBPC under the EWMP will cease.

Major modifications to the CIMP (such as adding, deleting or moving a monitoring site location) will be proposed in the Annual Report and in a separate letter to the Regional Board requesting Executive Officer approval of the change.

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¹³ The Permit-required Reasonable Assurance Analysis (RAA) requires the identification and evaluation of potential BMP implementation scenarios within the Peninsula CIMP area. Specifically, the Permit requires that this RAA be conducted for the prioritized WBPCs identified in the EWMP. The RAA must demonstrate achievement of appropriate standards as developed through applicable TMDLs and other Permit limitations for each WBPC addressed in the EWMP.

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Peninsula CIMP Appendix A Monitoring Site Information

Appendix A Monitoring Site Information For the Peninsula CIMP Group

CIMP Monitoring Site Summary

				Approxima	proximate Location Parameters to Sample For											
	Station ID	Туре	Description (including historical site ID, if any)	Latitude	Longitude	Bacteria (TC, FC, Entero) ^a	PCBs/ DDT ^b	Nutrients (NO3+NO2, TN, TP) ^c	Metals (Cu, Pb, Zn, Hg)	Pesticides (Dieldrin, Chlordane)	PAHs, benzo(a)pyrene	Flow	TSS	Field Measurements ^d	Screening Parameters ^e	Aquatic Toxicity ^f
1DLs	SMB 7-1	Open Beach	Malaga Cove: 300 Paseo Del Mar, Palos Verdes Estates (LACSDM)	33.80500	-118.39470	X										
rial TN	SMB 7-2	Open Beach	Bluff Cove: 600 Paseo del Mar, Palos Verdes Estates (LACSDB)	33.80330	-118.39589	X										
Bacte	SMB 7-3	Open Beach	Long Point: 7200 Palos Verdes Drive South, Rancho Palos Verdes (LACSD1)	33.79362	-118.40684	X										
eaches	SMB 7-4	Open Beach	Albone Cove: 6000 Palos Verdes Drive South, Rancho Palos Verdes (LACSD2)	33.73872	-118.39394	X										
SMB Beaches Bacterial TMDLs CSMP	SMB 7-5	Open Beach	Portuguese Bend Cove: 4100 Palos Verdes Drive South, Rancho Palos Verdes (LACSD3)	33.74183	-118.37912	X										
Machado Lake Nutrient and Pest/PCB and LA Harbor Toxics TMDL Sampling Plan	RHE City Hall	Manhole	RDD 275, Ranchview and Chadwick Canyons, also surrogate for areas not directly monitored	33.78405	-118.35289	X	X	X	X	X	X	X	X	X	As Needed	As Needed
ke Nut LA Ha amplin	Valmonte	Open Channel	Valmonte and Ferncreek subdrainage	33.79539	-118.35483		X	X				X	X			
hado La SB and D MDL Sa	Lariat	Grate Opening	Agua Magna/Sepulveda/Blackwater Canyon subdrainages	33.78111	-118.34718		X	X				X	X			
Mac Pest/PC	Solano	Manhole	PVP subdrainage to Walteria Lake	33.80201	-118.36008		X	X				X	X			
	Peninsula- RW1	Ocean	1,000 ft offshore (due west) of SMB 7- 1. A paired MS4 outfall is tributary to this site via Malaga Creek, and other major outfalls discharge in this vicinity.	33.80339	-118.39919	X	X						X		X	X
MS4 Receiving Water Monitoring Locations	Peninsula- RW2	Ocean	1,000 ft offshore (due southwest) of SMB 7-4. A paired MS4 outfall is located approximately 1,000 yards west of this location, within Abalone Cove.	33.73965	-118.38152	X	X						X		X	X
MS4 Stormwater Outfall Monitoring Locations	Peninsula- SD1	Manhole	The storm drain can be accessed via a manhole that is located in the parkway along Via Corta, adjacent to the intersection of Via Corta and Via del Puente.	33.80129	-118.39107	X	X					X	X	X	As Needed	As Needed
	Peninsula- SD2	Manhole	The storm drain can be accessed via a one of two manholes located on Seagate Drive. The preferable outfall to monitor is presumably located in a grass area on the Palos Verdes Bay Club property on the west side of Seagate Drive (near 32861 Seagate Drive).	33.74123	-118.38799	X	X					X	X	X	As Needed	As Needed

^a Per SMB Beaches Bacteria TMDLs for dry and wet weather, and Reconsideration of Certain Technical Matters of the SMBB Bacteria TMDL, Resolution R12-007

^b Per the SMB PCB/DDT TMDL and the Machado Lake Pesticide & PCB TMDL and Greater LA Harbor Toxics TMDL

^c Per the Machado Lake Nutrients TMDL

^d Field measurements include pH, dissolved oxygen, temperature, and specific conductivity. Hardness will be measured in the lab as part of the Screening Parameter suite, as there is currently no EPA-approved field testing method for hardness.

^e Screening parameters are listed in Attachment B (Table E-2 of the Permit MRP)

^f As detailed in the Permit MRP.

Stormwater	Outfall	Monitoring	Sites

Peninsula Cities

Coordinated Integrated Monitoring Program Stormwater Outfall Monitoring Locations

Monitoring Location ID: Peninsula-SD1

Latitude: 33°48.0552'

Longitude: -118°23.46'

Monitoring Location Description: Malaga Creek is a natural channel that drains a significant portion of the City of Palos Verdes Estates as well as a small portion of the City of Rancho Palos Verdes. The outlet of Malaga Creek is adjacent to SMB 7-1, an ongoing receiving water monitoring location in SMB. Of the known major outfalls that discharge to Malaga Creek, the one with the largest drainage area is proposed for CIMP monitoring. This storm drain outfall primarily drains single family residential and open space land uses, but also includes multifamily residential, commercial, and education land uses. After discharging, water from this outfall follows Malaga Creek for approximately 2,200 feet before discharging adjacent to SMB 7-1 at the beach. The storm drain can be accessed via a manhole that is located approximately 10 feet from the curb (on the Memorial Garden side) on Via Corta, and approximately 75 feet south of the intersection of Via Corta and Via del Puente. See Figure A-1 for a map of this area.

Site Photographs

View of Peninsula-SD1. This manhole requires traffic control, but provides access to the storm drain network that discharges to Malaga Creek.



©2014 Google

Stormwater Outfall Monitoring Locations

Peninsula-SD1

Point where Malaga Creek discharges at the beach. SMB-1 is located adjacent to this location, up-coast approximately 100 yards.



Peninsula Cities

Coordinated Integrated Monitoring Program Stormwater Outfall Monitoring Locations

Monitoring Location ID: **Peninsula-SD2**<u>Latitude</u>: 33°44.474'

Longitude: -118°23.279'

Monitoring Location Description: McCarrell Canyon Creek, a natural channel that drains a large undeveloped area, including the Three Sisters Reserve, transitions to an underground storm drain on the north side of Palos Verdes Drive South. The storm drain runs due south along Seagate Drive, receiving runoff from a Southern California Edison electrical substation, a single family residential neighborhood, a church (St. Peter's By the Sea), and a multi-family residential neighborhood (the Palos Verdes Bay Club), before discharging to Abalone Cove. The storm drain can be accessed via a one of two manholes located on Seagate Drive. The preferable manhole to monitor is presumably located in a grass area on the Palos Verdes Bay Club property on the west side of Seagate Drive. However, this manhole appears to have been landscaped over, and will need to be uncovered if sampling is to be conducted here. An additional manhole is located in the same vicinity, slightly upstream of the other manhole on the east side of Seagate Drive. See Figure A-2 for a map of this area.

Site Photographs

View of the grass lawn believed to contain Peninsula-SD2. This photo is taken from the east curb of Seagate Drive, facing south.



Stormwater Outfall Monitoring Locations

Peninsula-SD2

Bottom of McCarrell Canyon Creek, where it transitions to an underground storm drain. Photo is taken facing north. The majority of tributary area to here is undeveloped/parkland.



Bottom of McCarrell Canyon Creek, where it transitions to an underground storm drain. The two pipes seen in the image continue south towards Palos Verdes Dr S. and Peninsula-SD2. The Southern California Edison substation can be seen on the top of the image.



Peninsula Cities

Coordinated Integrated Monitoring Program Stormwater Outfall Monitoring Locations

Monitoring Location ID: RHE City Hall

Longitude: -118.35289

Monitoring Location Description: Located in the parking lot behind Rolling Hills Estates City Hall (4045 Palos Verdes Drive N.), this monitoring location is accessed via a manhole upstream of the Rolling Hills Estates city boundary. This monitoring location receives runoff from County unincorporated land and all of the Peninsula Cities with the exception of Palos Verdes Estates. Additionally, tributary land uses to this site include single family residential, vacant, education, and the largest commercial area in the Peninsula Cities. See Figure A-3 for a map of this area.

Site Photographs

The major outfall at RHE City Hall. The outfall is located in the back of the parking lot, and allows for easy, safe access.

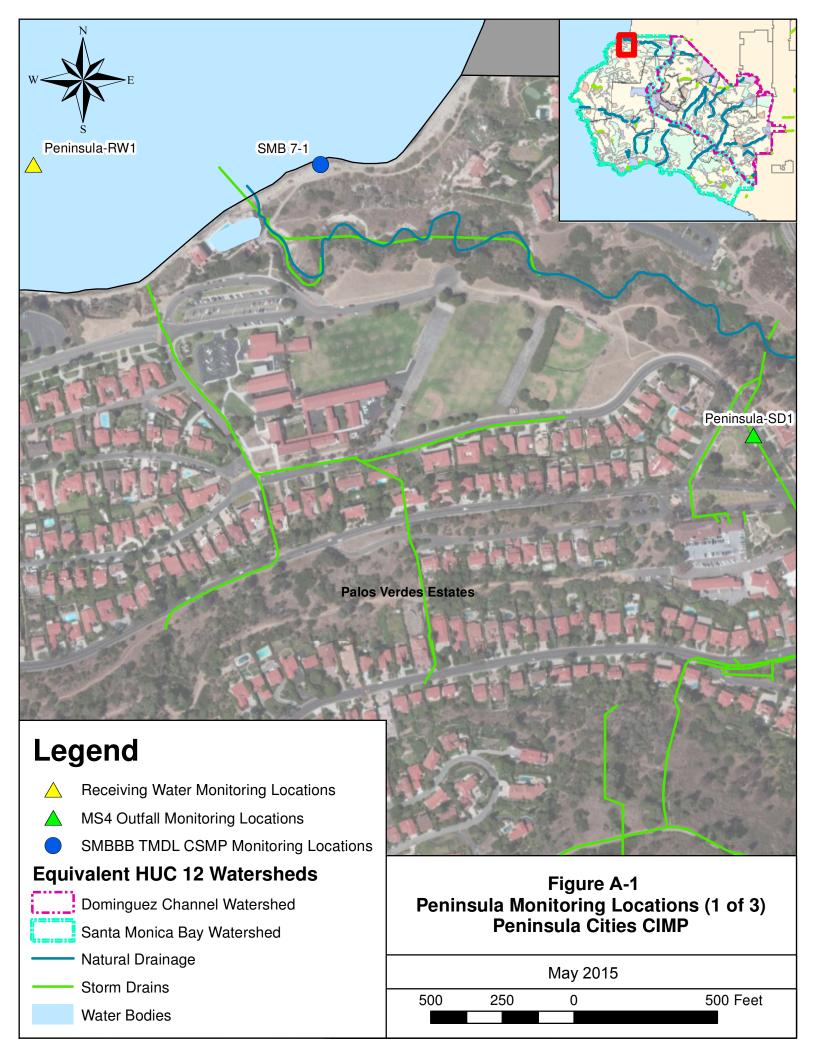
Stormwater Outfall Monitoring Locations

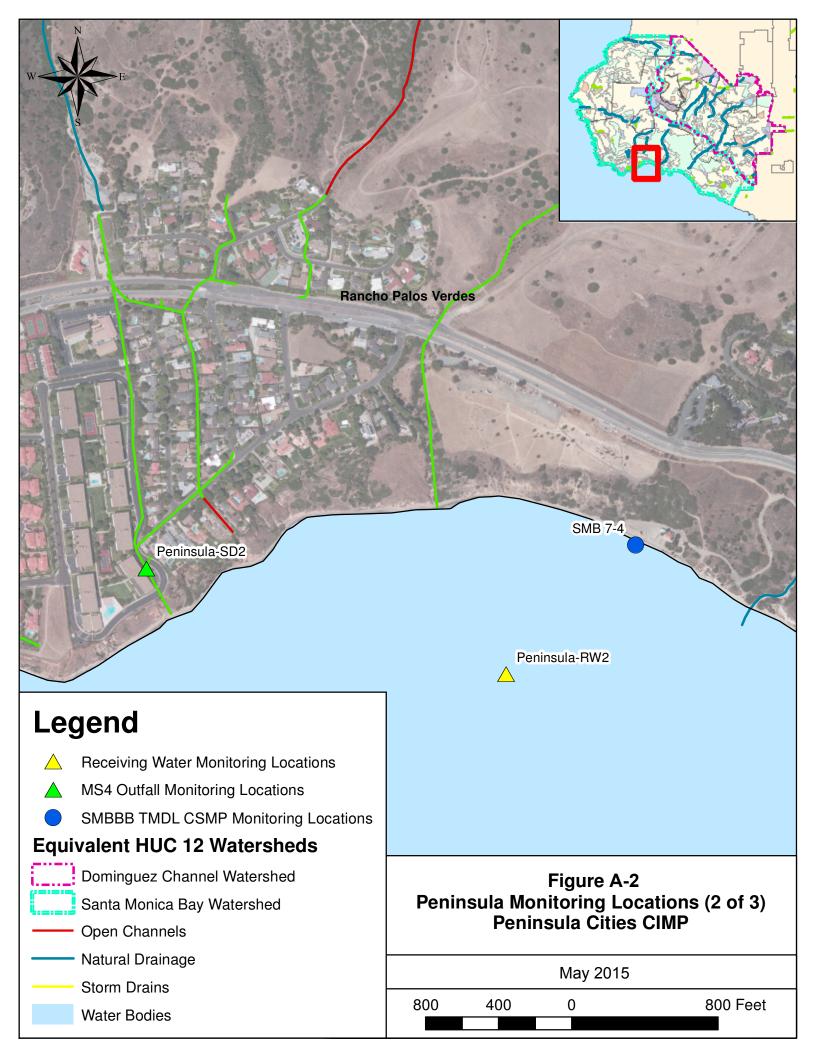
RHE City Hall

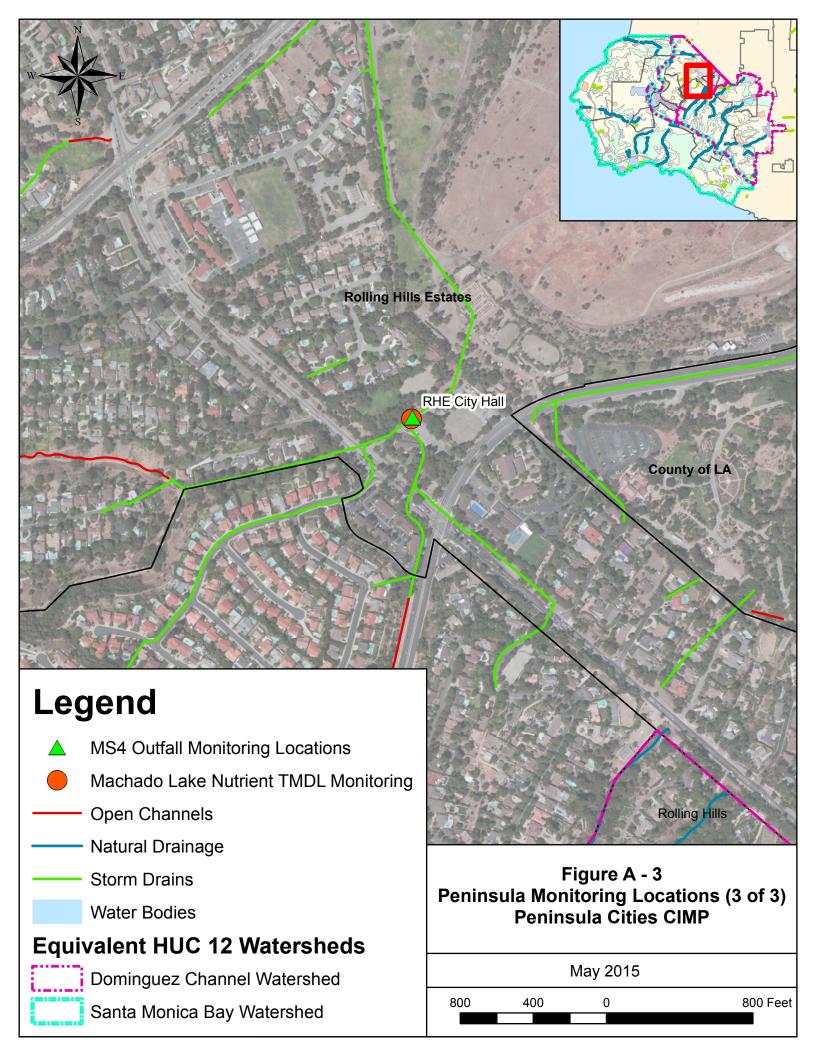
Northgate Environmental Field staff sampling at RHE City Hall.



Monitoring Site Figures







Peninsula CIMP Appendix B Analytical Method Requirements and Water Quality Objectives for Constituents Listed in MRP Table E-2

CIMP Analytical Method Requirements and Water Quality Objectives for Constituents Listed in Permit MRP Table E-2 (with Additional Requirements for Constituents with TMDLs and/or 303(d)-Listed, as applicable)

	Minimum (Permit Ta			Analysis Holding		Water Quali	ty Objective / Cri	iterion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
CONVENTIONAL POLL	UTANTS							
Oil and Grease	5	mg/L	EPA 1664A SM 5520 B	28 d	$G / Cool$, ≤ 6 °C, H_2SO_4 , to $pH < 2$	Basin Plan	Waters shall not greases, waxes o materials in conc that result in a vi coating on the su water or on object water, that cause that otherwise ac affect beneficial	r other centrations sible film or arface of the cts in the a nuisance, or liversely
Total Phenols	100	μg/L	EPA 420.1 SM 5530 D	28 d	$G / Cool$, ≤ 6 °C, H_2SO_4 to pH < 2	CTR Human Health Protection (Sources of Drinking water)	21,000	μg/L
Cyanide (Total)	5	μg/L	SM 4500 CN F ASTM D7511	14 d	P, FP, G / Cool, ≤ 6 °C, 1:1 NaOH to pH > 12, add 0.6g ascorbic acid if residual chlorine present	CTR Freshwater (1 hr avg.)	22	μg/L
						CTR Freshwater (4 day avg.)	5.2	μg/L

¹ "P" is for polyethylene; "FP" is fluoropolymer (polytetrafluoroethylene (PTFE); Teflon®), or other fluoropolymer, "G" is glass; "PA" is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic); "LDPE" is low density polyethylene.

	Minimum (Permit Tal			Analysis Holding		Water Quali	ty Objective / Criterion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value Units
pН	0 - 14	N/A	Field measurement using approved method (i.e., electrometric [EPA 150.2], potentiometric [SM 4500 H B], or equivalent)	Field (15 m)	P, FP, G / Cool, ≤ 6 °C	Basin Plan	The pH of inland surface waters shall not be depressed below 6. 5 or raised above 8. 5 as a result of waste discharges. Ambient pH levels shall not be changed more than 0. 5 units from natural conditions as a result of waste discharge. The pH of bays or estuaries shall not be depressed below 6. 5 or raised above 8. 5 as a result of waste discharges. Ambient pH levels shall not be changed more than 0. 2 units from natural conditions as a result of waste discharge.

	Minimum (Permit Tal			Analysis Holding		Water Quality Objective / Criterion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Temperature	None	°F	Field measurement using approved method (i.e., thermometer [SM 2550 B] or equivalent)	Field (15 minutes)	P, FP, G / None	Basin Plan	The natural receit temperature of alwaters shall not be unless it can be of to the satisfaction Regional Board of alteration in temperature of always beneficial uses. At that are allowed the requirements For waters designed WARM, water than 5 °F above temperature. At these WARM dewaters be raised as a result of was discharges. For waters designed color, water terms at the self-color, water terms at the self-color waters designed color, water terms at the self-color waters designed color, water terms at the self-color waters designed color wa	Il regional be altered lemonstrated in of the chat such berature ly affect Alterations must meet below. In ated comperature ed by more che natural ino time shall signated above 80 °F ste In ated in perature ed by more
Dissolved Oxygen	Sensitivity to 5 mg/L	mg/L	Field measurement	Field (15 m)	G, Bottle and top / None	Machado Lake Nutrient TMDL	>5 mg/L measure meters above the	

	Minimum (Permit Tal			Analysis Holding		Water Qual	ity Objective / Cr	iterion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
			using approved method (i.e., membrane electrode method [SM 4500 O G] or equivalent)			Basin Plan	At a minimum (selow), the mean dissolved oxyger concentration of shall be greater to and no single deshall be less than except when naticonditions cause concentrations. The dissolved oxyger concentrations. The dissolved oxyger concentrations. The dissolved oxyger concentrations. The dissolved oxyger content of all surface designated as both and SPWN shall depressed below result of waste dissolved oxyger content of all surface designated as both and SPWN shall depressed below result of waste dissolved oxyger content of waste dissolved oxyger content of all surface designated as both and SPWN shall depressed below result of waste dissolved oxyger content of waste dissolved oxyger content of all surface designated as both and SPWN shall depressed below result of waste dissolved oxyger content of all surface designated as both and SPWN shall depressed below result of waste dissolved oxyger content of all surface designated as both and SPWN shall depressed below result of waste dissolved oxyger content oxyger cont	an annual an annual an all waters han 7 mg/L, termination a 5.0 mg/L, ural lesser aygen face waters ARM shall below 5 of waste aygen face waters DLD shall below 6 of waste aygen face waters CLD shall below 6 of waste

	Minimum (Permit Ta			Analysis Holding		Water Quali	ty Objective / Cr	iterion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
BACTERIA (single sample	limits)							
Fecal coliform	20	MPN/10 0 ml	SM 9221 C E	8 h	PA, G / Cool < 10 °C, 0.0008% Na ₂ S ₂ O ₃	SMB Beaches (daily maximum)	400	MPN/100 mL
						SMB Beaches (geometric mean)	200	MPN/100 mL
						Basin Plan (REC-1, log mean, >= 4 samples for any 30-day period)	200	MPN/100 mL
						Basin Plan (REC-1, <10% samples during any 30-day period)	400	MPN/100 mL
E. coli (fresh waters)	1	MPN/10 0 ml	SM 9221 F	8 h	PA, G / Cool < 10 °C, 0.0008% Na ₂ S ₂ O ₃	none	none	none
GENERAL CONSTITUEN	NTS							
Dissolved Phosphorus ²	0.05	mg/L	EPA 365.3	28 d	$P / Cool$, ≤ 6 °C, H_2SO_4 to $pH < 2$	Basin Plan	Waters shall not contain biostimulatory substances ir concentrations that promote aquatic growth to the extent that such growth causes nuisance or adversely affect beneficial uses.	

² All dissolved constituents must be filtered upon arrival at analysis laboratory as the official US EPA holding time is 15 minutes.

	Minimum (Permit Tal			Analysis Holding		Water Quali	ty Objective / Cri	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Total Phosphorus	0.05	mg/L	SM 3120 B EPA 365.1	28d	$G / Cool$, ≤ 6 °C, H_2SO_4 to pH < 2	MS4 MAL	0.80	mg/L
						Machado Lake Nutrient TMDL (monthly average)	0.1	mg/L
Turbidity	0.1	NTU	EPA 180.1 SM 2130 B	48 h	P, FP, G / Cool, ≤ 6 °C	Basin Plan	Waters shall be f changes in turbid cause nuisance of affect beneficial Increases in natural attributable to convert quality fact not exceed the following increases shall not exceed the following incre	lity that r adversely uses. ral turbidity introllable tors shall following rbidity is O NTU, fot exceed rbidity is of dilution ther ther ther ther ther ther ther ther

	Minimum (Permit Tal			Analysis Holding		Water Quali	ty Objective / Cri	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Total Suspended Solids (TSS)	2	mg/L	SM 2540 D	7 d	P, FP, G / Cool, ≤ 6 °C	Basin Plan	Waters shall not suspended or sett material in conce that cause nuisan adversely affect l uses.	tleable entrations ace or
						MS4 MAL	264.1	mg/L
Suspended Sediment Concentration (SSC)	0.5	mg/L	ASTM D-3977- 97	7 d	P, G / Cool to ≤6° C, store in the dark	Basin Plan	Waters shall not suspended or sett material in conce that cause nuisan adversely affect t uses.	tleable entrations ace or
Total Dissolved Solids (TDS)	2	mg/L	SM 2540 C	7 d	P, FP, G / Cool, ≤ 6 °C	USEPA Secondary MCL	500	mg/L
						CA Dept. Public Health Recommended Upper Level	1,000	mg/L
						CA Dept. Public Health Recommended Short-term Level	1,500	mg/L
Volatile Suspended Solids (VSS)	2	mg/L	SM 2540 E EPA 160.4	7 d	P, FP, G / Cool, ≤ 6 °C	Basin Plan	Waters shall not suspended or sett material in conce that cause nuisan adversely affect l uses.	tleable entrations ace or

	Minimum (Permit Tal			Analysis Holding		Water Quali	ty Objective / Cri	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Total Organic Carbon (TOC)	1	mg/L	SM 5310C	28 d	$P, FP, G / Cool, \leq$ $6 °C, HCl, H2SO4,$ or $H3PO4$ to pH < 2	None	None	N/A
Total Petroleum Hydrocarbons (extractable fraction, i.e., diesel and motor oil range hydrocarbons)	5	mg/L	EPA 8015B	14 d to ext. / 40 d to analyze	G / Cool, ≤ 6 °C	None	None	none
Biochemical Oxygen Demand	2	mg/L	5210 B	48 h	P, FP, G / Cool, ≤ 6 °C, add 1 gram FAS crystals per liter if chlorine residual present	Basin Plan	Waters shall be f substances that re increases in the F adversely affect uses.	esult in BOD which
Chemical Oxygen Demand	20-900	mg/L	EPA 410.4 SM 5220 D	28 d	P, FP, G / Cool, ≤ 6 °C, H ₂ SO ₄ to pH < 2	MAL	247.5	mg/L
Total Ammonia-Nitrogen (NH ₃ -N)	0.1	mg/L	EPA 350.1	28 d	$P, FP, G / Cool, \leq 6 ^{\circ}C, H_2SO_4 \text{ to} $ $pH < 2$	Basin Plan	Varies based on temperature for Cand Warm Water to 3-4 of Basin P	Cold waters rs (Table 3-1
						Machado Lake Nutrient TMDL (one-hour average)	5.95	mg/L
						Machado Lake Nutrient TMDL (30 day average)	2.15	mg/L
Total Kjeldahl Nitrogen (TKN)	0.1	mg/L	EPA 351.2 SM 4500-NH _s	7 d or 28 d if acidified	P, FP, G / Cool, ≤ 6 °C, H ₂ SO ₄ to pH < 2	MS4 MAL	4.59	mg/L

	Minimum (Permit Ta			Analysis Holding		Water Quali	ty Objective / Cri	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Nitrate+Nitrite (NO ₂ +NO ₃ as N)	0.1	mg/L	EPA 300.0	24 h or 28 d if acidified	$P, FP, G / Cool, \le 6 °C, H_2SO_4 to pH < 2$	MS4 MAL	1.85	mg/L
						Basin Plan	10 as NO ₃ -N + NO ₂ -N	mg/L
Total Nitrogen (TKN+ NO ₂ -N+NO ₃ -N)	N/A		Sum of TKN, Nitrate, and Nitrite	N/A	N/A	Machado Lake Nutrient TMDL (monthly average)	1.0	mg/L
Alkalinity	2	mg/L	EPA 310.2 SM 2320B	14 d	P, FP, G / Cool, ≤ 6 °C	USEPA National Recommended Water Quality Criteria (Freshwater)	20,000	ug/L
Specific Conductance	1	umho/cm	Field measurement using approved method (i.e., conductivity meter [EPA 120.1] or equivalent)	Field (15 min) Lab (28 d) – sample should be filtered through a 0.45 micron filter and stored in dark	P, FP, G / Cool, ≤ 6 °C	CA Dept. Public Health Secondary MCL	900	µmhos/cm
Total Hardness (as CaCO ₃)	2	mg/L	EPA 130.1	6 mo	P, FP, G / HNO ₃ or H ₂ SO ₄ to pH < 2	None	None	N/A
Methylene Blue Active Substances (MBAS)	500	μg/L	SM 5540 C	48 h	P, FP, G / Cool, ≤ 6 °C	CA Dept. Public Health Secondary MCL	500	μg/L

	Minimum (Permit Ta			Analysis Holding		Water Qualit	Water Quality Objective / Criterion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units	
						Basin Plan Federal MCL	500	μg/L	
Chloride	2	mg/L	EPA 300.0 SM 4110B	28 d	P, FP, G / None	none	none	none	
Fluoride	100	μg/L	EPA 300.0 SM 4110B	28 d	P / None	Basin Plan	2,000	μg/L	
Methyl tertiary butyl ether (MTBE)	1000	μg/L	EPA 624	7	G, FP-lined septum / Cool \leq 6 °C, 0.008% Na ₂ S ₂ O ₃	Basin Plan	13	μg/L	
						CA Dept. Public Health Secondary MCL	5	μg/L	
Perchlorate	4	μg/L	EPA 314.0	28	P / None	Basin Plan	6	μg/L	
METALS (TOTAL & DISS	SOLVED³ FRA	CTIONS)	EPA 200.8 SM 3125B	6 mo	P, FP, G-acid rinsed / HNO ₃ to pH < 2, or at least 24 hours prior to analysis				
Aluminum	100	μg/L				USDFG (1 hr)	750	μg/L	
Antimony	0.5	μg/L				none	none	none	
Arsenic	1	μg/L				CTR Freshwater (1 hr avg.) dissolved	340	μg/L	
						CTR Freshwater (4 day avg.) dissolved	150	μg/L	
Beryllium	0.5	μg/L				none	none	none	

 $^{^3}$ All dissolved constituents must be filtered upon arrival at analysis laboratory. The official US EPA holding time is 15 minutes.

	Minimum (Permit Tal			Analysis Holding		Water Quality Objective / Criterion		erion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Cadmium	0.25	μg/L				MS4 MAL	2.52	μg/L
						CTR Freshwater (1 hr avg.) total	=(EXP(1.128* LN(Hardness)- 3.6867))	μg/L
						CTR Freshwater (1 hr avg.) dissolved	=(EXP(1.128* LN(Hardness)- 3.6867)) *(1.136672- (LN(Hardness) *0.041838))	μg/L
						CTR Freshwater (4 day avg.) total	=(EXP(0.7852 *LN(Hardness) -2.715))	μg/L
						CTR Freshwater (4 day avg.) dissolved	=(EXP(0.7852 *LN(Hardness) -2.715)) * (1.101672- (LN(Hardness) *0.041838))	μg/L
Chromium	0.5	μg/L				MS4 MAL	20.20	μg/L
Chromium (Hexavalent)	5	µg/L	EPA 218.6	28 d	P, FP, G / Cool, ≤ 6 °C, (NH ₄) ₂ SO ₄ / NH ₄ OH, pH = 9.3-9.7	CTR Freshwater (1 hr avg.) dissolved	16	µg/L
						CTR Freshwater (4 day avg.) dissolved	11	µg/L

	Minimum (Permit Tal			Analysis Holding		Water Quali	ty Objective / Crit	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Copper	0.5	μg/L				MS4 MAL (Total Fraction)	71.12	μg/L
						CTR Freshwater (1 hr avg.) total	=(EXP(0.9422 *LN(Hardness) -1.7))	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (1 hr avg.) dissolved	=(EXP(0.9422 *LN(Hardness) -1.7))*(0.96)	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Saltwater (1 hr avg.) dissolved	4.8	μg/L
						CTR Freshwater (4 day avg.) total	=(EXP(0.8545 *LN(Hardness) -1.702))	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (4 day avg.) dissolved	=(EXP(0.8545 *LN(Hardness) -1.702))*(0.96)	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Saltwater (4 day avg.) dissolved	3.1	μg/L

	Minimum (Permit Tal			Analysis Holding		Water Quali	terion	
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Iron	100,	μg/L				CA Dept. Public Health Secondary MCL	300	μg/L
Lead	0.5	μg/L				MS4 MAL	102.00	$\mu g/L$
						CTR Freshwater (1 hr avg.) total	=(EXP(1.273* LN(Hardness)- 1.46))	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (1 hr avg.) dissolved	=(EXP(1.273* LN(Hardness)- 1.46))*(1.4620 3- (LN(Hardness) *0.145712))	μg/L
						Greater LA and LB Harbor Toxics TMDL Saltwater (Acute) dissolved	210	µg/L
						CTR Freshwater (4 day avg.) total	=(EXP(1.273* LN(Hardness)- 4.705))	μg/L
						Greater LA and LB Harbor Toxics TMDL CTR Freshwater (4 day avg.) dissolved	=(EXP(1.273* LN(Hardness)- 4.705))*(1.462 03- (LN(Hardness) *0.145712))	μg/L
						Greater LA and LB Harbor Toxics TMDL (chronic) dissolved	8.1	μg/L

	Minimum (Permit Tal			Analysis Holding		Water Quali	Water Quality Objective / Criterio	
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Nickel	1	μg/L				MS4 MAL	27.43	μg/L
						CTR Freshwater (1 hr avg.) total	=(EXP(0.846* LN(Hardness) +2.255))	μg/L
						CTR Freshwater (1 hr avg.) dissolved	=(EXP(0.846* LN(Hardness) +2.255))*(0.99 8)	μg/L
						CTR Freshwater (4 day avg.) total	=(EXP(0.846* LN(Hardness) +0.0584))	μg/L
						CTR Freshwater (4 day avg.) dissolved	=(EXP(0.846* LN(Hardness) +0.0584))*(0.9 97)	μg/L
Selenium	1	μg/L						
						CTR Freshwater (1 hr avg.) total	20	μg/L
						CTR Freshwater (4 day avg.) total	5.0	μg/L
Silver	0.25	μg/L	ľ		-1	CTR Freshwater (max instant.) (total silver)	=(EXP(1.72*L N(Hardness)- 6.59))	μg/L
Thallium	1	μg/L				none	none	none

	Minimum (Permit Ta			Analysis Holding		Water Quality Objective / Cri		erion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Zinc	1	μg/L				MS4 MAL	641.3	$\mu g/L$
						CTR Freshwater (1 hr avg.) total	=(EXP(0.8473 *LN(Hardness) +0.884))	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (1 hr avg.) dissolved	=(EXP(0.8473 *LN(Hardness) +0.884))*(0.97 8)	μg/L
						Greater LA and LB Harbor Harbor Toxics TMDL Saltwater (acute) dissolved	90	μg/L
						CTR Freshwater (4 day avg.) total	=(EXP(0.8473 *LN(Hardness) +0.884))	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (4 day avg.) dissolved	=(EXP(0.8473 *LN(Hardness) +0.884))*(0.98 6)	μg/L
						Greater LA and LB Harbor Toxics TMDL Saltwater (chronic) dissolved	81	μg/L
Total & Dissolved Mercury	0.5	µg/L	EPA 245.7 (CVAFS)	90 d	FP, G, and FP- lined cap / 5 mL/L 12N HCl or 5 mL/L BrCl	NSWAL	0.051	μg/L

	Minimum (Permit Tal			Analysis Holding		Water Qualit	ty Objective / Crit	terion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units		
						MS4 MAL	0.32	μg/L		
						CTR Human Health Protection (30-d avg; fish consumption only)	0.051	μg/L		
VOLATILE ORGANIC CO	VOLATILE ORGANIC COMPOUNDS									
2-Chloroethyl vinyl ether ⁴	1	μg/L	EPA 624	7 d	G, FP-lined septum / Cool \leq 6 °C, 0.008% Na ₂ S ₂ O ₃	None	None	μg/L		
SEMIVOLATILE ORGAN	IIC COMPOUN	NDS	EPA 625 SM 6410 B	7 d to ext. / 40 d to analyze	G, FP-lined cap / Cool \leq 6 °C, 0.008% Na ₂ S ₂ O ₃					
ACID COMPOUNDS										
2-Chlorophenol	2	μg/L				CTR Human Health Protection (Sources of Drinking water)	120	μg/L		

⁴ Permit MRP Table E-2 lists 2-Chloroethyl vinyl ether as a base/neutral semi-volatile organic compound.

	Minimum (Permit Tal			Analysis Holding		Water Quali	ty Objective / Crit	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
4-Chloro-3-methylphenol	1	μg/L	ł			USEPA National Recommended Water Quality Criteria (Taste & Odor)	3,000	μg/L
2,4-Dichlorophenol	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	93	μg/L
2,4-Dimethylphenol	2	μg/L	1			CTR Human Health Protection (Sources of Drinking water)	540	μg/L
2,4-Dinitrophenol	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	70	μg/L
2-Nitrophenol	10	μg/L				None	None	N/A
4-Nitrophenol	5	μg/L				None	None	N/A
Pentachlorophenol	2	μg/L				CTR Fresh Water (4 day avg.)	=EXP(1.005*p H-5.134)	μg/L
						CTR Freshwater (1 hr avg.)	=EXP(1.005*p H-4.869)	μg/L
Phenol	1	μg/L	1			CTR Human Health Protection (Sources of Drinking water)	21,000	μg/L
2,4,6-Trichlorophenol	10	µg/L				CTR Human Health Protection (Sources of Drinking water)	2.1	μg/L

	Minimum (Permit Ta			Analysis Holding		Water Qualit	y Objective / Cr	iterion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
BASE/NEUTRAL COMPO	DUNDS							
Acenaphthene	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	1,200	μg/L
Acenaphthylene	2	μg/L				None	None	N/A
Anthracene	2	μg/L				CTR Human Health Protection (Sources of Drinking water)	9,600	μg/L
Benzidine	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.00012	μg/L
1,2 Benzanthracene	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0044	μg/L
Benzo(a)pyrene	2	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0044 None	μg/L N/A
Benzo(g,h,i)perylene	5	μg/L				None		
3,4 Benzoflouranthene	10	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0044	μg/L
Benzo(k)flouranthene	2	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0044	μg/L

	Minimum (Permit Ta			Analysis Holding		Water Qualit	y Objective / Cr	iterion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Bis(2-Chloroethoxy) methane	5	μg/L				None	None	N/A
Bis(2-Chloroisopropyl) ether	2	μg/L				CTR Human Health Protection (Sources of Drinking water)	1,400	μg/L
Bis(2-Chloroethyl) ether	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.031	μg/L
Bis(2-Ethylhexl) phthalate	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	1.8	μg/L
4-Bromophenyl phenyl ether	5	μg/L				None	None	N/A
Butyl benzyl phthalate	10	μg/L				CTR Human Health Protection (Sources of Drinking water)	3,000	μg/L
2-Chloronaphthalene	10	μg/L				CTR Human Health Protection (Sources of Drinking water)	1700	μg/L
4-Chlorophenyl phenyl ether	5	μg/L				None	None	N/A
Chrysene	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0044	μg/L
Dibenzo(a,h)anthracene	0.1	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0044	μg/L

	Minimum (Permit Ta			Analysis Holding		Water Qualit	Water Quality Objective / Criterion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units	
1,3-Dichlorobenzene	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	400	μg/L	
1,4-Dichlorobenzene	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	400	μg/L	
1,2-Dichlorobenzene	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	2,700	μg/L	
3,3-Dichlorobenzidine	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.04	μg/L	
Diethyl phthalate	2	μg/L				CTR Human Health Protection (Sources of Drinking water)	23,000	μg/L	
Dimethyl phthalate	2	μg/L				CTR Human Health Protection (Sources of Drinking water)	313,000	μg/L	
Di-n-Butyl phthalate	10	μg/L				CTR Human Health Protection (Sources of Drinking water)	2,700	μg/L	
2,4-Dinitrotoluene	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.11	μg/L	

	Minimum (Permit Ta			Analysis Holding		Water Quali	erion	
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
2,6-Dinitrotoluene	5	μg/L				USEPA Toxicity LOEL	330 (acute) 230 (chronic)	μg/L
4,6 Dinitro-2-methylphenol	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	13.4	μg/L
1,2-Diphenylhydrazine	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.04	μg/L
Di-n-Octyl phthalate	10	μg/L				USEPA Toxicity LOEL	940 acute 3 chronic	μg/L
Fluoranthene	0.05	µg/L				CTR Human Health Protection (Sources of Drinking water)	300	μg/L
Fluorene	0.1	µg/L				CTR Human Health Protection (Sources of Drinking water)	1,300	μg/L
Hexachlorobenzene	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.00075	μg/L
Hexachlorobutadiene	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.44	μg/L
Hexachloro- cyclopentadiene	5	μg/L				Basin Plan	50	μg/L
						CTR Human	240	μg/L

	Minimum (Permit Ta			Analysis Holding		Water Qualit	ty Objective / Cri	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
						Health Protection (Sources of Drinking water)		
Hexachloroethane	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	1.9	µg/L
Indeno(1,2,3-cd)pyrene	0.05	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0044	µg/L
Isophorone	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	8.4	μg/L
Naphthalene	0.2	μg/L				USEPA Toxicity LOEL	2300 acute 620 chronic	μg/L
Nitrobenzene	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	17	μg/L
N-Nitroso-dimethyl amine	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.00069	μg/L
N-Nitroso-diphenyl amine	1	μg/L				CTR Human Health Protection (Sources of Drinking water)	5.0	μg/L
N-Nitroso-di-n-propyl amine	5	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.005	μg/L

	Minimum (Permit Tal			Analysis Holding		Water Quali	Water Quality Objective / Criteri		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units	
Phenanthrene	0.05	μg/L				None	None	N/A	
Pyrene	0.05	μg/L				CTR Human Health Protection (Sources of Drinking water)	960	μg/L	
1,2,4-Trichlorobenzene	1	μg/L				Basin Plan	5	μg/L	
CHLORINATED PESTIC	CHLORINATED PESTICIDES			7 d to ext. / 40 d to analyze	$G, FP-lined cap / \\ Cool \leq 6 \ ^{\circ}C, \\ NaOH \ or \ H_2SO_4, \\ pH \ 5-9, \ 0.008\% \\ Na_2S_2O_3$				
Aldrin	0.005	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.00013	µg/L	
alpha-BHC	0.01	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.0039	μg/L	
beta-BHC	0.005	μg/L				CTR Human Health Protection (Sources of Drinking water)	0.014	µg/L	
delta-BHC	0.005	μg/L				None	None	N/A	
gamma-BHC (lindane)	0.02	μg/L				CTR Freshwater (1 hr avg.)	0.95	μg/L	
alpha-chlordane ^a	0.1	μg/L				none	none	none	
gamma-chlordane ^a	0.1	μg/L				none	none	none	

	Minimum (Permit Tal			Analysis Holding		Water Qualit	y Objective / Cri	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
4,4'-DDD	0.00004	μg/L				Annual WLA Permit Att. M SMB DDT TMDL Water Column Target	27.08 0.00017	g/yr µg/L
						Machado Lake Toxics TMDL Water Column Target	0.00084	μg/L
4,4'-DDE	0.00008	μg/L				Annual WLA Permit Att. M SMB DDT TMDL Water Column Target	27.08 0.00017	g/yr µg/L
						Machado Lake Toxics TMDL Water Column Target	0.00059	μg/L
4,4'-DDT	0.00008	µg/L				Annual WLA Permit Att. M SMB DDT TMDL Water Column Target	27.08 0.00017	g/yr µg/L
						Machado Lake Toxics TMDL Water Column Target	0.00059	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (4 day avg.)	0.001	μg/L

	Minimum Level (Permit Table E-2)			Analysis Holding		Water Quality Objective / Criterion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
						Greater LA and LB Harbor Toxics TMDL/CTR Saltwater (4 day avg.)	0.001	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (1 hr avg.)	1.1	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Saltwater (1 hr avg.)	0.13	μg/L
Dieldrin	0.01	μg/L				Machado Lake Toxics TMDL Water Column Target	0.00014	ug/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (4 day avg.)	0.056	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Saltwater (4 day avg.)	0.0019	μg/L
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (1 hr avg.)	0.24	μg/L

	Minimum Level (Permit Table E-2)			Analysis Holding		Water Quality Objective / Criterion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
						Greater LA and LB Harbor Toxics TMDL/CTR Saltwater (1 hr avg.)	0.71	μg/L
alpha-Endosulfan	0.02	μg/L				CTR Freshwater (4 day avg.)	0.056	μg/L
						CTR Freshwater (max instant.)	0.22	μg/L
beta-Endosulfan	0.01	μg/L				CTR Freshwater (4 day avg.)	0.056	μg/L
						CTR Fresh Water (max instant.)	0.22	μg/L
Endosulfan sulfate	0.05	μg/L	-			USEPA 24 hr avg	0.056	μg/L
Endrin	0.01	μg/L				CTR Freshwater (4 day avg.)	0.036	μg/L
						CTR Freshwater (1 hr avg.)	0.086	μg/L
Endrin aldehyde	0.01	µg/L				CTR Human Health Protection (Sources of Drinking water)	0.76	μg/L
Heptachlor	0.01	μg/L				CTR Freshwater (4 day avg.)	0.0038	μg/L
						CTR Fresh Water (max instant.)	0.52	μg/L
Heptachlor epoxide	0.01	μg/L				CTR Freshwater (4 day avg.)	0.0038	μg/L
						CTR Freshwater (max instant.)	0.52	μg/L

	Minimum Level (Permit Table E-2)		Analysis Holding			Water Quality Objective / Criterion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Toxaphene	0.5	μg/L				CTR Freshwater (4 day avg.)	0.0002	μg/L
						CTR Freshwater (1 hr avg.)	0.73	μg/L

	Minimum (Permit Tal			Analysis Holding		Water Quali	ty Objective / Cri	ctive / Criterion	
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units	
POLYCHLORINATED BIPHENYLS									
Total PCBs (sum of at least 40congeners)	range for all congeners: 0.000005- 0.000020	μg/L	Most sensitive, commercially available analysis in the region (i.e., Method 1668c, if feasible; otherwise, Method 8270)	1 yr to extract / 1 yr to analyze	G, FP-lined cap / Cool ≤ 6 °C	Basin Plan (30 day average)	0.014	μg/L	
	Total PCBs: 0.000020	μg/L	,			Basin Plan (1 day average)	0.030	μg/L	
						Basin Plan (Human Health)	0.000070	μg/L	
						SMB PCB TMDL Water Column Target	0.000019	μg/L	
						PCB TMDL Annual WLA (Permit Att. M)	140.25	g/yr	
						Basin Plan	0.5	μg/L	
						Machado Lake Toxics TMDL Water Column Target	0.00017	ug/L	
						Greater LA and LB Harbor Toxics TMDL/CTR Freshwater (4 day avg.)	0.014	μg/L	

	Minimum (Permit Tal			Analysis Holding		Water Quality Objective / Criterion		
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
						Greater LA and LB Harbor Toxics TMDL/CTR Saltwater (4 day avg.)	0.03	μg/L
						CTR Human Health Protection (Sources of Drinking water)	0.00017	μg/L
ORGANOPHOSPHATE PESTICIDES		EPA 525.2	7 d to ext. / 40 d to analyze	G, FP-lined cap / Cool ≤ 6 °C, pH 5-9				
Atrazine	2	μg/L				Basin Plan	1	μg/L
Chlorpyrifos	0.05	μg/L				CADFG Freshwater Aquatic Life (4 day Avg)	0.014	μg/L
						CADFG Freshwater Aquatic Life (1 hr maximum)	0.02	μg/L
Cyanazine	2	μg/L	EPA 629 / 507			None	None	N/A
Diazinon	0.01	μg/L				CADFG Freshwater Aquatic Life (4 day Avg)	0.05	µg/L
						CADFG Freshwater Aquatic Life (1 hr maximum)	0.08	µg/L

	Minimum (Permit Tal			Analysis Holding		Water Qualit	ty Objective / Cri	terion
Constituent	Value	Units	Analytical Methods	Time (Max)	Container Type ¹ / Preservative	Source	Value	Units
Malathion	1	μg/L			-	USEPA National Recommended Water Quality Criteria for Freshwater Aquatic Life (max instant.)	0.1	μg/L
Prometryn	2	μg/L				None	None	N/A
Simazine	2	μg/L				Basin Plan	4	μg/L
						USEPA National Recommended Water Quality Criteria for Freshwater Aquatic Life (max instant.)	10	μg/L
HERBICIDES				7 d to ext. / 40 d to analyze	G, FP-lined cap / Cool ≤ 6 °C, pH 5-9			
2,4-D	10	μg/L	EPA 615 SM 6640B			Basin Plan	70	μg/L
Glyphosate	5	μg/L	EPA 547			Basin Plan	700	μg/L
2,4,5-TP-SILVEX	0.5	μg/L	EPA 615 SM 6640B			USEPA National Recommended Water Quality Criteria for Human Health	10	μg/L

^aThere are no water quality objectives explicitly listed for alpha-chlordane and gamma-chlordane; however, total chlordane (which includes alpha-chlordane, gamma-chlordane, oxychlordane, cis-nonachlor, and trans-nonachlor) is listed in the Greater LA and LB Harbor Toxics TMDL with the following water quality criteria:

Peninsula CIMP

Appendix B

• Freshwater (acute): 2.4 μg/L

• Freshwater (chronic): 0.0043 μg/L

• Saltwater (acute): 0.09 µg/L

• Saltwater (chronic): 0.004 µg/L

Data Sources:

Los Angeles County Permit Order No. R4-2012-0175

USEPA Santa Monica Bay TMDL for DDTs and PCBs (March 2012)

Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters Toxic Pollutants TMDL (May 2011)

Los Angeles Region Basin Plan CH. 3 Water Quality Objectives (1994)

Machado Lake Eutrophic, Algae, Ammonia, and Odors (Nutrient) TMDL (April 2008)

Machado Lake Pesticides and PCBs TMDL (September 2010)

State Water Resources Control Board Online Water Quality Goals Database: (http://www.waterboards.ca.gov/water-issues/programs/water-quality-goals/search.shtml)

USEPA Federal Register Vol. 77, No. 97, Part II. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures (May 2012)

Quality Assurance Program Plan (QAPP), The State of California's Surface Water Ambient Monitoring Program (SWAMP) (September 2008)

Peninsula CIMP Appendix C CIMP Standard Operating Procedures (SOPs)

Appendix C

CIMP: Water Quality Monitoring Standard Operating Procedures

For the Peninsula CIMP Group

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List of Attachments

Attachment C.1: USGS protocols for Field Measurements (from National Field Manual for the Collection of Water-Quality)

Attachment C.2: Example Chain of Custody Forms (blank)

Attachment C.3: Dry Weather Outfall Screening Field Data Sheet (Example)

1 INTRODUCTION

This document summarizes the Standard Operation Procedures (SOPs) for water quality and flow sampling and measurement. This document is organized by procedures including an overview of the Permit¹ monitoring requirements, protocols for collecting water quality samples and performing flow monitoring and estimation, dry weather outfall screening requirements, and quality assurance and quality control requirements.

1.1 Definition of SOP Terms

- Aliquot: A discrete sample collected as part of a composite sample.
- <u>Grab Sample:</u> A discrete sample. The sample is typically collected within a short period of time, usually less than 15 minutes. It is analyzed as a single sample and represents an instantaneous point in time. This method is used to collect samples for constituents not amenable to composite sampling due to short holding times and/or specific collection or preservation needs.
- <u>Composite Sample:</u> A sample composed of multiple aliquots. The aliquots are collected at regular intervals based on time or flow rate and composited into one single composite sample for analysis. Composite samples are used to determine an event mean concentration (to the extent that the aliquots are representative of the entire storm hydrograph) or loading of a constituent in water.
- <u>Clean Hands/Dirty Hands:</u> The sampling protocol to be used to handle the sampling equipment and sample bottles (as appropriate) (see Section 4.1.1).

2 PROCEDURES

2.1 Sample Collection Procedures

The Permit requires that samples and measurements taken for the purpose of monitoring shall be representative of the monitored activity. Three types of sampling procedures will be implemented to obtain representative measurements of the monitoring constituents:

• Time-weighted composite samples, which will be used for the majority of constituents for wet weather outfall monitoring. Collection of a time-weighted composite sample will entail collecting one aliquot every 20 minutes during a three (3) hour continuous period of a qualifying storm event, or over the entire storm if the storm duration is predicted to be less than 3 hours (for a total of ten (10) aliquots), weather permitting (Reference: EPA

¹ This CIMP SOP was developed in accordance with Order No. R4-2012-0175, Monitoring and Reporting Program (MRP) No. CI-6948, dated November 8, 2012.

NPDES Storm Water Sampling Guidance Document EPA 833-B-92-001, 40 CFR 122.21 (g)(7)(ii)). Manual composite sample collection will be performed using a depth integrated sampler and/or a properly cleaned sample container with a pole attachment to collect discrete aliquots that will be combined to form one composite sample per monitoring event. Alternatively a peristaltic pump (such as a Masterflex E/S Portable Sampler with laboratory-cleaned fluoropolymers tubing) or portable autosampler (such as the ISCO 6712 with laboratory-cleaned fluoropolymers tubing) may be used to collect the discrete aliquots that will form the composite sample;

- Grab samples, which will be used for receiving water monitoring and dry weather outfall monitoring. Additionally, grab samples will be collected for wet weather outfall monitoring for bacteria, oil and grease, total petroleum hydrocarbons (TPH), cyanide, total phenols and volatile organic compounds (i.e., MTBE and 2-Chloroethyl vinyl ether only). Grab samples should be collected at the same time field measurements are performed. More details on the sampling procedures are provided in Section 2.4; and
- Field measurements. Field measurements will be gathered for readings that may change in transit between the sampling site and the laboratory. These parameters will include pH, dissolved oxygen, temperature, and specific conductivity. Procedures for measuring these parameters in the field are provided in Section 2.6.3.

In the first year of the monitoring program, outfall monitoring sites will be assessed for the feasibility of installing automated flow monitoring and sampling equipment. Automated monitoring equipment would facilitate the collection of more representative samples that represent a greater portion of flow hydrograph. If automated monitoring equipment is installed at one or more outfall monitoring locations after the first year, this SOP will be updated accordingly.

2.2 Monitoring Program Analytical Requirements

A summary of the monitoring program analytical requirements is provided in Appendix B.^{2,3} Appendix B includes the required analytical method, minimum reporting level⁴ (i.e., practical

² Appendix B is based on the Permit Attachment E (Monitoring and Reporting Program [MRP] Table E-2 (Storm Water Monitoring Program's Constituents with Associated Minimum Levels) and with requirements added for 303(d)-listed constituents and constituents with Total Maximum Daily Loads (TMDLs), as applicable.

³All monitoring, sampling, sample preservation, and analyses must be conducted according to test procedures approved under 40 CFR Part 136 for the analysis of pollutants, unless another test procedure is required under 40 CFR subchapter N or O or is otherwise specified in the Permit for such pollutants. If a particular Minimum Level is not attainable in accordance with procedures set forth in 40 CFR Part 136, the lowest quantifiable concentration of the lowest calibration standard analyzed by a specific analytical procedure may be used instead.

quantitation limit), analysis holding time and container type and preservative. A summary of the sample volume requirements is provided in Table C-1. Note that the sample volume requirements could be reduced after the first significant storm event and the first June dry weather event, if constituents from Permit MRP Table E-2 no longer need to be analyzed because they were either not detected above the analytical method detection limit, or they were detected below the lowest applicable water quality objective.

This SOP is based on information provided by Weck Laboratories in City of Industry, California, Vista Analytical Laboratory in El Dorado Hills California, and Aquatic Bioassay & Consulting laboratories, Inc. (ABC) in Ventura, California (toxicity analyses). Other analytical laboratories may be substituted for monitoring program implementation provided the laboratories meet the following requirements:

- 1. Certified for such analyses by an appropriate governmental regulatory agency.
- 2. Participated in "Intercalibration Studies" for stormwater pollutant analysis conducted by the Southern California Municipal Storm Water Monitoring Coalition (SMC)⁵.
- 3. Performs laboratory analyses consistent with the stormwater monitoring guidelines as specified in, the Stormwater Monitoring Coalition Laboratory Guidance Document, 2nd Edition R. Gossettt and K. Schiff (2007), and its revisions.

Additional Volume Needed Bottle for MS/MSD **Container** No. **Constituents** Volume **Containers Type Bottle** No. (mL) **Containers** Volume (mL) **Composite Samples** Total Hardness, total and Polyethylene 1 1.000 0 0 dissolved metals VOA Cr6, Total 1 40 0 0 Cr6. Dissolved VOA 1 40 0 0 Ammonia, COD, NO3+NO2 as Polyethylene 500 0 0 1 N, TKN

Table C-1. CIMP Sample Volume Requirements

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⁴ The Minimum Reporting Level is specified for all constituents listed in MRP Table E-2.

⁵The 'Intercalibration Studies' are conducted periodically by the SMC to establish a consensus based approach for achieving minimal levels of comparability among different testing laboratories for stormwater samples to minimize analytical procedure bias. Stormwater Monitoring Coalition Laboratory Document, Technical Report 420 (2004) and subsequent revisions and augmentations.

	Container Type	No. Containers	Bottle Volume (mL)	Additional Volume Needed for MS/MSD	
Constituents				No. Containers	Bottle Volume (mL)
BOD, Alkalinity, pH, EC, MBAS, TDS, TSS, Turbidity, VSS	Polyethylene (1 Gallon)	1	3,785	0	0
Chlorinated Herbicides (EPA 515.3)	Amber Glass	1	250	0	0
Organophosphate Pesticides (EPA 525.2)	Amber Glass	2	1,000	2	1,000
Glyphosate (EPA 547)	Amber VOA	1	40	1	40
Chlorinated Pesticides	Amber Glass	2	1,000	2	1,000
Semivolatile Organic Compounds (EPA 625)	Amber Glass	2	1,000	2	1,000
Fluoride (EPA 300.0)	Polyethylene	1	250	0	0
Perchlorate (EPA 314)	Polyethylene	1	250	0	0
Total & Dissolved Phosphorus	Polyethylene	1	500	0	0
Total Organic Carbon	Amber Glass	1	250	0	0
Toxicity (3 test species and TIE for most sensitive species)	Cubitainer (5 Gallon)	1	18,927	N/A	N/A
Composite Sample Subtotal		18	28,832	7	3,040
	Grab Samples				
Cyanide	Polyethylene	1	500	0	0
Bacteria	Sterile	3	125	0	0
Volatile organic Compounds (EPA 624)	VOA	3	40	3	40
TPH-Diesel, TPH-Motor Oil (EPA 8015)	Amber Glass	2	1,000	2	1,000
Oil & Grease (EPA 1664)	Glass	2	1,000	2	1,000
Phenolics (EPA 420.4)	Amber Glass	1	500	0	0
TOTAL		30	31,997	14	5,080

2.3 Aquatic Toxicity Testing and Toxicity Identification Evaluations

The aquatic toxicity testing requirements outlined in the Permit are intended to determine whether water column toxicity is observed in targeted receiving waters and then assess which pollutant categories may potentially be causing the adverse aquatic effects. The results of aquatic toxicity testing are intended to guide future receiving and outfall water quality monitoring and contribute to the identification and control of toxicity causing pollutants in urban runoff through

watershed control measures that may include: pollutant source controls, modified minimum control measures (MCMs) and Best Management Practices (BMPs). The following subsections outline the approach for conducting the Peninsula CIMP Group's aquatic toxicity monitoring and evaluation. Control measures and management actions to address confirmed toxicity caused by urban runoff are addressed by the EWMP, either via currently identified management actions or those that are identified via adaptive management of the EWMP.

The approach to conducting aquatic toxicity monitoring is presented in Figure C-1, which describes a general evaluation process for each sample collected as part of routine sampling conducted twice per year in wet weather and once per year in dry weather. Monitoring begins in the receiving water and the information gained is used to identify constituents for monitoring at outfalls to support the identification of pollutants that need to be addressed in the EWMP. The sub-sections below describe the detailed process and its technical and logistical rationale. Although not specified for testing at this time, the freshwater toxicity testing approach is also provided if such testing is initiated at any point during the life of the CIMP.

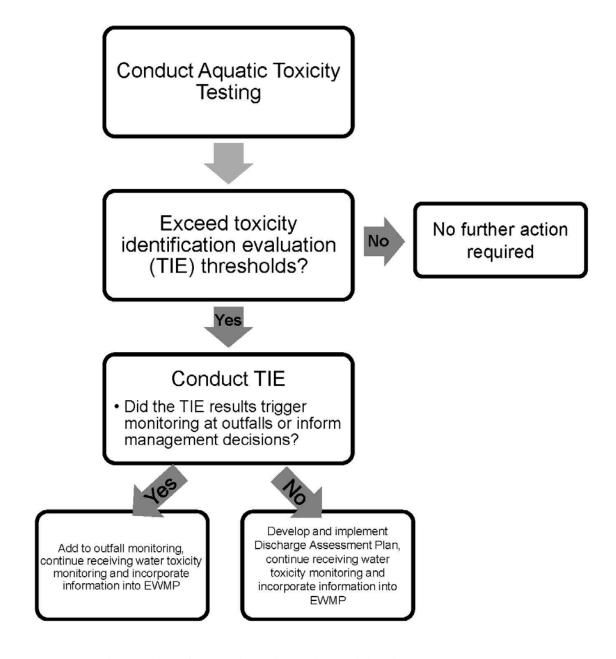


Figure C-1. Generalized Aquatic Toxicity Assessment Process

2.3.1 <u>Sensitive Species Selection</u>

The MRP (page E-32) states that a sensitivity screening to select the most sensitive test species should be conducted unless "a sensitive test species has already been determined, or if there is prior knowledge of potential toxicant(s) and a test species is sensitive to such toxicant(s), then monitoring shall be conducted using only that test species." Previous relevant studies conducted in the watershed should be considered. Such studies may have been completed via previous MS4 sampling, wastewater NPDES sampling, or special studies conducted within the watershed. The following sub-sections discuss the species selection process for assessing aquatic toxicity in receiving waters.

2.3.1.1 Freshwater Sensitive Species Selection

As described in the MRP (page E-31), if samples are collected in receiving waters with salinity less than 1 part per thousand (ppt), or from outfalls discharging to receiving waters with salinity less than 1 ppt, toxicity tests should be conducted on the most sensitive test species in accordance with species and short-term test methods in Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms (EPA/821/R-02/013, 2002; Table IA, 40 CFR Part 136). Static renewal freshwater toxicity test species identified in the MRP are:

- Fathead minnow, *Pimephales promelas* (Larval Survival and Growth Test Method 1000.04).
- Daphnid, Ceriodaphnia dubia (Survival and Reproduction Test Method 1002.05).
- ➤ Green alga, Selenastrum capricornutum (Raphidocelis subcapitata) (Growth Test 1003.0).

Low salinity (fresh) receiving water toxicity testing data from within the Peninsula CIMP Area were not identified during CIMP preparation. Toxicity data from the Dominguez Channel and other regional receiving waters, suggest that organophosphate pesticides, pyrethroids, and metals may contribute to aquatic toxicity. Assuming the potential presence of these toxicants in the WMG area, relative sensitivity to these pollutants was a primary consideration in selecting from among the three common test species.

Ceriodaphnia dubia (C. dubia) is often used locally and reported upon nationally, as a broad spectrum test species that is sensitive for historical and current use pesticides and metals, and studies indicate that it is more sensitive to the toxicants of concern than Pimephales promelas (P. promelas) or Selenastrum capricornutum (S. capricornutum). In Aquatic Life Ambient Freshwater Quality Criteria - Copper, the USEPA reports greater sensitivity of C. dubia to copper (species mean acute value of 5.93 μg/l) than for P. promelas (species mean acute value of 69.93 μg/l; EPA, 2007). C. dubia's relative sensitivity to copper extends to multiple metals. Additionally, researchers at the University of California (UC), Davis reviewed available reported

species sensitivity values in developing pesticide criteria for the Central Valley Regional Water Quality Control Board. In developing pesticide criteria for the Central Valley Regional Water Quality Control Board, researchers at University of California at Davis, reported higher sensitivity of *C. dubia* to diazinon and bifenthrin (species mean acute value of 0.34 µg/l and 0.105 µg/l) compared to *P. promelas* (species mean acute value of 7804 µg/l and 0.405 µg/l; Palumbo et al., 2010a,b). Additionally, in a stormwater study for the City of Stockton, urban stormwater runoff found acute and chronic toxicity to *C. dubia*, with no toxicity to *S. capricornutum* or *P. promelas* (Lee and Lee, 2001). The toxicity was attributed to organophosphate pesticides, indicating a higher sensitivity of *C. dubia* compared to *S. capricornutum* or *P. promelas*. While *P. promelas* is generally less sensitive to metals and pesticides, this species can be more sensitive to ammonia than *C. dubia*. However, as ammonia is not typically a constituent of concern for urban runoff and ammonia is not consistently observed above the toxic thresholds in the watershed, *P. promelas* is not considered a particularly sensitive species for evaluating the impacts of urban runoff in receiving waters in the watershed.

S. capricornutum is a species sensitive to herbicides; however, while sometimes present in urban runoff, herbicides are not identified as a potential toxicant in the watershed. Additionally, S. capricornutum is not considered the most sensitive species as it is not sensitive to pyrethroids or organophosphate pesticides and is not as sensitive to metals as C. dubia. Additionally, the S. capricornutum growth test can be affected by high concentrations of suspended and dissolved solids, color, and pH extremes, which can interfere with the determination of sample toxicity. As a result, it is common to manipulate the sample by centrifugation and filtration to remove solids in order to conduct the toxicity test; however, this process may affect the toxicity of the sample. In a study of urban highway stormwater runoff (Kayhanian et. al, 2008), S. capricornutum response to the stormwater samples was more variable than the C. dubia and the P. promelas and in some cases the algal growth was possibly enhanced due to the presence of stimulatory nutrients. Also, in a study on the City of Stockton urban stormwater runoff (Lee and Lee, 2001) the S. capricornutum tests rarely detected toxicity where the C. dubia and the P. promelas regularly detected toxicity.

Based on best professional judgment and local experience with the Permit-identified freshwater species, *C. dubia* is most sensitive to the broadest range of potential toxicant(s) typically found in local fresh receiving waters impacted by urban runoff and will be selected for freshwater toxicity testing by the Peninsula CIMP Group. The species can be maintained in laboratory cultures making them generally available year round. The simplicity of the test, the ease of interpreting results, and relatively small sample volume necessary to run the test, make the test a valuable screening tool. The ease of sample collection and higher sensitivity will support assessing the presence of ambient receiving water toxicity or long term effects of toxic stormwater over time. As such, toxicity testing in the freshwater portions of the watershed will be conducted using *C. dubia*. However, *C. dubia* test organisms are typically cultured in

moderately hard waters (80-100 mg/L CaCO₃) and can have increased sensitivity to elevated water hardness greater than 400 mg/L CaCO₃), which is beyond their typical habitat range. Because of this, in instances where hardness in site waters exceeds 400 mg/L (CaCO₃), an alternative test species may be used. Daphnia magna is more tolerant to high hardness levels and is a suitable substitution for *C. dubia* in these instances (Cowgill and Milazzo, 1990).

2.3.1.2 Saltwater Sensitive Species Selection

Samples collected in receiving waters with salinity equal to or greater than 1 ppt or from outfalls discharging to receiving waters with salinity that is equal to or greater than 1 ppt, should be tested using the most sensitive test species in accordance with *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms (EPA/600/R-95/136, 1995)*. The marine and estuarine test species identified in the MRP are:

- A static renewal toxicity test with the topsmelt, *Atherinops affinis* (Larval Survival and Growth Test Method 1006.015).
- A static non-renewal toxicity test with the purple sea urchin, *Strongylocentrotus* purpuratus (Fertilization Test Method 1008.0).
- A static non-renewal toxicity test with the giant kelp, *Macrocystis pyrifera* (Germination and Growth Test Method 1009.0).

In addition to the three species identified in the MRP, the red abalone, *Haliotis rufescens* (*H. rufescens*), larval development test was also considered given its extensive use in the region.

Although all the species mentioned have been demonstrated as sensitive to a wide variety of toxicants and have been subject to numerous inter- and intra-laboratory testing using standardized toxicants, two species: *Macrocystis pyrifera* (*M. pyrifera*) and *Atherinops affinis* (*A. affinis*); have limitations when used to assess the toxicity of stormwater, as compared to the sea urchin fertilization test and the red abalone larval development test.

The method for *M. pyrifera* is a 48-hour chronic toxicity test that measures the percent zoospore germination and the length of the gametophyte germ tube. Although the test may be sensitive to herbicides, fungicides, and treatment plant effluent, the use of *M. pyrifera* as a test species for stormwater monitoring may not be ideal. Obtaining sporophylls for stormwater testing could also be a limiting factor for selecting this test. Collection of *M. pyrifera sporophylls* from the field is necessary prior to initiating the test and the target holding time for any receiving water or stormwater sample is 36 hours; however, 72 hours is the maximum time a sample may be held prior to test initiation. During the dry season, meeting the 36-72 hour holding time will be achievable; however, field collection during wet weather may be delayed beyond the maximum holding time due to heavy seas and inaccessible collection sites. In addition, collection of *M*.

pyrifera sporophylls during the storm season may include increased safety risks that can be avoided by selection of a different species.

The *A. affinis* test measures the survival and growth test of a larval fish over seven days. At the end of seven days of exposure to a suspected toxicant, the number of surviving fish are recorded, along with their weights, and compared to those exposed to non-contaminated seawater. Positive characteristics of the *A. affiniss* chronic test include the ability to purchase test organisms from commercial suppliers as well as being one of the few indigenous test species that may be used to test undiluted stormwater by the addition of artificial sea salts to within the range of marine receiving waters. Unfortunately, the tolerance of *A. affinis* to chemicals in artificial sea salts may also explain their lack of sensitivity to changes in water quality compared to other test organisms such as the sea urchin or red abalone. There are concerns with the comparability of conducting a seven-day exposure test when most rain events do not occur over a seven-day period.

The Strongylocentrotus purpuratus (S. purpuratus) fertilization test measures the ability of S. purpuratus sperm to fertilize an egg when exposed to a suspected toxicant. The S. purpuratus fertilization has been selected as a chronic toxicity test organism in previous MS4 permits and has been used to assess ambient receiving water toxicity, sediment pore water toxicity, as well as stormwater toxicity. The S. purpuratus fertilization test is also among the most sensitive test species to metals. The adult test organisms may be purchased and held in the lab prior to fertilization, and the sample volume necessary to conduct the test is small with respect to the other suggested tests. The minimal exposure period (20 min) allows for a large number of tests to be conducted over a short period of time and permits the testing of toxicants that may lose their potency over long periods of time.

The red abalone larval development test measures the percent of abnormal shell development in larvae exposed to toxic samples for 48 hours. The red abalone is commonly used to test treatment plant effluent, but has had limited use in stormwater compared to the *S. purpuratus* fertilization test. The advantages of the red abalone test include a sensitive endpoint, the ability to purchase abalone from commercial suppliers and hold test organisms prior to spawning, and low variability in results compared to other species (e.g., *S. purpuratus* fertilization test). Thus, though not listed as a potential test species for use in stormwater monitoring in the Permit, it was considered as a potentially sensitive species for the purposes of selecting the most sensitive species.

Due to the limitations of the giant kelp germination and growth test and the topsmelt survival and growth test, in addition to not being particularly sensitive to the constituents identified as problematic in stormwater water runoff from the watershed, these tests are not considered particularly helpful in supporting the identification of pollutants of concern. Based on the sensitivity, smaller test volume requirements, their ability to be housed in the lab prior to testing, and shorter exposure times, the *S. purpuratus* fertilization test and the red abalone development

test will be considered during sensitive species selection to measure toxicity in marine and estuarine environments. Based on historical data of the sensitivity of the *S. purpuratus* and red abalone tests, and the limiting factors associated with the topsmelt and giant kelp tests, the sensitive species test for marine and estuarine species will be conducted with the *S. purpuratus* and red abalone tests. Species screening was determined to be appropriate for these two species (as opposed to selecting just one) as testing conducted within the region with both species have shown varying sensitivity. Thus, it is appropriate to test both to determine sensitivity at a given site. After the screening testing is completed, monitoring will be conducted with the most-sensitive species.

2.3.2 Testing Period

The following subsections characterize the toxicity testing periods for samples collected during dry and wet weather conditions.

2.3.2.1 Freshwater Testing Periods

Acute toxicity tests would normally be utilized for stormwater toxicity testing to be consistent with the relatively shorter exposure periods of watershed species to potential urban stormwater toxicants and would be conducted in accordance with Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms (EPA, 2002b). Despite the test duration not being typical of stormwater flows, Board staff has recommended that a chronic testing period (typically 7 days) be used for toxicity testing for both survival and reproductive/growth endpoints for *C. dubia* in samples. Chronic testing will be conducted on undiluted samples in accordance with Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms (USEPA, 2002a). Utilization of chronic tests to assess wet weather samples may generate results that are not representative of receiving water conditions.

2.3.2.2 Saltwater Testing Period

Two marine and estuarine toxicity species tests utilize methods that have short durations (20 minutes for the *S. purpuratus* fertilization test and 48 hours for the *H. rufescens* development test), the end points are sub-lethal and can be considered representative of acute or chronic effects. Both test species and test methods are suitable for wet weather and dry weather monitoring.

2.3.3 Toxicity Endpoint Assessment and Toxicity Identification Evaluation Triggers

As directed by the Permit MRP, acute and chronic toxicity test endpoints will be analyzed using the Test of Significant Toxicity (TST) t-test approach specified by the USEPA (USEPA, 2010). The Permit specifies that the chronic in-stream waste concentration (IWC) be set at 100%

receiving water for receiving water samples and 100% discharge for outfall samples. Follow-up triggers are generally based on the Permit specified statistical assessment as described below.

For acute *C. dubia* toxicity testing, follow up toxicity identification evaluation (TIE) testing is warranted if a statistically significant 50% difference in mortality is observed between the sample and laboratory control, a toxicity identification evaluation (TIE) will be performed. TIE procedures are further discussed in detail in the following subsection. Experience conducting TIEs in regional receiving waters supports using a 50% mortality trigger to provide a reasonable opportunity for a successful TIE. During 2003 and 2004 TMDL monitoring in the Calleguas Creek Watershed (CCW), TIEs were initiated for samples exceeding the 50% threshold, the majority of which displayed 100% mortality. In that study, toxicity had degraded in approximately 40% of the samples on which the procedures were initiated making the effort unsuccessful in pinpointing specific toxicants. The Regional Board approved monitoring program for the CCW Toxicity, Chlorpyrifos and Diazinon TMDL utilizes a 50% threshold for TIE initiation. Additionally, a 50% mortality threshold is utilized in the Ventura County MS4 Permit.

For chronic *C. dubia* toxicity testing, if a statistically significant 50% difference in mortality is observed between the sample and laboratory control, a TIE will be performed. If a statistically significant 50% difference in a sub-lethal endpoint is observed between the sample and laboratory control, a confirmatory sample will be collected from the receiving water within two weeks of obtaining the results of the initial sample. If a statistically significant 50% difference in mortality or sub-lethal endpoint is observed between the sample and laboratory control on the confirmatory sample, a TIE will be performed.

For the chronic marine and estuarine tests, the percent effect will be calculated. The percent effect is defined as the difference between the mean control response and the mean IWC response divided by the control response, multiplied by 100. A TIE will be performed if the percent effect value is equal to or greater than 50 percent. The TIE procedures will be initiated as soon as possible after the toxicity trigger threshold is observed to reduce the potential for loss of toxicity during sample storage. If the cause of toxicity is readily apparent or is caused by pathogen related mortality (PRM) or epibiont interference, the result will be rejected. In cases where significant endpoint toxicity effects greater than 50% are observed in the original sample, but the follow-up TIE positive control "signal" is not statistically significant, the cause of toxicity will be considered non-persistent and no sample follow-up testing is required. Future test results should be evaluated to determine if parallel TIE treatments are necessary to provide an opportunity to identify the cause of toxicity.

2.3.4 <u>Toxicity Identification Evaluation Approach</u>

The results of toxicity testing will be used to trigger further investigations to determine the cause of observed laboratory toxicity. The primary purpose of conducting TIEs is to support the identification of management actions that will remove toxicants from the receiving waters. Successful TIEs will guide adaptive outfall monitoring strategies to identify and analyze for suspect pollutant(s) and guide source control efforts.

The TIE approach is divided into three phases as described in USEPA's 1991 Methods for Aquatic Toxicity Identification Evaluations – Phase I Toxicity Characterization Procedures – Second Edition (EPA/600/6-9/003) and briefly summarized as follows:

- ➤ Phase I utilizes methods to characterize the physical/chemical nature of the constituents which cause toxicity. Such characteristics as solubility, volatility and filterability are determined without specifically identifying the toxicants. Phase I results are intended as a first step in specifically identifying the toxicants but the data generated can also be used to develop treatment methods that remove the toxicity without specifically identifying the toxicants.
- ➤ Phase II utilizes methods to specifically identify toxicants, or toxicant pollutant class.
- ➤ Phase III utilizes methods to confirm the identity of suspected toxicant(s).

TIE methods will generally adhere to USEPA procedures documented in conducting TIEs (USEPA, 1991, 1992, 1993a-b). A Phase I TIE will be conducted on samples that exceed the TIE. Water quality data will be reviewed to support future evaluation of potential toxicants. TIEs will perform the manipulations described in Table C-2.

Toxicity causation will be tentatively identified based on the treatments in Table C-2 and, when possible, the results verified based on water column chemistry analyses. After an initial determination of the cause of toxicity, the information may be used during future TIEs to target the expected toxicant(s) or provide new treatments to narrowly identify the toxicant cause(s). Moreover, if the toxicant or toxicant class is not initially identified, toxicity monitoring during subsequent events will confirm if the toxicant is persistent or a short-term episodic occurrence.

Table C-2 Aquatic Toxicity Identification Evaluation (TIE) Sample Manipulations

TIE Sample Manipulation	Expected Response		
Adjust to between pH 7 and 8.5	Alters toxicity in pH sensitive compounds (i.e., ammonia and some trace metals)		
Filtration or centrifugation	Removes particulates and associated toxicants		
Ethylene Diamine Tetra Acetic Acid (EDTA)	Chelates trace metals, particularly divalent cationic metals		
Sodium thiosulfate (STS) addition	Reduces toxicants attributable to oxidants (i.e., chlorine) and some trace metals		
Piperonyl Butoxide (PBO)	Reduces toxicity from organophosphate pesticides such as diazinon, chlorpyrifos and malathion, and enhances pyrethroid toxicity		
Carboxylesterase addition ⁽¹⁾	Hydrolyzes pyrethroids		
Solid Phase Extraction (SPE) with C18 column	Removes non-polar organics (including pesticides) and some relatively non-polar metal chelates		
Sequential Solvent Extraction of C18 column	Further resolution of SPE-extracted compounds for chemical analyses		
No Manipulation	Baseline test for comparing the relative effectiveness of other manipulations		

Carboxylesterase addition has been used in recent studies to help identify pyrethroid-associated toxicity (Wheelock et al., 2004; Weston and Amweg, 2007). However, this treatment is experimental in nature and should be used along with other pyrethroid-targeted TIE treatments (e.g., PBO addition).

As the primary goals of conducting TIEs is to identify pollutants for incorporation into outfall monitoring, narrowing the list of toxicants following Phase I TIEs via Phase II or III TIEs is not necessary if the toxicant class determined during the Phase I TIE is sufficient for: (1) identifying additional pollutants for outfall monitoring; and/or (2) identifying control measures. Thus, if the specific pollutant(s) or the analytical class of pollutant (e.g., metals that are analyzed via USEPA Method 200.8) are identified then sufficient information is available to inform the addition of pollutants to outfall monitoring.

Phase II TIEs may be utilized to identify specific toxicants in a sample if information beyond that gained via the Phase I TIE and review of chemistry data is needed to identify monitoring or management actions. Phase III TIEs will be conducted following any Phase II TIEs.

TIEs will be considered inconclusive if:

- The toxicity is persistent (i.e., observed in the positive control), and
- The cause of toxicity cannot be attributed to a class of constituents (e.g., insecticides, metals, etc.) that can be targeted for monitoring or additional source controls.

If (1) a combination of causes act in a synergistic or additive manner are identified; (2) the toxicity can be removed with a treatment or combination of the TIE treatments; or (3) the analysis of water quality data collected during the same event identifies the pollutant or analytical class of pollutants, the result of a TIE is considered conclusive.

Note that the MRP (page E-33) allows a TIE Prioritization Metric to be used in ranking sites for TIEs. As the extent to which TIEs will be conducted is unknown, prioritization cannot be assessed at this time, but may be utilized in the future based on the results of toxicity monitoring and the CIMP adaptive management.

2.3.5 <u>Discharge Assessment</u>

The Peninsula CIMP Group will prepare a Discharge Assessment Plan (DAP), if TIEs, from consecutive sampling events, are inconclusive. The Discharge Assessment will only be initiated after consecutive inconclusive TIEs, because of the inherent variability associated with the toxicity and TIE testing methods. The DAP will consider observed receiving and outfall toxicants above known species effect levels and the relevant exposure periods compared to the duration of the observed toxicity. The DAP will identify:

- Additional potential receiving water toxicity monitoring to evaluate the spatial extent of toxicity.
- > The toxicity test species to be utilized. If a different species is proposed, justification for the substitution will be provided.
- > The number and location of monitoring sites and their spatial relation to the observed receiving water toxicity.
- ➤ The number of monitoring events that will be conducted, a schedule for conducting the monitoring, and a process for evaluating the completion of the assessment monitoring.

The DAP will be submitted to Regional Board staff for comment within 60 days of receipt of notification of the second consecutive inconclusive result. If no comments are received within 30 days, it will be assumed that the approach is appropriate for the given situation and the DAP will be implemented within 90-days of submittal. If comments are received within 30 days, the Plan will be resubmitted to Regional Board staff and the DAP will be implemented within 90-days of submittal of a version of the Plan that does not receive comments from Regional Board staff.

2.3.6 Follow Up on Toxicity Testing Results

The MRP (page E-33) indicates the following actions should be taken when a toxicant or class of toxicants is identified through a TIE:

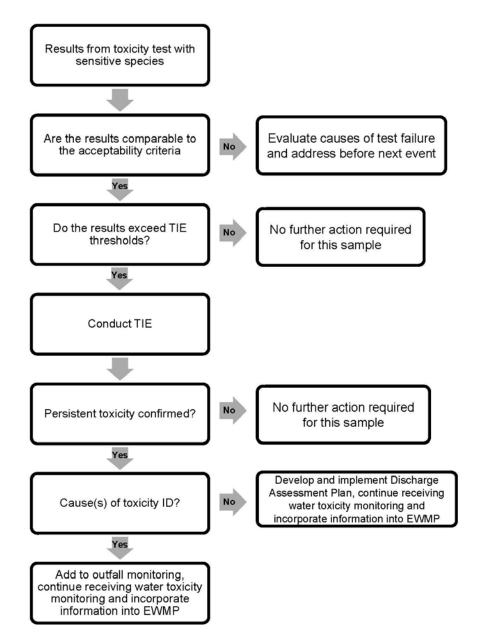
- ➤ The Peninsula CIMP Group shall analyze for the toxicant(s) during the next scheduled sampling event in the discharge from the outfall(s) upstream of the receiving water location.
- ➤ If the toxicant is present in the discharge from the outfall at levels above the applicable receiving water limitation, a toxicity reduction evaluation (TRE) will be performed for that toxicant.
- The list of constituents monitored at outfalls identified in the CIMP will be modified based on the results of the TIEs.

Monitoring for constituents identified based on the results of a TIE will occur as soon as feasible following the completion of a successful TIE (i.e., the next monitoring event that is at least 45 days following the toxicity laboratory's report transmitting the results of a successful TIE).

The requirements of the TREs will be met as part of the adaptive management process in the Peninsula EWMP rather than conducted via the CIMP. The identification and implementation of control measures to address the causes of toxicity are tied to management of the stormwater program, not the CIMP. It is expected that the requirements of TREs will only be conducted for toxicants that are not already addressed by an existing Permit requirement (i.e., TMDLs) or existing or planned management actions.

2.3.7 **Summary of Aquatic Toxicity Monitoring**

The approach to conducting aquatic toxicity monitoring as described in the previous sections is summarized in detail in Figure C-2. The intent of the approach is to identify the cause of toxicity observed in receiving water to the extent possible with the toxicity testing tools available, thereby directing outfall monitoring for the pollutants causing toxicity with the ultimate goal of supporting the development and implementation of management actions.



Test failure includes pathogen or epibont interference, which should be addressed prior to the next toxicity sampling event.

For freshwater, the TIE threshold is equal to or greater than 50% (\geq 50%) mortality in an acute (wet weather) or chronic (dry weather) test. If a \geq 50% effect in a sub-lethal endpoint for chronic test is observed during dry weather, a follow up sample will be collected within two weeks of the completion of the initial sample collection. If the follow up sample exhibits a \geq 50% effect, a TIE will be initiated.

For marine waters and estuarine waters, the TIE threshold is the percent effect value $\geq 50\%$. If a $\geq 50\%$ or greater effect is observed during dry weather a follow up sample will be collected within two weeks of the initial sample collection and if the follow up sample exhibits a $\geq 50\%$ effect, a TIE will be initiated.

The goal of conducting Phase I TIEs is to identify the cause of toxicity so that outfall monitoring can incorporate the toxicant(s) into the list of constituents monitored during outfall monitoring. Thus, if specific toxicant(s) or the analytical class of toxicants (i.e., metals that are analyzed via EPA Method 200.8) are identified, sufficient information is available to inform the addition of pollutants to the list of pollutants monitored during outfall monitoring.

Figure C-2. Detailed Aquatic Toxicity Assessment Process

2.3.8 <u>List of Laboratories Conducting Analysis</u>

The chosen laboratories will be able to meet the measurement quality objectives set forth in the CIMP. Laboratories will meet California Environmental Laboratory Accreditation Program (ELAP) and/or National Environmental Laboratory Accreditation Program (NELAP) certifications and any data quality requirements specified in this document. Due to contracting procedures and solicitation requirements, qualified laboratories have not yet been selected to carry out the analytical responsibilities described in this CIMP. Selected laboratories will be listed, per the example shown in Table C-3, along with lab certification information. Following the completion of the first monitoring year, the pertinent laboratory specific information will be included in the Integrated Monitoring Compliance Report Section of the Annual Report. At the end of each subsequent monitoring year, the Peninsula CIMP Group will assess the laboratories performance and at that time a new laboratory may be chosen.

Table C-3 Summary of Laboratories Conducting Analysis for the Peninsula CIMP

Laboratory ⁽¹⁾	General Category of Analysis	Lab Certification No. & Expiration Date ⁽²⁾

Information for all laboratories will be added to this table following their selection and upon CIMP update. Lab certifications are renewed on an annual basis.

2.3.8.1 Alternate Laboratories

In the event that the laboratories selected to perform analyses for the CIMP are unable to fulfill data quality requirements outlined herein (e.g., due to instrument malfunction), alternate laboratories will be selected to meet the same requirements that the primary labs have met. The original laboratory selected may recommend a qualified laboratory to act as a substitute. However, the final decision regarding alternate laboratory selection rests with the Peninsula CIMP Group.

2.4 Safety Considerations

Stormwater monitoring activities create hazardous conditions and safety is a primary concern. Prior to the commencement of field monitoring activities, a project Health and Safety Plan should be developed. The information in this SOP should be used as general guidance for developing a Health and Safety Plan for field activities.

General hazardous conditions associated with sampling include:

- Hazardous weather conditions (e.g., wind, lightning, flooding, etc.)
- Hazards associated with chemicals
- Biological hazards (e.g., rodents and snakes)
- Physical hazards (e.g., traffic, falling objects, sharp edges, slippery footing, and the
 potential for lifting injuries from opening or removing access panels and manhole covers,
 etc.)
- The CIMP monitoring program does not require sampling in confined spaces (e.g., manholes). If this were the case, the sampling team would need to be trained in and follow confined spaced entry procedures.

Preparation and training of all sampling personnel will be completed before beginning any sampling task. Extreme care will be taken to allow for safety precautions including proper equipment and appropriate operational techniques, sufficient time to accomplish the task, training on potential hazards, and emergency procedures. Sampling crews will consist of a minimum of three people.

If for any reason manual sample collection appears to be unsafe, samples will not be collected. If possible, samples will be collected at a later time when conditions are safe. A throw rope will be easily accessible in each truck cab and at the ready during manual sample collection if conditions warrant.

Basic emergency precautions include having access to both local emergency phone numbers and communication equipment (i.e., smart phones/cellular phones) and ensuring that personnel are trained in first aid and carry first aid equipment.

2.4.1 Hazardous Weather Conditions

Common sense should dictate whether sampling should be conducted during adverse weather conditions. No sampling personnel should place themselves in danger during high winds, lightning storms, or flooding conditions which might be unsafe. Under extreme conditions, a less hazardous storm event should be sampled.

2.4.2 Chemical Hazards

Sampling personnel can also be at risk of exposure to hazardous chemicals-either chemicals in the actual stormwater discharge or the preservatives in some of the sample containers. Therefore, direct contact with the bottle preservatives and the stormwater (if hazardous chemicals are suspected to be present; pathogens which are biological hazards are also likely present in stormwater) should be avoided. Sampling personnel should wear gloves and safety glasses to avoid skin and eye exposure to harmful chemicals. Sampling personnel should be trained to avoid exposure and instructed as to what to do if exposure occurs (e.g., flush the eyes, rinse the skin, ventilate the area, etc.).

Sampling personnel should keep Safety Data Sheets (SDS) (formerly Material Safety data Sheets) readily available for all solutions used for field measurements and refer to them to ensure that pH buffers or other chemicals are handled safely.

2.4.3 Biological Hazards

Stormwater sampling personnel may also encounter biological hazards such as rodents, snakes, and insects. The sampling crew should remain alert to these hazards. Monitoring supplies for certain locations should include insect repellant and a first aid kit.

2.4.4 Physical Hazards

The sampling crew should be aware of a number of physical hazards that could cause accidents at the sampling site. These hazards include traffic hazards, sharp edges, falling objects, slippery footing, and lifting injuries from removing manhole covers. Sampling personnel should pay close attention in order to prevent these safety hazards at all times.

If the monitoring activity encroaches on the public right of way, traffic cones, warning signs, and barricades should be placed in appropriate places around the monitoring activities. Sampling personnel should wear a reflective safety vest in high-traffic areas.

Working in and around water bodies carries the inherent risk of drowning. Life jackets should be worn when sampling in more than a few feet of water, or when sampling in swift currents.

2.5 Water Quality Sampling Procedures

The methods summarized below are for the collection and recording of samples needed to assess water quality parameters. This includes manual composite and grab sampling techniques that include using a depth integrated sampler or an intermediate sample container attached to a pole. Alternatively, composite sample aliquots may be collected manually using a peristaltic pump or portable autosampler.

Field measurements will be made for parameters that have the potential to change in transit between the monitoring location and analytical laboratory. Detailed notes of all activities conducted in the field will be kept in a site specific field logbook for eventual electronic database entry and reporting purposes. All records made in the field and reported by the analytical laboratory will follow the proper sample identification protocol and will be consistent with the chain of custody form.

2.5.1 Outfall Composite Sample Aliquots

Wet weather outfall samples, when feasible, will be collected before the associated receiving water sample is collected, at locations where paired outfall and receiving water locations exist.

For inaccessible sample locations, a Nasco swing sampler equipped with a borosilicate glass or Teflon bottle (or similar equipment) will be used to collect 10 time-weighted aliquots. Refer to Section 2.1 for a discussion of time-weighted composite sample aliquot collection times. Sample aliquots will be collected from the middle of the outfall flow, to the extent feasible. The same procedures for grab sample collection as stated in Section 2.5.2 for receiving water sampling will be conducted for the outfall sampling. Aliquots may be composited in the field by the sample personnel, or may be delivered individually to the laboratory for lab compositing.

2.5.2 <u>Receiving Water and Outfall Grab Samples</u>

Receiving water sampling will be conducted after the outfall sampling is performed, where paired outfall and receiving water locations exist, as feasible. At Peninsula-RW1 and Peninsula-RW2, grab samples will be collected from a boat in accordance with City of Los Angeles Environmental Monitoring Division (EMD) standard operating procedures.

Outfall grab samples will be collected upon arrival at approximately the same time as when the field measurements are performed, as feasible. Outfall grab samples will be collected directly into sample bottles, where feasible, or using equipment equivalent to that used for stormwater outfall monitoring (see Section 2.5.1).

All dry weather outfall sampling will be conducted using grab samples due to the unknown frequency and duration of flows. For stormwater outfall sampling, grab samples will be collected for the following parameters:

- Oil and grease
- TPH
- Total phenols
- Bacteria
- Other VOCs

These samples should be collected directly in the sample bottles that will be provided to the analytical lab (i.e., a transfer bottle should not be used). Where practical, samples collected by direct submersion will be collected mid-channel/outfall. The bottles should therefore not contain preservatives that could be lost when immersing the bottle in the receiving water; therefore the sample bottles will be preserved immediately upon arrival at the laboratory.

Grab sample containers designated for volatile organic compound analysis will have zero headspace.

2.5.3 Receiving Water and Outfall Field Measurements

Field measurements are to be performed for pH, dissolved oxygen, temperature, and specific conductivity. If the field instrumentation malfunctions these parameters should be analyzed at

the analytical laboratory; however there will be holding time issue that could affect data quality. For example, the holding time for pH analysis is 15 minutes, which is why pH should be measured in the field. Field measurements will be performed upon arrival, as feasible.

Field measurements will be performed as follows:

- Perform field measurements at the same time the grab samples are collected.
- Water temperature and dissolved oxygen must be measured directly within the water body (in situ). pH and conductivity often are measured in situ but may also be measured in a subsample of a composite or grab sample.
- Make field measurements only with properly calibrated instruments. Calibration is required at the field site for many, but not all, instruments and depends on the technology employed by the instrument. Follow the manufacturer's instructions about instrument calibration.
- Review the instrument log book(s) before leaving for the field site to ensure that problems previously encountered have been resolved and that the appropriate instrument and site maintenance were performed.
- Backup instruments and batteries should be readily available and in good working condition.
- Allow at least 60 seconds (or follow the manufacturer's guidelines) for sensors to equilibrate with sample water. Record the median of the final three or more readings as the value to be reported for that measurement point.
- Check instrument precision and accuracy (variability and bias) periodically while at a field site; precision and accuracy may vary, depending on the instrument used, sampling conditions, and the expertise of personnel.

Detailed information about field instruments including required supplies, maintenance, calibration, measurement, and troubleshooting is available from the USGS National Field Manual for the Collection of Water-Quality. This information is included as Attachment C.1 of this SOP.

2.5.4 Field Logbook

All visits to the sampling stations should be recorded in the site-specific logbook (such as a Rite-in-the-Rain bound journal No. 390F). Logbook entries should include: names of personnel performing the sample collection and field measurements; date and time for all measurements recorded and sample aliquots/grabs collected, receiving water flow measurements; and tasks performed while on site. Field measurement information will be recorded in the field logbook including the date

The logbooks will be filled out with a blue or black indelible ballpoint pen. If recording in a Rite-in-the-Rain logbook or on other water-resistant surface, an all-weather or bullet pen should be used. Using a pencil is not acceptable. In addition, felt-tipped pens (for example, Sharpie®) should not be used as their use could compromise the quality of data for samples for analysis of volatile organic compounds.

2.5.5 Sample Identification Protocol

The sample identification naming convention for each wet and dry weather event will be as follows:

Location Coordinates Station ID Location⁶ Sample Type Sample Event ID Latitude Longitude Receiving Peninsula-RW1-DATE 33.80339 -118.39919 Peninsula-RW1 Malaga Cove Water/Ocean (MM-DD-YY) Peninsula-SD1-DATE Peninsula-SD1 Storm Drain Malaga Creek 33.80092 -118.39100 (MM-DD-YY) Receiving Peninsula-RW2-DATE 33.73965 Peninsula-RW2 Abalone Cove -118.38152 Water/Ocean (MM-DD-YY) McCarrell Canyon Peninsula-SD2-DATE Peninsula-SD2 Storm Drain 33.74123 -118.38799 Creek (MM-DD-YY) Adjacent to parking lot behind Rolling RHECH-DATE (MM-DD-RHE City Hall 34.03141 -118.84124 Storm Drain Hills Estates City YY) Hall

Table C-4. CIMP Monitoring Locations and Descriptions

In addition, field QA/QC samples including duplicate samples and field blank will be submitted to the laboratory "blind", which means these samples will be given fictitious IDs. For example, the field duplicate collected at Peninsula-RW1 could be named on the chain of custody form as "Peninsula-RW3-DATE".

2.5.6 Chain of Custody Procedures

All samples will be submitted to the analytical laboratories under proper chain of custody (COC) procedures. Sample custody must be traceable from the time of sample collection until results are reported. A sample is considered under custody if the sample is:

• In actual possession.

⁶ The receiving water and outfall monitoring locations are shown on Figure 3 of the CIMP, and descriptions of the monitoring locations are provided in Appendix B of the CIMP.

- In view after in physical possession.
- Placed in a secure area (accessible by or under the scrutiny of authorized personnel only after in possession).

The following special notes should be added to COC forms when applicable:

- Filter for all dissolved constituents immediately upon arrival at the laboratory (and properly preserve the sample).
- Identify the sample for MS/MSD analysis.
- Preserve samples for oil and grease and TPH immediately upon arrival at the laboratory (these bottles should not contain preservative which could be lost during the sampling process).

Example COCs provided by Weck and ABC laboratories are included in Attachment C.2.

2.6 Flow Estimation and Monitoring Methods

The Permit requires flow monitoring for receiving waters and monitoring or estimation for outfalls. Flow monitoring activities will be performed after the water quality samples are collected, to minimize the potential for sample contamination from wading and other water disturbance activities.

2.6.1 Outfalls

Depending on site conditions and safety, the appropriate field methodology for monitoring flow will be selected. The following list includes the recommended flow monitoring methods (in order of prioritization):

- 1. Continuous automated flow monitoring devices;
- 2. Portable area velocity flow meter; or
- 3. Recording the time required to fill a container of known volume.

If none of the aforementioned methodologies are suitable due to safety hazards or site conditions, the flow will be estimated for stormwater outfall monitoring events using drainage area, impervious cover, and precipitation data. Discharge from monitored outfalls will be characterized in accordance with EPA flow estimation procedures in the NPDES Storm Water Sampling Guidance Document (US EPA, 1992). The EWMP Group is responsible for developing accurate drainage area and runoff coefficient information for each monitored outfall.

The US EPA provides an example in which rain gauge data are used to approximate flow rate using a variation of the rational method to incorporate measured rainfall data (US EPA, 1992). The general form of this equation gives flow rate (Q) in terms of hourly rainfall intensity (i), drainage area (A), and runoff coefficient (C).

Classic Rational Method:
$$Q = C \times i \times A$$

A simple example calculation is shown below for a drainage area less than 40 acres.

Site Characteristics:

Drainage Area (A): 31.5 Acres

Runoff Coefficient (C): 0.21 for low-density single family residential (per LA

Hydrology Manual)

Rainfall Characteristics:

Total Rainfall Depth for Storm Event: 0.4 inches

Measured 15-minute Rainfall Intensity: 0.12 inches/15 minutes

Incremental Flow Rate (Q) =
$$0.21 \times \frac{0.12 \text{ in}}{15 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times 31.5 \text{ ac} = 3.2 \text{ cfs}$$

The incremental flow rate will be calculated for each collected sample, based on the hourly rainfall intensity for the hour preceding the sample collection (e.g., a sample collected at 8:30 will rely on the hourly rainfall total recorded between 7:30 and 8:30).

Similarly, the runoff volume can be estimated using rainfall data. The following example uses the catchment and rainfall data to approximate discharge volume:

Total Runoff Volume =
$$0.21 \times 0.4$$
 in $\times \frac{1 \text{ ft}}{12 \text{ in}} \times 31.5$ ac = 0.221 ac ft

2.6.2 Receiving Waters

Flow monitoring of the receiving waters is not applicable for the ocean monitoring locations proposed herein.

3 NON-STORMWATER OUTFALL SCREENING

The non-stormwater outfall screening process and schedule is described in Section 4 of the CIMP. The field data sheet included in Attachment C.3 will be used to record data collected during non-stormwater outfall screening activities. These data will be entered into the CIMP Group's electronic inventory as described in the CIMP.

4 QUALITY ASSURANCE/QUALITY CONTROL

4.1 Clean Sampling Techniques

Due to the analytical practical quantitation limits required for certain parameters (e.g., trace metals, organics, and bacteria), and the potential for improper sampling techniques (including exposure from the ambient environment) to result in sample contamination at levels detectable by the analytical accuracy of the method, Clean Sampling Techniques will be used during the collection of samples. Moreover, because a sampling apparatus (e.g., swing sampler) may be used to collect composite sample aliquots for some of the monitoring program parameters, the sampling equipment will be properly cleaned by the laboratory (see Sections 4.5.3 and 4.5.4). Therefore, dedicated sampling equipment is required for each site. The sampling equipment will also be properly stored in between sample aliquot collection in accordance with Clean Sampling Techniques. In terms of handling sample containers, bottles will be handled following the "Clean Hands/Dirty Hands" procedure outlined below.

There are numerous routes by which samples may become contaminated. For example, 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 (dirt and dust from automobile exhaust, cigarette smoke, nearby roads, corroded or rusted bridges, wires, and poles). Even human contact can be a source of trace metals contamination (e.g., mercury amalgam fillings). The following materials have been found to contain trace metals and therefore should 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,
- Vycor
- 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.

All sampling equipment and sample containers used for metals determinations will be nonmetallic and free from any material that may contain metals. Sampling personnel are required to wear clean, non-talc gloves at all times when handling sampling equipment and sample containers. Personnel should avoid hand contact with contaminating surfaces (such as equipment, coins, food).

4.1.1 <u>Clean Hands/Dirty Hands Procedures</u>

Due to the logistics of manual composite sample collection, field procedures require a minimum of two field people assuming the "Dirty Hands" (DH1 and DH2) role. The second DH person can also assist with completing the necessary sample documentation (e.g., filling out the logbook and sample bottle labels).

Upon arrival at the sampling site, two members of the sampling team are designated as "Dirty Hands" (DH1) and "Clean Hands" (CH); if available, a third member is designated as DH2. All operations involving contact with the sample bottle are handled by CH. DH1 (and DH2, if available) is responsible for unsealing outer plastic bags and operating the sampling equipment (avoiding contact with the cleaned parts and the sample bottle for the DH-81 and the Swing Sampler bottle), and for all other activities that do not involve direct contact with the sample (e.g., opening coolers, calibrating field instruments).

The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the equipment. If it is not possible to approach from both, the site should be approached from downwind.

Sampling personnel are to implement the following procedures "Clean Hands/Dirty Hands" procedures:

- 1. At the site, all sampling personnel must put on clean gloves before commencing sample collection activity.
- 2. "Dirty Hands" must open the cooler or storage container, remove the double-bagged sampling equipment from storage, and unzip the outer bag.
- 3. Next, "Clean Hands" opens the inside bag containing the portion of the DH-81 sampler in contract with the sample bottle, or the sample bottle for the Swing Sampler, removes the DH-81/bottles, and reseals the inside bag. "Dirty Hands" then reseals the outer bag.
- 4. "Clean Hands" unscrews the bottle cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes.
- 5. "Dirty Hands" operates the DH-81 and Swing Sampler making sure to not come into contact with the laboratory-cleaned portions of the DH-81 or the sample bottles. Discard the first sample aliquot that is collected for each sampling round to generate the composite sample; begin filling the sample bottles with the second sample collected.
- 6. Collection of Non-Metallic Constituents: Dirty Hands unscrews the bottle caps for all containers except for the metals containers. Dirty Hands pours an aliquot from the DH-81 or Swing Sampler bottle into each sample container. Dirty Hands should not touch the DH-81 or Swing Sampler bottle (Clean Hands to provide assistance as needed).

- 7. Collection of Samples for Metals Analysis: Sample bottles designated for metals analysis are double-bagged at the analytical laboratory. Dirty Hands opens the outer bag. Clean Hands opens the inside bag and removes the sample bottle and uncaps the lid. Dirty Hands pours the sample aliquot into the metals bottle. Clean Hands screws the cap on the bottle and places the bottle back in the inner bag and seals the inner bad. Dirty Hands seals the outer bag. (Note that the sample label cannot contact the sample bottle and should be placed on the outer bag).
- 8. All parties should change gloves for the collection of each sample aliquot. Wearing multiple layers of gloves allows rapid glove changes.
- 9. If additional sample aliquots are required, rinse DH-81 bottle and Swing Sample bottle with the laboratory-provided deionized water and place back in the plastic double bag following CH/DH procedures.
- 10. If the sampler will not be reused during a field trip, rinse sampler components with laboratory-provided deionized water before they dry and place them into a plastic bag for transporting to the office laboratory to be cleaned for the next sampling event.

4.2 Quality Control Requirements for Field Measurements

Quality control requirements for field measurements are summarized below in Table C-5; these requirements are adapted from the State Water Boards' Surface Water Ambient Monitoring Program Requirements.

Table C-5. Field Measurement Quality Control Requirements

Parameter	Dissolved Oxygen	pН	Specific Conductance	Temperature
Analytical Method	Field measurement using approved method (i.e., membrane electrode method [SM 4500 O G] or equivalent)	Field measurement using approved method (i.e., electrometric [EPA 150.2], potentiometric [SM 4500 H B], or equivalent)	Field measurement using approved method (i.e., conductivity meter [EPA 120.1] or equivalent)	Field measurement using approved method (i.e., thermometer [SM 2550 B] or equivalent)
Units	mg/L	pН	μS/cm	°C
Resolution	0.01	0.01	1	0.1
Instrument Accuracy	±0.2	±0.2	±0.5%	±0.15
Points per Calibration	1	2	Per manufacturer	Per manufacturer
Pre-Sampling Calibration Check Frequency	Before every monitoring day on-site (re-calibrate if change of elevation is >500 m or barometric pressure > 2 mm Hg)	Per manufacturer	Per manufacturer	Per manufacturer

Parameter	Dissolved Oxygen	pН	Specific Conductance	Temperature
Post-Sampling Calibration Check Frequency	After every monitoring day (within 24 hours)	Per manufacturer	Per manufacturer	Per manufacturer
Allowable Drift	±0.5 or 10%	±0.2 units	±10%	±0.5

4.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The monitoring program goal is to collect one MS/MSD per sampling event (the MS/MSD can be either an outfall or receiving water sample). Whether the MS/MSD analysis is feasible using a project sample depends on the feasibility of obtaining the additional sample volume required for the MS/MSD analysis (see Table 2-1).

If sufficient sample cannot be collected for the MS/MSD, the laboratory will use a non-project sample that is analyzed part of the analysis batch as the MS/MSD sample; MS/MSD results for a non-project sample will not be used in the QA/QC evaluation of project samples.

4.4 Field Duplicate

Field duplicates will be collected at a frequency of one duplicate per year for wet weather events and one duplicate per year for dry weather events (for a total of two field duplicates per year). For each time-weighted aliquot, the field duplicate will be collected immediately after all the original sample is collected. The field duplicate will be analyzed for all monitoring parameters required at the specific site selected. Field duplicates will be submitted to the laboratory as "blind" samples.

4.5 Field Equipment Blanks

Field equipment blanks will be collected at a frequency of once per year for the purposes of evaluating sample contamination from the monitoring equipment and procedures. One blank will be collected for the DH-81 assembly and one blank will be collected for the Swing Sampler. The field blank will consist of by filling a large carboy or other appropriate container with reagent water in the laboratory, transporting the filled container to the sampling site, processing the water through the normal sampling steps (e.g., immersing the DH-81 or Swing Sampler bottle in the carboy) including implementing CH/DH sampling protocols.

Field equipment blanks will only be analyzed for trace metals, PCBs and DDTs, and any other constituents detected at less than one order of magnitude above the analytical practical quantitation limit. Therefore, the field equipment blanks should be collected after the data from the first storm event sampled have been evaluated.

4.5.1 Trip Blank

Trip blanks are provided by the laboratory and should be placed in coolers containing samples designated for volatile organic compound analysis, which for the monitoring program are only MTBE and EPA 624 constituents.

4.5.2 **Bottle Blanks**

Bottle blanks will be performed at the analytical laboratory by analyzing reagent water poured into any cleaned transfer bottles (e.g., the swing sampler bottle). Bottle blanks will be performed by the laboratory once per year and analyzed for trace metals and PCBs/DDTs.

4.5.3 Sampling Equipment Cleaning Procedures

Whenever possible, sampling devices should be cleaned and prepared for field use in a class 100 clean room. The laboratory will implement the following steps for cleaning the US DH-81 sampler prior to each use:

- 1. Disassemble the DH-81 (making sure that the nozzle is unscrewed from the cap) and soak components in detergent solution for 30 minutes. Put on appropriate disposable, powderless gloves. Scrub components with a soft brush or sponge and rinse thoroughly. Change gloves.
- 2. Soak each nonmetallic component in a 5-percent trace-metal-grade HCl solution for 30 minutes, followed by copious rinsing with deionized water. Acid rinse only nonmetal parts (acid must not contact the metal collar on the DH-81 sampler). Change gloves.
- 3. That the DH-81 should not be rinsed with methanol because samples will be analyzed for total organic carbon (TOC) and use of methanol could result in false positive detections.
- 4. Reassemble the sampler. Place the sampler into double plastic bags and seal for storage and transport.

4.5.4 Laboratory Sample Bottle Cleaning Procedures

US DH-81 and Swing Sampler bottle cleaning will be performed following US EPA cleaning procedures for trace elements (USEPA, 1996a):

- 1. Fill a precleaned basin with a sufficient quantity of a 0.5% solution of liquid detergent (alkaline Detergent such as Liquinox, Alconox, or equivalent.), and completely immerse the bottle. Allow to soak in the detergent for at least 30 minutes.
- 2. Using a pair of clean gloves and clean nonmetallic brushes, thoroughly scrub down all materials with the detergent.

- 3. Place the scrubbed materials in a precleaned basin. Change gloves.
- 4. Thoroughly rinse the inside and outside of each piece with reagent water until there is no sign of detergent residue (e.g., until all soap bubbles disappear).
- 5. After soaking, use clean gloves and tongs to remove the bottle and thoroughly rinse with distilled, deionized water.
- 6. Change gloves and immerse the bottle in a hot (50-60°C) bath of 1 N trace metal grade HCl, and allow to soak for at least 48 hours. Then thoroughly rinse the bottle with reagent water.
- 7. Fill the bottle with a weak acid solution (0.1% (v/v)) ultrapure HCl).
- 8. Double-bag the bottle in a polyethylene bag to prevent contamination of the surfaces with dust and dirt. Store at room temperature until sample collection.
- 9. Perform a bottle blank after the first bottle cleaning procedure of the year.

5 REFERENCES

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May 2015

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Ventura County Watershed Protection District, 2011. Ventura Countywide Stormwater Quality Management Program. Stormwater Program: Water Quality Monitoring Standard Operating Procedures 2009-2014. April 2011.

Attachment C.1: USGS protocols for Field Measurements (from National Field Manual for the Collection of Water-Quality)

Reference-Selected Chapters from:
National Field Manual for the Collection of Water-Quality Data
Techniques of Water-Resources Investigations
Book 9
Handbooks for Water-Resources Investigations

http://water.usgs.gov/owq/FieldManual/

TEMPERATURE 6.1

Revised by Franceska D. Wilde

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TEMPERATURE 6.1

Measurements of air and water temperature at a field site are essential for water-quality data collection. Determination of dissolved-oxygen concentrations, conductivity, pH, rate and equilibria of chemical reactions, biological activity, and fluid properties relies on accurate temperature measurements.

Accurate air- and water-temperature data are essential to document thermal alterations to the environment caused by natural phenomena and by human activities. Water temperature can be subject to environmental regulation and monitoring by State and local agencies.

TEMPERATURE:

a measure of
warmth or coldness

of a substance
with reference to
a standard value.

This section describes methods for measuring temperature in air, surface water, and ground water. The methods are appropriate for fresh to saline waters.

- ► A thermometer is any device used to measure temperature, consisting of a temperature sensor and some type of calibrated scale or readout device. Liquid-in-glass thermometers and thermistor thermometers are commonly used to measure air and water temperature. ¹
- ► The U.S. Geological Survey (USGS) uses the Centigrade or Celsius (C) scale for measuring temperature.

¹Some of the equipment and procedures recommended herein may not reflect the most recent technological advances; in this case, follow the manufacturer's instructions but comply with standard USGS quality-control practices.

6.1.1 EQUIPMENT AND SUPPLIES

Thermometers and other temperature-measurement equipment and supplies must be tested before each field trip and cleaned soon after use (table 6.1–1). Each temperature instrument must have a log book in which all calibrations and repairs are recorded, along with the manufacturer make and model and serial or property number.

Table 6.1–1. Equipment and supplies used for measuring temperature 1 [–, minus; +, plus; $^{\circ}$ C, degrees Celsius; L, liter; μ S/cm, microsiemens per centimeter at 25 $^{\circ}$ C]

- ✓ Calibration thermometer, liquid-in-glass or electronic-thermistor thermometer, either National Institute of Standards and Technology (NIST) certified or manufacturer-certified as NIST traceable. Must carry certificate of NIST traceability; its use not allowed after expiration of certification.
 - Temperature range, at least -5 to +45°C
 - 0.1°C graduations (liquid-in-glass) or less
- ✓ Thermometer, liquid-in-glass sensor, nonmercury-filled for field use
 - Temperature range, at least -5 to +45°C
 - Minimum 0.5°C graduated
 - Calibrated accuracy within 1 percent of full scale or 0.5°C, whichever is less
 - Calibrated and office-laboratory certified against a properly certified calibration thermometer (see above)
- ✓ Thermistor Thermometer
 - Calibrated accuracy within 0.1°C to 0.2°C
 - Digital readout to at least 0.1°C
 - Office-laboratory certified against a calibration thermometer (see above)
- Dewar flask and (or) plastic beakers (assorted sizes)
- ✓ Water bath, refrigerated (if available—see section 6.1.2)
- ✓ Soap solution (1 L), nonphosphate laboratory detergent
- ✓ Deionized water (1 L), maximum conductivity of 1 μS/cm
- ✓ Flowthrough chamber (for ground-water applications as an alternative to instruments with downhole capabilities)
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Log book, for recording all calibrations, maintenance, and repairs

¹Modify this list to meet specific needs of the field effort.

Temperature-measuring instruments for field and laboratory (calibration) use can be either a liquid-in-glass or thermistor thermometer. Field personnel should be familiar with the instructions for use of the thermometer that are provided by the manufacturer.

- ▶ Liquid-in-glass field thermometer—Total immersion thermometers that are filled with a stable liquid, such as alcohol, are recommended for water measurements in the field. (Partial immersion thermometers are not recommended: these have a ring or other mark to indicate the required immersion depth.) Thermometers for field use must not be mercury filled. Before making temperature measurements, check the type of liquid-filled thermometer being used.
- ▶ Thermistor thermometer—A thermistor thermometer is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity. An electrical signal processor (meter) converts changes in resistance to a readout calibrated in temperature units. Thermistors are incorporated into digital thermometers, individual-parameter instruments (such as conductivity and pH meters), and multiparameter instruments used for surface-water and ground-water measurements.

CAUTION:

Do not use mercury-filled thermometers in the field.

MAINTENANCE, CLEANING, AND STORAGE

Liquid-in-glass and thermistor thermometers can become damaged or out of calibration, especially as a consequence of thermal shock or extended exposure to direct sunlight. It is important to be familiar with and to follow the manufacturer's instructions for use and care.

- ► Keep a log book for each thermometer in which the date, time, and location of every calibration are recorded.
 - Avoid direct exposure of the thermometer to sunlight.
 - Avoid submerging the thermometer sensor in corrosive solutions.
 - Follow the calibration guidelines and protocols described in section 6.1.2.

- Digital thermometer casings should not be submerged in water unless the manufacturer affirms that they are waterproof. Do not allow any liquid to enter open jacks that are part of some digital thermometers.
- ► Keep thermometers clean.
 - Clean thermometer sensors with a soft cloth dipped in a mild solution of lukewarm water and nonphosphate detergent.
 - If the digital thermometer case needs to be disinfected, use a weak (0.005 percent) bleach solution.
 - **Do not autoclave the thermometer** (unless autoclaving is sanctioned by the manufacturer).
 - If your digital thermometer has a detachable sensor with a plug termination, periodically wipe off or clean the sensor contacts. Dirty contacts can affect temperature readings.
 - Blot the thermometer sensor dry after use.
 - To clean an LCD lens, use only plastic-approved lens cleaners; do not use alcohol, acetone, or other harsh chemicals, as these will fog the lens.
- ▶ Store thermometers securely when not in use.
 - Keep thermometers in a clean protective case when not in use. Each thermometer sensor and the case must be free of sand and debris.
 - Keep thermometers dry and in a protective case during transit.
 - Store liquid-filled thermometers with the bulb down.
 - Store thermometers in a cool place and inside a building when not in use; do not leave a thermometer in a vehicle that could change in temperature to very hot or very cold, resulting in thermal shock to the thermometer.
 - Check the batteries of thermistor-type thermometers for proper voltage before using.
 - Record the calibration data in the log book for each thermometer—liquid-in-glass, thermistor thermometer, or thermistor-containing field-measurement instrument. Note if a thermometer has been serviced or replaced.

CALIBRATION 6.1.2

Thermometer calibration differs from the process by which a pH or conductivity sensor is adjusted until the accuracy of its performance conforms to that of an accepted calibration standard. For temperature measurements, calibration² refers to a comparison or accuracy check at specified temperatures against a thermometer that is certified by the National Institute of Standards and Technology (NIST), or is manufacturer-certified as NIST traceable. Calibration should be performed in a laboratory environment every 6 to 12 months, depending on the manufacturer's recommendation.

- ▶ **Field thermometers:** Only calibration thermometers having current NIST certification or traceability can be used for checking the accuracy of (calibrating) field thermometers.
 - In the case of continuous monitors, a nonmercury calibration thermometer can be used in the field to check or monitor temperature readings whenever other field-measurement sensors are calibrated. See Wagner and others (2006) for specific guidelines for continuous monitors.
- ▶ Calibration thermometers are calibrated during their manufacture and certified as NIST-certified or NIST-traceable at the manufacturing laboratory. The USGS requires that calibration thermometers be recertified by a professional calibration service at least every 2 years, or be replaced with a calibration thermometer having current certification.
 - Calibration thermometers should be reserved for calibration and should not be used routinely as field thermometers (see TECHNICAL NOTE). Mercury-filled thermometers must never be used outside of the laboratory.
 - The thermistors included in other field-measurement instruments must be calibrated (checked) routinely, as specified below for thermistor thermometers, since accurate determination of other field measurements depends on the accuracy of temperature measurements. Thermistors that are incorporated into instruments designed to measure, for example, specific electrical conductance, dissolved oxygen, and pH commonly provide automatic temperature compensation.

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²Calibrate: "To check, adjust, or systematically standardize the graduations of a quantitative measuring instrument" (American Heritage Dictionary, 1976).

- All thermometers must be tagged with their most recent date and source of certification (NIST-certified or -traceable source for calibration thermometers and office-laboratory source for field thermometers).
- ▶ A log book is required in which the calibration and certification history of each calibration and field thermometer is recorded.

TECHNICAL NOTE: The accuracy of a thermometer may vary over time, depending on factors such as the quality of its manufacture, the frequency of its use, and the conditions to which it is exposed. Shock, contamination, rapid heating and cooling, and mechanical stress are some factors that can affect the stability of a liquid-inglass or thermistor thermometer (ICL Calibration Laboratories, 2003, 2005; ASTM International, 2005).

6.1.2.A CALIBRATION THERMOMETERS

Calibration thermometers (table 6.1-1) can be either a liquid-in-glass (mercury or spirit) or thermistor (digital) type thermometer, but must carry a current NIST certification or NIST-traceable certification that is no more than 2 years old. The actual duration of the calibration depends on the date of thermometer certification (not the date of purchase), how frequently the thermometer is used, and the conditions (thermal, chemical, and physical) to which it has been subjected during field operations and storage (see "Maintenance, cleaning, and storage" in section 6.1.1).

- ► Check that the calibration thermometer has an NIST certification or traceable certificate that is within a 2-year period of original certification or recertification.
- ► Liquid-in-glass calibration thermometer:
 - Before each use, inspect the thermometer for cracks, internal condensation, and liquid separation; if any of these conditions are observed, the thermometer must be replaced.
 - If the thermometer has been stored or used improperly, exposed at some length to sunlight or heat, or if its accuracy is otherwise in question, check its readings at temperatures of approximately 0°, 25°, and 40°C, against those of another calibration thermometer that has been certified within the past 2 years. If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.

▶ Thermistor calibration thermometer:

- Before each use, inspect the instrument (temperature sensor, digital display, wires or leads, and plugs) for signs of wear or damage; check that batteries are at full voltage.
- If the thermometer has been improperly stored or used, exposed at some length to sunlight or heat or extreme cold, or if its accuracy is otherwise in question, check its readings at five temperatures within the range of 0° to 40°C, against those of another currently certified calibration thermometer. If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.
- ► Once NIST certification has expired (exceeded the 2-year USGS limit):
 - The thermometer either must be replaced with a currently certified thermometer or be recertified through a professional calibration service.³ An office-laboratory calibration check does not constitute recertification of NIST traceability of a calibration thermometer.
 - It is advisable to replace all mercury thermometers with a spirit or thermistor thermometer in order to avoid potential mercury contamination. The mercury thermometer must be disposed of in strict accordance with safety regulations.

Do not use calibration thermometers as routine field thermometers. Reserve their use for calibrating field thermometers.

FIELD THERMOMETERS 6.1.2.B

Field thermometers, whether of the liquid-in-glass or thermistor (digital) type, and whether or not they are themselves NIST-traceable,

³The cost of commercial calibration services can vary widely. Examples of laboratories that are accredited to perform thermometer calibrations and certification include: National Institute of Standards and Technology (http://ts.nist.gov/ts/htdocs/230/233/calibrations/); ICL Calibration Laboratories (www.icllabs.com); Lab Safety Supply, Inc. (https://www.labsafety.com/calibration). (URLs cited were accessed 11/28/2005).

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require regular accuracy checks against a calibration thermometer. Carry an extra thermometer in the event that the accuracy of a field thermometer is in question. Note, however, that field checking of a thermometer's accuracy does not substitute for the required annual laboratory calibration.

- At a minimum, calibrate each field thermometer every 12 months—the time interval depends on the amount of use and abuse to which the thermometer has been subjected and on its manufacture. According to thermometer manufacturers, some models of thermistor thermometers require calibration every 6 months (YSI, 2005). Quarterly or possibly monthly calibration can be required if the thermometer is in heavy use; was exposed to thermal shock, an extended period of direct sunlight, or extreme shifts in temperature; or was exposed to aggressive chemical solutions. The calibration history from the log book can indicate the expected life of the thermometer.
- ► Each thermometer that passes the accuracy check must be tagged with the date of calibration. Thermometers that do not pass the accuracy check must be repaired, if possible, or else discarded or otherwise retired from use.
- ▶ The annual calibration of field thermometers can be performed in the office laboratory or by an NIST-accredited commercial laboratory. To calibrate a thermometer, check its readings across a range of temperatures as described below in the instructions for water-bath calibration procedures. Temperature checks must bracket and include points that represent the temperature range expected to be encountered in the field. **EXCEPTION:** Thermistors in continuous water-quality monitors can be field-checked annually (or more frequently, if necessary) with a nonmercury NIST-certified or NIST-traceable thermometer.
 - Fully submerge the bulb and liquid column if using a totalimmersion liquid-in-glass thermometer.
 - Keep calibration and field temperature sensors (thermistor or liquid-in-glass type) submerged throughout the calibration process.
 - Record thermometer readings throughout the bath warming and cooling periods and while keeping the water stirred or otherwise circulated (thermistor readings will be recorded with greater frequency).
 - Check meter batteries periodically for proper voltage when using a thermistor-type thermometer.

 Record the calibration data in the instrument log book for each thermistor thermometer (including thermistor-containing field meters), noting if a temperature sensor has been replaced.

Calibrate field thermometers every 12 months.

To calibrate field thermometers when a commercial refrigerated water bath is available:

- 1. Precool the sensor of the thermometer(s) being tested (field thermometer) to 0°C by immersing it in a separate ice/water bath.
- 2. Immerse the field and calibration temperature sensors in the refrigerated bath with a water temperature of approximately 0°C.
- 3. Position the temperature sensor(s) so that they are properly immersed and so that the scales can be read. Stir the water bath and allow at least 2 minutes for the thermometer readings to stabilize.
- 4. Without removing the temperature sensor(s) from the refrigerated water bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
 - a. Take three readings within a 5-minute span for each field thermometer.
 - b. Calculate the mean of the three temperature readings for each field thermometer and compare its mean value with the calibration thermometer.
 - c. If a liquid-filled field thermometer is found to be within ± 1 percent of full scale or ± 0.5 °C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
 - d. If a field thermistor is found to be within $\pm 0.2^{\circ}$ C of the calibration thermometer, set it aside for calibration checks at higher temperatures.
- 5. Repeat steps 1–4 in 25°C and 40°C water. Keep the bath temperature constant. Check the thermistors at two or more additional intermediate temperatures (for example, 15°C and 30°C).
- 6. Tag acceptable thermometers as "office-laboratory certified" with calibration date and certifier's initials.

To calibrate field thermometers when a commercial refrigerated water bath is not available:

A. For the 0°C calibration

- 1. Freeze several ice cube trays filled with deionized water.
- 2. Fill a 1,000-milliliter (mL) plastic beaker or Dewar flask three-fourths full of crushed, deionized ice. Add chilled, deionized water to the beaker. Place the beaker of ice/water mixture in a larger, insulated container or Dewar flask. Place the calibration thermometer into the ice/water mixture and make sure that the temperature is uniform at 0°C by stirring and checking at several locations within the bath.
- 3. Precool the sensor of the field thermometer(s) to 0°C by immersing in a separate ice/water bath.
- 4. Insert the field thermometer(s) into the ice/water mixture. Position the calibration and field thermometers so that they are properly immersed and so that the scales can be read. Periodically stir the ice/water mixture and allow at least 2 minutes for the thermometer readings to stabilize.
- 5. After the readings stabilize, compare the temperature of one field thermometer at a time with that of the calibration thermometer. Without removing the temperature sensor(s) from the test bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
 - a. Take three readings for each thermometer within a 5-minute span.
 - b. Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the calibration thermometer.
 - c. If the field liquid-filled thermometer is found to be within ± 1 percent of full scale or ± 0.5 °C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
 - d. If the field thermistor is found to be within ±0.2°C of the calibration thermometer, set it aside for calibration checks at higher temperatures.

B. For the "room temperature" calibration (25° C)

- 1. Place a Dewar flask or container filled with about 1 gallon of water in a box filled with packing insulation. (A partially filled insulated ice chest can be used for multiparameter instruments.) Place the calibration container in an area of the room where the temperature is fairly constant (away from drafts, vents, windows, and harsh lights).
- 2. Properly immerse the calibration and field thermometer(s) in the water. Cover the container and allow the water bath and thermometers to equilibrate.
- 3. Stir the water and, using the calibration thermometer, check the bath for temperature uniformity. Repeat this every 2 hours. It may be necessary to let the bath equilibrate overnight.
- 4. Compare one field thermometer at a time against the calibration thermometer, following the procedures described above in step A5 for the 0°C calibration.

C. For each temperature that is greater than 25°C

- 1. Warm a beaker of 1,000 mL or more of water to the desired temperature (for example, 40°C) and place it on a magnetic stirrer plate.
- 2. Follow the procedures described above in step A5 for the 0°C calibration.

Tag acceptable field thermometers as "office-laboratory certified" with the calibration date and certifier's initials.

Corrections can be applied to measurements made with a thermometer that is within ± 1 percent of full scale or $\pm 0.5^{\circ}$ C of the calibration thermometer. Corrections should be applied by using a calibration curve or table, which is plotted in the log book for the instrument. **Thermistors found to be out of calibration by more than 0.2^{\circ}C must be returned to the manufacturer for repair or replacement.**

Remember to tag and date acceptable field thermometers after calibration.

6.1.3 MEASUREMENT

Air temperature, in addition to water temperature, should be measured and recorded whenever water-quality samples are collected. Water temperature must always be measured in situ and in a manner that ensures that the measurement accurately represents the intended sample conditions. Before measuring air or water temperature:

- ► Inspect the liquid-in-glass thermometer to be certain that the liquid column has not separated.
 - Inspect the glass bulb to be sure it is clean.
 - Inspect the protective case to be sure it is free of sand and debris.
- ► Check that batteries are fully charged for thermister thermometers or temperature sensors incorporated into other field meters.

6.1.3.A AIR

Measure air temperature using a dry, calibrated thermometer.

- ▶ Place or hang the thermometer about 5 feet above the ground in a shaded area that is protected from strong winds but open to air circulation. Avoid areas of possible radiant heat effects, such as metal walls, rock exposures, or sides of vehicles.
- ▶ Allow 3 to 5 minutes for the thermometer to equilibrate, then record the temperature and time of day.
- ▶ Measure the air temperature as close as possible to the time when the temperature of the water sample is measured.
- ► Report routine air temperature measurements to the nearest 0.5°C. If greater accuracy is required, use a thermistor thermometer that has been calibrated to the accuracy needed.

6.1.3.B SURFACE WATER

The reported surface-water temperature must be measured in situ—do not measure temperature on subsamples from a sample compositing device. Measure temperature in such a manner that the mean or median temperature at the time of observation is represented (consult NFM 6.0 and fig. 6.0–1). Record any deviation from this convention in the data base and report it with the published data.

To measure the temperature of surface water:

- ▶ Making a cross-sectional temperature profile first, to determine the temperature variability of the stream section, is recommended—a hand-held digital thermometer works best for this purpose.
- ► To determine which sampling method to use (NFM 6.0), examine the cross-sectional profile and consider study objectives.
- ▶ Measure temperature in those sections of the stream that represent most of the water flowing in a reach. Do not make temperature measurements in or directly below stream sections with turbulent flow or from the stream bank (unless this specifically represents the intended condition to be monitored).
- 1. Use either a liquid-in-glass thermometer or a thermistor thermometer tagged as "office-laboratory certified" and dated within the past 12 months.
- 2. Record on field forms the temperature variation from the cross-sectional profile, and the sampling method selected.
 - **Flowing, shallow stream**—wade to the location(s) where temperature is to be measured. To prevent erroneous readings caused by direct solar radiation, stand so that a shadow is cast on the site for temperature measurement.
 - Stream too deep or swift to wade—measure temperature by lowering from a bridge, cableway, or boat a thermistor thermometer attached to a weighted cable. Do not attach a weight directly onto the sensor or sensor cable.
 - **Still-water conditions**—measure temperature at multiple depths at several points in the cross section.

3. Immerse the sensor in the water to the correct depth and hold it there for no less than 60 seconds or according to the manufacturer's guidelines until the sensor equilibrates thermally. The sensor must be immersed properly while reading the temperature; this might require attaching the thermistor to a weighted cable.

TECHNICAL NOTE: For in-situ measurement with liquid-filled, full-immersion thermometers—the water depth to which the thermometer is immersed must be no greater than twice the length of the liquid column of the thermometer in order to make an accurate measurement.

- 4. Read the temperature to the nearest 0.5°C for liquid-in-glass and 0.2°C for thermistor readings—do not remove the sensor from the water.
 - When using a liquid-in-glass thermometer, check the reading three times and record on field forms the median of these values.
 - When using a thermistor thermometer, wait until the readings stabilize to within 0.2°C, then record the median of approximately the last five values.
- 5. Remove the temperature sensor from the water, rinse it thoroughly with deionized water, blot it dry, and store it.
- 6. Record the stream temperature on field forms. Determine the values as follows:
 - In still water—median of three or more sequential values.
 - For equal discharge increments (EDI)—mean value of subsections measured (use median value if measuring one vertical at the centroid of flow).
 - For equal width increments (EWI)—mean or median value of subsections measured.

6.1.3.C GROUND WATER

Measurements of ground-water temperature must be made downhole or with a flowthrough system at the end of purging to ensure that the temperature measured accurately represents ambient aquifer water conditions (consult NFM 6.0 for guidance). **Do not report a temperature value measured from a bailed ground-water sample.**

To measure the temperature of ground water:

- ► Select either the downhole or flowthrough-chamber sampling system (see NFM 6.0, fig. 6.0–4) and record the method used.
- ▶ Measure temperature with a thermometer that has been officelaboratory certified within the past 12 months and within the temperature range to be encountered.
- 1. Prepare the instruments for either the downhole or the flowthrough-chamber system.
 - Downhole system—lower the sensor in the well to just below the pump intake (the intake location depends on the sampling objectives).
 - Flowthrough-chamber system—properly immerse the thermistor or liquid-in-glass thermometer in the chamber. Keep the pump tubing from the well to the chamber as short as possible, out of direct sunlight, and off the ground. Keep the chamber out of direct sunlight and wind.
- Begin water withdrawal from the well. Allow the thermometer to equilibrate with ground-water temperature for no less than 60 seconds or in accordance with the manufacturer's guidelines; record the readings and time intervals throughout the period of purging.
- 3. Toward the end of purging, record five or more sequential measurements, spaced at increments of 3 to 5 minutes or more.
 - If the thermistor temperature is stable within the 0.2°C criterion, report the median of the final five measurements (table 6.0–1). (For a liquid-in-glass thermometer, there should be only slight fluctuation around 0.5°C.)
 - If the stability criterion has not been met, extend the purge time and consult the well-purging objectives of the study. Report the median of the last five (or more) sequential measurements and record any instability on field forms.
- 4. Remove the thermometer from the water, rinse it thoroughly with deionized water, blot it dry, and store it as described in 6.1.1.

6.1.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions on table 6.1-2 fail to resolve the problem, or if additional information is needed.

When using thermistor thermometers:

- ► Check the voltage of the batteries.
- ▶ Start with good batteries in instruments and carry spares.

Table 6.1–2. Troubleshooting guide for temperature measurement

Symptom	Possible cause and corrective action	
Liquid-in-glass thermometer does not read accurately	• Check thermometer to see that the liquid is not separated—if separated, take back to the office laboratory to reunite column or for disposal.	
Thermistor thermometer does not read accurately	 Dirty sensor—remove dirt and oil film. Weak batteries—replace with new batteries. 	
Erratic thermistor thermometer readings	 Bad or dirty connection at meter or sensor—tighten or clean connections. Break in the cables—replace cables. Weak batteries—replace with new batteries. 	
Thermistor thermometer slow to stabilize	Dirty sensor—clean sensor to remove dirt and oily film.	

6.1.5 REPORTING

USGS temperature measurements should be stored in the National Water Information System (NWIS) data base. These data may be published electronically and (or) on paper as the verified negative or positive value measured, as described below.

- ▶ Thermistor thermometer measurements: Store manually recorded temperature measurements in the data base to the user-verified precision of the instrument (generally, 0.1 or 0.2°C, provided that the thermometer calibration verifies this accuracy). Electronically recorded temperature data may be stored unrounded. Unrounded temperature data in the database must be rounded when retrieved for publication.
- ► Liquid-in-glass thermometer measurements: Record temperature measurements in the data base to the nearest 0.5°C.
- ► Any values less than 0.1°C are highly questionable and should be published only after a complete calibration check of the equipment used.
- ▶ USGS field measurements of air and water temperature must be entered on the paper or electronic field form and stored in the NWIS data base.
 - Be sure to store all data under the correct parameter and method (if available) codes.
 - Store air and water temperature measurement data with replicate samples only if replicate measurements were made. Enter replicate measurements under the correct medium code for quality-control (QC) samples; alternatively, distinguish the replicate from the regular sample by using the unique time-of-sampling that was assigned to QC samples for that site and date.
 - Do not store the regular-sample measurement data with the replicate-sample data. Enter regular-sample data only once in the NWIS data base.
- ▶ Record the accuracy range of the instrument in the data base, if possible. Report the accuracy range with the published values.

Report only those water temperature values that were measured in situ.

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National Field Manual for the Collection of Water-Quality Data



Chapter A6 Field Measurements

Section 6.2 DISSOLVED OXYGEN

Revised by Stewart A. Rounds, Franceska D. Wilde, and George F. Ritz

Techniques of Water-Resources Investigations Book 9-A6

U.S. Department of the Interior

U.S. Geological Survey

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This National Field Manual for the Collection of Water-Quality Data (National Field Manual) responds to advances in technology and science and to the ever-developing needs for water-quality monitoring. Its aim is to provide scientifically sound guidance to U.S. Geological Survey (USGS) personnel and to document USGS requirements for collecting water-quality data. As a result, the expertise of numerous scientists has been tapped in developing the various chapters of this manual and keeping them current.

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6.2 Dissolved Oxygen

Revised by Stewart A. Rounds, Franceska D. Wilde, and George F. Ritz

The concentration of dissolved oxygen in water is affected by many factors, including ambient temperature, atmospheric pressure, and ion activity (ionic strength of the water body). Accurate dissolved-oxygen (DO) data are essential for understanding and documenting effects on environmental water resources that result from natural phenomena and human activities. Sources of DO in water include atmospheric aeration and photosynthetic activities of aquatic plants. Sinks of DO in water include respiration, aerobic decomposition processes, ammonia nitrification, and other chemical/biological reactions. Many chemical and biological reactions in groundwater and surface water depend directly or indirectly on the amount of available oxygen. The presence of DO in aquatic systems is necessary for the survival and growth of many aquatic organisms and is used as an indicator of the health and geochemical quality of surface-water and groundwater systems.

DISSOLVED OXYGEN: Molecular oxygen (oxygen gas) dissolved in water.

Standard procedures used by the U.S. Geological Survey (USGS) for determining concentrations of DO in surface water and groundwater involve the use of luminescence-based (optical sensor), amperometric (Clark cell¹), or spectrophotometric methods of analysis. The iodometric (Winkler) method (section 6.2.3) no longer is used by the USGS for routine measurement of DO at field sites, but remains a standard method for verifying the results of DO measurements made using other methods.

The selection of field equipment and measurement methods takes into consideration (a) whether equipment will be used at varying and discrete locations and times or be deployed at a single location over a period during which it will be unattended, (b) anticipated environmental conditions, (c) the specific data-quality objectives of the data-collection program, and (d) the inherent benefits of a given technology as applied to given site characteristics and project or program objectives. The measurement methods described are employed by the USGS onsite for routine determination of DO concentrations in fresh to saline surface water and groundwater.

The primary USGS field procedure employed for DO determinations during the past two decades required the use of amperometric sensors until luminescence-based (optical) sensors became more common (around 2005). Although both optical and amperometric methods yield accurate results, optical DO sensors are considered a major technological advance over amperometric sensors because optical DO sensors are more robust in the field environment.

▶ Optical and amperometric sensor methods (section 6.2.1) are applicable to the same aqueous environmental conditions. Both sensor technologies are available in single-parameter DO meters or in multiparameter sondes and can be either handheld for discrete measurements or deployed for longer term, unattended continuous and real-time measurements.

¹ This document refers to the "amperometric" method or sensor interchangeably with the "Clark cell" sensor. Other terms applied to amperometric methods include polarographic and galvanic technology.

- ▶ Spectrophotometric (colorimetric) methods (section 6.2.2) yield consistent results when applied to the determination of DO concentrations in oxygen-depleted waters (for example, in certain aquifers and deep-lake horizons). Noninstrumental colorimetric methods that are available for visually determining DO concentrations to zero milligram per liter (mg/L) can be useful for a quick reconnaissance of DO conditions and an accuracy check of DO sensor performance.
- ▶ The iodometric (Winkler) method (section 6.2.3) is regarded as an accurate and precise method for the calibration of DO sensors and the determination of DO concentration in water, when performed under controlled laboratory conditions. Before sensors that could be immersed directly in the water column became commonly available, USGS personnel were trained to perform Winkler titrations onsite. Standard USGS practice no longer sanctions the transport of field samples offsite for DO determination.
- Some procedures for equipment operation as recommended in this guidance document may not apply to your equipment because of technological advances or other changes.
- Be sure to record any modifications made to the standard USGS procedures given in this field manual.

6.2.1 Optical (Luminescence) and Amperometric Sensor Methods

Either the optical or amperometric sensor methods can yield accurate results for measurement of DO concentrations under most of the field conditions encountered for routine USGS data-collection activities. Both methods are relatively simple to use, whether deployed for single (discrete) or continuous (unattended) DO measurements in surface water or groundwater. Because of the advantages introduced by advances in applying luminescence technology to DO measurement, optical sensors are generally favored for most standard USGS field operations.

- ▶ Optical sensors. The technology used in optical DO sensors involves the measurement of light-emission characteristics of a luminescence-based reaction at the sensor-water interface (see TECHNICAL NOTE 1). In contrast to amperometric sensors:
 - Oxygen is not consumed at the sensor-water interface.
 - The optical sensor is not dependent on water flow; consequently, no stirring mechanism is required at sites with slow or stagnant waters.
 - Optical sensors are stable. They are considerably more robust than amperometric sensors in maintaining calibration over long-term deployment and over a wide range of environmental conditions, and sensor drift over time is minimal when the sensor is kept clean.
 - There are no known sources of interference to the luminescence method in natural aquatic systems. Optical sensors will measure accurately in the presence of hydrogen sulfide (H₂S) and also when deployed in fresh, brackish, and mildly polluted waters. Contact, however, with organic solvents can compromise sensor integrity or performance.
 - Cleaning and maintenance are simplified. The optical sensor contains no anode or cathode to service, and uses no electrolyte solution, amperometric-type membranes, O-rings, or stirrer.

- The maintenance routine and schedule for optical sensors is less frequent than for amperometric sensors. Optical-sensor maintenance is dictated by manufacturer guidelines that are specific to the type of sensor in use and the conditions to which the sensor has been subjected.
 - Optical-sensor luminophore-containing modules² (referred to as sensor caps, probe tips, or luminophore-coated membranes or foil, depending on the manufacturer) are rugged and resistant to punctures or other damage in storm or high-flow conditions, while amperometric (Teflon-membrane) sensors are considerably more vulnerable and require frequent replacement.
 - Compared with the amperometric sensor, the frequency of a calibration check for an unattended (for example, continuously deployed) optical sensor should occur at least every 4 to 8 weeks, which depends primarily on environmental conditions and the age and condition of the luminophore, while the amperometric sensor typically requires recalibration every week or two, depending on environmental conditions.
 - The manufacturers generally recommend annual to biannual replacement of the luminophorecontaining module. The modules are easily replaced and should be calibrated or undergo a calibration check after being replaced.

TECHNICAL NOTE 1. The luminescence sensor employs a light-emitting diode (LED) to provide incident light of a specific wavelength, which excites a luminescent-dye molecule substrate (luminophore) of the sensor. After some dissipation of the excitation energy, longer wavelength light is emitted. The intensity of the fluorescence is proportional to the DO concentration because the presence of oxygen can quench, or suppress, the fluorescence response of the dye. Higher DO concentrations result in greater quenching and a decreased fluorescence response. More importantly, the timescale, or lifetime, of the fluorescence reaction is dependent also on the DO concentration and is not dependent on the light intensity of excitation or fluorescence, therefore allowing reliable determination of the DO concentration. Temperature stability during calibration and measurement is extremely important for optical and amperometric sensors alike.

- ▶ Amperometric sensors (Clark cell). The amperometric measurement method was the most commonly used field method for DO determination for USGS water data-collection efforts before introduction of the luminescence method. In this method, the DO concentration is determined using a temperature-compensating meter connected to an amperometric-membrane type of sensor or an amperometric sensor bundled with other sensors in a multiparameter sonde.
 - Amperometric sensors require use of membranes and electrolyte solutions (*see* TECHNICAL NOTE 2 below).
 - The method is flow-dependent, requiring that an adequate flow of water (approximately 1 foot per second (ft/s)) passes across the membrane.³ Manual stirring is required when making handheld measurements. Use of an additional stirring mechanism fitted to the sensor or sonde is needed for discrete or continuous measurements at sites with slow or stagnant waters.
 - Contact of the amperometric sensor with hydrogen sulfide (H₂S) interferes with the DO determination by degrading the electrode surfaces under the membrane.

² See TECHNICAL NOTE 1 for definitions of luminescence and luminophore.

³ The "Rapid Pulse" (YSI) sensor, however, does not require a stirrer and was designed to be virtually flow-independent for DO measurement in environmental waters. As of this writing, it is the only amperometric technology designed for this purpose and that allows a two-point calibration.

- Amperometric sensors are vulnerable to changes in temperature and the instrument must be temperature compensating. Be cognizant of the relation between sensor membranes and temperature.
 The permeability of the membrane changes as a function of temperature, as does the solubility of oxygen in water.
- Method performance can be negatively affected by:
 - calibration drift
 - a loose, wrinkled, or damaged membrane
 - air bubbles in the electrolyte
 - use of expired or contaminated electrolyte solution
 - loose-fitting O-rings and membranes
 - damaged, dirty, or otherwise contaminated electrodes under the membrane
- Extreme temperature change and (or) shock/vibration may cause a shift in the calibration, resulting in biased data.

TECHNICAL NOTE 2. Some manufacturers provide amperometric-sensor membranes of various thicknesses, the selection of which depends on the intended use of the instrument. Select the sensor membrane based on manufacturer's recommendations. Two basic types of membrane design are available: (a) individual membranes and (b) membrane-cap assemblies. Individual membranes are considerably less expensive but require more care and skill to install properly. Sensor performance can be affected by the manner in which individual membranes are installed and conditioned after installation.

6.2.1.A Equipment and Field Preparations

DO instruments (meters and sensors) are available from a number of commercial vendors. Because of differences among manufacturers in the instrument design and instructions for use, calibration, and maintenance, it is important that the user be thoroughly familiar with the instructional manual for the specific instrument system to be used in addition to the guidance given here.

Equipment Description and Maintenance

Meters, sondes, and the DO sensors used in these instruments are sophisticated electronic equipment that require care in handling and operation. Information about the equipment and supplies required for the optical and amperometric methods of determining aqueous DO concentrations is summarized in table 6.2–1.

▶ Amperometric sensor. The amperometric "instrument system" refers to the entire sensor assembly, including electrolyte solutions, membranes, and thermistors. Protect all sensors and supplies from being jostled during transportation, from sudden impacts, sudden temperature changes, and from extremes of heat and cold below 0 °C.

- ▶ **Optical sensor.** Guidance for when to replace the luminophore-containing cap or membrane varies among manufacturers and can be based on the specific design and materials used, the environmental conditions to which the sensor is exposed, the age of the sensor, and (or) the amount of time it is deployed. For example:
 - Hach Company states that the need for replacement of the luminophore module depends on environmental factors to which their LDO (Luminescent Dissolved Oxygen) probe is exposed, rather than be scheduled solely on the basis of frequency or length of use. Environmental factors such as photobleaching of the luminophore surface from irradiation (for example, overexposure to sunlight), and substantial changes in water properties such as salinity or atmospheric conditions (air pressure), can affect the need for luminophore-module replacement.
 - YSI Environmental advises annual replacement of the luminophore membrane assembly for their ROX (Reliable Oxygen) optical sensor.
 - In-Situ, Inc. advises that the RDO (Rugged Dissolved Oxygen) sensor cap has a 2-year shelf life
 from the time of manufacture when not in service, but the cap must be replaced after one year of
 field deployment.
- ▶ Storage of optical and amperometric sensors. Become familiar with the specific manufacturer's recommendations for short-term (field) and long-term (office) storage.
 - Amperometric sensors should not be allowed to dry out and should be kept moist during storage.
 - Storage of optical sensors in a humid environment differs among manufacturers; consult the manual provided for the sensor.

Table 6.2-1. Equipment and supplies for the optical and amperometric sensor methods of dissolved oxygen determination.¹

[DO, dissolved oxygen; mg/L, milligram per liter; NFM, National Field Manual for the Collection of Water-Quality Data; -, minus; +, plus; °C, degrees Celsius; ±, plus or minus]

For amperometric method only

Amperometric instruments must be pressure-compensated (as well as temperature-compensated).

DO sensor membrane replacement kit includes membranes, O-rings, electrolyte (filling) solution; electrode reconditioning supplies; stirring attachment for low- or no-flow waters.

For optical and amperometric measurement methods

Instrument must be equipped with temperature compensation

- · DO instrument and DO sensor or multiparameter instrument with DO capability and digital temperature readout display
- Operating range in water, from at least –5 °C to +45 °C
- Measure concentrations from 0.05 to 20 mg/L (instrument capability can range to 50 mg/L)
- Minimum scale readability (display resolution), preferably 0.01 mg/L DO
- Calibrated accuracy within ±0.1 mg/L DO²

Calibration equipment, per manufacturer's recommendation.³

Pocket altimeter-barometer or DO instrument with built-in barometer; barometer measures to nearest 1 millimeter of mercury and its calibration has been checked before use.

Thermometer (see NFM 6.1 and 6.8 for calibration-check criteria) (for verification of air and water temperature and accuracy of instrument built-in thermistor).

Zero DO solution.⁴ Dissolve 1 gram sodium sulfite in 1 liter of deionized water (0.008M solution, prepared fresh just before the field trip or during week of use).⁵

Flowthrough chamber for determining groundwater DO, if downhole sensor deployment is impractical.

Oxygen-solubility table (table 6.2–6), or access http://water.usgs.gov/software/DOTABLES/.

Waste-disposal containers.

Spare batteries.

- Calibration and maintenance log books for DO instrument and barometer.
- Calibrated specific conductance sensor, if working in saline or brackish systems.
- ¹ Modify this list to meet specific needs of the field effort.
- ² Refer to Wagner and others (2006) for long-term sensor deployment.
- ³ Equipment needs and additional information specific to each calibration procedure are provided in section 6.2.1.B.
- ⁴ Optionally, a few crystals of cobalt chloride (CoCl₂) can be added to the solution as a catalyst in order to speed up the reaction; however, routine USGS field operations omit the addition of CoCl₂, as it is a toxic substance, is regulated for proper disposal, and is not a necessary component to achieve a solution of the zero DO. If CoCl₂ will be used, personnel are advised to check the Material Safety Data Sheet for proper handling and disposal of the solution.

⁵Take special note of the manufacturer's guidance as applicable to your sensor. Some manufacturers supply the zero-DO solution required or document the specific instructions for preparing the zero-DO solution recommended for their sensors, including an alternative by which nitrogen gas is forced into tap or deionized water to produce a zero-DO solution (consult with the manufacturer's division of technical support).

Field trip preparations

The service performed on all equipment, whether a full calibration, calibration check, or replacement or repair of parts for the instrument, and whether performed in the office, laboratory, or field, must be accurately recorded and dated in the log book using black or blue non-erasable ink.

Field-measurement instruments are to be maintained on a regular schedule and performance-tested before field deployment, as described below:

- 1. Check all electrical connections and the charge on the batteries, as applicable for the instrument in use.
- 2. Thermistors/thermometers must be calibrated and field checked before use, as described in NFM 6.1 ("Temperature").

- 3. Perform a 100-percent saturation calibration check (see section 6.2.1.B). This performance check does not negate the need for onsite sensor calibration at oxygen saturation.
- 4. Perform a zero-DO sensor-performance check.
 - a. Prepare the zero-DO sodium sulfite solution (see table 6.2–1).
 - b. Before immersing sensor in the zero-DO solution, it is imperative to **remove the wiper** (or sponge) from the unit to avoid saturating it with the sodium sulfite solution. (Not all instruments have a DO sensor wiper.)
 - c. Rinse sensor and wiper thoroughly and then reinstall wiper elements. Multiple and thorough rinses with deionized water are necessary to restore the sensor to proper operating condition and prevent bias to subsequent measurements.
- 5. Review the care and maintenance guidance provided by the manufacturer for the specific sensor being used; instructions can differ appreciably depending on the instrument type, make, and model.
 - a. **Optical DO-sensor instrument:** Check the condition and (or) deployment history of the luminophore-containing sensor module, referring to the manufacturer's guidance for replacement of the luminophore module.
 - Depending on the instrument, sensor modules are replaced annually or at least every 2 years, even if the probe is idle.
 - If the instrument reading exceeds 0.2 mg/L in the zero-DO solution, check DO again with a freshly prepared zero-DO solution; if a greater than 0.2 mg/L reading persists, contact the instrument manufacturer and inquire if the luminophore module should be replaced.

b. Amperometric instrument:

- Inspect the instrument closely, checking for loose, wrinkled, or torn membrane; air bubbles beneath the membrane; a loose O-ring, and a tarnished or discolored cathode or anode. If any of these problems are detected, do not use the sensor until it has been serviced according to the manufacturer's guidance.
- If the instrument reading exceeds 0.2 mg/L in the zero-DO solution, check DO again with a freshly prepared zero-DO solution; if a greater than 0.2 mg/L reading persists, replace the sensor membrane and electrolyte (if present) or repair.
- **Membrane type** Consult manufacturer recommendations to select a sensor membrane of the thickness required for the field operation. (Only one membrane thickness is available for some amperometric sensor makes or models.)
- **Membrane replacement** After replacing, the new membrane should be allowed to condition over a given period of time before sensor calibration and deployment.
 - Depending on the manufacturer and whether replacement involves using the O-ring or membrane-cap method, conditioning time depends on the type of membrane. Conditioning of membranes with O-rings, for example, generally ranges from a minimum of 2 hours up to 6 hours. For greater stability during calibration, allow the new membrane to condition overnight before calibration and use.
 - Membranes in caps are prestretched and require less conditioning.

- For continuous monitoring applications with field-replaceable sensors, either condition
 the replacement sensor before the site visit, or replace the sonde with a second, clean and
 calibrated sonde and perform maintenance of the replaced sonde at the office.
- When the sonde is deployed for discrete measurement, and conditions necessitate use of a new membrane before the recommended overnight conditioning time, more frequent calibration checks and possibly recalibration may be needed to ensure accurate DO measurements.⁴ This is not recommended for continuous monitoring applications.
- 6. Remember to document field preparations and all instrument tests and adjustments in the meter log book. **Do not use an instrument that fails calibration.**

CAUTION:

Before handling sodium sulfite, cobalt chloride, or any other chemicals, refer to safety precautions on the Material Safety Data Sheet (MSDS) for that chemical.

6.2.1.B Calibration of Optical and Amperometric Sensors

Sensor-based instrument systems used to determine DO in water must be calibrated properly before being deployed. Proper calibration procedures are necessary to ensure the overall accuracy and precision of DO measurements. Amperometric sensors are more likely to require frequent calibration than optical sensors. While equipment manufacturers advise performing the calibration in the office laboratory before going onsite, USGS protocols call for onsite calibration checks and possible recalibration at the field site, as necessary to meet the specific data-quality requirements of the project.

The accuracy required by the project for sites at which DO will be determined and the capabilities of the selected instrument will govern whether a one-point calibration will be sufficient or a two-point calibration should be used. In addition, some manufacturers of the DO equipment commonly used for USGS data-collection efforts recommend testing of the equipment in a laboratory setting to determine the accuracy of room-temperature calibrations compared with measurements made under the anticipated warmer or colder field conditions. Project personnel are advised to be familiar with recommendations from the manufacturer of their equipment.

- ▶ One-point calibration. The main goal of the one-point calibration procedure is to create a 100-percent saturated oxygen environment where the DO sensor (optical or amperometric) and its regulating thermistor are at the same temperature. Amperometric sensors used in multiparameter instruments, for the most part, are capable of only a one-point calibration).⁵
 - **Procedure 1** (Air calibration chamber in air)
 - **Procedure 2** (Calibration with air-saturated water)
 - **Procedure 3** (Air calibration with a wet towel)

⁴ One sensor manufacturer recommends running the DO sensor for at least 15 minutes after a membrane change or if the electrodes were reconditioned. Check the manual or handbook of your instrument for corroboration.

⁵ The "Professional Plus" multiparameter instrument (YSI Incorporated) with amperometric sensor can be calibrated at zero DO and 100 percent saturation. Other such instruments also may be in production.

- **Procedure 4** (Air calibration chamber in water). Unlike Procedures 1, 2, and 3, this procedure currently is applied to amperomeric instrument systems only. The potential applicability of this procedure to calibration of optical sensors is a topic of discussion and review that can be followed in the chapter 6 section of the NFM Comments and Errata page (http://water.usgs.gov/owq/FieldManual/mastererrata.html).
- ▶ Two-point calibration (for optical sensors). The two-point calibration typically involves calibration of the sensor at 100 percent saturation, followed by calibration at zero DO. Only specific makes and models of optical DO sensors have the capacity to be calibrated to two points. The two-point calibration adds complexity to the calibration process and is not recommended by all manufacturers of optical sensors. Be sure first to understand the instrument capabilities and then determine the best course of action for your field work.
 - For routine applications, it is advisable to rely on a zero-DO performance check rather than a zero-DO recalibration, which would risk corrupting the manufacturer's zero-DO calibration.
 - Use of a two-point calibration should be considered if (a) the calibration is needed to satisfy the data-quality objectives of the project, (b) oxygen concentrations of less than 1 mg/L are likely to be encountered and zero-DO performance tests fail at this concentration level, or (c) the calibration is deemed necessary by experienced field personnel knowledgeable of site conditions.
 - Before starting or planning for a two-point calibration, it is advisable to consult the manufacturer's instructions or technical support for the specific optical DO sensor being used.
 - If using a two-point DO calibration, calibrate the DO sensor only after calibrating other field-measurement sensors to prevent possible interference of the sodium sulfite (zero-DO) solution with the calibration of the other sensors. Complete the DO calibration at 100 percent saturation before the zero calibration.
- ▶ **Sensor-performance checks.** Verifying sensor performance (calibration checks) is a required standard procedure in USGS field operations (*see* section 6.2.1.A)
 - All DO sensors have the capability to undergo a performance check at zero DO as well as at saturation.⁷
 - Verifying instrument performance at zero DO and using the two-point calibration can be particularly important for data accuracy when the instrument will be used to measure low DO concentrations (for example, DO less than 5 mg/L).

Do not use an instrument that fails to calibrate properly.

⁶ Although optical instruments undergo zero-calibration procedures by the manufacturer, the accuracy of factory calibrations may not satisfy the data-quality objectives of some USGS field studies.

⁷ It should be underscored that manufacturers uniformly caution against zero recalibration of sensors but allow for zero DO checks, stipulating the need to thoroughly rinse the zero-solution from the sensor.

Correction for Atmospheric Pressure and Salinity

Calibration procedures include corrections for atmospheric pressure and ionic strength (ionic strength is estimated from the conductivity or salinity measurement for routine field applications). Atmospheric pressure, the temperature of the water or water vapor, and the ionic strength (estimated by conductivity or salinity) of the water must be known to determine the theoretical amount of oxygen that can be dissolved in water. **Record all calibration information in instrument log books and copy calibration data onto field forms at the time of calibration.**

TECHNICAL NOTE 3. DO sensors do not actually measure oxygen in milligrams per liter or parts per million. Both of these expressed concentrations are based on calculations that relate instrument reading with the temperature and salinity of the sample water. The actual sensor measurement is proportional to the ambient partial pressure of oxygen, which can be displayed either as percent saturation or in milligrams per liter, depending on user input.

Ambient atmospheric pressure is true atmospheric pressure at the measurement site, not that which has been adjusted to sea level. Atmospheric pressure reported by the National Weather Service generally is not the true (ambient) value. National Weather Service atmospheric readings usually are adjusted to sea level and must be adjusted back to the elevation of the weather station. Upon request, a weather station may provide ambient atmospheric pressure.

- ▶ Determine the ambient atmospheric pressure to the nearest 1 millimeter (mm) of mercury. A calibrated pocket altimeter-barometer typically has been used to determine atmospheric pressure; however, many instruments that now are in common use include an internal barometer.
- ► Check the accuracy of all field barometers before each field trip (including barometers built into instrument systems) and record readings and adjustments in the instrument log book. If possible, check barometer accuracy while at an official weather station. If this is not an option, adjust the official weather station barometric pressure to the elevation at the field site at which the barometer reading is being recorded.
- ► To correct weather-station readings adjusted to sea level to ambient atmospheric pressure: subtract appropriate values shown (table 6.2–2, fig. 6.2–1) from atmospheric readings adjusted to sea level (shown in millimeters of mercury).

Although atmospheric pressure does not decrease linearly with increases in elevation, linear interpolation is acceptable within the elevation ranges given in table 6.2–2. Alternatively, plot the values from table 6.2–2 and extrapolate subtraction factors directly from the graph (fig. 6.2–1). Section 6.2.5 contains the table of oxygen solubility at various temperatures and pressures.

Most modern multiparameter instruments (see NFM 6.8) incorporate a pressure-temperature and salinity compensation algorithm in their firmware for DO measurements; the instruments have a built-in conductivity sensor that corrects the DO-concentration (in milligrams per liter) data for salinity automatically. For instruments that are not equipped with a conductivity/specific conductance (SC) sensor, a manual salinity correction of the DO data would be required.

▶ If a user-specified salinity correction is needed, the preferred USGS method is to apply salinity correction factors after calibrating and measuring DO concentration of the environmental water body (see section 6.2.5). Interactive tables are available for user-specified temperature, pressure, and salinity at http://water.usgs.gov/software/DOTABLES/.

▶ When a manual salinity correction is made by the user during calibration, the instrument requires recalibration for each field variation in salinity (see section 6.2.5).

TAKE NOTE: If using a multiparameter sonde that includes a calibrated conductivity sensor, salinity corrections to the DO concentration reading (in mg/L) are performed automatically in the sonde; that is, the DO sensor communicates with the SC sensor.

Table 6.2–2. Factors used to correct reported atmospheric pressures that have been adjusted to sea level. [NGVD, National Geodetic Vertical Datum of 1929]

Elevation of weather station (in feet, NGVD)	Value to subtract (millimeters of mercury)
0	0
1,000	27
2,000	53
3,000	79
4,000	104
5,000	128
6,000	151

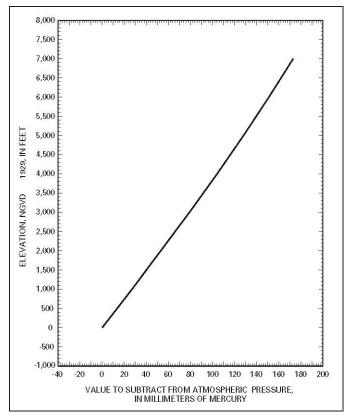


Figure 6.2–1. Factors used to correct reported atmospheric pressures that have been adjusted to sea level. NGVD 1929, National Geodetic Vertical Datum 1929.

Selection of Calibration Method

A saturated-oxygen calibration of DO sensors is recommended uniformly by manufacturers, regardless of which of the following methods is used: Air Calibration Chamber in Air (Procedure 1), Calibration in Air-Saturated Water (Procedure 2), or Air Calibration with a Wet Towel (Procedure 3). With minor modifications, these procedures can be applied to a one-point calibration of either luminescent-sensor (optical) or amperometric instruments (not all instruments allow or can accommodate a two-point calibration). A fourth method, Air Calibration Chamber in Water (Procedure 4), is described in the section on calibration for amperometric sensors. Although Procedure 4 has, in some cases, been applied when calibrating optical sensors, the pressure differentials and aqueous vapor properties at various temperatures experienced at the field site increases the potential for undetected water droplets on the thermistor and luminophore membrane and the risk for larger measurement error compared with the other calibration methods described below. It is important to refer to the manufacturer-provided guidance, as each of the procedures has inherent advantages and disadvantages and may include instrument-specific sources of error.

- ▶ The saturated-water method (Procedure 2) tends to be favored by manufacturers for calibrations in an office laboratory because it ensures equilibration of the temperature sensor with the DO amperometric membrane or the optical luminescence-coated sensor. Procedure 2 is considered to provide the best accuracy for calibration of optical sensors.
- ▶ The air calibration with a wet towel method (Procedure 3) is performed at the field site and is the method recommended most commonly by manufacturers for calibrating the amperometric (Clark cell) sensor, given advances in instrument technology. While the Wet Towel method can be used in the calibration of optical as well as amperometric sensors, the Air Calibration Chamber in Water method is applicable to amperometric sensors only. In previous versions of this field manual, the Air Calibration Chamber in Water (Procedure 4) method was published as "Procedure 3."
- Check DO meter calibration at each field site.
- Calibration of amperometric sensors should be checked each time after an instrument has been powered off and recalibrated, as necessary.

Optical (Luminescence) DO Sensors: Calibration Procedures

The introduction of luminescence technology to DO field instruments has improved and simplified the data-collection process for field determination of DO. In addition to being more rugged, having fewer interferences, and undergoing decreased calibration drift relative to amperometric sensors, optical DO sensors tend to be more accurate, with accuracy specifications of ± 0.1 mg/L or 1 percent after calibration.⁸ This level of accuracy is best achieved by calibrating under controlled conditions in a laboratory or simulated laboratory environment.

⁸ USGS field scientists have corroborated the accuracy of the optical sensor to 0.05 mg/L DO by using repeated comparisons of results with the Rhodazine-D spectrophotometric method described in section 6.2.2 of this field manual (Gerolamo Casile, U.S. Geological Survey, written commun., 2012). These results can be entered into the USGS NWIS database.

TECHNICAL NOTE 4. Optical DO sensors often contain internal calibration information from the manufacturer. Although some manufacturers advise that no further calibration is warranted, the accuracy of factory calibrations do not necessarily satisfy the data-quality objectives required for USGS applications. Because the validity of a calibration can substantially affect the overall accuracy and precision of DO measurements, users are advised to check the calibration frequently in order to meet specific data-quality objectives.

- ▶ Because the optical DO sensors are not subject to drift, shock, or temperature extremes, the office-performed calibration is likely to remain stable after transport to the field; nevertheless, calibrations must be verified at the field site.⁹
- ▶ The Rhodazine-D spectrophotometric and iodometric methods for DO measurement described in sections 6.2.2 and 6.2.3, respectively, have been used to check the calibration of these instruments (see footnote 8).
- ▶ All calibration information is to be recorded in instrument-specific log books and the calibration data copied onto field forms at the time of calibration. Some instruments produce calibration reports generated by manufacturer-specific firmware; such reports that can be downloaded should be reviewed and incorporated in the instrument log book.
- ▶ Procedure 1 (air calibration chamber in air), Procedure 2 (calibration with air-saturated water) and Procedure 3 (air calibration with a wet towel) are described below for calibration of optical sensors at 100 percent saturation.
 - Refer to the NFM Comments and Errata, chapter 6, for the potential applicability of the "air calibration chamber in water" method to calibration of optical sensors (http://water.usgs.gov/owq/FieldManual/mastererrata.html).
 - A description of the "air calibration chamber in water" method is given below as Procedure 4 in the section titled "Amperometric (Clark cell) DO Sensors: Calibration procedures".

Procedure 1: Air calibration chamber in air

This procedure (which is similar to Procedure 3) is commonly used for calibrating **handheld** optical DO instruments. Calibration chambers either are built into the instrument case or are provided as separate components by the manufacturer. Use the calibration chamber that is provided or recommended by the manufacturer.

- 1. Wet the inside of the calibration chamber with water and then pour out the water, leaving a few drops.
 - a. Remove any water droplets on the temperature and optical sensors.
 - b. Insert the sensor into the chamber (this ensures 100 percent humidity).
 - If using a screw-on calibration cup, make sure it is loose and not making an airtight seal in order to maintain ambient pressure.
 - Keep the calibration assembly in a stable temperature environment and out of direct sunlight.

⁹ Laboratory calibration is favored by manufacturers in general, who advise that DO instruments rarely should require recalibration in the field.

- 2. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the calibration chamber to equilibrate. If appropriate for the instrument being used, run the instrument during the equilibration period.
- 3. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.
- 4. Monitor the temperature and DO outputs in the calibration chamber, observing readings until the instrument readings stabilize. Read the temperature to the nearest 0.1 °C.

TECHNICAL NOTE 5. To maximize accuracy, a recommended practice is to maintain or approximate air temperatures during calibration that are within 10 °C of the ambient temperature of the water to be measured (see Procedure 3 – Wet Towel Method).

- 5. If calibrating to a given DO concentration rather than calibrating to a condition of 100 percent saturation, use table 6.2–6 or the online software DOTABLES (http://water.usgs.gov/software/DOTABLES/) to determine DO saturation at the calibration temperature and atmospheric pressure.
- 6. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
 - If using an instrument that allows calibration simply to a 100-percent saturation condition, all that may be needed is to provide the ambient atmospheric pressure for the instrument to determine (with internal software) the resulting DO concentration.
- 7. Verify that the instrument reading is within ± 0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study.
- 8. Remove the sensor from the calibration chamber to check if water droplets were on the optical tip or membrane during calibration; water droplets on the sensor tip or membrane and on the temperature sensor can cause improper calibration.
 - Recalibrate the instrument if water droplets were present.
 - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
- 9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

During saturated-air calibration, it is necessary to keep water droplets off of the optical sensor module (luminescence tip or membrane) and temperature probe.

Procedure 2: Calibration with air-saturated water

This procedure, in which the DO sensor or instrument system is calibrated in water that is saturated with oxygen at a known temperature and ambient atmospheric pressure, generally is preferred by manufacturers for optical-sensor calibration. ¹⁰ Procedure 2 is considered the most accurate for optical measurements of DO because the saturated water ensures that all equipment parts equilibrate with water temperature simultaneously, and the method eliminates the need to check for water droplets on the optical tip/membrane or temperature sensor. Great care is required, however, to ensure that the water is indeed saturated with oxygen.

E	quipment: Calibration with Air-Saturated Water
1	5-gallon bucket or manufacturer-provided aeration chamber
1	10-gallon-aquarium air pump with two outlets
1	10-foot-length of aquarium pump tubing
2	Gas-diffusion (air) stones

For this procedure, producing aerated water under controlled laboratory conditions is preferred; calibrate the DO sensor in the office laboratory before departing for the field site (step 4a below).

- 1. In the laboratory, fill a 5-gallon bucket to three-quarters full with tap water.
- 2. Attach the pump tubing to the pump and then the two air stones to the ends of the tubing. Place the tubing with air stones at the bottom of the filled bucket.
- 3. Turn on the pump and aerate the water for a minimum of 30 minutes.¹¹ **Tip:** The pump could be left to operate continuously (24/7) in order to have a ready supply of air-saturated water on hand for calibration in the laboratory or for transport and calibration in the field.
- 4. **Calibration**—Take care to keep air bubbles off of the optical sensor (the luminescence tip or membrane).
 - a. For laboratory calibration, place the DO sensor (or multiparameter sonde) in the bucket and allow 5 to 10 minutes for the sensor to come to thermal equilibrium with the aerated water. Take care not to place the sensor over or in the bubbles from the air stone!
 - b. For field calibration of a handheld DO sensor:
 - Fill a 1-gallon (approximately 4-liter) container to three-quarters full with the laboratory-aerated water for transport to the field. In the field vehicle, shake the container vigorously for 2 minutes to fully aerate the water and immerse the DO sensor. Allow about 5 minutes for the sensor to come to thermal equilibrium with the aerated water.
 - Alternatively, use the Wet Towel Method (Procedure 3).
- 5. Read and record the temperature of the calibration water to the nearest 0.1 °C.

¹⁰ Some manufacturers provide the necessary aeration equipment with the instrument.

¹¹ Previous versions of this procedure described in this field manual specified that a sensor or sonde be immersed in the water while the water is being aerated with a battery-operated aquarium pump. Owing to uncertainties in pump quality, battery power, and possible supersaturation, this technique is not universally recommended by the manufacturers who reviewed this protocol and has been modified accordingly. If the former procedure is used, it is imperative to avoid placing the sensor in the stream of air bubbles.

- 6. Using a calibration-checked altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
- 7. Using oxygen-solubility table 6.2–6 or the online software DOTABLES (http://water.usgs.gov/software/DOTABLES/), determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)
- 8. Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value. Alternatively, use more stringent accuracy criteria that reflect the data-quality requirements of the study. If the field calibration or calibration check fails to meet the established criterion, (a) use a different instrument (if available), and (b) do not collect or report data using an instrument that has failed calibration.
- 9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

For accurate calibration, ensure that the water is 100 percent saturated with oxygen (see step 4b above).

Procedure 3: Air calibration with a wet towel

For many multiparameter instruments a 100-percent humidity environment can be created by wrapping a moist towel around the sensor guard and inserting into a plastic bag. The Wet Towel Method is almost identical to Procedure 1, the main difference being that the sensor (or sonde) guard will be wrapped in a wet towel instead of being inserted into a calibration cup or chamber.

	Equipment: Calibration with a Wet Towel
1	Towel, sized so that it will wrap around the sensor at least two full wraps
1	Trash bag, clear or white plastic

- 1. Bring sensor to thermal equilibrium.
 - a. If attempting to match the temperature of the water being monitored (for example, stream, lake, or groundwater), place the sensor directly in the water body (alternatively, for groundwater, into a flowthrough cell through which well water is being pumped continually).
 - b. Allow 5 to 10 minutes for thermal equilibration of the sensor with ambient water temperature until temperature readings have stabilized.
- 2. Once temperature readings are stable, soak the towel either (a) in the water for DO measurement, or (b) with tap or deionized water.

- 3. Remove the towel, wring it out, and then wrap the wet towel completely around the sensor guard, cup, or chamber, two full wraps or more.
 - As you wrap the sensor, ensure that no water droplets are either on the temperature sensor or on the luminescent sensor (sensor tip or membrane).
 - Place the wrapped sensor into the plastic bag and keep it out of direct sunlight in order to keep the temperature from changing.
- 4. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the towel (calibration chamber) to equilibrate. Run the instrument during the equilibration period, if so directed by manufacturer instructions.
- 5. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.
- 6. Monitor the temperature and DO outputs and observe readings until the instrument stabilizes. Read the temperature to the nearest 0.1 °C.
- 7. If calibrating to a DO concentration rather than to 100 percent saturation, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (http://water.usgs.gov/software/DOTABLES/) to determine the DO saturation concentration at the measured temperature and atmospheric pressure.
- 8. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
 - If using an instrument that allows calibration only to 100 percent saturation, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
 - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study.
- 9. Remove the sensor from the towel and check if any water droplets were on the membrane. Water droplets on the membrane and temperature probe can cause improper calibration.
 - Recalibrate the instrument if water droplets are observed.
 - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
- 10. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Amperometric (Clark cell) Do Sensors: Calibration Procedures

The calibration and operation of amperometric instruments differ among instrument types, makes, and models—refer to the instrument manual provided by the manufacturer. Calibration for amperometric sensors typically is performed using one of the following procedures for a one-point calibration at 100 percent saturation:

- ► Procedure 1 (Air Calibration Chamber in Air)
- ► Procedure 2 (Calibration with Air-Saturated Water)
- ► Procedure 3 (Air Calibration with Wet Towel)
- ► Procedure 4 (Air Calibration Chamber in Water)

Manufacturers recommend different calibration frequencies for membrane-electrode (amperometric) DO meters. Depending on equipment capabilities, instrument performance and data quality can be enhanced by checking sensor performance; that is, making calibration checks as frequently as needed or as directed by project protocols. Sensor manufacturers generally agree that optimum performance and data quality will be obtained by frequent calibration and performance checks. Sensor performance checks at zero DO are implemented routinely by trained USGS field personnel (see section 6.2.1.B).

Tip: Many amperometric DO sensors require the meter to be powered on for 10 to 15 minutes before calibration (and use) to stabilize the probe. Refer to the manufacturer's instrument-specific guidelines for the requirements of your instrument.

Procedure 1: Air calibration chamber in air

This procedure, similar to Procedure 3, is the most commonly used method for amperometric instruments. Calibration chambers are either built into the instrument case or are provided as separate components by the manufacturer. Use the calibration chamber provided or recommended by the manufacturer.

- 1. Wet the inside of the calibration chamber with water, then pour out the water (but leave a few drops).
- 2. Remove any water droplets on the sensor membrane and temperature sensor, then insert the sensor into the chamber (this ensures 100 percent humidity).
 - If using a screw-on calibration cup, ensure it is loose (not making an airtight seal) to avoid causing a change in the pressure around the sensor compared to the onsite barometric pressure. Alternatively, consider using the Wet Towel Method (Procedure 3).
 - Be sure to keep the DO assembly in a stable temperature environment and out of direct sunlight, as applicable for the instrument in use.
- 3. Allow 10 to 15 minutes for the air to saturate and for the DO sensor and the air inside the calibration chamber to equilibrate. Apply power to the instrument during the equilibration period, as applicable for the instrument in use
- 4. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.

5. Monitor the temperature and DO outputs in the calibration chamber and observe readings until the instrument stabilizes. Read the air temperature in the chamber to the nearest 0.1 °C. To the degree possible, the temperature in the chamber should approximate the temperature of the water body in which DO will be determined within about 10 °C.

TECHNICAL NOTE 6. Most instrument manufacturers recommend calibrating at temperatures that are at least within 10 °C of the ambient water temperature. The most accurate calibration will be achieved if the temperature difference between the environmental water and the calibration chamber is minimized as much as possible (see Procedure 3, the Wet Towel Method, for additional information). In addition, the manufacturers of DO equipment that currently (2013) is in common use for USGS data-collection efforts advise testing the equipment in a laboratory setting to determine the accuracy of room-temperature calibrations compared with measurements made under the anticipated warmer or colder field conditions.

- 6. If calibrating to a DO concentration rather than to a 100-percent saturation condition, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (http://water.usgs.gov/software/DOTABLES/) to determine the DO saturation value at the measured temperature and atmospheric pressure.
- 7. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
 - If using an instrument that allows calibration simply to a 100-percent saturation condition, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
 - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study. If the criteria are not met, repeat the calibration procedure after checking for water droplets in step 2 above.
- 8. Remove the sensor from the calibration chamber and again check for water droplets on the membrane. Water droplets on the membrane and temperature sensor can cause improper calibration.
 - Recalibrate the instrument if water droplets are observed.
 - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
- 9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Procedure 2: Calibration with air-saturated water

In this procedure, the DO sensor or instrument system is calibrated in water that is saturated with oxygen at a known temperature and ambient atmospheric pressure. Manufacturers advise that the calibration with air-saturated water is best done in the laboratory under controlled conditions.¹²

	Equipment: Calibration with Air-Saturated Water
1	5-gallon bucket or manufacturer-provided aeration chamber
1	10-gallon-aquarium air pump with two outlets
1	10-foot-length of aquarium pump tubing
2	Gas-diffusion (air) stones

- 1. In the laboratory, fill the 5-gallon bucket about three-quarters full with tap water.
- 2. Using two air stones, saturate the water for at least 30 minutes before use. However, some manufacturers recommend that the pump be left on continuously (24/7) so that the water is always saturated and ready to use.
- 3. Place the DO sensor in the water, avoiding contact with the bubble stream, and allow the sensor to come to thermal equilibrium.
- 4. Read the temperature of the calibration water to the nearest 0.1 °C.
- 5. Using a calibration-checked altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
- 6. Move the sensor so as to ensure a 1 foot per second (ft/s) flow across the membrane; alternatively, use a sensor that is equipped with a stirrer. Ensure that sufficient flow passes over the DO sensor during the saturated-water calibration method as well as when making a field measurement.
 - Move the sensor to stir the water, using either a horizontal stirring motion or a "teabag" dipping motion. Take care not to remove the sensor from the water.
 - The DO reading may rise as the water is stirred.
 - After the DO reading has peaked and is stable, start to calibrate the DO sensor.
 - Maintain this flow rate while monitoring measurements and adjusting the instrument calibration.

TECHNICAL NOTE 7. The various types of amperometric sensors can have different levels of flow dependency; however, the 1 ft/s flow is not detrimental to sensors with little or no flow dependence.

7. Using the oxygen-solubility table 6.2–6 or the online software DOTABLES (http://water.usgs.gov/software/DOTABLES/), determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)

¹² Field calibrations with battery-powered pumps are not recommended by manufacturers who reviewed this report (see footnote 11). Trained USGS field personnel have, however, demonstrated success using Procedure 2 in the field.

- 8. Verify that the instrument reading is within ± 0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality objectives of the study.
 - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
- 9. Record calibration information in instrument log books and transfer the calibration data into electronic records or onto paper field forms at the time of calibration.

For accurate calibration, ensure that the water is 100 percent saturated with oxygen.

Procedure 3: Calibration with a Wet Towel

This method is almost identical to Procedure 1, the main difference being that the sensor (or sonde) guard will be wrapped in a wet towel instead of being inserted into a calibration cup or chamber.

	Equipment: Wet-Towel Calibration
1	Towel, sized so that it will wrap around the sensor at least two full wraps
1	Trash bag, clear or white plastic

- 1. Bring the sensor to thermal equilibrium.
 - If attempting to match the temperature of the water being monitored (for example, stream, lake, or groundwater), place the sensor directly in the water body (alternatively, for groundwater, into a flowthrough cell through which well water is being pumped continually).
 - Allow 5 to 10 minutes for thermal equilibration of the sensor with the ambient water temperature until temperature readings have stabilized.
- 2. Once temperature readings are stable, soak the towel either (a) in the environmental water for DO measurement, or (b) with tap or deionized water.
- 3. Remove the towel, wring it out, and wrap the wet towel completely around the sensor guard, cup, or chamber, two full wraps or more.
 - As you wrap the sensor, ensure that no water droplets are either on the temperature sensor or on the sensor tip or membrane.
 - Place the wrapped sensor into the plastic bag and **keep it out of direct sunlight** to keep the temperature from changing.
- 4. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the towel (calibration chamber) to equilibrate. Run the instrument during the equilibration period, if so directed by manufacturer instructions.
- 5. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure to the nearest 1 mm of mercury.
- 6. Monitor the temperature and DO outputs and observe readings until the instrument stabilizes. Read the temperature to the nearest 0.1 °C.

- 7. If calibrating to a specific DO concentration rather than to 100 percent saturation, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (http://water.usgs.gov/software/DOTABLES/) to determine the DO saturation value at the measured temperature and atmospheric pressure.
- 8. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
 - If using an instrument that allows calibration to 100 percent saturation, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
 - Verify that the instrument reading is within ± 0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study or program.
- 9. Remove the sensor from the towel and check if any water droplets are on the membrane. Water droplets on the membrane or temperature sensor can cause improper calibration.
 - Recalibrate the instrument if water droplets are observed.
 - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
- 10. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Water droplets on the DO membrane and thermistor will result in improper calibration. Recalibration is required if water droplets are observed.

Procedure 4: Air calibration chamber in water

A specialized air-calibration chamber permits calibration of the DO sensor at the temperature of the water in which DO concentration is to be measured. This calibration procedure minimizes errors caused by temperature differences; for example, at sites having field conditions with a wide disparity between ambient air and water temperature. For many multiparameter water-quality instruments, the manufacturer-provided groundwater flow cell may be modified and used as an air calibration chamber in water. The modification requires the cell to be mounted on the sonde with one port of the cell tightly plugged and the other port vented to the atmosphere with tubing. The method is subject to large errors, especially in cold temperatures, if the port is not adequately vented to the environment. **Before using this method, check with the manufacturer for its applicability to the instrument to be used**.

- 1. Insert the sensor probe and calibration chamber into the surface water or groundwater to be measured. Once the temperature readings stabilize (allow 10 to 15 minutes), remove the sensors and calibration chamber from the water to be measured. Empty the calibration chamber, leaving a few drops of water.
 - Check for and remove any water droplets on the sensor membrane and the thermistor.
 - Insert the DO sensor into the wet chamber (this ensures 100 percent humidity).

¹³ Air calibration chambers for in-water calibrations no longer are available on the open market (for example, the YSI 5075A calibration chamber is no longer manufactured).

- Check that the port is adequately vented, that no water can leak into the calibration chamber, and that droplets of water are not adhering to the membrane and thermistor. The water droplets reduce the rate of oxygen diffusion through a membrane, producing erroneous results.
- 2. Immerse the calibration chamber into the water to be measured. Allow 10 to 15 minutes for the air temperature inside the chamber to equilibrate with the water (see TECHNICAL NOTE 6 in Procedure 1).
 - For streams, choose an area of the stream that closely approximates mean stream temperature. In shallow streams, try to place the chamber in an area that represents the stream but that is shaded from direct sunlight.
 - For groundwater, use temperature-stabilized purge water or other clean water having a temperature that closely approximates that of the groundwater.
- 3. Using a calibration-checked pocket altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
- 4. Read the temperature within the chamber to the nearest 0.1 °C, using a calibrated thermometer (NFM 6.1).
 - The temperature inside the chamber should approximate the water temperature.
 - If the two temperatures do not match, allow additional time for equilibration of the chamber with the water temperature.
 - If the temperature of the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Compare water temperature measured by the DO meter and a calibrated field thermometer. If the two measurements vary by more than ± 0.5 °C, the calibration should be discontinued and the DO meter thermistor should be repaired following the manufacturer's recommendations.
- 5. Use table 6.2–6 (section 6.2.5) to determine the DO saturation value at the measured water temperature and atmospheric pressure. If a salinity correction will be applied during calibration, consult the instructions in section 6.2.5 and table 6.2–7.
- 6. Following the manufacturer's instructions, set or adjust the calibration control until the instrument reads a DO saturation value determined from oxygen solubility (table 6.2–6).
 - Verify that the instrument reading is within ±0.2 mg/L of the computed saturation value, or use more stringent accuracy criteria per the data-quality objectives of the study.
 - Verify that no water droplets are on the membrane or thermistor. **Recalibrate the instrument if** water droplets are observed.
 - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
 - Remove the sensor from the calibration chamber for cleaning and storage.
- 7. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Water droplets on the DO membrane and thermistor will result in improper calibration. Recalibration is required if water droplets are observed.

6.2.1.C Measurement

The solubility of oxygen in water depends on the partial pressure of oxygen in air, the temperature of the water, and the content of dissolved solids in the water.

- ► The higher the atmospheric pressure and the lower the temperature and conductivity, the more oxygen can be dissolved in the water.
- ▶ Degassing, mineral precipitation, and other chemical, physical, and biological reactions can cause the DO concentration of a water sample to change substantially within minutes after sample collection. These sample reactions are especially important when sampling groundwater that is not in equilibrium with the atmosphere.

The solubility of oxygen in water decreases as salinity increases. Correction factors for salinity normally are applied after measuring DO for single-point samples; however, for continuously deployed DO probes on multiparameter instruments that include calibrated specific-conductance sensors, it is wise to activate the instrument's internal salinity correction algorithms to account for a dynamically changing environment. Information that pertains to oxygen solubility and salinity is given in section 6.2.5, including the link to an on-line program that generates tables of DO solubility values and (or) salinity correction factors over a range of user-specified temperature, pressure, and salinity or specific conductance (http://water.usgs.gov/software/DOTABLES/accessed March 11, 2013).

Surface water

Standard determinations of DO in riverine surface water represent the cross-sectional median or mean concentration of dissolved oxygen at the time of observation.

- ▶ Multiparameter instruments (sondes) are in common use for USGS measurement of DO and other field properties, both for in situ discrete measurements in surface water and for short- or long-term deployment in streams, lakes and reservoirs, and other bodies of surface water. Refer to NFM 6.8, Wagner and others (2006), and manufacturer guidance for additional information regarding the siting and use of multiparameter instruments.
- ▶ Measuring the DO concentration at one distinct point in a cross section is valid only for flowing water with a cross-sectional DO variation of less than 0.5 mg/L. Discerning such variation requires a reconnaissance cross-section measurement. Measurements made at multiple locations in the cross section are recommended as a routine practice, when possible.
- ▶ Determining DO concentration for a single channel at the centroid of flow at the midpoint of the vertical only represents the cross section under ideal mixing conditions.
- ▶ Do not measure DO in or directly below sections with turbulent flow, in still water, or from the bank, unless these conditions represent most of the reach or are required to fulfill study objectives.
- ▶ Verify whether or not the instrument in use applies salinity corrections automatically. If not, apply a salinity correction to the saturation values after the DO measurement, referring to section 6.2.5 and table 6.2–7.

Dissolved oxygen must be measured in situ. Never measure DO in subsamples from a sample splitter or other vessel.

Follow the steps below to measure DO in surface water:

- 1. Calibration checks:
 - Check that the thermistor is accurate and that its calibration has been certified by the USGS Water Science Center within the past 12 months; more frequent calibration checks are performed in the field, depending on the field conditions encountered (see NFM 6.1.2.B for specifics).
 - Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).
 - If a calibration adjustment is necessary or if it is required to address program protocols, dataquality requirements, or site-specific conditions, calibrate the DO sensor onsite, in accordance with the procedures described in section 6.2.1.B.
- 2. Examine the variation in DO measured at multiple locations along the cross section (if this reconnaissance step was performed) to help select the sampling method (NFM 6.0):
 - Flowing, shallow stream—Wade to the location(s) where DO is to be measured.
 - **Stream too deep or swift to wade**—Lower a weighted DO sensor with a calibrated temperature sensor from a bridge, cableway, or boat.
 - Do not attach the weight directly to the sensors or sensor cables, because this could damage the sensors or sensor cables.
 - To avoid damaging sensors or cables, contact the instrument manufacturer or vendor for information regarding the weights approved for use with the instrument and how to attach them.
 - **Still-water conditions**—Measure DO at multiple depths at several points in the cross section (see TECHNICAL NOTE 8).
 - Lakes and reservoirs—Measure DO at a series of specific depths to determine a vertical profile at each location of interest (see TECHNICAL NOTE 8).

TECHNICAL NOTE 8. For amperometric sensors: If the water velocity at the point of measurement is less than about 1 ft/s, use a stirring device to increase the flow velocity.¹⁴

- To hand stir, raise and lower the sensor at a rate of about 1 ft/s, but do not break the surface of the water. The stir-by-hand method may not be appropriate in lakes, reservoirs, or slow-moving waters (for example, bayous); these water bodies may be stratified at the point of measurement, making accurate DO measurements impossible with a non-stirred amperometric DO probe. This could be especially problematic in areas where DO concentrations change substantially over short distances, such as near the thermocline or bottom sediments.
- High stream velocity also can cause erroneous DO measurements.
- 3. Immerse the DO and temperature sensors directly into the water body and allow the sensors to equilibrate to the water temperature (no less than 60 seconds).
- 4. Record the temperature without removing the sensor from the water.

¹⁴ Refer to footnote 3 if using a YSI "Rapid Pulse" sensor, for which a stirrer is not needed.

- 5. After the instrument reading has stabilized, record the median DO concentration (see NFM 6.0). The reading should stabilize to within ± 0.2 mg/L.
- 6. For EWI, EDI, or multiple-vertical measurements, proceed to the next station in the cross section and repeat steps 3 through 5. When measurements for the stream have been completed, remove the sensor from the water, rinse it with deionized water, and store it according to the manufacturer's instructions.
- 7. Record DO concentrations on the field forms:
 - **In still water**—Median of three or more sequential values.
 - **EDI**—Mean value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
 - EWI—Mean (or median) of all subsections measured.

Groundwater

Before the concentration of DO in groundwater can be determined, standing water must be evacuated from the well to ensure that measurements of DO concentration in the well will be representative of formation-water concentration. An adequate well purge ensures the flow of freshwater from the formation into the well (refer to NFM 4.2 and NFM 6.0.3.A for detailed information). Measurement of ambient DO concentrations in groundwater additionally requires use of equipment and procedures that avoid aeration and mitigate losses or gains of dissolved gases in the water being sampled. A bailed sample, for example, is inadmissible for DO measurement because the field sample-decanting process exposes the sample to the atmosphere (NFM 6.0.3); this provision likewise applies to any type of sampling device from which the sample is brought in contact with air when transferred to a measurement or analysis vessel.

Project or program data-quality requirements and objectives, site characteristics, and equipment availability will dictate whether (a) measurements will be made *in situ* (DO measured downhole) or *ex situ* (DO measured above land surface, the inline-flow procedure), and if (b) optical, amperometric, or spectrophotometric methods will be used for DO measurement. This section addresses the use of optical and amperometric sensors, for which the lower threshold for measurement of aqueous DO concentrations is from 1 to 2 mg/L, depending on the instrument being used and the accuracy required.¹⁵ **If the anticipated DO concentration is less than 1.0 mg/L, consider use of spectrophotometric methods (section 6.2.2).**¹⁶

- ▶ If using an optical-sensor instrument at DO less than 1.0 mg/L, first perform a zero-DO calibration check or calibration (instrument permitting), and document the results.
- ▶ When anticipating DO concentrations in the hypoxic or suboxic range on a routine or regular basis,
 - Optical sensor: Readings to 0.05 mg/L should be verified using the methods described in sections 6.2.2 or 6.2.3. The presence of hydrogen sulfide, however, will not affect the accuracy of the measurement.
 - Amperometric sensor: The sensor can be adversely affected by hydrogen sulfide and misread the true DO value.

¹⁵ The accuracy of DO measurements to 0.05 mg/L with an optical sensor has been field verified against Rhodazine-D spectrophotometric measurement on numerous occasions by USGS field-methods instructors (Gerolamo Casile, U.S. Geological Survey, oral commun., 2012).

¹⁶ Note that spectrophotometric methods for determining DO concentration generally are not approved by the U.S. Environmental Protection Agency for regulatory assessments.

Refer to NFM sections 6.0.1 and 6.0.3 for guidance related to the selection, preparation, and procedures for in situ and ex situ measurement of field-determined properties. Study objectives and site characteristics will dictate the specific method selected. Select the field-measurement system that best fits the requirements for the data-collection effort.

- ▶ **Downhole (in situ) measurement** (see NFM 6.0.3.B). Submersible multiparameter sondes and single-parameter sensors are deployed downhole to the targeted depth interval. Deployment typically involves data collection for a single field trip. The sonde or sensor sometimes is deployed for unattended monitoring, but the appropriate conditions and protocols must be followed (see NFM 6.8). Use of the optical DO sensor makes longer-term deployment more practical, compared to that of the amperometric sensor.
- ▶ Inline flowthrough cell/chamber (ex situ) measurement. Sample is pumped directly (inline) to an airtight, transparent chamber or manufacturer-provided cell having either (1) leak-proof ports (compression fittings) that accommodate either the optical or amperometric DO single-parameter sensor (and other single-parameter sensors), or (2) a multiparameter sonde instrumented with either an optical or amperometric DO sensor. NFM 6.0, figure 6.0–3, diagrams a flowthrough cell system; figure 6.0–5 charts downhole and inline sampling processes.¹¹
 - Sample is transferred using a positive-displacement submersible pump fitted with high-density plastic or fluorocarbon-polymer tubing that is relatively gas impermeable.
 - Use of transparent materials for the tubing and chamber is needed to allow checking for air bubbles in the water stream or adhering to the sides of the tubing and flowthrough cell or chamber (that have been introduced as an artifact of the sampling procedure, as distinguished from gas bubbles that are native to the formation water). Such air bubbles add significant error to low-level DO measurements and should be excluded (A.F. White, U.S. Geological Survey, written commun., 1993).
 - Protect exposed sample tubing and the flow-through cell or chamber from direct sunlight.

Do not measure groundwater DO concentration in a sample extracted from a bailer or other sampling device that results in sample exposure to the atmosphere.

Follow the steps below to measure DO in groundwater:

- 1. Calibration checks: Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).
 - Check that the thermistor gives an accurate reading and that its calibration has been verified by the USGS Water Science Center within the past 12 months (see NFM 6.1).
 - Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).
 - If field calibration is necessary or if it is required to address program protocols, data-quality requirements, or site-specific conditions, calibrate the DO sensor in accordance with the procedures and restrictions described in section 6.2.1.B.

¹⁷ See section 6.0, "General Information and Guidelines," in chapter 6 of this field manual (http://water.usgs.gov/owq/FieldManual/Chapter6/6.0 contents.html).

- 2. Install the DO equipment (see NFM 6.0 for more detailed instructions):
 - **Downhole system**—Lower the DO and temperature sensors to the measuring point, followed by the pump, to monitor DO variation during purging. When an amperometric sensor is used, water needs to flow past the sensor at a velocity of no less than 1 ft/s; attach a mechanical stirrer, if necessary, to maintain this velocity. The optical sensor is not flow dependent.
 - Inline flowthrough system—Refer to NFM 6.0 for installation guidelines. If sensors are to be installed in a flowthrough cell or chamber, install the DO sensor immediately downstream of the point of sample inflow. For a system using a multiparameter instrument sonde, install the sonde in the flowthrough cell provided by the manufacturer and in accordance with manufacturer instructions. Be sure to:
 - Install the DO sensor through an airtight grommet, if using a chamber instrumented with single-parameter sensors. Check that the seal around the DO sensor is intact and that the sensors are properly immersed.
 - Shield the sample tubing and flowthrough cell/chamber from direct sunlight to minimize changes to sample temperature (this step is most critical for users of amperometric sensors).
 - Dislodge and flush entrained air bubbles from the tubing walls and flowthrough chamber by tapping the tubing with a blunt tool (see TECHNICAL NOTE 9 below). Note that air bubbles are an indication of air leakage into the sampling system and should be distinguished from gas bubbles that could be native to formation water chemistry.
 - Check for and eliminate backpressure in the flowthrough chamber.
- 3. **If using an amperometric instrument,** be sure to maintain constant, laminar flow past the DO sensor (refer to footnote 3). Measure and record DO at regular intervals throughout purging. Allow the sensors to equilibrate with groundwater for 5 minutes or more at the flow rate to be used for sampling.
- 4. Check the stability (measurement variability) of DO toward the end of purging. The stability criterion is met when five consecutive readings made at regularly spaced intervals of 3 to 5 minutes or more are within ±0.2 mg/L. (For each reading, monitor fluctuations for 30 to 60 seconds and record the median value, if necessary.) If the ±0.2 mg/L criterion is not met, increase the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals.
- 5. Report sample DO as the median of the final five DO readings recorded. Record on field forms any difficulty with stabilization.
- 6. Remove the sensor from the water and rinse it with deionized water.

Air bubbles in the lines and flowthrough chamber can add substantial error to DO readings in low DO or oxygen depleted groundwater.

TECHNICAL NOTE 9. Anomalously high DO measurements commonly are caused by aeration of groundwater during pumping. This can result from air leakage through loose fittings on production-well pumps (for example, turbine pumps) and also if drawdown in the aquifer introduces air into the cone of depression or through well-screen perforations. To avoid these problems, review information about the pump, well-construction and drawdown data, and previous data records (A.F. White, U.S. Geological Survey, written commun., 1993).

6.2.1.D Troubleshooting for Amperometric Instruments

The troubleshooting suggestions given in table 6.2–3 are for amperometric instruments and are not exhaustive; consult the manufacturer of your amperometric instrument for additional guidance. For problems with calibration or measurement using optical sensors, periodically wipe the sensor with a wet cloth. Do not wipe the Teflon membrane; rather, remove water droplets by shaking or other means. Wiping the Teflon membrane may scratch the membrane, resulting in erroneous readings. If problems with the amperometric sensor persist, consult the manufacturer. Faulty batteries can cause erratic readings.

- ► Check the voltage of the batteries.
- ► Start with good batteries in the instrument and carry spares.

Table 6.2–3. Troubleshooting guide for amperometric instruments.

Symptom	Possible cause and corrective action
Instrument drifts or takes excessive time to stabilize	 Thermal equilibrium of water and sensor has not been reached—wait longer. Weak batteries—replace. DO sensor needs maintenance—recondition.
Erratic instrument readings	 Break in cable—replace cable. Faulty connection at instrument or sensor—clean contact and tighten. Hole in membrane—replace membrane, recondition. Air bubble in sensor—recondition sensor. Weak batteries—replace.
Instrument too slow to react	 Gold or silver cathode tarnished—buff with pencil eraser, manufacturer-provided polishing paper, and recondition sensor. Fouled membrane—replace membrane and recondition sensor.
Instrument will not read zero in sodium sulfite solution	 Solution contains oxygen—make fresh solution. Instrument still does not read zero— replace membrane and recondition sensor.
Instrument cannot be calibrated to read standards	 Unable to adjust upward—check to see if more than one membrane is on the sensor. Unable to adjust downward (membrane is probably too tight or too thin)—replace membrane.
Instrument reads inaccurate temperature	Faulty thermistor or cable—repair or replace.

6.2.2 Spectrophotometric (Rhodazine-D and Indigo-Carmine) Methods

Various spectrophotometric methods (*see* TECHNICAL NOTE 10) are available for determining DO over a broad range of concentrations. The information given in this section, however, is limited to the application of spectrophotometric analysis of Rhodazine-D¹⁸ and Indigo-Carmine reagents for determining DO concentrations in relatively oxygen-deficient (hypoxic) and anoxic¹⁹ waters; that is, DO concentration from about 2 to zero mg/L.²⁰ The option to measure DO by spectrophotometry in the higher concentration ranges generally is selected when field conditions limit use of optical or amperometric sensor methods. (Non-instrumental analyses of Rhodazine-D and Indigo-Carmine reagent indicators also are available for measuring aqueous DO concentrations, but the analysis can be subject to considerable operator variability, is not applicable to standard USGS field protocols, and is thus beyond the scope of this guidance.)

TECHNICAL NOTE 10. The purpose of photometry is to measure light in a way that takes the sensitivity of human visual system into account. Photometry only measures in the visible spectral region from 360 nm to 830 nm, where human eyes are sensitive. Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength. The National Institute of Standards and Technology (NIST) maintains the national scales for reflectance and transmittance in the ultraviolet, visible, and near-infrared spectral regions; that is, 250 nm to 2,500 nm (see http://www.nist.gov/pml/div685/grp03/spectrophotometry.cfm).

Spectrophotometric methods for DO measurement have been used in USGS field work for measuring DO in oxygen-depleted groundwater and can be adapted for work in oxygen-depleted zones of lakes and reservoirs, but are not approved by the U.S. Environmental Protection Agency for application to regulatory assessments. The Rhodazine-D spectrophotometric method for determining DO in groundwater was introduced by White and others (1990) as a means for obtaining accurate DO data for groundwater at a time when sensor methods lacked the capability of in situ measurement.

- ► The Rhodazine-D spectrophotometric method is applicable to a range from 0.1 to 1.0 mg/L dissolved oxygen in aqueous environments. The Rhodazine-D (phenzone dye) compound, in reduced form, reacts with dissolved oxygen to form a deep rose to red-purple reaction product.
- ▶ Low-level Indigo-Carmine spectrophotometric methods are applicable to DO concentration ranges from either 0.006 to 0.8 or 0.2 to 2.0 mg/L, depending on the specific manufacturer kit ("ampul" or "ampoule" kit) being used for the range of interest. Indigo Carmine reacts with the dissolved oxygen present in the sample to form a highly colored blue reaction product.
- As mentioned previously, USGS technical staff have documented optical sensor measurements²¹ at DO concentrations of 0.05 mg/L and Rhodazine-D spectrophotometric readings to be of comparable accuracy. To date, these findings have not been published or verified using different types of optical sensors. Before measuring and reporting hypoxic to anoxic DO concentration data from optical

¹⁸ Rhodazine-DTM is a proprietary product of CHEMetrics, Inc. (White and others, 1990).

¹⁹ Hypoxic: *Hypoxia* – "A condition in which natural waters have a low concentration of dissolved oxygen (about 2 milligrams per liter compared with a normal level of 8 to 10 milligrams per liter). Stevenson and Wyman (1991); *http://toxics.usgs.gov/definitions/hypoxia.html*. *Anoxic*, in this document, refers to water that has a very low concentration of dissolved oxygen (that is, less than 0.5 milligrams per liter) (U.S. Geological Survey, 2010; *http://toxics.usgs.gov/definitions/anoxic.html*), or total deprivation of oxygen (U.S. Environmental Protection Agency, 2009).

²⁰ The information for the concentration range of the spectrophotometric methods discussed was provided from and reviewed by technical specialists representing CHEMetrics, Inc. and the Hach Company. See http://www.chemetrics.com and www.hach.com.

²¹ Unpublished data. Comparisons were made using an In-Situ Inc. TROLL 9500 Profiler equipped with a rugged dissolved oxygen (RDO) optical sensor (Gerolamo Casile, U.S. Geological Survey, oral commun., 2012).

sensors, the capability and accuracy of the optical sensor in this low DO-concentration range needs to be documented by making side-by-side measurements onsite to compare results with values obtained using a spectrophotometric method.

6.2.2.A Equipment and Supplies

The Rhodazine-D and Indigo-Carmine spectrophotometric methods were designed to minimize atmospheric interaction with the water sampled. Two sampling systems commonly are used: (1) an in situ (submersible or downhole) sampler, such as the assemblies discussed in White and others (1990), and (2) a plastic overflow cell through which sample water is pumped (see equipment and supplies in table 6.2–4).

The sampling system is configured to utilize a self-filling ampoule system with the Rhodazine-D or Indigo Carmine reagent vacuum-sealed inside. DO concentration is determined instrumentally on the resultant solution using a spectrophotometer or photometer. The ampoule kits and spectrophotometer (or photometer) are available commercially. The spectrophotometer (or photometer) selected must be able to be adjusted, either manually or automatically, to the appropriate wavelength of incident light needed for the determination of DO in the resultant colored sample, based on the reagent used. Applicable spectrophotometers, photometers, and ampoule kits are available commercially from various companies and for a variety of concentration ranges.

- ► The accuracy of commercially available reagent kits may not be included with the equipment or supplies purchased. Always check with the manufacturer regarding the accuracy of the specific test kit(s) of interest.
- ► The accuracy of the test kits will typically be a function of the concentration range of DO in the sample.
- ▶ A spectrophotometer is used to measure the amount of light that a sample absorbs. The instrument operates by passing a beam of light through a sample and measuring the intensity of light received by a detector (http://www.chm.davidson.edu/vce/spectrophotometry/Spectrophotometry.html).
- ➤ Some spectrophotometers are precalibrated specifically for the products or kits developed by the kit manufacturer. If using a spectrophotometer that is not precalibrated for the products being used, calculate the DO concentration using the regression equations provided by the manufacturer of the reagent kit.

Table 6.2–4. Equipment and supplies for the spectrophotometric method of dissolved-oxygen determination using Rhodazine-D™ and Indigo Carmine reagents.

[mm, millimeter; DO, dissolved-oxygen concentration; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Portable spectrophotometer (or photometer)

Appropriate reagent kits for the expected DO range of the environmental condition

Blank ampoule (zero DO), included in each kit

Submersible sampling tool, used in situ, to meet criteria described in White and others (1990). For example,

- Manganous sulfate reagent
- Plastic sampler device (overflow cell), length of C-flex tubing, and sample pump

Safety gloves, glasses, and apron

Waste disposal container

White background sheet

Deionized water (maximum conductivity of 1 µS/cm)

Bottle, squeeze dispenser, for deionized water

Lint-free wipes to remove moisture from surface of the ampoule

6.2.2.B Calibration and Interferences

DO is measured as percent absorbance by the spectrophotometer. A calibration chart typically is provided with each chemical reagent kit, along with a regression formula to convert absorbance to micrograms per liter (μ g/L) of DO for use with a spectrophotometer that does not perform the conversion in its firmware. Most current spectrophotometers and photometers available for measurement of dissolved oxygen are precalibrated for direct readout of DO concentration in milligrams per liter.

- ▶ Ensure that an appropriate blank ampoule is used to zero the spectrophotometer (or photometer).
- ▶ Additional calibration is needed if the method will be used to determine DO in heavily contaminated or acidic waters. This can be done by equilibrating a water sample with known partial pressures of atmospheric oxygen (White and others, 1990). Atmospheric oxygen standards are available from suppliers of gas chromatography equipment.

These chemical reagent-based methods are not subject to salinity or dissolved-gas interferences (ASTM D5543-09, ASTM D 888-12, White and others, 1990; Gilbert and others, 1982). Interferences from total salinity, major dissolved inorganic species, dissolved gases, or temperature are typically negligible with this method. However, color and turbidity in the environmental sample may interfere with both the Rhodazine-D and Indigo-Carmine methods, causing positively biased results. If using these methods in colored or turbid water, first conduct an assessment of the amount of bias attributable to such effects.

- ▶ Rhodazine-D. The spectrophotometric method using Rhodazine-D reagent is affected by the presence of oxidizing agents, including chlorine, ferric and cupric ions, and hexavalent chromium, resulting in high-biased DO readings (White and others, 1990).²²
 - The presence of cupric copper and ferric iron at a concentration less than 50 μ g/L may cause a bias of less than 1 μ g/L; at 100 μ g/L concentration, cupric copper may cause a bias of 5 μ g/L, and ferric iron may cause a bias of 7 μ g/L.
 - Sample pH at or below a pH of 2 may cause erroneous results.

²² See also http://www.chemetrics.com/products/pdf/oxygen_rhodazined.pdf, accessed September 20, 2012.

- A hydroquinone concentration greater than 200 μg/L is a positive interferent and its oxidation byproduct, benzoquinone, causes a false positive result. The effect from oxidizing agents can be corrected if the concentrations of the interfering species are known (White and others, 1990).
- ▶ Indigo Carmine. The spectrophotometric method using Indigo Carmine reagent²³ is affected by ferric iron, hypochlorite (chlorine), and chromate, which can cause a false positive at concentrations equal to or greater than 10 mg/L.
 - Cupric copper interferes positively at or above 100 mg/L.
 - Seawater may cause the reagent to precipitate.

6.2.2.C Measurement

USGS spectrophotometric measurement procedures have been tested and quality assured for the determination of DO concentration using the Rhodazine-D and Indigo-Carmine reagents provided in commercially available kits supplied by the CHEMetrics and Hach companies, respectively.²⁴ While the instructions provided by the manufacturers generally should be followed, augmented instructions and information are provided below to ensure that DO measurement meets USGS standards for accuracy and reproducibility. USGS personnel are advised to make the adjustments described here to the manufacturer-provided instructions.

Rhodazine-D and Indigo-Carmine reagents react with DO to produce an oxidized complex characterized by deep-rose or brightly blue-colored reaction products, respectively. The color intensity is proportional to the concentration of the initial DO present. **Timing is very important for colorimetric analyses made with a spectrophotometer.** Follow the explicit instructions for the waiting time after the sample mixes with the reagent. The reaction with the reagents occurs almost instantaneously for both the Rhodazine-D and Indigo-Carmine methods. Color development continues after the time interval specified for these methods because oxygen from the atmosphere continuously diffuses into the sample through the broken ampule tip.

- ▶ Do not extend the waiting times specified in the Rhodazine-D and Indigo-Carmine methods, but adhere to them strictly.
- Excessive mixing of the ampule before reading the spectrophotometer also may introduce atmospheric oxygen, which can bias the results, resulting in erroneous readings.

Follow the steps below to measure DO using the spectrophotometric method:

- 1. Familiarize yourself with instructions from the manufacturer for the kit to be used and adjust the instructions to incorporate the procedures that follow, as applicable.
- 2. Accounting for site characteristics and study objectives, purge the well following guidelines in NFM 4.2.
- 3. Set the spectrophotometer to an appropriate wavelength for the kit being used. When using a manufacturer-designated DO photometer (or spectrophotometer), verify whether or not introduction of the ampoule provided in the kit will trigger the correct wavelength setting automatically.

²³ ASTM D 888-12; ASTM D 5543-09; Gilbert and others (1982).

²⁴ Instructions from the Hach Company and CHEMetrics Inc. for selected colorimetry-based methods at DO concentration ranges relevant to routine USGS sampling were selected for testing because USGS field personnel currently use the equipment and reagent kits from these companies.

- 4. Zero the spectrophotometer using the blank provided in the kit (follow the manufacturer's instructions).²⁵
- 5. When collecting the sample:
 - Prevent sample aeration. Use a positive-displacement submersible pump and high-density plastic or fluorocarbon polymer sample tubing that is relatively gas impermeable, if possible, throughout measurement.
 - Operate equipment to mitigate losses or gains of dissolved gases. (Consult NFM 6.0 for proper downhole and inline flowthrough-chamber sampling procedures.)
- 6. Select your sample-collection method: Use either a downhole or overflow-sampler device.
 - Go to Step 7 for the downhole sampling tool method, ²⁶ or
 - Go to Step 8 for the plastic overflow-sampler device with a suitable pump method.
- 7. **Downhole system**: After purging the well (NFM 4.2), follow steps 7a through d.
 - a. Carefully immerse a reagent-containing ampoule on the sampling tool that is attached to a wire line.
 - b. At the desired depth of sample collection (in a well or in surface water), break the scored tip of the ampoule by using a sharp upward tug on the sampling tool.
 - This permits sample water to be drawn into the ampoule.
 - During transit to the surface, progressively decreasing pressure in the ampoule prevents cross contamination from overlying water through the ampoule tip.
 - c. Withdraw the ampoule from the sampling device and invert once to mix the contents of the ampoule, allowing the bubble to travel from end to end; follow the kit-specific instructions regarding the number of ampoule inversions.²⁷
 - Take care that this process does not introduce atmospheric oxygen into the ampoule.
 - Make sure the time required to bring the ampoule to the surface does not exceed the waiting times specified by the method. (This method may work best for shallow wells).
 - d. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue. Skip to step 9.
- 8. **Overflow device**: After purging the well (NFM 4.2), follow steps 8a through f.
 - a. Connect the plastic overflow-sampling device (table 6.2–4) to the outlet of the pump tubing with C-flex tubing 3 feet (ft) or less in length. The overflow device is used to break the ampoule in the flowing stream of water.
 - If using the **Rhodazine-D** method, the kit is equipped with the appropriate overflow sampling device needed to crack the ampoule.

²⁵ Native water may be used if this option is provided by the kit manufacturer.

²⁶ A downhole sampling tool is described by White and others (1990).

²⁷ Instructions provided by kit manufacturers specify inverting the ampoule several times with the bubble traveling from end to end to facilitate mixing of reagent and sample. USGS field observations, however, indicate that vigorous or repeated mixing can introduce atmospheric oxygen and bias the measurement (Gerolamo Casile, U.S. Geological Survey, written commun., 2013).

- If using the **Indigo-Carmine** method, adapt the Rhodazine-D instructions as follows, instead of using the directions provided²⁸:
 - Obtain a plastic funnel with a funnel size of approximately 1 cup.
 - Adapt the funnel to the end of a length of C-flex tubing. This funnel, while overflowing, will allow the tip of the Indigo-Carmine ampoule to be broken very close to where the sample water flows in.

TECHNICAL NOTE 11. Use optically clear materials to enable seeing whether bubbles are entrained in the tubing or flow cell (chamber). Air bubbles that adhere to the sides of the tubing and chamber will add significant error to low-level DO measurements (A.F. White, U.S. Geological Survey, written commun., 1993).

- b. Reduce the pumping rate to achieve an even, nonturbulent, laminar rate of flow (for groundwater, about 500 milliliters per minute) that is used for sample collection. While pumping, allow the sampling device to overflow during sample collection.
 - Check for air bubbles in or adhering to the tubing and flowthrough cell (chamber).
 - Tap the tubing with a blunt tool to dislodge entrained air bubbles.
- c. Insert the glass ampoule, tip first, into the overflowing sampling device so that the tapered tip is at the bottom of the device, close to the point of water inflow.
- d. Snap the tip by gently pressing the upper end of the ampoule toward the wall of the sampling device.
 - The vacuum ampoule will draw in the sample water, leaving a small bubble at one end.
 - Ensure that the ampoule is full before proceeding to step e; this will prevent entraining excess atmospheric oxygen and thereby producing erroneous readings.
- e. Withdraw the ampoule from the sampling device and invert to mix the contents of the ampoule, allowing the bubble to travel from end to end; follow the kit-specific instructions regarding the number of ampoule inversions (see footnote 27).
- f. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue.
- 9. Insert the ampoule directly into the spectrophotometer cell holder, either immediately after retrieval or as specified in the kit-specific instructions.
- 10. Read concentration or absorbance:
 - a. Make spectrophotometer readings, adhering as strictly as possible to the manufacturer-specified time interval.
 - **Rhodizine-D**—Record the reading within the time interval directed by the kit manufacturer (for example, within 30 seconds when using the CHEMetrics ampoule kit).

²⁸ The Hach Company Indigo Carmine kit instructs placing the sample tube at the bottom of an overflowing beaker, then breaking the ampoule near the sample tubing at the bottom of the beaker. Tests conducted by USGS personnel indicated that substituting the directions in step 8a substantially improve measurement accuracy and reproducibility. (Gerolamo Casile, U.S. Geological Survey, written communication, 2013).

- **Indigo-Carmine**—Record the reading within the time interval directed by the kit manufacturer.
- b. If using a spectrophotometer that does not convert absorbance values of DO measurements to milligrams per liter for the kit being used, use regression equations to make the conversion (see White and others, 1990).
- 11. **Quality control**: Consider utilizing multiple determinations to document the precision and (or) accuracy of the DO concentration to be reported.
 - Repeat steps 9 and 10 twice in rapid succession to document measurement precision.
 - To document the variability of DO concentrations within the water system being measured, repeat steps 4 through 10 on three sequentially collected samples.

Do not exceed the time interval specified for completion of color development.

6.2.3 **lodometric (Winkler) Method**

The USGS currently uses the Alsterberg-Azide modification to the Winkler titration procedure for iodometric determination of DO. The precision of measurements using the iodometric method should be within at least ± 0.05 mg/L²⁹ when performed by experienced analysts (American Public Health Association, 2005).

- ► The iodometric (Winkler) method no longer is being used routinely as a standard field method for measurement of DO in USGS investigations because (1) the accuracy and reproducibility achievable are dependent on the experience and expertise of the data collector, (2) potential environmental interferences (for example, the presence of nitrite, ferrous and ferric iron, and organic matter) require advanced knowledge of the chemistry of the sample, and (3) field conditions can make preventing exposure of the sample to atmospheric oxygen difficult. Nevertheless, the iodometric method is recognized as a reliable standard for producing accurate results when correctly implemented.
- ► The iodometric (Winkler) method is widely accepted in the scientific community and is used to check the calibration of, and the measurements made with, electrometric DO instrument systems.
 - The Winkler method was used to verify the accuracy of optically and amperometrically determined DO concentrations reported by the USGS in an oil spill investigation, in accordance with a request by the U.S. Environmental Protection Agency (Wilde and Skrobialowski, 2011).
 - Checking the calibration of electrometric instruments using the Winkler procedure is performed in a controlled (that is, laboratory) environment. The DO instrument is calibrated with air-saturated deionized water in which the DO concentration has been determined by the Winkler method; the DO instrument is then adjusted to the concentration determined from the titration.
 - If a saline solution is used to approximate the environmental water, do not apply a salinity correction factor.

²⁹ Based on a standard deviation (SD) of ± 0.02 mg/L for a three SD accuracy of ± 0.06 mg/L.

6.2.3.A Equipment and Supplies

Equipment and supplies needed for the iodometric method are listed in table 6.2–5. The procedure involves the use of reagents available in premeasured pillow packets from commercial suppliers. Alternatively, reagents may be prepared by a chemist or titration technician, as described in American Public Health Association (2005).

- ► The accuracy of commercially obtained reagent packets may differ among manufacturers and other preparers of the reagents and should be recorded in field notes.
- ► Clean all equipment before use.

Beaker 2 000 ml glass or Teffon

Table 6.2–5. Equipment and supplies for the iodometric (Winkler) method of dissolved-oxygen determination.

[mL, milliliter; N, normal; μS/cm, microsiemens per centimeter at 25 degrees Celsius; NFM, National Field Manual for the Collection of Water-Quality Data]

Beaker, 2,000 mL, glass or Teflon
Bottles for biochemical oxygen demand (BOD) analysis, glass stoppered, 300 mL
Stirrer, magnetic
Stirring bars, Teflon coated
Cylinder, graduated, 250 mL
Flask, Erlenmeyer, 250 mL
Buret, 25-mL capacity with 0.05-mL graduations and Teflon stopcock
Buret, support stand
Buret, clamp, double
Chemical reagents: Alkaline iodide-azide reagent Manganous sulfate reagent Sulfamic acid granules Sodium thiosulfate, 0.025 N titrant Starch indicator solution
Clippers, for opening reagent pillows
Appropriate safety gloves, glasses, and apron
Waste disposal container
White background sheet
Deionized water (maximum conductivity of 1 μS/cm)
Bottle, squeeze dispenser, for deionized water
Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
Pocket altimeter-barometer, calibrated, or DO-measurement equipment that includes barometer

¹ Use either commercially prepared reagent pillow packets or analyst-prepared reagents, depending on the data-quality requirements of the study.

6.2.3.B Measurement

This section describes how to make an iodometric determination of DO concentration.

- ▶ When the purpose of using the Winkler method is to check calibration of an amperometric or luminescent-sensor instrument, start at step 1 below and continue to the end. For quality control, steps 5 and 6 are written so as to verify the Winkler determination in duplicate. This is standard practice and should be followed
- ▶ If making a Winkler determination for the DO concentration of an environmental sample, start at step 5, substituting the sample water for deionized water (DIW). Collect the sample and perform the titration as described below on at least two subsamples to provide the appropriate quality control. When filling the BOD bottles, a minimum of three bottle volumes of sample should pass through the bottle to collect the final volume.
 - **In surface water:** To fill the bottles, use of a sewage sampler is recommended. If a hand-held method is needed, fill the bottles in the water body by tilting them slightly to allow the bottle to slowly fill in a manner so as to avoid turbulence, bubbling, or otherwise entraining air. Keep the filled bottles submerged (in the surface-water body) for about 30 seconds. Next, while the bottle is submerged, insert the stopper firmly in the bottle, taking care not to trap air bubbles.
 - **In groundwater:** A laminar-flow sample is pumped inline from the well into the bottle, from the bottom to overflowing the top of the bottle and in a manner so as to avoid any turbulence and bubbles. Allow the sample to overflow for at least 30 seconds. Next, while still overflowing, insert the stopper firmly into the bottle, taking care not to trap air bubbles.
 - Pour off excess water that is trapped on the lip of the stoppered bottle.
 - Follow step 6 procedures as described below, substituting the sample-filled biochemical oxygen demand (BOD) bottles.
- ▶ Results of two iodometric titrations should agree within 0.1 mg/L. If they do not agree, repeat the titration on one or more additional subsamples until this quality-assurance criterion is met.

Follow the steps below to check calibration of an optical or amperometric DO instrument using the Winkler Alsterberg-Azide titration:

- 1. Fill a clean 2,000-mL beaker with deionized water that is near DO saturation. The water temperature should be close to the ambient (field or laboratory) temperature.
- 2. Prepare the DO-sensing instrument for operation, in accordance with the manufacturer's instructions.
- 3. Place the DO sensor in a beaker of DIW. If using an amperometric sensor, maintain a water velocity of at least 1 ft/s flowing passed the sensor. If the sensor is not equipped with a stirring mechanism, use a magnetic stirrer.
- 4. Monitor the DO concentrations of the DIW with the DO instrument and record the value after the readings have stabilized.
- 5. Carefully fill two clean BOD bottles with three or more bottle volumes of DIW from the beaker, taking care not to introduce any air bubbles by slowly overflowing the bottles adequately to remove any trapped air bubbles.
- 6. Determine the DO concentration of the DIW in each BOD bottle, as follows:

- a. Add one each of the following dry reagent pillow packets³⁰
 - Alkaline iodide-azide (white powder).
 - Manganous sulfate (pinkish-colored powder).
- b. Recap the bottle to prevent air bubbles from being trapped in the bottle.
- c. Invert the bottle 25 times or more to completely dissolve the reagents.
 - An orange-brown flocculent indicates the presence of DO.
 - Allow the flocculent to settle halfway down the bottle (approximately 5 minutes).
 - Invert the bottle 25 times again; let the flocculent settle again until the upper half of the solution is clear.
- d. Add one reagent pillow of sulfamic acid (see footnote 30).
- e. Recap the bottle without introducing air or air bubbles. Invert the bottle 25 times until all of the flocculent and granules are dissolved, leaving a yellow color.
- f. Fill a clean 25-mL buret with 0.025 *N* (*Normal*) sodium thiosulfate titrant. Remove any air bubbles from the delivery tube beneath the stopcock and zero the meniscus.
- g. Using either a clean 200-mL pipet or a 200-mL volumetric flask, measure 200 mL of the sample and dispense the sample into a clean, wide-mouth Erlenmeyer flask.
- h. Place the flask on a magnetic stirrer. Carefully insert a clean Teflon stirring bar and stir the sample at a moderate rate without aerating the sample.
- i. Add increments of sodium thiosulfate titrant until the color turns pale straw-yellow.
- j. Add 1 to 2 mL of starch indicator solution. (This causes the sample to turn dark blue.)
- k. Very slowly add more sodium thiosulfate titrant until the sample just turns clear. (A white background behind or below the flask will help to see the color change.)
- 1. Record the volume of sodium thiosulfate titrant used, in milliliters.
 - For a 200-mL sample, the volume of titrant added is directly proportional to the amount of DO in milligrams per liter.
 - To calculate DO for a sample volume greater or less than 200 mL,

$$DO (mg/L) = (\frac{200}{sample \ volume}) \times titrant \ added, \ in \ mL$$
 (1)

- m. Record the DO value. Rinse the equipment thoroughly with deionized water.
- 7. **Quality control.** Titration values for the duplicate samples should agree within 0.1 mg/L.
 - If they do not agree, repeat the titration process (steps 5 and 6a through 6m, above) on one or more additional subsamples until this quality-assurance criterion is met.
 - Record the final, quality-assured value for DO concentration.

³⁰ Laboratory-prepared reagents might be prepared instead, depending on data-quality requirements, if titration will be performed by an analyst.

- 8. Recheck the field instrument for proper functioning, following the manufacturer's recommendations and instructions.
 - Consult the manufacturer if the field instrument does not calibrate properly.
 - Do not use an instrument that fails calibration.

6.2.4 Reporting

USGS personnel are instructed to enter the DO value on the field form indicating method (optical, amperometric, spectrophotometric, or iodometric) used for DO determination.

- ▶ DO concentrations for the amperometric and optical-sensor methods are measured to the nearest 0.01 mg/L, but currently are reported to the nearest 0.1 mg/L.
- ▶ DO concentrations for the spectrophotometric/Rhodazine-D and Indigo-Carmine methods are reported to the nearest 0.01 mg/L.
- ▶ Note that the percentage of DO saturation in water can be greater than 100. When the concentration exceeds 20 mg/L, check manufacturer's specifications and:
 - Report ">20 mg/L" if the manufacturer's instrument range specifications do not exceed 20 mg/L.
 - Report concentration values up to the maximum specified limit if the manufacturer's instrument range specifications exceed 20 mg/L.
 - Report "> the listed numerical limit" if the concentration exceeds the manufacturer's specified instrument range.

6.2.5 Correction Factors for Oxygen Solubility Concentrations and Salinity

Solubility concentrations of oxygen in freshwater at various temperatures and pressures (table 6.2–6) and correction factors for salinity based on specific conductance (table 6.2–7) were generated from the equations of Benson and Krause (1980, 1984) and can be customized to cover the range and decimal places needed; see U.S. Geological Survey Office of Water Quality Technical Memorandum 2011.03 (Myers, 2011). By accessing "DOTABLES," the interactive software that generated tables 6.2–6 and 6.2–7, the user can self-generate individual values or tables of a specific range of oxygen-solubility and salinity correction factors: http://water.usgs.gov/software/DOTABLES/.31

- ➤ To adjust freshwater oxygen-saturation values for the effects of salinity, use correction factors based on chloride concentration or specific conductance. Refer to the manufacturer's instructions for the DO instrument before applying a salinity correction.
- ➤ Correcting DO solubility for saline waters (greater than 2,000 microsiemens per centimeter or 1,000 mg/L chloride) varies with instrument type, calibration method, and the salts in solution.

³¹ DOTABLES is an online program that generates tables of dissolved oxygen (DO) solubility values and (or) salinity correction factors over a range of user-specified values for water temperature, barometric pressure, and salinity or specific conductance. In addition to generating tables, DOTABLES can compute a single-value of oxygen solubility and percent saturation for a specific instance of temperature, pressure, and salinity.

- The correction based on specific conductance (table 6.2–7) is more useful because accurate conductivity can be determined easily from a field measurement.
- Salinity correction factors based on chloride can be calculated using information provided in U.S.
 Geological Survey Quality of Water Branch Technical Memorandum 79.10 (Pickering, 1979).
- ▶ DO instruments either use an automatic internal salinity correction, a manual salinity control knob for internal correction, or the calibration control knob for manual correction of salinity. Check that instruments with automatic internal salinity correction use approved salinity correction factors.

Example of salinity correction

Suppose a DO measurement is made in water with a temperature of 20.0 degrees Celsius, an atmospheric pressure of 750 millimeters of mercury, and a specific conductance of 8,000 microsiemens per centimeter (μ S/cm). The freshwater oxygen solubility from table 6.2–6 is 8.97 mg/L for that temperature and pressure; the salinity correction factor from table 6.2–7 is 0.9733 for that temperature and specific conductance. The solubility of oxygen under these conditions then is:

$$8.97 \text{ mg/L } \times 0.97331 = 8.73 \text{ mg/L}$$
 (2)

The presence of more dissolved ions in the saline water decreases the oxygen solubility.

- ▶ If calibrating an instrument that does not have an internal salinity compensation algorithm, you could adjust the DO instrument to read 8.73 mg/L for a 100 percent saturation condition.
- ► If the DO measurement made with an amperometric or optical sensor under the above conditions were 7.50 mg/L and the DO probe did not have an internal salinity compensation algorithm, then the actual DO concentration should be reported as 7.50 mg/L multiplied by 0.9733, which equals 7.30 mg/L.
- ► Do not use a salinity correction factor for measurements made with the iodometric (Winkler) or spectrophotometric methods.

Example of percent saturation calculation

To express results as percent saturation, use the following equation:

$$DO (percent \ saturation) = \frac{measured \ DO \ (mg \ / L)}{DO \ (mg \ / L \ at \ 100 \ percent \ saturation)} \times 100$$
(3)

For a salinity-corrected DO measurement of 7.30 mg/L for a sample in which the oxygen solubility (salinity corrected) is 8.73 mg/L as in the above example, the percent DO saturation would be the dividend of 7.30 divided by 8.73, multiplied by 100, which equals 83.6 percent. Note that for measurements with the iodometric (Winkler) or spectrophotometric methods, salinity correction factors are not applied to the measurement concentration.

Solubility of oxygen infreshwater at various temperatures and pressures. Table 6.2–6.

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

(deg C) 0.0 0.5 1.0	200	705	710	715	720	725	730	735	740	745	735 740 745 750 755 760	755	760	765	770	775	780	785	790	795
0.0 0.5 1.0	>			•)	1	2)			,)				
0.5	13.46	13.56	13.65	13.75	13.85	13.94	14.04	14.14	14.23	14.33	14.43	14.52	14.62	14.72	14.81	14.91	15.01	15.10	15.20	15.30
1.0	13.27	13.37	13.46	13.56	13.65	13.75	13.84	13.94	14.03	14.13	14.23	14.32	14.42	14.51	14.61	14.70	14.80	14.89	14.99	15.08
	13.09	13.18	13.28	13.37	13.46	13.56	13.65	13.75	13.84	13.93	14.03	14.12	14.22	14.31	14.40	14.50	14.59	14.69	14.78	14.87
1.5	12.91	13.00	13.09	13.19	13.28	13.37	13.46	13.56	13.65	13.74	13.84	13.93	14.02	14.11	14.21	14.30	14.39	14.48	14.58	14.67
2.0	12.73	12.82	12.91	13.01	13.10	13.19	13.28	13.37	13.46	13.56	13.65	13.74	13.83	13.92	14.01	14.10	14.20	14.29	14.38	14.47
2.5	12.56	12.65	12.74	12.83	12.92	13.01	13.10	13.19	13.28	13.37	13.46	13.55	13.64	13.73	13.82	13.91	14.00	14.10	14.19	14.28
3.0	12.39	12.48	12.57	12.66	12.75	12.84	12.93	13.02	13.10	13.19	13.28	13.37	13.46	13.55	13.64	13.73	13.82	13.91	14.00	14.09
3.5	12.23	12.31	12.40	12.49	12.58	12.67	12.75	12.84	12.93	13.02	13.11	13.19	13.28	13.37	13.46	13.55	13.63	13.72	13.81	13.90
4.0	12.07	12.15	12.24	12.33	12.41	12.50	12.59	12.67	12.76	12.85	12.93	13.02	13.11	13.20	13.28	13.37	13.46	13.54	13.63	13.72
4.5	11.91	11.99	12.08	12.17	12.25	12.34	12.42	12.51	12.59	12.68	12.77	12.85	12.94	13.02	13.11	13.20	13.28	13.37	13.45	13.54
5.0	11.75	11.84	11.92	12.01	12.09	12.18	12.26	12.35	12.43	12.52	12.60	12.69	12.77	12.86	12.94	13.03	13.11	13.19	13.28	13.36
5.5	11.60	11.69	11.77	11.86	11.94	12.02	12.11	12.19	12.27	12.36	12.44	12.52	12.61	12.69	12.78	12.86	12.94	13.03	13.11	13.19
0.9	11.46	11.54	11.62	11.70	11.79	11.87	11.95	12.04	12.12	12.20	12.28	12.37	12.45	12.53	12.61	12.70	12.78	12.86	12.94	13.03
6.5	11.31	11.39	11.48	11.56	11.64	11.72	11.80	11.88	11.97	12.05	12.13	12.21	12.29	12.37	12.46	12.54	12.62	12.70	12.78	12.86
7.0	11.17	11.25	11.33	11.41	11.49	11.58	11.66	11.74	11.82	11.90	11.98	12.06	12.14	12.22	12.30	12.38	12.46	12.54	12.62	12.70
7.5	11.03	11.11	11.19	11.27	11.35	11.43	11.51	11.59	11.67	11.75	11.83	11.91	11.99	12.07	12.15	12.23	12.31	12.39	12.47	12.55
8.0	10.90	10.98	11.06	11.14	11.21	11.29	11.37	11.45	11.53	11.61	11.69	11.76	11.84	11.92	12.00	12.08	12.16	12.24	12.32	12.39
8.5	10.77	10.84	10.92	11.00	11.08	11.16	11.23	11.31	11.39	11.47	11.54	11.62	11.70	11.78	11.86	11.93	12.01	12.09	12.17	12.24
0.6	10.64	10.71	10.79	10.87	10.94	11.02	11.10	11.18	11.25	11.33	11.41	11.48	11.56	11.64	11.71	11.79	11.87	11.94	12.02	12.10
9.5	10.51	10.59	10.66	10.74	10.81	10.89	10.97	11.04	11.12	11.19	11.27	11.35	11.42	11.50	11.57	11.65	11.73	11.80	11.88	11.95
10.0	10.39	10.46	10.54	10.61	10.69	10.76	10.84	10.91	10.99	11.06	11.14	11.21	11.29	11.36	11.44	11.51	11.59	11.66	11.74	11.81
10.5	10.26	10.34	10.41	10.49	10.56	10.64	10.71	10.78	10.86	10.93	11.01	11.08	11.16	11.23	11.30	11.38	11.45	11.53	11.60	11.68
11.0	10.15	10.22	10.29	10.37	10.44	10.51	10.59	10.66	10.73	10.81	10.88	10.95	11.03	11.10	11.17	11.25	11.32	11.39	11.47	11.54
11.5	10.03	10.10	10.17	10.25	10.32	10.39	10.47	10.54	10.61	10.68	10.76	10.83	10.90	10.97	11.05	11.12	11.19	11.26	11.34	11.41
12.0	9.91	66.6	10.06	10.13	10.20	10.27	10.35	10.42	10.49	10.56	10.63	10.71	10.78	10.85	10.92	10.99	11.06	11.14	11.21	11.28
12.5	9.80	9.87	9.94	10.02	10.09	10.16	10.23	10.30	10.37	10.44	10.51	10.58	10.66	10.73	10.80	10.87	10.94	11.01	11.08	11.15
13.0	69.6	9.76	9.83	9.90	6.97	10.04	10.11	10.19	10.26	10.33	10.40	10.47	10.54	10.61	10.68	10.75	10.82	10.89	10.96	11.03
13.5	9.59	9.65	9.72	9.79	98.6	9.93	10.00	10.07	10.14	10.21	10.28	10.35	10.42	10.49	10.56	10.63	10.70	10.77	10.84	10.91
14.0	9.48	9.55	9.62	69.6	92.6	9.82	68.6	96.6	10.03	10.10	10.17	10.24	10.31	10.37	10.44	10.51	10.58	10.65	10.72	10.79

Table 6.2-6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

Temp.							A	tmosphe	ric pres	sure, in	Atmospheric pressure, in millimeters of mercury	ters of n	nercury							
(deg C)	700	705	710	715	720	725	730	735	740	745	750	755	260	292	770	775	780	785	790	795
14.5	9.38	9.44	9.51	9.58	9.65	9.72	9.78	9.85	9.92	66.6	10.06	10.13	10.19	10.26	10.33	10.40	10.47	10.53	10.60	10.67
15.0	9.27	9.34	9.41	9.48	9.54	9.61	89.6	9.75	9.81	88.6	9.95	10.02	10.08	10.15	10.22	10.29	10.35	10.42	10.49	10.56
15.5	9.18	9.24	9.31	9.38	9.44	9.51	9.58	9.64	9.71	9.78	9.84	9.91	86.6	10.04	10.11	10.18	10.24	10.31	10.38	10.44
16.0	80.6	9.14	9.21	9.28	9.34	9.41	9.47	9.54	9.61	6.67	9.74	9.80	9.87	9.94	10.00	10.07	10.13	10.20	10.27	10.33
16.5	86.8	9.05	9.11	9.18	9.24	9.31	9.37	9.44	9.50	9.57	9.64	9.70	9.77	9.83	9.90	96.6	10.03	10.09	10.16	10.22
17.0	8.89	8.95	9.03	80.6	9.15	9.21	9.28	9.34	9.41	9.47	9.54	09.6	99.6	9.73	9.79	98.6	9.92	66.6	10.05	10.12
17.5	8.80	8.86	8.92	8.99	9.05	9.12	9.18	9.24	9.31	9.37	9.44	9.50	9.57	9.63	69.6	9.76	9.82	68.6	9.95	10.01
18.0	8.70	8.77	8.83	8.90	8.96	9.03	60.6	9.15	9.21	9.28	9.34	9.40	9.47	9.53	9.59	99.6	9.72	9.78	9.85	9.91
18.5	8.62	89.8	8.74	8.80	8.87	8.93	8.99	90.6	9.12	9.18	9.24	9.31	9.37	9.43	9.50	9.56	9.62	69.6	9.75	9.81
19.0	8.53	8.59	8.65	8.72	8.78	8.84	8.90	8.96	9.03	60.6	9.15	9.21	9.28	9.34	9.40	9.46	9.53	9.59	9.65	9.71
19.5	8.44	8.50	8.57	8.63	8.69	8.75	8.81	8.87	8.94	9.00	90.6	9.12	9.18	9.25	9.31	9.37	9.43	9.49	9.55	9.62
20.0	8.36	8.42	8.48	8.54	8.60	99.8	8.73	8.79	8.85	8.91	8.97	9.03	60.6	9.15	9.21	9.28	9.34	9.40	9.46	9.52
20.5	8.28	8.34	8.40	8.46	8.52	8.58	8.64	8.70	8.76	8.82	88.88	8.94	9.00	90.6	9.12	9.18	9.25	9.31	9.37	9.43
21.0	8.19	8.25	8.31	8.37	8.43	8.49	8.55	8.61	8.67	8.73	8.79	8.85	8.92	86.8	9.04	9.10	9.16	9.22	9.28	9.34
21.5	8.11	8.17	8.23	8.29	8.35	8.41	8.47	8.53	8.59	8.65	8.71	8.77	8.83	8.89	8.95	9.01	9.07	9.13	9.19	9.25
22.0	8.04	8.09	8.15	8.21	8.27	8.33	8.39	8.45	8.51	8.57	8.63	89.8	8.74	8.80	8.86	8.92	86.8	9.04	9.10	9.16
22.5	7.96	8.02	80.8	8.13	8.19	8.25	8.31	8.37	8.43	8.48	8.54	8.60	99.8	8.72	8.78	8.84	8.89	8.95	9.01	9.07
23.0	7.88	7.94	8.00	8.06	8.11	8.17	8.23	8.29	8.35	8.40	8.46	8.52	8.58	8.64	8.69	8.75	8.81	8.87	8.93	86.8
23.5	7.81	7.86	7.92	7.98	8.04	8.09	8.15	8.21	8.27	8.33	8.38	8.44	8.50	8.56	8.61	8.67	8.73	8.79	8.84	8.90
24.0	7.73	7.79	7.85	7.90	7.96	8.02	8.08	8.13	8.19	8.25	8.30	8.36	8.42	8.48	8.53	8.59	8.65	8.70	8.76	8.82
24.5	99.7	7.72	7.77	7.83	7.89	7.94	8.00	8.06	8.11	8.17	8.23	8.28	8.34	8.40	8.45	8.51	8.57	8.62	89.8	8.74
25.0	7.59	7.65	7.70	7.76	7.81	7.87	7.93	7.98	8.04	8.10	8.15	8.21	8.26	8.32	8.38	8.43	8.49	8.54	8.60	99.8
25.5	7.52	7.58	7.63	69.7	7.74	7.80	7.85	7.91	7.97	8.02	8.08	8.13	8.19	8.24	8.30	8.35	8.41	8.47	8.52	8.58
26.0	7.45	7.51	7.56	7.62	7.67	7.73	7.78	7.84	7.89	7.95	8.00	8.06	8.11	8.17	8.22	8.28	8.33	8.39	8.44	8.50
26.5	7.38	7.44	7.49	7.55	7.60	99.7	7.71	7.77	7.82	7.88	7.93	7.99	8.04	8.10	8.15	8.20	8.26	8.31	8.37	8.42
27.0	7.32	7.37	7.43	7.48	7.53	7.59	7.64	7.70	7.75	7.81	7.86	7.91	7.97	8.02	80.8	8.13	8.19	8.24	8.29	8.35
27.5	7.25	7.30	7.36	7.41	7.47	7.52	7.57	7.63	7.68	7.74	7.79	7.84	7.90	7.95	8.01	8.06	8.11	8.17	8.22	8.27
28.0	7.19	7.24	7.29	7.35	7.40	7.45	7.51	7.56	7.61	7.67	7.72	7.77	7.83	7.88	7.93	7.99	8.04	8.10	8.15	8.20
28.5	7.12	7.18	7.23	7.28	7.33	7.39	7.44	7.49	7.55	7.60	7.65	7.71	7.76	7.81	7.87	7.92	7.97	8.02	8.08	8.13

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward] Solubility of oxygen in freshwater at various temperatures and pressures.—Continued Table 6.2–6.

Temp.							A	tmosph	eric pres	ssure, in	Atmospheric pressure, in millimeters of mercury	ters of n	nercury							
(deg C)	200	705	710	715	720	725	730	735	740	745	750	755	260	765	770	775	780	785	790	795
29.0	7.06	7.11	7.16	7.22	7.27	7.32	7.38	7.43	7.48	7.53	7.59	7.64	69.7	7.74	7.80	7.85	7.90	7.95	8.01	8.06
29.5	7.00	7.05	7.10	7.15	7.21	7.26	7.31	7.36	7.42	7.47	7.52	7.57	7.62	7.68	7.73	7.78	7.83	7.89	7.94	7.99
30.0	6.94	66.9	7.04	7.09	7.14	7.20	7.25	7.30	7.35	7.40	7.46	7.51	7.56	7.61	7.66	7.71	7.77	7.82	7.87	7.92
30.5	88.9	6.93	86.9	7.03	7.08	7.13	7.19	7.24	7.29	7.34	7.39	7.44	7.49	7.55	7.60	7.65	7.70	7.75	7.80	7.85
31.0	6.82	6.87	6.92	6.97	7.02	7.07	7.12	7.17	7.23	7.28	7.33	7.38	7.43	7.48	7.53	7.58	7.63	69.7	7.74	7.79
31.5	92.9	6.81	98.9	6.91	96.9	7.01	7.06	7.11	7.16	7.21	7.27	7.32	7.37	7.42	7.47	7.52	7.57	7.62	7.67	7.72
32.0	6.70	6.75	08.9	6.85	6.90	6.95	7.00	7.05	7.10	7.15	7.20	7.25	7.30	7.36	7.41	7.46	7.51	7.56	7.61	99.7
32.5	6.64	69.9	6.74	6.79	6.84	68.9	6.94	66.9	7.04	7.09	7.14	7.19	7.24	7.29	7.34	7.39	7.44	7.49	7.54	7.59
33.0	6.59	6.64	69.9	6.74	6.79	6.84	68.9	6.93	86.9	7.03	7.08	7.13	7.18	7.23	7.28	7.33	7.38	7.43	7.48	7.53
33.5	6.53	6.58	6.63	89.9	6.73	87.9	6.83	88.9	6.93	86.9	7.02	7.07	7.12	7.17	7.22	7.27	7.32	7.37	7.42	7.47
34.0	6.48	6.53	6.57	6.62	29.9	6.72	6.77	6.82	6.87	6.92	6.97	7.02	7.06	7.11	7.16	7.21	7.26	7.31	7.36	7.41
34.5	6.42	6.47	6.52	6.57	6.62	6.67	6.71	92.9	6.81	98.9	6.91	96.9	7.01	7.06	7.10	7.15	7.20	7.25	7.30	7.35
35.0	6.37	6.42	6.47	6.51	95.9	6.61	99.9	6.71	92.9	08.9	6.85	06.9	6.95	7.00	7.05	7.09	7.14	7.19	7.24	7.29
35.5	6.32	6.36	6.41	6.46	6.51	95.9	09.9	6.65	6.70	6.75	08.9	6.84	68.9	6.94	66.9	7.04	7.08	7.13	7.18	7.23
36.0	6.26	6.31	98.9	6.41	6.45	6.50	6.55	09.9	6.65	69.9	6.74	6.79	6.84	88.9	6.93	86.9	7.03	7.08	7.12	7.17
36.5	6.21	6.26	6.31	6.35	6.40	6.45	6.50	6.54	6.59	6.64	69.9	6.73	82.9	6.83	88.9	6.92	6.97	7.02	7.07	7.11
37.0	6.16	6.21	6.26	6.30	6.35	6.40	6.44	6.49	6.54	6.59	6.63	89.9	6.73	6.77	6.82	6.87	6.92	96.9	7.01	7.06
37.5	6.11	6.16	6.20	6.25	6.30	6.35	6:39	6.44	6.49	6.53	6.58	6.63	29.9	6.72	6.77	6.81	98.9	6.91	6.95	7.00
38.0	90.9	6.11	6.15	6.20	6.25	6.29	6.34	6:39	6.43	6.48	6.53	6.57	6.62	6.67	6.71	92.9	6.81	6.85	06.9	6.95
38.5	6.01	90.9	6.10	6.15	6.20	6.24	6.29	6.34	6.38	6.43	6.47	6.52	6.57	6.61	99.9	6.71	6.75	08.9	6.84	68.9
39.0	5.96	6.01	6.05	6.10	6.15	6.19	6.24	6.29	6.33	6.38	6.42	6.47	6.52	95.9	6.61	6.65	6.70	6.75	6.79	6.84
39.5	5.91	5.96	6.01	6.05	6.10	6.14	6.19	6.23	6.28	6.33	6.37	6.42	6.46	6.51	95.9	09.9	6.65	69.9	6.74	82.9
40.0	5.87	5.91	5.96	00.9	6.05	60.9	6.14	6.19	6.23	6.28	6.32	6.37	6.41	6.46	6.50	6.55	6.59	6.64	69.9	6.73

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius] Table 6.2-6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

Temp.							A	\tmosph	eric pre	ssure, in	Atmospheric pressure, in millimeters of mercury	ters of r	nercury							
(deg C)	009	909	610	615	620	625	630	632	640	645	650	655	099	999	670	675	089	685	069	695
0.0	11.53	11.62	11.72	11.82	11.91	12.01	12.11	12.20	12.30	12.40	12.49	12.59	12.69	12.78	12.88	12.98	13.07	13.17	13.27	13.36
0.5	11.36	11.46	11.56	11.65	11.75	11.84	11.94	12.03	12.13	12.22	12.32	12.41	12.51	12.60	12.70	12.80	12.89	12.99	13.08	13.18
1.0	11.21	11.30	11.39	11.49	11.58	11.68	11.77	11.86	11.96	12.05	12.15	12.24	12.34	12.43	12.52	12.62	12.71	12.81	12.90	12.99
1.5	11.05	11.14	11.24	11.33	11.42	11.52	11.61	11.70	11.79	11.89	11.98	12.07	12.17	12.26	12.35	12.44	12.54	12.63	12.72	12.81
2.0	10.90	10.99	11.08	11.18	11.27	11.36	11.45	11.54	11.63	11.72	11.82	11.91	12.00	12.09	12.18	12.27	12.37	12.46	12.55	12.64
2.5	10.75	10.84	10.93	11.02	11.11	11.20	11.29	11.39	11.48	11.57	11.66	11.75	11.84	11.93	12.02	12.11	12.20	12.29	12.38	12.47
3.0	10.61	10.70	10.79	10.88	10.96	11.05	11.14	11.23	11.32	11.41	11.50	11.59	11.68	11.77	11.86	11.95	12.03	12.12	12.21	12.30
3.5	10.47	10.55	10.64	10.73	10.82	10.91	10.99	11.08	11.17	11.26	11.35	11.43	11.52	11.61	11.70	11.79	11.87	11.96	12.05	12.14
4.0	10.33	10.42	10.50	10.59	10.68	10.76	10.85	10.94	11.02	11.11	11.20	11.28	11.37	11.46	11.54	11.63	11.72	11.81	11.89	11.98
4.5	10.19	10.28	10.36	10.45	10.54	10.62	10.71	10.79	10.88	10.97	11.05	11.14	11.22	11.31	11.39	11.48	11.57	11.65	11.74	11.82
5.0	10.06	10.15	10.23	10.32	10.40	10.48	10.57	10.65	10.74	10.82	10.91	10.99	11.08	11.16	11.25	11.33	11.42	11.50	11.59	11.67
5.5	9.93	10.02	10.10	10.18	10.27	10.35	10.43	10.52	10.60	10.68	10.77	10.85	10.94	11.02	11.10	11.19	11.27	11.35	11.44	11.52
0.9	9.80	68.6	9.97	10.05	10.14	10.22	10.30	10.38	10.47	10.55	10.63	10.71	10.80	10.88	10.96	11.04	11.13	11.21	11.29	11.37
6.5	89.6	9.76	9.84	9.93	10.01	10.09	10.17	10.25	10.33	10.42	10.50	10.58	10.66	10.74	10.82	10.91	10.99	11.07	11.15	11.23
7.0	9.56	9.64	9.72	9.80	88.6	96.6	10.04	10.12	10.20	10.29	10.37	10.45	10.53	10.61	10.69	10.77	10.85	10.93	11.01	11.09
7.5	9.44	9.52	09.6	89.6	9.76	9.84	9.92	10.00	10.08	10.16	10.24	10.32	10.40	10.48	10.56	10.64	10.72	10.80	10.87	10.95
8.0	9.33	9.40	9.48	9.56	9.64	9.72	9.80	88.6	9.95	10.03	10.11	10.19	10.27	10.35	10.43	10.51	10.58	10.66	10.74	10.82
8.5	9.21	9.29	9.37	9.44	9.52	09.6	89.6	9.76	9.83	9.91	66.6	10.07	10.14	10.22	10.30	10.38	10.46	10.53	10.61	10.69
0.6	9.10	9.18	9.25	9.33	9.41	9.48	9.56	9.64	9.71	62.6	8.87	9.95	10.02	10.10	10.18	10.25	10.33	10.41	10.48	10.56
9.5	8.99	9.07	9.14	9.22	9.29	9.37	9.45	9.52	09.6	6.67	9.75	9.83	9.90	86.6	10.05	10.13	10.21	10.28	10.36	10.43
10.0	8.88	8.96	9.03	9.11	9.18	9.26	9.33	9.41	9.49	9.56	9.64	9.71	9.79	98.6	9.94	10.01	10.09	10.16	10.24	10.31
10.5	8.78	8.85	8.93	9.00	80.6	9.15	9.23	9.30	9.37	9.45	9.52	09.6	29.6	9.75	9.82	68.6	6.97	10.04	10.12	10.19
11.0	89.8	8.75	8.82	8.90	8.97	9.04	9.12	9.19	9.26	9.34	9.41	9.48	9.56	9.63	9.71	82.6	9.85	9.93	10.00	10.07
11.5	8.58	8.65	8.72	8.79	8.87	8.94	9.01	80.6	9.16	9.23	9.30	9.38	9.45	9.52	9.59	29.6	9.74	9.81	88.6	96.6
12.0	8.48	8.55	8.62	8.69	8.77	8.84	8.91	86.8	9.05	9.12	9.20	9.27	9.34	9.41	9.48	9.56	9.63	9.70	9.77	9.84
12.5	8.38	8.45	8.52	8.59	8.67	8.74	8.81	8.88	8.95	9.02	60.6	9.16	9.23	9.31	9.38	9.45	9.52	9.59	99.6	9.73
13.0	8.29	8.36	8.43	8.50	8.57	8.64	8.71	8.78	8.85	8.92	8.99	90.6	9.13	9.20	9.27	9.34	9.41	9.48	9.55	9.62
13.5	8.19	8.26	8.33	8.40	8.47	8.54	8.61	89.8	8.75	8.82	8.89	8.96	9.03	9.10	9.17	9.24	9.31	9.38	9.45	9.52
14.0	8.10	8.17	8.24	8.31	8.38	8.45	8.52	8.58	8.65	8.72	8.79	8.86	8.93	00.6	6.07	9.14	9.20	9.27	9.34	9.41

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius] Solubility of oxygen in freshwater at various temperatures and pressures.—Continued Table 6.2–6.

Temn							٥	tmosuh	Atmospheric pressure in millimeters of mercury	in eine	millime	ters of n	Jerciiry							
(deg C)	009	902	610	615	620	625	630	635	640	645	650	655	, 099	999	0/9	675	089	685	069	695
14.5	8.01	8.08	8.15	8.22	8.29	8.35	8.42	8.49	8.56	8.63	8.69	8.76	8.83	8.90	8.97	9.04	9.10	9.17	9.24	9.31
15.0	7.93	7.99	8.06	8.13	8.20	8.26	8.33	8.40	8.47	8.53	8.60	8.67	8.74	8.80	8.87	8.94	9.00	9.07	9.14	9.21
15.5	7.84	7.91	7.97	8.04	8.11	8.17	8.24	8.31	8.37	8.44	8.51	8.57	8.64	8.71	8.77	8.84	8.91	8.97	9.04	9.11
16.0	7.76	7.82	7.89	7.95	8.02	8.09	8.15	8.22	8.28	8.35	8.42	8.48	8.55	8.61	89.8	8.75	8.81	8.88	8.95	9.01
16.5	7.67	7.74	7.80	7.87	7.93	8.00	8.07	8.13	8.20	8.26	8.33	8.39	8.46	8.52	8.59	8.65	8.72	8.79	8.85	8.92
17.0	7.59	99.7	7.72	7.79	7.85	7.92	7.98	8.05	8.11	8.17	8.24	8.30	8.37	8.43	8.50	8.56	8.63	8.69	8.76	8.82
17.5	7.51	7.58	7.64	7.70	7.77	7.83	7.90	7.96	8.03	8.09	8.15	8.22	8.28	8.35	8.41	8.47	8.54	8.60	8.67	8.73
18.0	7.43	7.50	7.56	7.62	7.69	7.75	7.81	7.88	7.94	8.01	8.07	8.13	8.20	8.26	8.32	8.39	8.45	8.51	8.58	8.64
18.5	7.36	7.42	7.48	7.55	7.61	7.67	7.73	7.80	7.86	7.92	7.99	8.05	8.11	8.18	8.24	8.30	8.36	8.43	8.49	8.55
19.0	7.28	7.34	7.41	7.47	7.53	7.59	99.7	7.72	7.78	7.84	7.90	7.97	8.03	8.09	8.15	8.22	8.28	8.34	8.40	8.47
19.5	7.21	7.27	7.33	7.39	7.45	7.52	7.58	7.64	7.70	7.76	7.82	7.89	7.95	8.01	8.07	8.13	8.20	8.26	8.32	8.38
20.0	7.13	7.20	7.26	7.32	7.38	7.44	7.50	7.56	7.62	7.68	7.75	7.81	7.87	7.93	7.99	8.05	8.11	8.17	8.24	8.30
20.5	7.06	7.12	7.18	7.24	7.31	7.37	7.43	7.49	7.55	7.61	7.67	7.73	7.79	7.85	7.91	7.97	8.03	8.09	8.15	8.21
21.0	66.9	7.05	7.11	7.17	7.23	7.29	7.35	7.41	7.47	7.53	7.59	7.65	7.71	7.77	7.83	7.89	7.95	8.01	8.07	8.13
21.5	6.92	86.9	7.04	7.10	7.16	7.22	7.28	7.34	7.40	7.46	7.52	7.58	7.64	7.70	7.76	7.82	7.88	7.94	7.99	8.05
22.0	6.85	6.91	6.97	7.03	7.09	7.15	7.21	7.27	7.33	7.39	7.45	7.50	7.56	7.62	7.68	7.74	7.80	7.86	7.92	7.98
22.5	6.79	6.85	06.9	96.9	7.02	7.08	7.14	7.20	7.26	7.31	7.37	7.43	7.49	7.55	7.61	7.67	7.72	7.78	7.84	7.90
23.0	6.72	82.9	6.84	06.9	6.95	7.01	7.07	7.13	7.19	7.24	7.30	7.36	7.42	7.48	7.53	7.59	7.65	7.71	7.77	7.82
23.5	99.9	6.71	6.77	6.83	68.9	6.94	7.00	7.06	7.12	7.17	7.23	7.29	7.35	7.40	7.46	7.52	7.58	7.63	69.7	7.75
24.0	6.59	6.65	6.71	92.9	6.82	88.9	6.94	66.9	7.05	7.11	7.16	7.22	7.28	7.33	7.39	7.45	7.51	7.56	7.62	7.68
24.5	6.53	6:59	6.64	6.70	92.9	6.81	6.87	6.93	86.9	7.04	7.10	7.15	7.21	7.27	7.32	7.38	7.44	7.49	7.55	7.61
25.0	6.47	6.52	6.58	6.64	69.9	6.75	6.81	98.9	6.92	6.97	7.03	7.09	7.14	7.20	7.25	7.31	7.37	7.42	7.48	7.53
25.5	6.41	6.46	6.52	6.57	6.63	69.9	6.74	08.9	6.85	6.91	96.9	7.02	7.08	7.13	7.19	7.24	7.30	7.35	7.41	7.46
26.0	6.35	6.40	6.46	6.51	6.57	6.62	89.9	6.73	62.9	6.84	06.9	6.95	7.01	7.07	7.12	7.18	7.23	7.29	7.34	7.40
26.5	6.29	6.34	6.40	6.45	6.51	95.9	6.62	6.67	6.73	87.9	6.84	68.9	6.95	7.00	7.06	7.11	7.16	7.22	7.27	7.33
27.0	6.23	6.28	6.34	6.39	6.45	6.50	95.9	6.61	29.9	6.72	6.77	6.83	88.9	6.94	66.9	7.05	7.10	7.15	7.21	7.26
27.5	6.17	6.23	6.28	6.33	6:39	6.44	6.50	6.55	09.9	99.9	6.71	6.77	6.82	6.87	6.93	86.9	7.04	7.09	7.14	7.20
28.0	6.12	6.17	6.22	6.28	6.33	6.38	6.44	6.49	6.54	09.9	6.65	0.70	92.9	6.81	6.87	6.92	6.97	7.03	7.08	7.13
28.5	90.9	6.11	6.17	6.22	6.27	6.33	6.38	6.43	6.49	6.54	6.59	6.64	6.70	6.75	08.9	98.9	6.91	96.9	7.02	7.07

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius] Table 6.2-6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

44.0 64.0 <th< th=""><th>Temp.</th><th></th><th></th><th></th><th></th><th></th><th></th><th>¥</th><th>tmosph</th><th>eric pre</th><th>ssure, in</th><th>mIIIme</th><th>Atmospheric pressure, in millimeters of mercury</th><th>nercury</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></th<>	Temp.							¥	tmosph	eric pre	ssure, in	mIIIme	Atmospheric pressure, in millimeters of mercury	nercury							
6.01 6.06 6.11 6.16 6.22 6.27 6.32 6.37 6.43 6.48 6.53 6.59 6.64 6.69 6.74 6.89 6.99 6.91 6.10 6.12 6.22 6.23 6.31 6.32 6.31 6.32 6.31 6.32 6.31 6.32 6.31 6.32 6.31 6.32 6.31 6.32 6.31 6.32 6.31 6.32 6.31 6.32 6.31 <th< th=""><th>(deg C)</th><th>009</th><th>902</th><th>610</th><th>615</th><th>620</th><th>625</th><th>630</th><th>635</th><th>640</th><th>645</th><th>650</th><th>655</th><th>099</th><th>999</th><th>029</th><th>675</th><th>089</th><th>982</th><th>069</th><th>695</th></th<>	(deg C)	009	902	610	615	620	625	630	635	640	645	650	655	099	999	029	675	089	982	069	695
5.96 6.00 6.06 6.11 6.10 6.21 6.23 6.37 6.42 6.47 6.33 6.38 6.36 6.03 6.04 6.10 6.10 6.11 6.10 6.21 6.22 6.31 6.37 6.47 6.47 6.32 6.37 6.47 6.47 6.32 6.37 6.42 6.47 6.32 6.37 6.42 6.47 6.47 6.49 6.47 6.47 6.27 <th< td=""><td>29.0</td><td>6.01</td><td>90.9</td><td>6.11</td><td>6.16</td><td>6.22</td><td>6.27</td><td>6.32</td><td>6.37</td><td>6.43</td><td>6.48</td><td>6.53</td><td>6.59</td><td>6.64</td><td>69.9</td><td>6.74</td><td>6.80</td><td>6.85</td><td>06.90</td><td>6.95</td><td>7.01</td></th<>	29.0	6.01	90.9	6.11	6.16	6.22	6.27	6.32	6.37	6.43	6.48	6.53	6.59	6.64	69.9	6.74	6.80	6.85	06.90	6.95	7.01
5.90 5.95 6.00 6.05 6.11 6.16 6.21 6.24 6.37 6.47 6.52 6.57 6.69 6.79 6.79 5.85 5.90 6.90 6.00 6.01 6.10 6.11 6.12 6.24 6.31 6.49 6.49 6.59 6.79 6.70 6.70 6.10 6.	29.5	5.95	00.9	90.9	6.11	6.16	6.21	6.27	6.32	6.37	6.42	6.47	6.53	6.58	6.63	89.9	6.74	6.79	6.84	68.9	6.95
5.8 5.90 5.95 6.00 6.05 6.10 6.11 6.12 6.21 6.23 6.31 6.34 6.41 6.46 6.25 6.31 6.36 6.41 6.46 6.25 6.31 6.36 6.41 6.46 6.25 6.31 6.36 6.41 6.46 6.25 6.41 6.46 6.25 6.41 6.46 6.25 6.41 6.46 6.27 6.41 6.46 6.27 6.41 6.46 6.27 6.41 6.46 6.27 6.40 6.57 6.50	30.0	5.90	5.95	00.9	6.05	6.11	6.16	6.21	6.26	6.31	6.37	6.42	6.47	6.52	6.57	6.63	89.9	6.73	82.9	6.83	88.9
5.79 5.88 5.90 5.95 6.00 6.05 6.10 6.15 6.20 6.23 6.31 6.46 6.41 6.46 6.51 6.50 6.50 5.74 5.79 5.84 5.90 6.00 6.01 6.15 6.15 6.25 6.30 6.35 6.40 6.45 6.50 6.50 6.50 6.70 6.10 6.10 6.12 6.25 6.30 6.35 6.40 6.45 6.50 6.50 6.50 6.50 6.50 6.50 6.70 6.	30.5	5.85	5.90	5.95	00.9	6.05	6.10	6.16	6.21	6.26	6.31	98.9	6.41	6.46	6.52	6.57	6.62	6.67	6.72	6.77	6.82
5.4 5.79 5.84 5.90 5.95 6.00 6.10 6.15 6.20 6.25 6.30 6.35 6.40 6.45 6.50 6.50 5.64 5.79 5.84 5.89 5.94 5.99 6.04 6.10 6.15 6.20 6.25 6.30 6.35 6.40 6.79 6.7	31.0	5.79	5.85	5.90	5.95	00.9	6.05	6.10	6.15	6.20	6.25	6.31	6.36	6.41	6.46	6.51	95.9	6.61	99.9	6.71	6.77
5.69 5.74 5.79 5.84 5.89 6.94 6.10 6.15 6.20 6.25 6.35 6.34 6.89 6.94 6.10 6.15 6.20 6.25 6.34 6.39 6.94 6.10 6.14 6.19 6.24 6.29 6.34 6.39 6.44 6.19 6.14 6.19 6.24 6.29 6.44 6.19 6.24 6.29 6.44 6.19 6.14 6.19 6.24 6.29 6.44 6.19 6.14 6.19 6.24 6.29 6.44 6.29 6.44 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.19 <th< td=""><td>31.5</td><td>5.74</td><td>5.79</td><td>5.84</td><td>5.90</td><td>5.95</td><td>00.9</td><td>6.05</td><td>6.10</td><td>6.15</td><td>6.20</td><td>6.25</td><td>6.30</td><td>6.35</td><td>6.40</td><td>6.45</td><td>6.50</td><td>6.55</td><td>6.61</td><td>99.9</td><td>6.71</td></th<>	31.5	5.74	5.79	5.84	5.90	5.95	00.9	6.05	6.10	6.15	6.20	6.25	6.30	6.35	6.40	6.45	6.50	6.55	6.61	99.9	6.71
5.64 5.69 5.74 5.89 5.84 5.89 6.94 6.09 6.14 6.19 6.24 6.29 6.34 6.99 6.14 6.19 6.24 6.39 6.44 5.59 5.64 5.69 5.74 5.89 5.84 5.89 6.94 6.99 6.14 6.19 6.24 6.29 6.34 6.39 6.44 6.19 6.14 6.19 6.24 6.39 6.44 6.99 6.14 6.19 6.14 6.19 6.24 6.39 6.44 6.99 6.14 6.19 6.14 6.19 6.14 6.19 6.24 6.39 6.44 6.99 6.04 6.09 6.14 6.19 6.24 6.39 6.44 6.99 6.04 6.09 6.14 6.19 6.24 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.	32.0	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.10	6.15	6.20	6.25	6.30	6.35	6.40	6.45	6.50	6.55	09.9	6.65
5.59 5.64 5.69 5.74 5.79 5.84 5.89 6.84 6.04 6.09 6.14 6.19 6.24 6.29 6.34 6.39 5.54 5.59 5.64 5.89 5.84 5.89 5.94 5.99 6.04 6.09 6.14 6.19 6.24 6.39 6.34 6.39 5.50 5.54 5.69 5.74 5.89 5.94 5.99 6.04 6.09 6.14 6.19 6.24 6.39 6.34 6.39 6.34 6.39 6.34 6.99 6.04 6.09 6.14 6.19 6.14 6.19 6.14 6.19 6.14 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39 6.34 6.39<	32.5	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	60.9	6.14	6.19	6.24	6.29	6.34	6.39	6.44	6.49	6.54	6.59
5.54 5.59 5.64 5.59 5.64 6.03 6.04 6.03 6.04 6.03 6.03 6.03 6.03 <th< td=""><td>33.0</td><td>5.59</td><td>5.64</td><td>5.69</td><td>5.74</td><td>5.79</td><td>5.84</td><td>5.89</td><td>5.94</td><td>5.99</td><td>6.04</td><td>60.9</td><td>6.14</td><td>6.19</td><td>6.24</td><td>6.29</td><td>6.34</td><td>6.39</td><td>6.44</td><td>6.49</td><td>6.54</td></th<>	33.0	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	60.9	6.14	6.19	6.24	6.29	6.34	6.39	6.44	6.49	6.54
5.505.545.695.645.695.745.795.845.895.946.046.086.136.186.236.285.455.505.555.645.695.745.795.845.895.946.096.036.086.136.186.235.405.455.505.645.695.745.795.845.885.936.086.136.186.235.315.405.455.505.545.695.745.795.845.885.935.986.036.086.136.185.215.315.405.455.605.445.695.745.795.845.895.935.986.036.086.125.225.315.365.555.605.645.695.745.795.885.935.895.935.995.135.315.365.415.455.505.645.695.745.795.885.935.895.935.995.135.145.455.505.555.605.645.695.745.795.835.885.935.895.135.185.225.275.315.365.415.465.505.545.695.745.795.895.745.795.835.895.045.095.135.135.215.325.315.415.465.505.54 <td< td=""><td>33.5</td><td>5.54</td><td>5.59</td><td>5.64</td><td>5.69</td><td>5.74</td><td>5.79</td><td>5.84</td><td>5.89</td><td>5.94</td><td>5.99</td><td>6.04</td><td>60.9</td><td>6.14</td><td>6.19</td><td>6.24</td><td>6.28</td><td>6.33</td><td>6.38</td><td>6.43</td><td>6.48</td></td<>	33.5	5.54	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	60.9	6.14	6.19	6.24	6.28	6.33	6.38	6.43	6.48
5.455.505.545.645.695.745.795.845.895.945.986.036.086.136.186.235.405.455.505.555.645.695.745.795.845.895.935.986.036.086.136.185.355.405.555.645.695.745.795.845.885.935.986.036.086.135.315.365.455.505.555.605.645.695.745.795.835.885.935.976.025.225.215.365.415.455.505.565.645.695.745.795.835.885.935.976.025.175.225.275.315.365.415.455.605.645.695.745.785.835.885.935.975.135.185.225.215.325.415.455.505.555.605.645.695.745.785.835.885.935.135.185.225.275.325.345.465.505.555.605.645.695.745.785.835.835.045.095.135.135.235.345.345.355.355.355.355.355.355.355.355.355.355.355.355.355.355.355.355.355.35 <td>34.0</td> <td>5.50</td> <td>5.54</td> <td>5.59</td> <td>5.64</td> <td>5.69</td> <td>5.74</td> <td>5.79</td> <td>5.84</td> <td>5.89</td> <td>5.94</td> <td>5.99</td> <td>6.04</td> <td>80.9</td> <td>6.13</td> <td>6.18</td> <td>6.23</td> <td>6.28</td> <td>6.33</td> <td>6.38</td> <td>6.43</td>	34.0	5.50	5.54	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	80.9	6.13	6.18	6.23	6.28	6.33	6.38	6.43
5.405.455.505.545.695.745.795.845.885.935.986.036.086.136.185.355.405.555.505.565.645.695.745.795.845.885.935.986.036.086.125.315.365.405.555.605.645.695.745.795.885.935.986.026.075.225.215.315.365.415.455.505.555.605.645.695.745.785.885.935.976.025.175.225.215.315.365.415.455.505.565.645.695.745.785.835.885.935.975.135.135.365.415.455.505.565.645.695.745.785.835.835.925.135.135.245.415.455.505.555.605.645.695.745.785.835.835.935.135.185.225.275.325.345.465.505.565.565.565.565.565.565.565.565.565.575.595.745.785.785.785.785.045.095.135.135.235.345.345.465.505.555.565.565.565.565.565.565.575.595.54 <td>34.5</td> <td>5.45</td> <td>5.50</td> <td>5.55</td> <td>5.59</td> <td>5.64</td> <td>5.69</td> <td>5.74</td> <td>5.79</td> <td>5.84</td> <td>5.89</td> <td>5.94</td> <td>5.98</td> <td>6.03</td> <td>80.9</td> <td>6.13</td> <td>6.18</td> <td>6.23</td> <td>6.28</td> <td>6.32</td> <td>6.37</td>	34.5	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.98	6.03	80.9	6.13	6.18	6.23	6.28	6.32	6.37
5.355.405.455.505.555.605.645.695.745.795.845.885.935.986.036.086.125.315.365.405.455.505.645.695.745.795.835.885.935.986.026.075.245.315.365.415.455.505.565.645.695.745.785.835.885.935.976.025.255.275.315.365.415.455.505.645.695.745.785.835.885.935.975.175.225.275.315.365.415.465.695.745.785.835.885.935.975.135.185.225.275.315.365.415.465.505.645.695.745.785.835.885.935.095.135.185.225.275.325.365.415.465.505.555.595.445.695.735.785.835.095.095.135.135.235.365.375.415.465.505.555.595.645.695.735.785.005.055.055.055.055.555.595.645.695.735.735.735.005.055.055.055.555.595.645.695.735.735.735.0	35.0	5.40	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.88	5.93	5.98	6.03	80.9	6.13	6.18	6.22	6.27	6.32
5.315.365.405.455.505.555.605.645.695.745.795.835.885.935.976.075.265.315.365.415.455.505.555.605.645.695.745.785.835.895.935.975.125.275.315.365.415.455.505.555.605.645.695.745.785.835.895.975.135.185.225.275.325.415.465.505.555.605.645.695.745.785.835.895.095.135.185.225.275.325.365.415.465.505.555.695.745.785.835.895.045.095.135.185.235.365.415.465.505.555.595.645.695.735.785.835.045.095.145.185.235.375.315.415.465.505.555.595.645.695.735.785.005.055.055.055.555.505.555.595.645.695.735.785.005.055.055.055.555.505.555.595.645.695.735.785.005.055.055.055.055.555.595.555.595.645.695.735.005.0	35.5	5.35	5.40	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.88	5.93	5.98	6.03	80.9	6.12	6.17	6.22	6.27
5.265.315.365.415.455.505.555.605.645.695.745.785.835.835.976.025.225.275.315.365.415.455.505.565.605.645.695.745.785.835.935.975.135.145.365.415.455.505.555.605.645.695.745.785.835.895.975.135.185.225.275.325.415.465.505.565.645.695.735.785.835.875.045.095.135.185.235.365.415.465.505.555.595.645.695.735.785.785.005.055.095.145.185.235.375.415.465.505.555.595.595.645.695.005.055.055.055.055.575.595.595.595.645.69	36.0	5.31	5.36	5.40	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.79	5.83	5.88	5.93	5.98	6.02	6.07	6.12	6.17	6.22
5.225.275.315.365.415.455.505.555.605.645.695.745.785.885.935.975.175.225.275.315.365.415.455.505.555.605.645.695.745.785.835.895.925.135.185.225.275.325.365.415.465.505.555.595.645.695.735.785.835.875.045.095.135.185.235.375.415.465.505.555.595.645.695.735.785.785.005.055.095.145.185.235.375.315.415.465.505.555.595.645.695.735.784.965.005.055.095.145.185.235.275.225.275.235.275.235.315.415.465.505.555.595.645.695.735.73	36.5	5.26	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.93	5.97	6.02	6.07	6.12	6.16
5.175.225.275.315.365.415.455.505.555.605.645.695.745.785.835.895.925.135.185.225.275.325.365.415.465.505.555.605.645.695.735.785.835.875.095.135.185.225.275.325.315.415.465.505.555.595.645.095.735.785.785.005.055.095.145.185.235.275.325.375.415.465.505.555.595.645.695.734.965.005.055.095.145.185.235.235.375.415.465.505.555.595.645.695.73	37.0	5.22	5.27	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.93	5.97	6.02	6.07	6.11
5.135.185.225.275.325.365.415.465.505.555.645.695.735.785.835.875.095.135.185.225.275.325.365.415.465.505.555.595.645.695.735.785.835.045.095.135.185.235.275.325.375.415.465.505.555.595.645.695.734.965.005.055.095.145.185.235.235.235.375.415.465.505.555.595.645.695.73	37.5	5.17	5.22	5.27	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.92	5.97	6.05	90.9
5.09 5.13 5.18 5.22 5.27 5.32 5.36 5.41 5.46 5.50 5.55 5.59 5.64 5.69 5.73 5.78 5.83 5.89 5.04 5.09 5.13 5.18 5.23 5.27 5.32 5.34 5.41 5.46 5.50 5.55 5.59 5.64 5.69 5.73 5.78 5.78 5.78 5.79 5.00 5.05 5.09 5.14 5.18 5.23 5.23 5.23 5.37 5.41 5.46 5.50 5.55 5.59 5.59 5.64 5.69 5.73 5.95 5.95 5.95 5.95 5.95 5.95 5.95 5.9	38.0	5.13	5.18	5.22	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.60	5.64	5.69	5.73	5.78	5.83	5.87	5.92	5.97	6.01
5.04 5.09 5.13 5.18 5.23 5.27 5.32 5.36 5.41 5.46 5.50 5.55 5.59 5.64 5.69 5.73 5.78 5 5.00 5.05 5.09 5.14 5.18 5.23 5.23 5.37 5.41 5.46 5.46 5.50 5.55 5.59 5.64 5.69 5.73 5 5.40 5.00 5.05 5.09 5.14 5.18 5.23 5.23 5.32 5.37 5.41 5.46 5.50 5.55 5.59 5.64 5.69 5.64 5.69 5.84	38.5	5.09	5.13	5.18	5.22	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.83	5.87	5.92	5.97
5.00 5.05 5.09 5.14 5.18 5.23 5.27 5.32 5.37 5.41 5.46 5.50 5.55 5.59 5.64 5.69 5.73 4.96 5.00 5.05 5.09 5.14 5.18 5.23 5.28 5.32 5.37 5.41 5.46 5.50 5.55 5.59 5.64 5.69 5.69	39.0	5.04	5.09	5.13	5.18	5.23	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82	5.87	5.92
4.96 5.00 5.05 5.09 5.14 5.18 5.23 5.28 5.32 5.37 5.41 5.46 5.50 5.55 5.59 5.64 5.69	39.5	5.00	5.05	5.09	5.14	5.18	5.23	5.27	5.32	5.37	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82	5.87
	40.0	4.96	5.00	5.05	5.09	5.14	5.18	5.23	5.28	5.32	5.37	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

)		'		,											
Temp.				S	pecific co	nductance,	in microsi	emens per (Specific conductance, in microsiemens per centimeter at 25 degrees Celsius	at 25 degre	es Celsius				
(deg C)	0	1000	2000	3000	4000	2000	0009	2000	8000	0006	10000	11000	12000	13000	14000
0.0	1.0000	0.9961	0.9922	0.9882	0.9843	0.9804	0.9764	0.9724	0.9684	0.9644	0.9604	0.9564	0.9524	0.9483	0.9443
1.0	1.0000	0.9961	0.9923	0.9884	0.9845	0.9805	9926.0	0.9727	0.9687	0.9648	8096.0	0.9568	0.9528	0.9488	0.9448
2.0	1.0000	0.9962	0.9923	0.9885	0.9846	0.9807	8926.0	0.9729	0.696.0	0.9651	0.9611	0.9572	0.9532	0.9493	0.9453
3.0	1.0000	0.9962	0.9924	9886.0	0.9847	6086.0	0.9770	0.9732	0.9693	0.9654	0.9615	0.9576	0.9536	0.9497	0.9458
4.0	1.0000	0.9962	0.9925	0.9887	0.9849	0.9811	0.9772	0.9734	9696.0	0.9657	0.9618	0.9579	0.9541	0.9502	0.9462
5.0	1.0000	0.9963	0.9925	0.9888	0.9850	0.9812	0.9774	0.9736	8696.0	0996.0	0.9622	0.9583	0.9545	0.9506	0.9467
0.9	1.0000	0.9963	0.9926	0.9889	0.9851	0.9814	9226	0.9739	0.9701	0.9663	0.9625	0.9587	0.9549	0.9510	0.9472
7.0	1.0000	0.9963	0.9927	0.9890	0.9853	0.9816	0.9778	0.9741	0.9703	9996.0	0.9628	0.9590	0.9552	0.9514	0.9476
8.0	1.0000	0.9964	0.9927	0.9891	0.9854	0.9817	0.9780	0.9743	9026.0	6996.0	0.9631	0.9594	0.9556	0.9519	0.9481
0.6	1.0000	0.9964	0.9928	0.9892	0.9855	0.9819	0.9782	0.9745	0.9708	0.9672	0.9634	0.9597	0.9560	0.9523	0.9485
10.0	1.0000	0.9964	0.9928	0.9893	0.9856	0.9820	0.9784	0.9747	0.9711	0.9674	0.9637	0.9601	0.9564	0.9527	0.9489
11.0	1.0000	0.9965	0.9929	0.9893	0.9858	0.9822	9826.0	0.9750	0.9713	2296.0	0.9640	0.9604	0.9567	0.9530	0.9494
12.0	1.0000	0.9965	0.9930	0.9894	0.9859	0.9823	0.9787	0.9752	0.9716	0.9680	0.9643	2096.0	0.9571	0.9534	0.9498
13.0	1.0000	0.9965	0.9930	0.9895	0.9860	0.9825	0.9789	0.9754	0.9718	0.9682	0.9646	0.9610	0.9574	0.9538	0.9502
14.0	1.0000	0.9965	0.9931	9686.0	0.9861	0.9826	0.9791	0.9756	0.9720	0.9685	0.9649	0.9613	0.9578	0.9542	0.9506
15.0	1.0000	9966.0	0.9931	0.9897	0.9862	0.9827	0.9793	0.9758	0.9723	0.9687	0.9652	0.9617	0.9581	0.9545	0.9510
16.0	1.0000	9966.0	0.9932	8686.0	0.9863	0.9829	0.9794	0926.0	0.9725	0696.0	0.9655	0.9620	0.9584	0.9549	0.9513
17.0	1.0000	9966.0	0.9932	8686.0	0.9864	0.9830	9626.0	0.9761	0.9727	0.9692	0.9657	0.9622	0.9587	0.9552	0.9517
18.0	1.0000	0.9967	0.9933	6686.0	0.9865	0.9831	0.9797	0.9763	0.9729	0.9695	0.9660	0.9625	0.9591	0.9556	0.9521
19.0	1.0000	0.9967	0.9933	0.9900	9986.0	0.9833	0.9799	0.9765	0.9731	2696.0	0.9663	0.9628	0.9594	0.9559	0.9524
20.0	1.0000	1966.0	0.9934	0.9901	0.9867	0.9834	0.9800	1926.0	0.9733	6696.0	0.9665	0.9631	0.9597	0.9562	0.9528
21.0	1.0000	1966.0	0.9934	0.9902	8986.0	0.9835	0.9802	6926.0	0.9735	0.9701	8996.0	0.9634	0.96.0	0.9566	0.9531
22.0	1.0000	8966.0	0.9935	0.9902	6986.0	0.9836	0.9803	0.9770	0.9737	0.9704	0.9670	0.9636	0.9603	0.9569	0.9535
23.0	1.0000	8966.0	0.9935	0.9903	0.9870	0.9838	0.9805	0.9772	0.9739	9026.0	0.9672	0.9639	0.9605	0.9572	0.9538
24.0	1.0000	8966.0	0.9936	0.9904	0.9871	0.9839	9086.0	0.9774	0.9741	0.9708	0.9675	0.9642	8096.0	0.9575	0.9541
25.0	1.0000	8966'0	0.9936	0.9904	0.9872	0.9840	8086.0	0.9775	0.9743	0.9710	0.9677	0.9644	0.9611	0.9578	0.9545
26.0	1.0000	8966'0	0.9937	0.9905	0.9873	0.9841	6086.0	0.9777	0.9744	0.9712	6.9679	0.9647	0.9614	0.9581	0.9548
27.0	1.0000	6966.0	0.9937	9066.0	0.9874	0.9842	0.9810	0.9778	0.9746	0.9714	0.9681	0.9649	0.9616	0.9584	0.9551
28.0	1.0000	6966.0	0.9938	9066.0	0.9875	0.9843	0.9812	0.9780	0.9748	0.9716	0.9684	0.9651	0.9619	0.9586	0.9554
29.0	1.0000	6966.0	0.9938	0.9907	9286.0	0.9844	0.9813	0.9781	0.9750	0.9718	9896.0	0.9654	0.9621	0.9589	0.9557

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp.				S	pecific co	nductance,	in microsie	emens per (entimeter	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius	es Celsius				
(deg C)	15000	16000	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000
0.0	0.9402	0.9361	0.9321	0.9280	0.9239	0.9198	0.9157	0.9116	0.9074	0.9033	0.8992	0.8950	6068.0	0.8867	0.8826
1.0	0.9408	0.9367	0.9327	0.9286	0.9246	0.9205	0.9164	0.9124	0.9083	0.9042	0.9001	0.8960	0.8918	0.8877	0.8836
2.0	0.9413	0.9373	0.9333	0.9293	0.9252	0.9212	0.9172	0.9131	0.9091	0.9050	0.9009	6968.0	0.8928	0.8887	0.8846
3.0	0.9418	0.9378	0.9339	0.9299	0.9259	0.9219	0.9179	0.9139	0.9099	0.9058	0.9018	8268.0	0.8937	0.8897	0.8856
4.0	0.9423	0.9384	0.9345	0.9305	0.9266	0.9226	0.9186	0.9146	0.9107	0.9067	0.9027	9868.0	0.8946	9068.0	9988.0
5.0	0.9428	0.9389	0.9350	0.9311	0.9272	0.9233	0.9193	0.9154	0.9114	0.9075	0.9035	0.8995	0.8955	0.8915	0.8875
0.9	0.9433	0.9395	0.9356	0.9317	0.9278	0.9239	0.9200	0.9161	0.9122	0.9082	0.9043	0.9004	0.8964	0.8924	0.8885
7.0	0.9438	0.9400	0.9361	0.9323	0.9284	0.9246	0.9207	0.9168	0.9129	0.606.0	0.9051	0.9012	0.8973	0.8933	0.8894
8.0	0.9443	0.9405	0.9367	0.9329	0.9290	0.9252	0.9213	0.9175	0.9136	0.9098	0.9059	0.9020	0.8981	0.8942	0.8903
0.6	0.9447	0.9410	0.9372	0.9334	0.9296	0.9258	0.9220	0.9182	0.9143	0.9105	0.9067	0.9028	0.8989	0.8951	0.8912
10.0	0.9452	0.9415	0.9377	0.9340	0.9302	0.9264	0.9226	0.9188	0.9150	0.9112	0.9074	0.9036	8668.0	0.8959	0.8921
11.0	0.9457	0.9419	0.9382	0.9345	0.9308	0.9270	0.9233	0.9195	0.9157	0.9119	0.9082	0.9044	9006.0	8968.0	0.8929
12.0	0.9461	0.9424	0.9387	0.9350	0.9313	0.9276	0.9239	0.9201	0.9164	0.9126	0.9089	0.9051	0.9014	9268.0	0.8938
13.0	0.9465	0.9429	0.9392	0.9355	0.9319	0.9282	0.9245	0.9208	0.9171	0.9133	9606.0	0.9059	0.9021	0.8984	0.8946
14.0	0.9470	0.9433	0.9397	0.9361	0.9324	0.9287	0.9251	0.9214	0.9177	0.9140	0.9103	9906.0	0.9029	0.8992	0.8954
15.0	0.9474	0.9438	0.9402	0.9366	0.9329	0.9293	0.9257	0.9220	0.9183	0.9147	0.9110	0.9073	0.9036	6668.0	0.8962
16.0	0.9478	0.9442	0.9406	0.9370	0.9334	0.9298	0.9262	0.9226	0.9190	0.9153	0.9117	0.9080	0.9044	0.9007	0.8970
17.0	0.9482	0.9446	0.9411	0.9375	0.9340	0.9304	0.9268	0.9232	0.9196	0.9160	0.9123	0.9087	0.9051	0.9014	8268.0
18.0	0.9486	0.9451	0.9415	0.9380	0.9345	0.9309	0.9273	0.9238	0.9202	0.9166	0.9130	0.9094	0.9058	0.9022	0.8985
19.0	0.9490	0.9455	0.9420	0.9385	0.9349	0.9314	0.9279	0.9243	0.9208	0.9172	0.9136	0.9101	0.9065	0.9029	0.8993
20.0	0.9493	0.9459	0.9424	0.9389	0.9354	0.9319	0.9284	0.9249	0.9214	0.9178	0.9143	0.9107	0.9071	0.9036	0.9000
21.0	0.9497	0.9463	0.9428	0.9394	0.9359	0.9324	0.9289	0.9254	0.9219	0.9184	0.9149	0.9114	0.9078	0.9043	0.9007
22.0	0.9501	0.9467	0.9432	0.9398	0.9363	0.9329	0.9294	0.9260	0.9225	0.9190	0.9155	0.9120	0.9085	0.9049	0.9014
23.0	0.9504	0.9470	0.9436	0.9402	0.9368	0.9334	0.9299	0.9265	0.9230	0.9196	0.9161	0.9126	0.9091	0.9056	0.9021
24.0	0.9508	0.9474	0.9440	0.9406	0.9372	0.9338	0.9304	0.9270	0.9236	0.9201	0.9167	0.9132	0.9097	0.9063	0.9028
25.0	0.9511	0.9478	0.9444	0.9411	0.9377	0.9343	0.9309	0.9275	0.9241	0.9207	0.9172	0.9138	0.9104	6906.0	0.9034
26.0	0.9515	0.9481	0.9448	0.9415	0.9381	0.9347	0.9314	0.9280	0.9246	0.9212	0.9178	0.9144	0.9110	0.9075	0.9041
27.0	0.9518	0.9485	0.9452	0.9419	0.9385	0.9352	0.9318	0.9285	0.9251	0.9217	0.9183	0.9149	0.9115	0.9081	0.9047
28.0	0.9521	0.9488	0.9455	0.9422	0.9389	0.9356	0.9323	0.9289	0.9256	0.9222	0.9189	0.9155	0.9121	0.9087	0.9053
29.0	0.9524	0.9492	0.9459	0.9426	0.9393	0.9360	0.9327	0.9294	0.9261	0.9228	0.9194	0.9161	0.9127	0.9093	0906.0

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward] Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

Temn					Specific conductance, in microsiemens ner centimeter at 25 deurees Celsius	ndiictance	in microsie	mens ner (centimeter	at 25 deure	es Celsius				
(deg C)	30000	31000	32000	33000	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000
0.0	0.8784	0.8742	0.8701	0.8659	0.8617	0.8575	0.8533	0.8491	0.8449	0.8407	0.8365	0.8323	0.8281	0.8239	0.8197
1.0	0.8795	0.8753	0.8712	0.8670	0.8629	0.8587	0.8546	0.8504	0.8462	0.8421	0.8379	0.8337	0.8296	0.8254	0.8212
2.0	0.8805	0.8764	0.8723	0.8682	0.8641	0.8599	0.8558	0.8517	0.8476	0.8434	0.8393	0.8351	0.8310	0.8268	0.8227
3.0	0.8815	0.8775	0.8734	0.8693	0.8652	0.8611	0.8570	0.8529	0.8488	0.8447	0.8406	0.8365	0.8324	0.8283	0.8242
4.0	0.8825	0.8785	0.8745	0.8704	0.8664	0.8623	0.8582	0.8542	0.8501	0.8460	0.8419	0.8379	0.8338	0.8297	0.8256
5.0	0.8835	0.8795	0.8755	0.8715	0.8675	0.8635	0.8594	0.8554	0.8513	0.8473	0.8433	0.8392	0.8351	0.8311	0.8270
0.9	0.8845	0.8805	99/8.0	0.8726	9898.0	0.8646	9098.0	0.8566	0.8526	0.8485	0.8445	0.8405	0.8365	0.8325	0.8284
7.0	0.8855	0.8815	922	0.8736	0.8697	0.8657	0.8617	0.8577	0.8538	0.8498	0.8458	0.8418	0.8378	0.8338	0.8298
8.0	0.8864	0.8825	0.8786	0.8746	0.8707	8998.0	0.8628	0.8589	0.8549	0.8510	0.8470	0.8431	0.8391	0.8351	0.8311
0.6	0.8873	0.8834	96/8.0	0.8757	0.8718	8298.0	0.8639	0.8600	0.8561	0.8522	0.8482	0.8443	0.8404	0.8364	0.8325
10.0	0.8882	0.8844	0.8805	9928.0	0.8728	0.8689	0.8650	0.8611	0.8572	0.8533	0.8494	0.8455	0.8416	0.8377	0.8338
11.0	0.8891	0.8853	0.8815	922	0.8738	0.8699	0.8661	0.8622	0.8583	0.8545	0.8506	0.8467	0.8428	0.8389	0.8351
12.0	0.8900	0.8862	0.8824	0.8786	0.8748	0.8709	0.8671	0.8633	0.8594	0.8556	0.8517	0.8479	0.8440	0.8402	0.8363
13.0	8068.0	0.8871	0.8833	0.8795	0.8757	0.8719	0.8681	0.8643	0.8605	0.8567	0.8529	0.8490	0.8452	0.8414	0.8375
14.0	0.8917	0.8879	0.8842	0.8804	0.8767	0.8729	0.8691	0.8654	0.8616	0.8578	0.8540	0.8502	0.8464	0.8426	0.8388
15.0	0.8925	0.8888	0.8851	0.8813	922	0.8739	0.8701	0.8664	0.8626	0.8588	0.8551	0.8513	0.8475	0.8437	0.8400
16.0	0.8933	9688.0	0.8859	0.8822	0.8785	0.8748	0.8711	0.8674	0.8636	0.8599	0.8561	0.8524	0.8486	0.8449	0.8411
17.0	0.8941	0.8905	8988.0	0.8831	0.8794	0.8757	0.8720	0.8683	0.8646	0.8609	0.8572	0.8535	0.8497	0.8460	0.8423
18.0	0.8949	0.8913	928870	0.8840	0.8803	9928.0	0.8730	0.8693	0.8656	0.8619	0.8582	0.8545	0.8508	0.8471	0.8434
19.0	0.8957	0.8921	0.8884	0.8848	0.8812	0.8775	0.8739	0.8702	9998.0	0.8629	0.8592	0.8556	0.8519	0.8482	0.8445
20.0	0.8964	0.8928	0.8892	0.8856	0.8820	0.8784	0.8748	0.8711	0.8675	0.8639	0.8602	0.8566	0.8529	0.8493	0.8456
21.0	0.8972	0.8936	0.8900	0.8864	0.8828	0.8793	0.8757	0.8720	0.8684	0.8648	0.8612	0.8576	0.8539	0.8503	0.8467
22.0	6268.0	0.8943	8068.0	0.8872	0.8837	0.8801	0.8765	0.8729	0.8693	0.8658	0.8622	0.8585	0.8549	0.8513	0.8477
23.0	9868.0	0.8951	0.8915	0.8880	0.8845	0.8809	0.8774	0.8738	0.8702	0.8667	0.8631	0.8595	0.8559	0.8523	0.8487
24.0	0.8993	0.8958	0.8923	0.8888	0.8853	0.8817	0.8782	0.8747	0.8711	9298.0	0.8640	0.8605	0.8569	0.8533	0.8497
25.0	0.9000	0.8965	0.8930	0.8895	0.8860	0.8825	0.8790	0.8755	0.8720	0.8685	0.8649	0.8614	0.8578	0.8543	0.8507
26.0	9006.0	0.8972	0.8937	0.8903	0.8868	0.8833	0.8798	0.8763	0.8728	0.8693	0.8658	0.8623	0.8588	0.8552	0.8517
27.0	0.9013	6268.0	0.8944	0.8910	0.8875	0.8841	9088.0	0.8771	0.8736	0.8702	0.8667	0.8632	0.8597	0.8562	0.8527
28.0	0.9019	0.8985	0.8951	0.8917	0.8883	0.8848	0.8814	0.8779	0.8745	0.8710	0.8675	0.8641	9098.0	0.8571	0.8536
29.0	0.9026	0.8992	0.8958	0.8924	0.8890	0.8856	0.8821	0.8787	0.8753	0.8718	0.8684	0.8649	0.8615	0.8580	0.8545

Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp.				S	pecific con	nductance,	in microsi	emens per (sentimeter	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius	es Celsius				
(deg C)	45000	46000	47000	48000	49000	20000	51000	52000	53000	54000	22000	26000	57000	28000	20000
0.0	0.8155	0.8112	0.8070	0.8028	0.7986	0.7944	0.7901	0.7859	0.7817	0.7775	0.7733	0.7691	0.7648	9092.0	0.7564
1.0	0.8170	0.8128	9808.0	0.8045	0.8003	0.7961	0.7919	0.7877	0.7835	0.7793	0.7751	0.7709	0.7668	0.7626	0.7584
2.0	0.8185	0.8144	0.8102	0.8061	0.8019	0.7978	0.7936	0.7894	0.7853	0.7811	0.7770	0.7728	0.7686	0.7645	0.7603
3.0	0.8200	0.8159	0.8118	0.8077	0.8035	0.7994	0.7953	0.7911	0.7870	0.7829	0.7788	0.7746	0.7705	0.7664	0.7623
4.0	0.8215	0.8174	0.8133	0.8092	0.8051	0.8010	0.7969	0.7928	0.7887	0.7846	0.7805	0.7764	0.7723	0.7682	0.7641
5.0	0.8230	0.8189	0.8148	0.8108	0.8067	0.8026	0.7986	0.7945	0.7904	0.7863	0.7823	0.7782	0.7741	0.7700	0.7660
0.9	0.8244	0.8204	0.8163	0.8123	0.8082	0.8042	0.8002	0.7961	0.7921	0.7880	0.7840	0.7799	0.7759	0.7718	0.7678
7.0	0.8258	0.8218	0.8178	0.8138	8608.0	0.8057	0.8017	0.7977	0.7937	0.7897	0.7857	0.7816	9.7776	0.7736	0.7696
8.0	0.8272	0.8232	0.8192	0.8152	0.8112	0.8073	0.8033	0.7993	0.7953	0.7913	0.7873	0.7833	0.7793	0.7753	0.7713
0.6	0.8285	0.8246	0.8206	0.8167	0.8127	0.8088	0.8048	8008.0	0.7969	0.7929	0.7889	0.7850	0.7810	0.7770	0.7731
10.0	0.8299	0.8259	0.8220	0.8181	0.8141	0.8102	0.8063	0.8023	0.7984	0.7945	0.7905	0.7866	0.7826	0.7787	0.7748
11.0	0.8312	0.8273	0.8234	0.8195	0.8156	0.8117	0.8077	0.8038	0.7999	0.7960	0.7921	0.7882	0.7843	0.7804	0.7764
12.0	0.8324	0.8286	0.8247	0.8208	0.8170	0.8131	0.8092	0.8053	0.8014	0.7975	0.7936	0.7898	0.7859	0.7820	0.7781
13.0	0.8337	0.8299	0.8260	0.8222	0.8183	0.8145	0.8106	0.8067	0.8029	0.7990	0.7952	0.7913	0.7874	0.7836	0.7797
14.0	0.8349	0.8311	0.8273	0.8235	0.8197	0.8158	0.8120	0.8082	0.8043	0.8005	9962.0	0.7928	0.7890	0.7851	0.7813
15.0	0.8362	0.8324	0.8286	0.8248	0.8210	0.8172	0.8134	0.8095	0.8057	0.8019	0.7981	0.7943	0.7905	0.7867	0.7828
16.0	0.8374	0.8336	0.8298	0.8260	0.8223	0.8185	0.8147	0.8109	0.8071	0.8033	0.7995	0.7958	0.7920	0.7882	0.7844
17.0	0.8385	0.8348	0.8310	0.8273	0.8235	0.8198	0.8160	0.8123	0.8085	0.8047	0.8010	0.7972	0.7934	0.7896	0.7859
18.0	0.8397	0.8360	0.8322	0.8285	0.8248	0.8210	0.8173	0.8136	8608.0	0.8061	0.8023	0.7986	0.7948	0.7911	0.7873
19.0	0.8408	0.8371	0.8334	0.8297	0.8260	0.8223	0.8186	0.8149	0.8112	0.8074	0.8037	0.8000	0.7963	0.7925	0.7888
20.0	0.8419	0.8383	0.8346	0.8309	0.8272	0.8235	0.8198	0.8161	0.8124	0.8087	0.8050	0.8013	0.7976	0.7939	0.7902
21.0	0.8430	0.8394	0.8357	0.8321	0.8284	0.8247	0.8211	0.8174	0.8137	0.8100	0.8064	0.8027	0.7990	0.7953	0.7916
22.0	0.8441	0.8405	0.8368	0.8332	0.8296	0.8259	0.8223	0.8186	0.8150	0.8113	0.8076	0.8040	0.8003	0.7967	0.7930
23.0	0.8451	0.8415	0.8379	0.8343	0.8307	0.8271	0.8234	0.8198	0.8162	0.8126	0.8089	0.8053	0.8016	0.7980	0.7943
24.0	0.8462	0.8426	0.8390	0.8354	0.8318	0.8282	0.8246	0.8210	0.8174	0.8138	0.8102	0.8065	0.8029	0.7993	0.7957
25.0	0.8472	0.8436	0.8400	0.8365	0.8329	0.8293	0.8257	0.8222	0.8186	0.8150	0.8114	0.8078	0.8042	9008.0	0.7970
26.0	0.8482	0.8446	0.8411	0.8375	0.8340	0.8304	0.8269	0.8233	0.8197	0.8162	0.8126	0.8090	0.8054	0.8018	0.7983
27.0	0.8491	0.8456	0.8421	0.8386	0.8350	0.8315	0.8280	0.8244	0.8209	0.8173	0.8138	0.8102	9908.0	0.8031	0.7995
28.0	0.8501	0.8466	0.8431	0.8396	0.8361	0.8326	0.8290	0.8255	0.8220	0.8184	0.8149	0.8114	0.8078	0.8043	0.8007
29.0	0.8510	0.8476	0.8441	0.8406	0.8371	0.8336	0.8301	0.8266	0.8231	0.8196	0.8160	0.8125	0.8090	0.8055	0.8019

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius] Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

Temp.				-	Specific co	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius	in microsi	emens per	centimeter	at 25 degre	es Celsius				
(deg C)	0	1000	2000	3000	4000	2000	0009	2000	8000	0006	10000	11000	12000	13000	14000
30.0	1.0000	6966.0	0.9939	8066.0	0.9877	0.9845	0.9814	0.9783	0.9751	0.9720	0.9688	0.9656	0.9624	0.9592	0.9560
31.0	1.0000	0.9970	0.9939	8066.0	0.9877	0.9846	0.9815	0.9784	0.9753	0.9721	0.9690	0.9658	0.9626	0.9595	0.9563
32.0	1.0000	0.9970	0.9939	0.9909	0.9878	0.9847	0.9817	0.9785	0.9754	0.9723	0.9692	0.9660	0.9629	0.9597	0.9565
33.0	1.0000	0.9970	0.9940	0.9909	0.9879	0.9848	0.9818	0.9787	0.9756	0.9725	0.9694	0.9662	0.9631	0.96.0	0.9568
34.0	1.0000	0.9970	0.9940	0.9910	0.9880	0.9849	0.9819	0.9788	0.9757	0.9727	9696.0	0.9665	0.9633	0.9602	0.9571
35.0	1.0000	0.9970	0.9940	0.9911	0.9880	0.9850	0.9820	0.9790	0.9759	0.9728	8696.0	0.9667	0.9636	0.9605	0.9573
Temp.					specific co	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius	in microsie	emens per o	sentimeter	at 25 degre	es Celsius				
(deg C)	15000	16000	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000
30.0	0.9527	0.9495	0.9463	0.9430	0.9397	0.9364	0.9332	0.9299	0.9266	0.9232	0.9199	0.9166	0.9133	6606.0	9906.0
31.0	0.9530	0.9498	0.9466	0.9434	0.9401	0.9369	0.9336	0.9303	0.9270	0.9237	0.9204	0.9171	0.9138	0.9105	0.9071
32.0	0.9533	0.9501	0.9469	0.9437	0.9405	0.9373	0.9340	0.9308	0.9275	0.9242	0.9209	0.9176	0.9143	0.9110	0.9077
33.0	0.9536	0.9505	0.9473	0.9441	0.9409	0.9376	0.9344	0.9312	0.9279	0.9247	0.9214	0.9181	0.9149	0.9116	0.9083
34.0	0.9539	0.9508	0.9476	0.9444	0.9412	0.9380	0.9348	0.9316	0.9284	0.9251	0.9219	0.9186	0.9154	0.9121	0.9088
35.0	0.9542	0.9511	0.9479	0.9448	0.9416	0.9384	0.9352	0.9320	0.9288	0.9256	0.9224	0.9191	0.9159	0.9126	0.9094
Temp.					Specific col	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius	in microsi6	emens per o	Sentimeter	at 25 degre	es Celsius				
(deg C)	30000	31000	32000	33000	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000
30.0	0.9032	8668.0	0.8964	0.8931	0.8897	0.8863	0.8829	0.8795	0.8760	0.8726	0.8692	0.8658	0.8623	0.8589	0.8554
31.0	0.9038	0.9005	0.8971	0.8937	0.8904	0.8870	0.8836	0.8802	89/8.0	0.8734	0.8700	9998.0	0.8632	0.8597	0.8563
32.0	0.9044	0.9011	0.8977	0.8944	0.8910	0.8877	0.8843	0.8809	9249	0.8742	0.8708	0.8674	0.8640	9098.0	0.8572
33.0	0.9050	0.9017	0.8984	0.8950	0.8917	0.8884	0.8850	0.8817	0.8783	0.8749	0.8716	0.8682	0.8648	0.8614	0.8580
34.0	0.9056	0.9023	0.8990	0.8957	0.8923	0.8890	0.8857	0.8824	0.8790	0.8757	0.8723	0.8690	0.8656	0.8622	0.8588
35.0	0.9061	0.9028	9668.0	0.8963	0.8930	0.8897	0.8864	0.8830	0.8797	0.8764	0.8731	0.8697	0.8664	0.8630	0.8597

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius] Table 6.2-7. Salinity correction factors for dissolved oxygen in water (based on specific conductance).—Continued

Temp.				Spo	Specific cond	luctance, i	in microsie	fic conductance, in microsiemens per centimeter at 25 degrees Celsius	entimeter	at 25 degr	ees Celsiu	2			
(deg C)	45000	46000	47000	48000	49000	20000	51000	52000	53000	54000	22000	26000	2,000	28000	23000
30.0	0.8520	0.8485	0.8450	0.8416	0.8381	0.8346	0.8311	0.8276	0.8241	0.8207	0.8172	0.8137	0.8102	9908.0	0.8031
31.0	0.8529	0.8494	0.8460	0.8425	0.8391	0.8356	0.8321	0.8287	0.8252	0.8217	0.8182	0.8148	0.8113	8208.0	0.8043
32.0	0.8537	0.8503	0.8469	0.8435	0.8400	0.8366	0.8331	0.8297	0.8262	0.8228	0.8193	0.8159	0.8124	0.8089	0.8054
33.0	0.8546	0.8512	0.8478	0.8444	0.8410	0.8375	0.8341	0.8307	0.8272	0.8238	0.8204	0.8169	0.8135	0.8100	9908.0
34.0	0.8555	0.8521	0.8487	0.8453	0.8419	0.8385	0.8351	0.8317	0.8282	0.8248	0.8214	0.8180	0.8145	0.8111	0.8077
35.0	0.8563	0.8529	0.8496	0.8462	0.8428	0.8394	0.8360	0.8326	0.8292	0.8258	0.8224	0.8190	0.8156	0.8122	0.8087

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pH 6.4

Revised by George F. Ritz and Jim A. Collins

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pH 6.4

Revised by George F. Ritz and Jim A. Collins

pH is a primary factor governing the chemistry of natural water systems and is measured routinely in U.S. Geological Survey (USGS) studies of water quality. The pH of water directly affects physiological functions of plants and animals and is, therefore, an important indicator of the health of a water system.

pH: A mathematical notation defined as the negative base-ten logarithm of the hydrogen-ion activity, measured in moles per liter of a solution.

The pH of an aqueous system can be understood as an estimation of the activity, or effective concentration, ¹ of hydrogen ions (H⁺) affecting that system. The theoretical basis of H⁺ activity and measurement are described in greater detail in Hem (1989) and in Pankow (1991).

By definition,

$$pH = -log_{10}[H^+]$$
, and $[H^+] = 10^{-pH}$.

- ► Logarithmic units are used to express H⁺ activity because the concentration of H⁺ in most environmental waters is usually too low to be expressed as milligrams per liter, micrograms per liter, or moles per liter, in contrast to most other chemical species (Hem, 1989).
- ▶ pH is reported on a scale that most commonly is shown to range from 0 to 14 (see TECHNICAL NOTE below). The pH scale is related directly to H⁺ and hydroxide (OH⁻) concentrations at a given temperature.
 - A solution is defined as having a neutral pH (pH = 7.00 at 25° C) when the H⁺ concentration is equal to the OH⁻ concentration.
 - A solution is defined as acidic if the H⁺ activity (concentration) is greater than that of the OH⁻ ion (pH is less than 7 at 25°C).
 - A solution is defined as basic, or alkaline, when the OH⁻ concentration is greater than the H⁺ concentration (pH is greater than 7 at 25°C).

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¹The majority of natural freshwater systems for which water-quality data are routinely collected by the USGS are considered to be dilute; that is, the volume of dissolved solids is less than 50 milligrams per liter and the ionic strength of the solution (the strength of the electrostatic field caused by the ions) is less than 10⁻⁴. For dilute solutions, activity values can be assumed to be equal to measured ion concentrations (Hem, 1989). Therefore, throughout the text of this section, the terms "activity" and "concentration," as they relate to the hydrogen ion, are used interchangeably.

► Temperature affects the chemical equilibria of ionic activities in aqueous solutions, including that of H⁺ (Hem, 1989). For example, neutral pH for pure water at 30°C is calculated to be 6.92, whereas at 0°C, neutral pH is 7.48. The pH of pure water at 25°C is defined as 7.00. Therefore, the temperature of the solution must be taken into account when measuring and recording pH.

TECHNICAL NOTE: Although pH commonly is reported on a scale ranging from 0 to 14, pH values of less than 0 can be measured in highly acidic solutions, and pH values greater than 14 can be measured in concentrated base solutions (Nordstrom and Alpers, 1999; Hem, 1989).

6.4.1 EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH consists of a pH meter, sensor(s) (a pH electrode and often a temperature sensor), and buffer solutions (table 6.4–1). Since a variety of instrument systems are available from manufacturers (multiparameter instruments, for example, are described in NFM 6.8), the procedures described in this section may not be applicable or may need to be modified, depending on the specific instrument system being used. Field personnel should:

- ▶ Be thoroughly familiar with the information provided in the manufacturer's user manual.
- ▶ Adhere to USGS protocols for quality control and assurance of pH measurements.
- ► Test the meter and electrode before each field trip.

Temperature affects the operation of pH meters, electrodes, and buffer solutions.

Table 6.4–1. Equipment and supplies used for measuring pH¹

[mL, milliliters; mV, millivolt; °C, degrees Celsius; μS/cm, microsiemens per centimeter at 25 degrees Celsius; +, plus: ±, plus or minus; MSDS, Material Safety Data Sheets]

✓ pH meter and pH electrodes

Battery powered, solid state, with automatic temperature compensation (for multiparameter instruments, see NFM 6.8)

Range of at least 2 to 12 pH, preferably 0 to 14 pH

Accuracy of at least ± 0.01 units

Temperature range of at least 0 to +45°C

Millivolt readout with accuracy of ±1.0 mV

- ✓ pH electrodes, gel-filled or liquid-filled, as appropriate, for study objectives and site conditions
- ✓ pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)
- ✓ pH electrode storage solution
- ✓ Thermistor (or thermometer), calibrated
- ✓ Buffer solutions for pH 4, 7, and 10; temperature correction chart(s) for buffers; labeled with expiration dates
- ✓ Stand for holding pH electrode
- ✓ Bottle, delivery (squeeze), to dispense deionized water
- ✓ Deionized water, maximum conductivity of 1 μS/cm
- ✓ Beakers or measurement vessels, polyethylene or Teflon[®] preferable, assorted volumes of 50 to 150 mL, clean but not acid rinsed
- ✓ Flowthrough chamber (for ground-water measurements)
- ✓ Minnow bucket (or mesh bag) with tether or equivalent, used for temperature equilibration of buffer solutions
- ✓ Waste-disposal container
- ✓ pH-meter/electrode logbook for recording calibrations, maintenance, and repairs
- ✓ MSDS for all pH buffers and other reagents to be used

¹This list pertains to single-parameter instruments for measuring pH. Refer to NFM 6.8 for information on and general use of multiparameter instruments. This list may be modified to meet the specific needs of the field effort.

CAUTION: Keep Material Safety Data Sheets (MSDS) readily available and refer to them to ensure that pH buffers or other chemicals are handled safely.

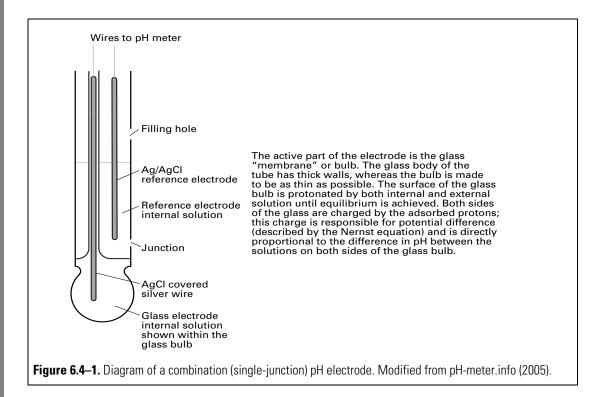
6.4.1.A pH METERS

A pH meter is a high-impedance voltmeter that measures the very small, direct current potential (in millivolts (mV)) generated between a glass pH electrode and a pH reference electrode. The potentiometric measurement is displayed as a pH value. The meter uses potentiometric differences to generate these pH values and is programmed with (1) the ideal Nernstian response relating hydrogenion activity (concentration) and electrical response (59.16 mV/unit pH), and (2) an automatic temperature compensation (ATC) factor. Since the ideal Nernstian slope response from the electrode varies with temperature, the meter's software adjusts the slope to be in accordance with the Nernst equation at the corresponding environmental temperature during calibration and measurement (refer to section 6.4.3 for an explanation of the Nernst equation).

6.4.1.B pH ELECTRODES

The pH electrode is a special type of ion selective electrode (ISE) that is designed specifically for the measurement of hydrogen-ion concentration in a dilute aqueous solution.

- ▶ Diodes or triodes (combination electrodes) are used in most USGS field studies.
 - Combination electrodes are housed either in a glass or an epoxy body. Diodes contain a pH reference electrode and pH measurement electrode. Triodes contain the reference and measurement electrodes plus a thermistor. In either case, the basic electrode operation is the same (IC Controls, 2005a).
 - All combination pH electrodes have a glass membrane, a reference and a measurement electrode, an ionic (filling) solution, and a reference junction (shown on fig. 6.4–1); these are described below.



- ▶ Electrode performance naturally degrades over time with normal use. However, field personnel need to be alert to those chemical environments that can cause serious and more rapid degradation of electrode performance (IC Controls, 2005a). Many such environments are coincident with industrial, mined, and urban areas (table 6.4–2).
 - Field personnel should be aware of the effect on the pH measurement when deploying the electrode in such environments: document field conditions on field forms.
 - When measuring pH under specific adverse chemical conditions, the use of electrodes with properties designed to withstand such conditions is recommended (table 6.4–2).

Table 6.4–2. pH electrodes recommended for water having elevated concentrations of sodium and other monovalent major cations, sulfide, cyanide, and ferric chloride.

[H ⁺ , h	ıydrogen	ion; N	a+,	sodium	ion; >	 greater 	than; ≥,	greater than	or equal to
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Chemical condition	Description of water	Degradation effect on a common combination pH electrode	Recommended pH electrode
Basic ions dominant in solution	pH high (>10 pH units); low H ⁺ activity results in measurement of other monovalent ions in solution.	Sluggish response to changes in pH, resulting from dehydration of the glass membrane. The pH measurement is	Glass pH electrode designed for measuring high values of pH.
	Elevated Na ⁺ at pH ≥11.0, H ⁺ activity is low. The electrode senses Na ⁺ activity as if it were H ⁺ because of the similar charge and structure of the Na ⁺ and H ⁺ ions.	negatively biased.	designed for measuring high values of pH.
Elevated concentrations of sulfide or cyanide	Elevated concentrations of sulfides or cyanides are found in industrial, mined, or urban areas.	Sulfide or cyanide contamination of the internal reference electrode.	Double-junction electrodes and plasticized reference electrodes.
Elevated concentration of ferric chloride	Ferric chloride is used as a flocculating agent in wastewater treatment plants, for example.	Ferric chloride attacks the glass membrane of the pH electrode, deactivating many of the sensing sites on the glass surface.	Consult the manufacturer for (1) selecting pH electrodes that can withstand this environment; and (or) (2) specific cleaning procedures for the glass membrane.

Glass membrane. The most essential and vulnerable element of the pH electrode is the sensitive glass membrane, which permits the sensing of hydrogen-ion activity in most natural waters. When the pH electrode is immersed in a solution (for example, a calibration buffer or a sample solution), ions from the glass diffuse into a thin layer on the outside of the membrane, while hydrogen ions diffuse through this layer until an equilibrium is reached between the internal and external ionic concentrations. In this way, an electrical potential is developed across the sensing surface, which is proportional to the concentration of hydrogen ions in the surrounding solution (pH-meter.info, 2005).

A clean, undamaged glass membrane is necessary for performing an accurate measurement of pH.

Reference and measurement electrodes. Contained within the pH-sensor body are a reference electrode (that generates a constant electrical potential) and a pH-measurement electrode. The measurement electrode generates a separate electrical potential that is proportional to the concentration of hydrogen ions in the sample solution. The electrodes together form a complete electrical circuit; when the diffusion of hydrogen ions reaches equilibrium, no electrical current is present, and the difference in electrical potential that exists between the reference and the measurement electrodes is an indication of the hydrogen-ion concentration in the solution. The pH meter, sensing this minute difference in electrical potentials, converts this difference into a pH value based on the latest calibration of the pH electrode.

Ionic (filling) solutions. An ionic solution used to fill the space within the pH electrode is the source of mobile, chemical ions that serve to complete the electrical circuit between the internal reference and pH-measurement electrodes. The pH electrode may be filled either with an ionic liquid solution (liquid-filled pH electrode) or an ionic gel solution (gel-filled pH electrode). Typically, these ionic solutions contain a chloride salt (usually silver or potassium) of a known and specific molarity (strength). For liquid-filled electrodes, maintaining a sufficient volume and the correct molarity of the filling solution within the electrode is very important to achieving meaningful measurements. Most standard pH electrodes are designed to function well when the electrode filling solution strength is similar to the sample ionic strength, typically having a relatively high ionic strength of 3 molar (M) or greater. Using low ionic-strength or high ionic-strength pH electrodes and a filling solution of appropriate composition and molarity—as recommended by the electrode manufacturer—is recommended when working with environmental samples having conductivities less than $100 \, \mu \text{S/cm}$ or greater than $20,000 \, \mu \text{S/cm}$, respectively.

Reference junction. The liquid reference junction (sometimes called the "salt bridge") is an electrically conductive bridge within the pH electrode, between the reference ionic solution and the sample being measured. This junction is necessary for the proper functioning of the pH-sensing electrical cell; it must allow free movement of electrons, but at the same time, isolate the ionic solution from the bulk environmental sample. Typically, this junction is made of a porous material such as ceramic, Teflon, or glass fiber, and may clog and malfunction if not maintained properly. The function of the reference junction is characterized by a chemical memory. In a correctly functioning pH electrode, a small amount of time lapses before the appropriate ionic bridge is formed between the electrode reference ionic solution and the external environmental sample or external calibration-buffer solution. The length of time necessary for the establishment of this ionic equilibrium is a primary reason for the requirement that pH be measured in a quiescent sample solution. (Sections 6.4.4 and 6.4.5 provide further discussion.)

Remember to check that the junction on the pH electrode is not clogged; a clogged electrode will not function properly.

Electrode performance naturally deteriorates over time under normal operating conditions. However, use of the electrode in severe chemical environments can cause more rapid deterioration (table 6.4–2). Many of these environments are coincident with industrial and urban locations: immersing a pH electrode in such environments should be avoided or minimized to the extent possible (IC Controls, 2005a). Whenever the pH electrode is exposed to conditions such as those listed on table 6.4–2, this information should be recorded in the pH-meter/electrode logbook and documented in field notes.

pH BUFFER SOLUTIONS 6.4.1.C

pH buffer solutions (buffers) are ionic solutions that are used to calibrate the pH instrument system. Buffers maintain constant pH values because of their ability to resist changes to the specific pH value for which they are produced. **Measurements of pH are only as accurate as the buffers used to calibrate the electrode.**

- ▶ Use only buffers that have been certified traceable to an NIST standard reference material.
- ▶ Select the buffer molarity that is appropriate for the ionic strength of the water to be measured and the instrument system that will be used.
 - For pH measurements of dilute waters with conductivities less than 100 μS/cm, use of buffers having lower-than-standard molarity and a low ionic-strength pH electrode is recommended (refer to section 6.4.3.B).
 - For pH measurements in high ionic-strength waters with conductivities greater than 20,000 μS/cm, use of buffers having a higher-than-standard molarity is recommended (refer to section 6.4.3.C).
- ▶ Label pH buffer containers with the acquisition date and the expiration date. Copy the expiration date and the buffer lot number onto any reagent containers into which the buffer is transferred. Copy the temperature-correction information onto the respective buffer container or keep a copy of this information with the buffers being transported to the field.
- ▶ **Discard the pH buffer on its expiration date**. The pH of a buffer can be altered substantially because of temperature fluctuation, carbon dioxide (CO₂) absorption, mold growth, or evaporation.

Use the following precautions and protocols to help ensure the accuracy of the pH measurement (modified from Busenberg and Plummer, 1987):

- Cap buffer bottles firmly after use to prevent evaporation and contamination from atmospheric CO₂. The pH 10 buffer has the greatest sensitivity to CO₂ contamination, whereas the pH 4 buffer is the least sensitive. Buffers are stable for the short exposure time during electrode calibration.
- Never pour used buffer back into a bottle containing the stock buffer solution.
- Do not insert an electrode or other material into a bottle containing stock buffer solution always pour the buffer into a separate container and discard the solution after use.
- Take care not to contaminate the buffer with another buffer or with other fluids.
- **Do not let the buffer become diluted** (this can happen, for example, if deionized water used to clean the electrode drips into the buffer).
- Protect buffers against wide temperature variations, whether in transit, during use, or in storage. Never expose buffers to extreme heat or freezing temperatures. If buffers experience these conditions, their pH values can no longer be assumed to be valid. Discard buffer solutions and any other reagents appropriately.
- Before using buffers in the calibration sequence, bring them to the temperature of the sample solution as much as possible. Since buffer composition differs among manufacturers; check the temperature-correction factors provided by the manufacturer in order to assign the correct pH value to the buffer for the temperature of the buffer at the time of calibration.

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In order of greatest to least sensitivity of standard buffers to ${\rm CO_2}$ contamination: pH 10 buffer > pH 7 buffer > pH 4 buffer. In order of greatest to least variation of buffer pH with change in temperature: pH 10 buffer > pH 7 buffer > pH 4 buffer.

6.4.2 MAINTENANCE OF pH INSTRUMENTS

Proper care of pH meters, and particularly of the electrode, is essential for maintaining the accuracy and precision required for pH measurements and promotes the longevity of the equipment. pH instrument maintenance includes adhering to the manufacturer's instructions for the use and care of the instrument, and routine use of appropriate electrode cleaning, reconditioning, and storage requirements. As always, follow the manufacturer's instructions for the specific type of electrode in use.

Electrode performance must be monitored before every water-quality field trip and again while at the field site.

6.4.2.A ELECTRODE CARE AND CLEANING

USGS field personnel should integrate the following guidance for the care and cleaning of pH electrodes into their routine field-measurement procedures.

- Never handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with the design characteristics of the glass membrane and affect subsequent pH measurements.
- ▶ Inspect the electrode and electrode cable for physical damage. For example, check for
 - Cut or frayed cable(s).
 - Broken connectors and mismatched or missing parts.
 - A visibly scratched or broken bulb, cracked electrode body, and broken or damaged internal electrode (reference and measurement electrodes).
- ► Gel-filled electrodes do not require filling and typically require less maintenance than liquid-filled electrodes. Do not store gel-filled electrodes in dilute water, even temporarily, as salts may leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.

To prepare and care for liquid-filled electrodes:

- 1. Remove salt crystal deposits from the electrode, membranes, and junctions by rinsing with deionized water (DIW). Visually check that the reference junction is not blocked or caked with salt. Thorough rinsing with DIW should remove these deposits. Be sure to unplug the fill hole before making pH measurements, as suction pressure may affect the proper movement of ions in the filling solution and the correct operation of the reference junction. Re-plug the fill hole after use.
 - If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the electrode in the air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet the junction.
 - After 15 minutes, visually inspect the junction for liquid or new salt accumulation. Ensure that the filling solution is flowing freely. Refer to the manufacturer's instructions.
- 2. Check the filling solution level and replenish it if necessary. The solution should reach the bottom of the fill hole. Filling solutions differ in molarity and composition—always check that the correct filling solution required by the manufacturer for a particular electrode is being used.
- 3. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (check the manufacturer's recommendations).
- 4. Keep a record of the electrode and meter operation and maintenance and repairs in the pH-meter/electrode logbook.
 - Record in the calibration logbook the operational history of each pH electrode.
 - Record the Nernst slope reading and the millivolt readings at pH 4, 7, 10, or other pertinent pH buffer values (based on field study objectives) during calibration. Properly working electrodes should give 95 to 102 percent response of that expected from the theoretical Nernst relationship (Busenberg and Plummer, 1987).

TECHNICAL NOTE: The theoretical Nernst response is 59.16 mV/pH unit at 25°C, but varies based on temperature. Adequate adjustment of the Nernstian relation requires manual or automatic temperature compensation (ATC). Most modern pH meters have the ATC feature. A slope of 95 percent or less signals probable electrode deterioration and the need to monitor closely any further decline in slope percent. Consider replacing the electrode if calibration slope values cannot be brought to greater than 95 percent. **Do not use an electrode with a slope of less than 95 percent.**

5. Keep the electrode bulb moist and capped when not in use. Use only the wetting solution recommended by the manufacturer.

For routine cleaning of the pH electrode:

Keeping electrodes clean and the liquid junction free-flowing is necessary for producing accurate pH measurements. Because of the variety of electrodes available, check the manufacturer's instructions for specific tips and precautions.

- 1. **Before and after each use**—rinse the electrode body thoroughly, using only DIW. Dispense the DIW from a squeeze bottle.
- 2. Do not wipe or wick moisture from electrodes with paper towels or ChemWipes[®] as these can scratch the pH glass membrane. Wiping the electrode body with paper also may cause a static charge (polarization) on the exterior of the pH electrode, which can also adversely affect the pH measurement.

6.4.2.B RECONDITIONING OF LIQUID-FILLED ELECTRODES

If problems persist during calibration of a liquid-filled electrode, or if there is reason to doubt that the electrode is in good working condition, check the manufacturer's instructions for how to test and recondition the electrode. Reconditioning procedures should be implemented only if the electrode's slope response has deteriorated to less than 95 percent. Document in the pH-meter/electrode logbook if the electrode has been reconditioned or replaced.

The following general procedures can be used to attempt to bring the liquid-filled electrode back into proper working condition:

- 1. Remove the old filling solution from the electrode.
 - a. Place the needle of a 1- or 3-milliliter (mL) syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).
 - b. Tilt the pH electrode until the filling solution is near the fill hole and the needle tip is covered with the filling solution.
 - c. Pull back on the syringe plunger until the syringe is full.
 - d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode.
- 2. Flush the pH electrode with DIW.
 - a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with DIW.
 - b. With a syringe, remove the DIW from the pH electrode chamber.
 - c. As a result of changes in pressure, temperature, and evaporation, visible crystals may form in the pH electrode. If these are present, continue to flush with DIW until all the crystals have been dissolved and removed from the pH electrode.
- 3. Fill the electrode with fresh filling solution. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.
 - a. Partially fill the pH electrode chamber with the filling solution.
 - b. Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
 - c. Remove and discard the filling solution to a waste container.
 - d. Refill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. Be sure to use the appropriate type and molarity of filling solution.
 - e. Rinse any excess filling solution from the outside of the electrode with DIW.
- 4. After following the reconditioning procedures, retest the electrode. If the procedures fail to remedy the problem, discard the electrode.

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ELECTRODE STORAGE 6.4.2.C

Electrodes must be clean before they are stored for any length of time. Refer to the manufacturer's instructions for the proper short-term (used daily or weekly) and long-term (2 to 4 months) storage requirements of the electrode.

General guidelines for short-term storage:

- 1. Storage solutions are specific to the type of electrode; check the manufacturer's manual for each electrode. **Do not store glass hydrogen-ion electrodes in DIW** unless instructed to do so by the manufacturer.
- 2. Storage solutions have a limited shelf life. Label storage solution containers with the expiration date and discard expired solutions on that date and in a proper manner.
- 3. Do not place a small piece of cotton or paper towel in the electrode cap to help keep it moist, as this can scratch the glass membrane sensor.
- 4. Store liquid-filled pH electrodes upright.
- 5. Store liquid-filled electrodes wet between uses to maximize their accuracy and response time.
 - The glass membrane (bulb) should be fully immersed in the proper electrode storage solution.
 - Between field sites, replace the plug on the fill hole and cover the electrode bulb with the cap.
 - Fill the cap with enough storage solution to keep the bulb wet.
- 6. Gel-filled electrodes should be stored according to the manufacturer's instructions.

General guidelines for long-term storage:

- 1. Liquid-filled electrodes may need to be drained of filling solution; follow the manufacturer's instructions.
- 2. Clean the electrode contacts and connector (with alcohol, if necessary). Allow the contacts to dry and seal and store them in a plastic bag.
- 3. Store every component of the pH measuring system in an area that is clean, dry, and protected from extremely hot or cold temperatures.

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6.4.3 CALIBRATION OF THE pH INSTRUMENT SYSTEM

Proper calibration of the pH instrument system is crucial to accurate pH measurement of environmental samples. During calibration, the pH electrodes are immersed in buffer solutions of known pH (section 6.4.1.C). The buffers are designed to produce a corresponding electrical response potential (usually in millivolts) for the specific pH buffer (for example, pH = 4, 7, or 10 buffer solution) within the pH electrode. These potentials are measured by the pH meter. The Nernst equation gives the expected (theoretical) response potential of the pH buffer at the specific temperature of the calibration (Hem, 1989; see TECHNICAL NOTE below). Note that the measured temperature must be programmed into the pH meter unless the meter has incorporated automatic temperature compensation. The calibration returns the actual, measured potential.

TECHNICAL NOTE: pH electrodes operate on the principle that differing concentrations of the H⁺, in buffers or environmental samples, produce differing potentiometric responses (measured in millivolts). The Nernst equation is used to establish the calibration of the pH instrument system by determining the slope of electrical potential versus pH at a given temperature. At 25°C, this Nernstian relation (the slope along any two points on the line plotted for electrical potential versus pH) is known to be 59.16 mV/pH units. To calculate the slope between two points along the line of measured potentials versus pH:

$$E=E^0$$
- $S(pH)$

where

S = slope

E = electrode pair potential, in mV, and

 E^0 = standard potential, in mV.

Thus, using two buffers of known pH (pH₁ and pH₂),

$$E_1 = E^0 - S(pH_1)$$
 and $E_2 = E^0 - S(pH_2)$.

Rearrange as:

$$s = \frac{E_2 - E_1}{pH_1 - pH_2}$$

The theoretical slope is temperature dependent; the theoretical slope (in mV) can be calculated as:

$$S_t = 0.19841(273.15 + t)$$

where

t = temperature in degrees Celsius, and

 S_t = slope at a given temperature.

The primary concept in accurate calibration of the pH electrode is to select pH buffers with values that bracket the expected pH of the environmental sample; this is known as a two-point calibration. Before field calibration of the pH instrument system, it is useful to estimate (or to anticipate from historical site data, if available) the pH and conductivity of the waters to be encountered at the field sites. If no data are available from which to estimate sample pH, then pH indicator paper can be used onsite as a gross indicator of the pH of the system. (Under no circumstances should a pH value from indicator paper be recorded as site pH.) For three-point or other multipoint calibrations, follow the manufacturer's instructions for (a) which buffers to use and (b) the sequence of buffer use.

EXAMPLE: When measuring pH in a stream that is within the normal range of specific electrical conductivity,

- a. If pH values are expected to be between 7 and 8, then the standard pH 7 and pH 10 buffers should be selected.
- b. If pH values are expected to be less than 7, then the standard pH 7 and pH 4 buffers should be selected.
- c. If the anticipated pH range in pH is large, a check of electrode performance using a third standard buffer value is advisable.

The following guidelines and standard procedures apply in general whenever a pH instrument system is to be calibrated. Because calibration and operating procedures can differ with differing instrument systems, check the manufacturer's recommended calibration procedures and calibration solutions. Digital pH meters automatically compensate for buffer temperatures and indicate appropriate Nernst values (in millivolts). When using these instruments, follow the manufacturer's calibration instructions precisely—do not take shortcuts.

- ▶ Before each field trip and field calibration, check pH meter/electrode logbook records for electrode performance. **Remember**—any noted calibration slope of 95 percent or less indicates probable electrode deterioration; at 94-percent slope or less, the electrode should not be used.
- ▶ Use at least two pH buffer solutions of documented, traceable pH value for adequate calibration of the pH instrument system.
- ▶ Pour the amount needed of each buffer from the source container into a clean, polyethylene bottle dedicated for the respective buffer, and label the bottle with the buffer's pH value, lot number, expiration date, and the temperature-adjusted pH values provided by the manufacturer for that buffer.
- ▶ The temperature of the buffer solutions should be near the same temperature as the water to be sampled. A calibration check of the temperature sensor must be performed at least annually (NFM 6.1).

TECHNICAL NOTE: Temperature has two effects on the pH measurement of a sample—temperature can affect meter and electrode potentials (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect) within the sample. The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample will be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

Do not use pH buffers that have exceeded their date of expiration.

6.4.3.A CALIBRATION PROCEDURE UNDER STANDARD AQUEOUS CONDITIONS

"Standard aqueous conditions" refers to environmental water with an ionic strength that is within the range in which a standard buffer solution and combination pH electrode can be appropriately used to achieve an accurate pH measurement. For routine USGS water-quality measurements, ionic strengths ranging from 100 to 20,000 µS/cm are considered standard.

When calibrating the pH electrode:

- 1. Bring the pH buffers to the ambient temperature of the stream or ground water to be measured, to the degree possible under the prevailing field conditions. The temperature sensor (liquid-in-glass or thermistor thermometer), measurement vessel, and electrode also should be at or near the ambient temperature of the environmental sample. Maintain each buffer as close to sample temperature as possible when calibrating the electrode.
 - Surface water and ground water—When equilibrating the buffer temperature to ambient surface-water temperature, one method is to place the buffer bottles in a minnow bucket or mesh bag and suspend them in the body of surface water. Alternatively, place the buffers into a bucket or insulated cooler (a) containing surface water, or (b) being filled with ground water.
 - When immersing buffer bottles in water, ensure that the bottle is firmly capped and that the water level remains below the cap so that water cannot enter the bottle and contaminate the buffer.
- 2. Inspect the pH electrode.
 - a. Check for damage to the electrode bulb, body, or cables.
 - b. Rinse any mineral precipitate off the electrode with DIW.
 - c. Uncover (unplug) the fill hole.
 - d. If you can visually see small bubbles within the electrode solution, **gently** tap the electrode body to dislodge them. Bubbles trapped in the sensing tip of the electrode will affect the physical conditions necessary for correct operation of the electrode. **Do not wipe moisture from the electrode.**
- 3. Power up the pH meter. The meter will perform an internal self-test. Note any discrepancies displayed by the meter and record these in the pH-meter/electrode logbook. Malfunctioning meters usually require manufacturer attention; do not try to fix malfunctioning meters in the field. Having backup meters for field trips is necessary for this reason.
- 4. Record in the ph-meter/instrument logbook the internal self-test information displayed by the pH meter. A calibration log is **mandatory** for all calibrations.

- 5. Initiate the calibration process by pushing the required calibration display sequences for the particular pH meter and electrode. Standard USGS procedure for calibration of a single-parameter pH meter-and-electrode system requires a two- or three-point calibration.
 - Some types of pH-instrument systems may use a different multipoint calibration procedure; in such cases, follow the instructions provided in the instrument manual.
 - A single-point calibration, recommended by some manufacturers, is not acceptable for USGS field measurement of pH.
- 6. Record in the pH-meter/electrode logbook: pH value, measured temperature, lot number, and expiration date of the first buffer. Typically, the meter will initially indicate the pH 7 buffer (isoelectric point).
- 7. Begin calibration procedures:
 - a. Note that the electrode and thermistor must be rinsed with DIW at least three times between uses of each buffer.
 - b. Rinse the electrode twice with the first buffer (usually the pH 7 buffer). Do not allow the glass membrane of the electrode to come in contact with the sides or bottom of the beaker or other measurement vessel.
 - i. **First rinse**—Pour enough buffer into a small beaker or other vessel so that it covers the electrode reference junction; swirl the buffer to rinse the electrode body from above the reference junction to the bottom of the bulb. Discard buffer appropriately.
 - ii. **Second rinse**—Pour the next aliquot of buffer into the vessel and immerse the electrode in the buffer for 1 minute. Discard buffer appropriately.
 - c. Pour another aliquot of buffer into the vessel. Immerse the electrode for 1 minute, without swirling the buffer solution.
 - d. Record the pH measurement shown on the meter display in the pH meter/electrode logbook, along with the buffer temperature reading and the pH value from the buffer and temperature table.
 - For pH meters displaying millivolt values, the meter will display the value associated with the pH 7 buffer, as compensated for the buffer temperature.
 - For properly functioning electrodes, the pH 7 millivolt value should be between +10 and -10 mV. Record the millivolt data in the pH-meter/electrode logbook.
 - e. Press "Cal" or other display instructions to lock in the pH 7 calibration.

TECHNICAL NOTE: During the calibration sequence, after the DIW and buffer rinses and when the specific buffer value is ready to be locked in to the calibration, some meters provide the opportunity to adjust the initially displayed pH value to a corrected pH value for that buffer solution.

- If this adjustment is equal to or less than 0.05 pH units, proceed with the adjustment, but specifically note this in the pH meter/electrode logbook.
- If the adjustment would exceed 0.05 pH units, the pH electrode is not functioning optimally; consider reconditioning the electrode or using another electrode until the cause of the substandard performance can be determined.

- 8. **Return to step 6 above, followed by step 7**, repeating each of the procedures just followed but using either the pH 4 or pH 10 buffer, whichever buffer solution, along with the pH 7 buffer, brackets the pH values of the environmental water to be sampled. Record all the calibration data, including the millivolt data, in the pH meter/electrode logbook (see step 7 to test the adequacy of the calibration using the slope test or millivolt test).
- 9. **At this point, the electrode should be calibrated**. Check the adequacy of the calibration and that the electrode is functioning properly, using the slope test or (and) the millivolt test. Some instruments have the capability to display the slope value; this datum should be recorded in the pH-meter/electrode logbook.
 - The slope test. Values ranging from 95 to 102 percent slope are acceptable—if the slope-percent value is outside of this range: clean the electrode and check the level of the filling solution, that the fill hole is open, and that the junction is free-flowing; then, recalibrate.

TECHNICAL NOTE: Since the theoretical Nernstian relation between electrical response and pH at the calibration temperature is programmed into the pH meter software, the calibration process provides the Nernstian response from the electrode/meter system being calibrated. The actual calibration slope is calculated and the **displayed slope value** represents the actual slope of the electrical potential (millivolt)— pH line that this calibration has produced.

- The millivolt test. For pH meters that display and store only millivolt readings (do not display the slope percent), use the following guidelines to ascertain adequate calibration:
 - pH 7 buffer: Displays between -10 to +10 mV
 - pH 4 buffer: Displays between +165 to +195 mV
 - pH 10 buffer: Displays between -165 to -195 mV
- If using buffers other than the standard pH 4, 7, and 10 buffers, refer to the information provided with the specific buffer lot to determine the correct, temperature-compensated millivolt potential for that buffer.
- 10. **Replace the electrode** if, after recalibration, the slope remains outside the acceptable range of 95 to 102 percent or if the acceptable range of the millivolt response is not met at any of the calibration points.

CALIBRATION FOR LOW IONIC-STRENGTH WATER 6.4.3.B

Calibration of pH instrument systems with standard buffers does not guarantee accurate and (or) timely pH measurement in low ionic-strength waters (conductivity less than $100~\mu\text{S/cm}$) and in very low ionic-strength waters (conductivity less than $50~\mu\text{S/cm}$). As sample ionic strength decreases, the efficiency of the standard pH instrument system also decreases. Low or very low ionic-strength waters have little buffering capacity and may readily absorb atmospheric CO_2 , resulting in the formation of carbonic acid in the sample. A continuous change in pH values can occur from the varying reaction rates of the sample water with CO_2 , resulting in an unstable measurement.

Standard pH electrodes do not respond well in waters with low ionic strength.

- ▶ Standard combination pH electrodes respond more slowly, the response is characterized by continual drift, and calibration is difficult to maintain. Equilibration with the sample water may not be completely achieved or the equilibration time may be on the order of hours.
- ▶ Standard pH electrodes exhibit a jumpy response and are more sensitive to conditions of flow and agitation, and measurement accuracy decreases (Wood, 1981).

When preparing to measure pH in low ionic-strength waters, the response time, accuracy, and reproducibility of the measurement can be improved by modifying the type of electrode and buffer.

To measure pH in water of low ionic strength:

- 1. Use a specific, low ionic-strength electrode. The pH electrode for low ionic-strength solutions typically is characterized by
 - A thin, responsive glass membrane;
 - A reference junction that allows rapid electrolyte flow; and
 - A pH-neutral ionic additive within the reference filling solution.
- 2. Use corresponding low ionic-strength pH buffers.
 - The low ionic-strength buffer should contain the same type of pH-neutral ionic additive as that in the electrode reference filling solution (the amount of pH neutral ionic additive must be the same in the electrode and buffer, so that the net pH effect is standardized).
 - Low ionic-strength buffers may not be of the standard pH buffer values (pH = 4, 7, 10). Check that your pH meter can accept these "nonstandard" buffer values for calibration.

Calibration of the pH instrument system and measurements made in low ionic-strength solutions should involve a specific combination of low ionic-strength buffers and low ionic-strength electrodes.

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6.4.3.C CALIBRATION FOR HIGH IONIC-STRENGTH WATER

USGS studies increasingly involve pH measurement and sampling of high ionic-strength waters (ionic strength greater than 3 M or conductivity greater than 20,000 μ S/cm) from sources such as industrial effluent (for example, from paper mills, oil refineries, carbonate processing or other mining activities that have corrosive properties), combined sewer/storm water from urban systems, seawater, and brines. Using standard buffers or standard equipment may not yield an accurate pH measurement for such waters.

- ▶ The high ionic strength of some industrial effluents or brines often are of greater or equal ionic strength than that of the filling solution in the standard pH electrode. This results in an ionic gradient toward the reference junction and into the pH electrode, which compromises the design parameters of the electrode and therefore the soundness of the calibration and the pH measurement.
- ▶ Standard buffers are not of an ionic strength that approximates or exceeds the ionic strength of the sample solution, and standard filling solutions in pH electrodes similarly may have too low of an ionic strength to be calibrated properly for measurement of pH in high ionic-strength waters.

When selecting the measurement system to be used to determine the pH of high ionicstrength waters, consider the following options:

- 1. Obtain high ionic-strength (conductivity greater than 20,000 μS/cm) pH buffer solutions from commercial sources, if available. Follow the guidelines for maintenance and use of pH buffers previously described in section 6.4.1.C, paying close attention to the effect of temperature on buffer values.
- 2. Obtain high ionic-strength pH glass electrodes, if available. These may be characterized by filling solutions of greater than 3 *M* ionic strength and more solution-specific glass sensors. Note specific uses recommended by the manufacturer and follow the manufacturer's instructions.
- 3. If no suitable pH glass electrode/buffer system is available for pH measurement in high ionic-strength environments, investigate the suitability of alternative instrumentation and methods, such as those that employ spectrophotometric or optical methods, with respect to the site-specific conditions to be encountered and study data-quality objectives (Bellerby and others, 1995; Farquharson and others, 1992; Sedjil and Lu, 1998).
 - Spectrophotometric methods typically involve the constant-rate introduction of acid-base indicator dyes into the sample; pH measurement is accomplished by measurement of the resultant spectra of the dye. An important limitation to this system is that acid-base indicator dyes are typically sensitive over very narrow pH ranges (Raghuraman and others, 2006).
 - Spectrophotometric measurement of pH in environmental samples is a methodology designed for specific environments; follow the guidelines provided by the equipment manufacturer.
 - As part of USGS studies, any pH data obtained by spectrophotometry or other nontraditional pH measurement method must be entered under the unique parameter and (or) method code designated in the USGS National Water Information System (NWIS) waterquality database.

CALIBRATION FOR THE pH SENSOR IN 6.4.3.D MULTIPARAMETER INSTRUMENTS

Before beginning calibration of the pH electrode in a multiparameter instrument sonde, read and follow carefully the instrument manual and manufacturer's instructions. Guidelines that incorporate USGS protocols for pH calibration and measurement are described in NFM 6.8.

General procedures for calibration of the pH sensor in a multiparameter sonde:

- 1. Select the pH 7 and one additional buffer solution that will bracket the anticipated pH of the sample. Equilibrate the temperature of the buffers to the temperature of the environmental sample.
- 2. Rinse the sonde and electrode thoroughly three times with DIW before and between use of each buffer solution.
- 3. Rinse the pH and temperature sensors three times with separate aliquots of the first pH buffer, using the "pour-swirl-discard, pour-sit-discard, pour-sit-measure" method described in section 6.4.3.A. Allow enough time for the sensors to equilibrate to buffer temperature before locking in the first calibration point.
- 4. Repeat step 3, using the second pH buffer, and lock in the second calibration point. (Depending on site conditions and study objectives, it might be useful to check the calibration range of the pH sensor using a third buffer; if appropriate, lock in a value.)
- 5. Always record temperature information with calibration information in the pH-meter/electrode logbook and on the field sheet.

MEASUREMENT 6.4.4

The pH of sample water is to be measured as soon as possible after removal of the sample from its environmental source. The pH of a water sample can change substantially within hours or even minutes after sample collection as a result of temperature change; degassing (loss of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); in-gassing (gain of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); mineral precipitation (formation of calcium carbonate, iron hydroxides); metabolic respiration by microorganisms; and other chemical, physical, and biological reactions (Hem, 1989). Field conditions, including rain, wind, cold, dust, direct sunlight, and direct exposure to vehicle exhaust can cause measurement problems.² Always protect the instrument system and the measurement process from the effects of harsh weather and transportation damage.

The pH value of an aqueous system should be determined by taking the median of three or more separate and stable measurements that are recorded in a quiescent sample. Recording a median value ensures that the reported pH value represents a true measurement, instead of a computed measurement, and avoids the mathematical procedure required to compute a mean pH from logarithmic operations.

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²The effects of field conditions on the quality of field measurements, water-quality samples, and data integrity must be anticipated by field personnel and protocols to minimize sample contamination as described in NFM 4 and 5 are to be implemented as standard operating procedure.

TECHNICAL NOTE: The pH value of a given sample always is recorded in the USGS database as a median of a series of stable measurements. For applications that require reporting pH over time (for example, an annual average pH) or space, however, computation of the mean of the hydrogen ion activity may be useful. To compute a series of pH measurements collected over time or space:

- a. Take the antilog of each pH measurement, using the following equation: Activity = 10^{-pH} .
- b. Add all the antilog values and divide the sum by the total number of values.
- c. Convert the calculated mean activity back to pH units, using the equation, pH = (-log10) (mean H⁺ activity).

If reporting pH as a computed mean, document this information and the procedure used. **Do not** enter a mean pH value in the USGS NWIS database under the parameter code for a median or direct determination of pH.

6.4.4.A pH MEASUREMENT IN SURFACE WATER

When using a single-parameter pH electrode/meter instrument system, the pH of surface water is determined ex situ, from a quiescent, non-stirred sample that is withdrawn from a churn or cone splitter or other approved sample-compositing device. Although referred to as a single-parameter method, most modern pH meters are equipped with a thermistor used to determine the temperature of the sample. Each pH measurement must be accompanied with a concurrent temperature measurement.

- ▶ It is not advisable to immerse the pH electrode into flowing surface water for the following reasons:
 - Placing the pH electrode into moving water risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. In addition, proper functioning of the glass membrane is affected when ionic equilibrium is not achieved with the surrounding sample solution.
 - Calibration of the electrode was accomplished in a quiescent sample, not in flowing or stirred water. Adequate calibration of the instrument system cannot be assumed to extend to moving water.
 - USGS methodology in surface-water measurement usually involves the collection of depthand width-integrated samples. In situ measurements of pH in a moving water system, either at a singular point in the waterway or across a section, do not meet these requirements.
 - Reference-junction equilibrium cannot be achieved in moving water; thus, correct electrode functioning will again be inhibited.
 - It is difficult to have electrode temperature come to equilibrium with sample temperature in moving water; correct pH instrument system functioning will be inhibited.
- ► The determination of pH in situ, using a multiparameter instrument system, is described in NFM 6.0 and 6.8. The system selected depends on the data-quality objectives of the study and on site-specific conditions.

Before collecting the sample and making ex situ measurements, it is advisable to determine the range of pH values in the cross section, or estimate the magnitude of lateral mixing of the waterway at the field site, using an in situ measurement method (for example, with a multiparameter sonde).

When making an ex situ pH measurement:

Set up the pH instrument system close to the sampling site in order to minimize the time lapse between sample collection and pH measurement.

- 1. The glass membrane of the electrode should not contact the sides or bottom of the beaker or other measurement vessel. Use only a clean measurement vessel.
- 2. Fill the measurement vessel with sufficient sample to ensure that the electrode reference junction is fully immersed, taking care not to aerate the sample.
- 3. After calibration (or measuring the pH of a different sample), rinse the electrode and thermistor three times with DIW. This crucial step must always be completed between differing solutions.
- 4. Rinse the electrode and thermistor sensors two times with the sample, as follows:
 - a. **First rinse**—Pour an aliquot of sample onto the sensors and swirl the sample water around the electrode sensors. Discard the sample appropriately.
 - b. **Second rinse**—Pour an aliquot of sample onto the sensors and allow the sensors to sit in the solution for 1 minute (do not swirl). Discard the sample appropriately.
- 5. **Measure pH**, as follows:
 - a. Pour a third aliquot of sample into the vessel. **Allow the sensors to sit in a quiescent sample** for 1 minute or until the pH value stabilizes within the established criterion. Record the pH value on the electronic or paper field-notes form.
 - b. Repeat the procedure in (a) above on at least two additional aliquots of the sample, recording the pH measurement for each aliquot on the field form(s).
- 6. Calculate a final sample pH as the median of the values measured for the sample aliquots and document the calculation on field forms.
- 7. **Record** the final pH value of the sample to the nearest 0.01 pH unit, along with the sample temperature, in paper and (or) electronic field forms, including forms that accompany samples being shipped to the laboratory.
- 8. The pH value should be reported to the nearest 0.1 pH unit when published and when recorded in the NWIS database.

Always record the temperature of the sample concurrently with each pH measurement.

6.4.4.B pH MEASUREMENT IN GROUND WATER

The pH of ground water should be measured under no-flow (quiescent sample) conditions. When using a single-parameter meter, the measurement can be made either with the pH electrode and temperature sensor inserted (a) into an airtight flowthrough cell or chamber to which the sample is pumped, or (b) in a vessel that contains an aliquot of sample either collected from pump discharge or withdrawn from a sampling device, such as a bailer (figs. 6.4–2 and 6.4–3, respectively). (See NFM 6.8 for pH measurement using a multiparameter sonde).

The central concept for measuring pH in ground water is to use equipment that minimizes aeration, chemical change, and temperature change. If possible, operate equipment in a manner that helps to mitigate losses and gains of dissolved gases in solution.

- ► The flowthrough cell/chamber method yields accurate pH data when implemented appropriately.
- ▶ Bailed or other methods for collecting discrete samples for pH measurement must be implemented carefully to avoid temperature change, turbulence, and sample aeration from decanting and mixing of the bailed water.
- ▶ Downhole deployment of a submersible sensor or sonde risks losing the equipment if it becomes lodged in the well.

Document on electronic or paper field forms the methodology used to obtain samples for pH measurement.

Unless specifically required by study objectives or environmental constraints, in situ measurement of pH by putting the sensor system directly into the well (downhole method) should be avoided for the following reasons:

- ▶ Placing the pH electrode directly into the borehole risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. Any accretions or coatings on the inside of the borehole may be transferred to the pH sensor and damage, or alter, the membrane.
- ▶ Pumps, wiring, and (or) other equipment within the borehole may damage or degrade the pH sensor and the sonde.
- Any static electrical charge on the inside of the well casing or borehole may be transferred to the pH electrode, a condition sometimes referred to as a "ground loop," which also compromises accurate pH measurement.

Always measure and record sample temperature concurrently with pH measurements.





Figure 6.4–2. Photographs of (\boldsymbol{A}) a flowthrough cell/chamber for use with single-parameter field-measurement sensors, shown without sensors installed; and (\boldsymbol{B}) a flowthrough cell attached to a multiparameter sonde. Photograph \boldsymbol{A} courtesy of Geotech Environmental. Photograph \boldsymbol{B} is a USGS stock image.

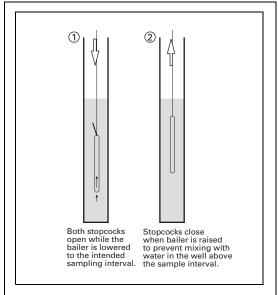


Figure 6.4–3. Use of a dual-valve (double stop-cock) Teflon bailer.

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Referring to figure 6.4–2, ground water is pumped directly from the well through tubing and into an airtight flowthrough cell/chamber containing either a calibrated pH electrode and other sensors (typically, dissolved oxygen, specific electrical conductance, and temperature sensors (fig. 6.4–2A), or a multiparameter sonde (fig. 6.4–2B).

After successful calibration of the pH instrument system on site, pH measurement of sample water may proceed either on discrete samples obtained from a bailer, or on pumped ground water circulated through a flowthrough cell/chamber.

- ▶ Use of the bailer to obtain ground-water samples is analogous to the approved use of samplers in a surface-water situation, as described below.
- ▶ Use of a flowthrough cell/chamber has the advantage of concurrent monitoring of ground-water field measurements in addition to pH, as described below.

To make a pH measurement using a flowthrough cell/chamber system instrumented with single-parameter sensors (fig. 6.4–2):

- 1. Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight.
- 2. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged.
- 3. Check for and eliminate any backpressure condition.
- 4. Monitor pH variation during purging:
 - a. Keep the flow constant and laminar.
 - b. Allow the sensors to equilibrate with the ground water for 5 minutes or more, at the flow rate to be used for collecting all of the other samples.
 - c. Record pH values at regularly spaced time intervals throughout purging (consult NFM 6.0 for detailed guidance). Compare the variability of pH values toward the end of purging. The stability of pH values is assumed when three to five readings made at regularly spaced intervals are constant. If readings continue to fluctuate, continue to monitor, or, if site conditions are demonstrably variable (degassing, ingassing, rapid thermal changes from water at depth), select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.
- 5. Determine sample pH toward the end of purging (for example, during removal of the final purge volume) as follows:
 - a. Divert flow from the chamber to allow the sample contained within the chamber to become quiescent (after recording the other field measurements). Record the pH value under quiescent conditions to the nearest 0.01 pH unit.
 - b. Determine the median of the pH values recorded under quiescent conditions and report this value as sample pH.
 - c. If field personnel have reason to suspect an electrode malfunction, a calibration check at the end of sampling is recommended.

To make a pH measurement on a bailed sample (fig. 6.4–3):

- 1. Withdraw subsamples from the well and transfer each bailed sample to a churn, cone splitter, or other appropriate compositing device (NFM 2).
- 2. Remove an aliquot from the sample composite for measurement of pH.

TROUBLESHOOTING 6.4.5

Consult the instrument manufacturer for recommended troubleshooting actions for specific single-parameter and multiparameter pH instrument systems.

- ▶ Nearly all problems encountered during pH calibration and measurement can be attributed directly to the condition and responsiveness of the pH electrode (table 6.4–3).
- ► For any problem, first test that the instrument batteries are fully charged. Keep spare batteries on hand that are fully charged.

Table 6.4–3. Troubleshooting guide for pH measurement.

[DIW, deionized water]

Symptom	Possible cause—Corrective action
Instrument system will not calibrate to full scale	 Buffers may be contaminated or old—Use fresh buffers. Faulty electrode—Recondition or replace electrode (see section 6.4.2). Weak batteries—Replace with new or fully charged batteries.
Slow response	 For liquid-filled electrodes: Weak or incorrect solution—Change filling solution to correct molarity. No or low filling solution—Add fresh solution of correct molarity. Dirty tip (for example, visible chemical deposits or organic or biological matter on the electrode)—Rinse tip with DIW; if residue persists, use solution and cleaning method recommended by the manufacturer. Take care not to scratch the electrode tip. Clogged or partially clogged junction—Follow the manufacturer's instructions to unclog the junction). Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B). Sluggish response to pH changes; pH measurement is biased negatively—Refer to table 6.4–2. For gel-filled electrodes: Dirty bulb—Rinse bulb carefully with DIW. If organic/inorganic/biological residue persists, consult the manufacturer's recommendations. Visibly clogged junction—Follow the manufacturer's instructions to unclog the junction Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B).
Erratic readings	 Loose or defective connections—Tighten, clean, or replace connections. Broken or defective cable—Repair or replace cable. Static charge—Polish face of meter with antistatic solution. Loose battery connection—Tighten. Air bubbles in the electrode bulb—Shake electrode gently. Too much pressure in flowthrough chamber—Release and reduce pressure. Weak batteries—Replace with new, fully charged batteries.

6.4.6 REPORTING

Due to the rapidity of pH reactions in environmental samples, the effect of temperature on the operation of the pH instrument system, and chemical and microbiological equilibria within the sample, pH measurements must be completed and recorded as soon as possible after removing the sample from the environmental medium. When entering the pH value for the site into the NWIS database, ensure that the method code selected correctly corresponds to the method that was used for the pH measurement.

- ▶ On field forms (electronic or paper) and in the pH-meter/electrode logbook, record pH calibration and environmental measurements to 0.01 standard pH units.
- ▶ In the USGS NWIS database, report pH values to the nearest 0.1 standard pH unit, unless study and data-quality objectives dictate otherwise and equipment of the appropriate precision and accuracy has been used.

6.4.7 SELECTED REFERENCES

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By D.B. Radtke, J.V. Davis, and F.D. Wilde

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SPECIFIC ELECTRICAL 6.3 CONDUCTANCE

By D.B. Radtke, J.V. Davis, and F.D. Wilde

Electrical conductance is a measure of the capacity of water (or other media) to conduct an electrical current. Electrical conductance of water is a function of the types and quantities of dissolved substances in water, but there is no universal linear relation between total dissolved substances and conductivity.

The USGS reports conductivity in microsiemens per centimeter at 25 degrees Celsius (μ S/cm at 25°C). The method described in this section for measuring conductivity is applicable to surface water and ground water, from fresh to saline.

SPECIFIC ELECTRICAL
CONDUCTANCE (CONDUCTIVITY)—
 a measure of the electrical
 conductance of a substance
 normalized to unit length
 and unit cross section at a
 specified temperature.

EQUIPMENT AND SUPPLIES 6.3.1

The instrument system used to measure conductivity must be tested before each field trip and cleaned soon after use. Many conductivity instruments are available, including multiparameter instruments that include conductivity sensors. This section provides detailed information on the use of conductivity-specific instruments only, although instructions regarding conductivity standards and measurement methods are applicable in general. Users must be familiar with the instructions provided by the manufacturer. Every conductivity (or multiparameter) instrument must have a log book in which repairs and calibrations are recorded, along with manufacturer make and model description and serial or property number.

Table 6.3–1. Equipment and supplies used for measuring conductivity¹ [°C, degrees Celsius; \leq , less than or equal to; >, greater than; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; L, liter]

✓ Conductivity instrument and conductivity sensor

Battery powered Wheatstone bridge

Direct readout

Temperature range at least -5 to +45°C

Temperature compensating (25°C)

Accuracy: Conductivity ≤100 µS/cm, within 5 percent of full scale Conductivity >100 µS/cm, within 3 percent of full scale

- ✓ Thermistor thermometer sensor (for automatic temperaturecompensating models)
- ✓ Thermometer, liquid-in-glass or thermistor
- ✓ Extra sensors (if possible) and batteries, or backup instrument
- Conductivity standards at conductivities that approximate and bracket field values
- ✓ Compositing and splitting device for surface-water samples
- √ Flowthrough chamber or downhole instrument for ground-water measurements
- ✓ Plastic beakers (assorted sizes)
- ✓ Soap solution, nonphosphate (1 L)
- ✓ Hydrochloric acid solution, 5 percent volume-to-volume (1 L)
- ✓ Deionized water, 1 L, maximum conductivity of 1 µS/cm
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Brush (small, soft)
- ✓ Waste disposal container
- ✓ Minnow bucket with tether (or equivalent) for equilibrating buffer solutions to sample temperature
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

As soon as possible after delivery to the office, label conductivity standards with the date of expiration. Secard standards that have expired, been frozen, have begun to evaporate, or that were decanted from the storage container. Quality-controlled conductivity standards ranging from 50 to $50,000~\mu$ S/cm at 25° C can be obtained by USGS personnel through "One Stop Shopping." Order standards outside this range from suppliers of chemical reagents. Conductivity standards usually consist of potassium chloride dissolved in reagent-grade water.

¹Modify this list to meet the specific needs of the field effort.

CONDUCTIVITY SENSORS 6.3.1.A

Conductivity sensors are either contacting-type sensors with electrodes or electrodeless-type sensors.

- ► Contacting-type sensors with electrodes. Three types of cells are available: (1) a dip cell that can be suspended in the sample, (2) a cup cell that contains the sample, or (3) a flow cell that is connected to a fluid line. Choose a cell constant on the basis of expected conductivity (table 6.3–2). The greater the cell constant, the greater the conductivity that can be measured. The cell constant is the distance between electrodes (in centimeters) divided by the effective cross-sectional area of the conducting path (in square centimeters).
- ▶ Electrodeless-type sensors. These operate by inducing an alternating current in a closed loop of solution, and they measure the magnitude of the current. Electrodeless sensors avoid errors caused by electrode polarization or electrode fouling.

Table 6.3–2. Example of cell constants for contacting-type sensors with electrodes and corresponding conductivity ranges

Conductivity range, in microsie- mens per centimeter	Cell constant, in 1/centimeter
0.005 - 20	.01
1 – 200	.1
10 - 2,000	1.0
100 - 20,000	10.0
1,000 – 200,000	50.0

CAUTION: Before handling conductivity standards or acids, refer to Material Safety Data Sheets (MSDS) for safety precautions.

6.3.1.B EQUIPMENT MAINTENANCE

Maintenance of conductivity equipment includes periodic office checks of instrument operation. To keep equipment in good operating condition:

- ▶ Protect the conductivity system from dust and excessive heat and cold.
- ▶ Keep all cable connectors dry and free of dirt.
- ▶ Protect connector ends in a clean plastic bag.

Sensor cleaning and storage

Conductivity sensors must be clean to produce accurate results; residues from previous samples can coat surfaces of sensors and cause erroneous readings. Refer to the manufacturer's instructions regarding long- and short-term storage of the sensor.

- ► Clean sensors thoroughly with deionized water (DIW) before and after making a measurement (this is sufficient cleaning in most cases).
- ▶ Remove oily residue or other chemical residues (salts) with a detergent solution. Sensors can soak in detergent solution for many hours without damage.
- ▶ If oil or other residues persist, dip the sensor in a dilute hydrochloric acid solution. Never leave the sensor in contact with acid solution for more than a few minutes. Check the manufacturer's recommendations before using acid solutions.
- ► Clean carbon and stainless steel sensors with a soft brush. Never use a brush on platinum-coated sensors.
- ► Sensors may be temporarily stored in deionized water between measurements and when the system is in daily use.
- ► For long-term storage, store sensors clean and dry.

CALIBRATION 6.3.2

Conductivity systems must be calibrated before every water-quality field trip and again at each site before samples are measured. Calibration readings are recorded in the instrument log book and on field forms at the time the instrument is calibrated. Remember, the temperature sensor on the conductivity sensor must be District certified within the past 4 months.

Calibration and operating procedures differ, depending on instrument and sensor type.

- ➤ Some conductivity sensors may need to be soaked overnight in deionized water before use—Check the manufacturer's instructions.
- ► Some analog instruments require an initial mechanical zero adjustment of the indicator needle.
- ► For a cup-type cell, calibration and measurement procedures described for the dip-type cell apply; the only difference is that standards are poured directly into the cup-type cell.
- ▶ When using a dip-type cell, do not let the cell rest on the bottom or sides of the measuring container.

Calibrate at your field site—bring standards to sample temperature.

Conductivity systems normally are calibrated with at least two standards. Calibrate sensors against a standard that approximates sample conductivity and use the second standard as a calibration check. The general procedures described in steps 1 through 15 below apply to most instruments used for field measurements—check the instrument manual for specific instructions.

- 1. Inspect the instrument and the conductivity sensor for damage. Check the battery voltage. Make sure that all cables are clean and connected properly.
- 2. Turn the instrument on and allow sufficient time for electronic stabilization.

- 3. Select the correct instrument calibration scale for expected conductivity.
- 4. Select the sensor type and the cell constant that will most accurately measure expected conductivity.
- Select two conductivity standards that will bracket the expected sample conductivity. Verify that the date on the standards has not expired.
- 6. Equilibrate the standards and the conductivity sensor to the temperature of the sample.
 - Put bottles of standards in a minnow bucket, cooler, or large water bath that is being filled with ambient water.
 - Allow 15 to 30 minutes for thermal equilibration. Do not allow water to dilute the standard.
- 7. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
 - **First**, rinse the sensor, the thermometer, and the container three times with deionized water.
 - **Next**, rinse the sensor, the thermometer, and the container three times with the standard to be used.
- 8. Put the sensor and the thermometer into the rinsed container and pour in fresh calibration standard.
- 9. Measure water temperature. Accurate conductivity measurements depend on accurate temperature measurements or accurate temperature compensation.
 - If the sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
 - If using a manual instrument without a temperature display or temperature compensation, adjust the instrument to the temperature of the standard using a calibrated liquid-in-glass or a thermistor thermometer.
- 10. Agitate a submersible-type conductivity sensor up and down under the solution surface to expel air trapped in the sensor. Read the instrument display. Agitate the sensor up and down under the solution surface again, and read the display. Repeat the procedure until consecutive readings are the same.

- 11. Record the instrument reading and adjust the instrument to the known standard value.
 - For nontemperature-compensating conductivity instruments, apply a temperature-correction factor to convert the instrument reading to conductivity at 25°C.
 - The correction factor depends to some degree on the specific instrument used—use the temperature-correction factor recommended by the manufacturer. If this is not available, use correction factors from table 6.3–3.
 - If an instrument cannot be adjusted to a known calibration standard value, develop a calibration curve. After temperature compensation, if the percentage difference from the standard exceeds 5 percent, refer to the troubleshooting guide (section 6.3.4).
- 12. Record in the instrument log book and on field forms:
 - The temperature of the standard solution.
 - The known and the measured conductivity of the standard solution (including ± variation).
 - The temperature-correction factor (if necessary).
- 13. Discard the used standard into a waste container. Thoroughly rinse the sensor, thermometer, and container with deionized water.
- 14. Repeat steps 7 through 13 with the second conductivity standard.
 - The purpose for measuring a second standard is to check instrument calibration over the range of the two standards.
 - The difference from the standard value should not exceed 5 percent.
 - If the difference is greater than 5 percent, repeat the entire calibration procedure. If the second reading still does not come within 5 percent of standard value, refer to the troubleshooting guide in section 6.3.4 or calibrate a backup instrument.
- 15. Record in the instrument log book and on field forms the calibration data for the second standard.

Do not use expired standards. Never reuse standards.

Table 6.3–3. Correction factors for converting non-temperature-compensated values to conductivity at 25 degrees Celsius, based on 1,000 microsiemens potassium chloride solution

[Use of potassium-based constants on non-potassium-based waters generally does not introduce significant errors for general purpose instruments used to measure conductivity]

Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor
0.5	1.87	10.5	1.39	20.5	1.09
1.0	1.84	11.0	1.37	21.0	1.08
1.5	1.81	11.5	1.35	21.5	1.07
2.0	1.78	12.0	1.33	22.0	1.06
2.5	1.76	12.5	1.32	22.5	1.05
3.0	1.73	13.0	1.30	23.0	1.04
3.5	1.70	13.5	1.28	23.5	1.03
4.0	1.68	14.0	1.27	24.0	1.02
4.5	1.66	14.5	1.26	24.5	1.01
5.0	1.63	15.0	1.24	25.0	1.00
5.5	1.60	15.5	1.22	25.5	0.99
6.0	1.58	16.0	1.21	26.0	0.98
6.5	1.56	16.5	1.19	26.5	0.97
7.0	1.54	17.0	1.18	27.0	0.96
7.5	1.52	17.5	1.16	27.5	0.95
8.0	1.49	18.0	1.15	28.0	0.94
8.5	1.47	18.5	1.14	28.5	0.93
9.0	1.45	19.0	1.13	29.0	0.92
9.5	1.43	19.5	1.12	29.5	0.91
10.0	1.41	20.0	1.11	30.0	0.90

To extend the temperature range shown in table 6.3–3, consult the manufacturer's guidelines. If these are unavailable, use the following equation:

$$C_{25} = \frac{C_m}{1 + 0.02(t_m - 25)}$$

where,

 C_{25} = corrected conductivity value adjusted to 25°C; C_m = actual conductivity measured before correction; and t_m = water temperature at time of C_m measurement.

MEASUREMENT 6.3.3

In situ measurement generally is preferred for determining the conductivity of surface water; downhole or flowthrough-chamber measurements are preferred for ground water. Be alert to the following problems if conductivity is measured in an isolated (discrete) sample or subsample:

- ► The conductivity of water can change over time as a result of chemical and physical processes such as precipitation, adsorption, ion exchange, oxidation, and reduction—Do not delay making conductivity measurements.
- ► Field conditions (rain, wind, cold, dust, direct sunlight) can cause measurement problems—Shield the instrument to the extent possible and perform measurements in a collection chamber in an enclosed vehicle or an on-site laboratory.
- ► For waters susceptible to significant gain and loss of dissolved gases, make the measurement within a gas-impermeable container (Berzelius flask) fitted with a stopper—Place the sensor through the stopper and work quickly to maintain the sample at ambient surface-water or ground-water temperature.
- ▶ Avoid contamination from the pH electrode filling solution— Measure conductivity on a separate discrete sample from the one used for measuring pH; in a flowthrough chamber, position the conductivity sensor upstream of the pH electrode.

Conductivity must be measured at the field site.

Document the precision of your measurements. Precision should be determined about every tenth sample or more frequently, depending on study objectives. Successive measurements should be repeated until they agree within 5 percent at conductivity $\leq 100 \, \mu \text{S/cm}$ or within 3 percent at conductivity $> 100 \, \mu \text{S/cm}$.

The conductivity measurement reported must account for sample temperature. If using an instrument that does not automatically temperature compensate to 25°C, record the uncompensated measurement in your field notes, along with the corrected conductivity value. Use correction factors supplied by the instrument manufacturer if available; otherwise, refer to table 6.3–3.

6.3.3.A SURFACE WATER

Surface-water conductivity should be measured in situ, if possible; otherwise, determine conductivity in discrete samples collected from a sample splitter or compositing device. Filtered samples may be needed if the concentrations of suspended material interfere with obtaining a stable measurement.

In situ measurement

Conductivity measurements in flowing surface water should represent the cross-sectional mean or median conductivity at the time of observation (see step 7, below). Any deviation from this convention must be documented in the data base and with the published data.

First:

- ➤ Take a cross-sectional conductivity profile to determine the degree of system variability. A submersible sensor works best for this purpose.
- ▶ Refer to NFM 6.0 for criteria to help decide which sampling method to use.

Next, follow the 7 steps listed below:

- 1. Calibrate the conductivity instrument system at the field site after equilibrating the buffers with stream temperature.
- 2. Record the conductivity variation from a cross-sectional profile on a field form and select the sampling method.
 - **Flowing, shallow stream**—wade to the location(s) where conductivity is to be measured.
 - Stream too deep or swift to wade—lower a weighted conductivity sensor from a bridge, cableway, or boat. Do not attach weight to the sensor or the sensor cable.
 - **Still-water conditions**—measure conductivity at multiple depths at several points in the cross section.
- 3. Immerse the conductivity and temperature sensors in the water to the correct depth and hold there (no less than 60 seconds) until the sensors equilibrate to water conditions.
- 4. Record the conductivity and corresponding temperature readings without removing the sensors from the water.
 - Values should stabilize quickly to within 5 percent at conductivity ≤100 μS/cm and within 3 percent at conductivity >100 μS/cm.
 - Record the median of the stabilized values on field forms.
 - If the readings do not meet the stability criterion after extending the measurement period, record this difficulty in the field notes along with the fluctuation range and the median value of the last five or more readings.
- 5. For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 and 4. Record on field forms the mean (or median, if appropriate) value for each subsection measured.
- 6. When the measurement is complete, remove the sensor from the water, rinse it with deionized water, and store it.
- 7. Record the stream conductivity on the field forms:
 - In still water—median of three or more sequential values.
 - **EDI**—mean value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
 - **EWI**—mean or median of all subsections measured (see NFM 6.0).

Subsample measurement

Representative samples are to be collected and split or composited according to approved USGS methods (NFM 4). Measure the conductivity of samples as soon as possible after collection. If the sample cannot be analyzed immediately, fill a bottle to the top, close it tightly, and maintain the sample at stream temperature until measurement.

Reported conductivity values normally are determined on an unfiltered sample. Large concentrations of suspended sediment can be a source of measurement error—record such conditions in the field notes.

- ▶ If sediment concentrations are heavy, measure conductivity on both unfiltered and filtered subsamples and record both values on the field form.
- ▶ If the conductivity value differs significantly between the filtered and unfiltered samples, report the filtered value as sample conductivity and identify it as a "filtered sample."
- 1. Calibrate the conductivity instrument system at the field site.
- 2. Select the sampling method (see NFM 6.0) and collect a representative sample.
- 3. Withdraw a homogenized subsample from a sample splitter or compositing device. Rinse the sample bottles three times with the sample—rinse them with sample filtrate, for filtered samples.
- 4. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
 - a. First, rinse the sensor, the thermometer, and the container three times with deionized water.
 - b. Next, rinse the sensor, the thermometer, and the container using sample water.
- 5. Allow the sensors to equilibrate to sample temperature, then discard the used sample water. Pour fresh sample water into a container holding the sensor and the thermometer. When using a diptype sensor, do not let the sensor touch the bottom or sides of the measuring container.

- 6. Measure water temperature.
 - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
 - If the instrument is not temperature compensating, use a calibrated thermistor or a liquid-in-glass thermometer.
 - Adjust the instrument to the sample temperature (if necessary) and remove the thermometer.

7. Measure conductivity.

- a. Remove any air trapped in the sensor by agitating the sensor up and down under the water surface.
- b. Read the instrument display.
- c. Agitate the sensor up and down under the water surface, and read the display again.
- d. Repeat the procedure until consecutive readings are the same.
- 8. Record the conductivity and the sample temperature on field forms.
 - If the instrument is not temperature compensating, record the raw data and convert the values to conductivity at 25°C using temperature-correction factors provided by the manufacturer.
 - Report the median of the readings to three significant figures on the field forms.
 - Discard the sample into a waste container and dispose according to regulations.

9. **Quality control**—

- Repeat steps 3 through 8 with at least two fresh subsamples, rinsing the instruments once only with sample water.
- Subsample values should be within ±5 percent for conductivity ≤100 μS/cm, or ±3 percent for conductivity >100 μS/cm.
- If criteria cannot be met: filter the samples, report the median of 3 or more samples, and record this difficulty in field notes.
- 10. Rinse the sensor, the thermometer, and the container with deionized water. If another measurement is to be made within the next day or two, store the sensor in deionized water. Otherwise, store the sensor dry.

6.3.3.B GROUND WATER

Measurements of ground-water conductivity must represent aquifer conditions. Temperature changes resulting from transporting a well sample to land surface can affect conductivity.

- ➤ To minimize the effect from temperature changes, measure conductivity as close to the source as possible, using either a downhole or flowthrough-chamber sampling system (refer to NFM 6.0 for details).
- ▶ Bailed or other methods for collecting discrete samples isolated from the source are not recommended as standard practice, although such methods are sometimes called for owing to site characteristics or other study requirements.
- ► The well should be purged or in the process of purging before sample conductivity is determined and recorded.

Downhole and flowthrough-chamber measurement

- 1. Calibrate the conductivity instrument system on site.
 - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
 - a. Check the temperature of the water flowing into the bucket against that of standards.
 - b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
 - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.
- 2. Install the conductivity and temperature sensors.
 - **Downhole system**—Lower the conductivity and temperature sensors to the sampling point, followed by the pump.

- a. Remove any air from the system by agitating the conductivity sensor up and down under the water; read the instrument display.
- b. Repeat this procedure until rapid consecutive readings are approximately the same.
- Flowthrough-chamber system—Install the chamber system
 as close to the well as possible and shield the system from
 direct sunlight.
 - a. Position the conductivity sensor upstream from the pH electrode.
 - b. Direct flow to the chamber after an initial discharge to waste to clear sediment from sample line.
 - c. Release any air trapped in the chamber.
 - d. Agitate the conductivity sensor up and down under the water to remove air from system. Rapid consecutive readings should be about the same.
- 3. During purging (table 6.0–1 in NFM 6.0):
 - Keep flow constant and laminar.
 - Allow the sensors to equilibrate with ground-water temperature for 5 minutes or more at the flow rate to be used for collecting all other samples.
- 4. Measure conductivity and associated temperature at regular intervals throughout purging; record the conductivity values and the associated temperature in the field notes.
 - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
 - If the instrument is not temperature compensating, install a calibrated thermometer in the flowthrough chamber, record raw data, and apply correction factors.
- 5. Check the variability of the conductivity values toward the end of purging.
 - The stability criterion is met when five readings taken at regularly spaced intervals of 3 to 5 minutes or more are within
 - ±5 percent for conductivity ≤100 µS/cm
 - ± 3 percent for conductivity >100 μ S/cm

- When readings fluctuate rapidly, record the median of three or more readings within about 60 seconds as the value for a specific time interval.
- If the criterion is not met, extend the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals. Record this difficulty on the field forms.
- 6. Report conductivity.
 - Record the final five values on field forms.
 - Report the median value of the final five measurements as the sample conductivity.
 - If values exceed the stability criterion, report the range of values observed for the time interval, along with the median of the final five or more values.

Subsample measurement

Conductivity measurements reported from bailed or other discrete samples need to be identified in the data base, indicating the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

- 1. Calibrate the conductivity instrument system onsite.
 - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
 - a. Check the temperature of the water flowing into the bucket against that of standards.
 - b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
 - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.

- 2. Draw off subsamples for measurement.
 - Quality control—Collect three subsamples to check precision.
 - If samples need to be stored for a short time, or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles—fill to the brim, cap tightly, and maintain at ambient ground-water temperature. Measure conductivity as soon as possible.
- 3. Follow procedures described in steps 4 through 10 for "Subsample measurement" of surface water (6.3.3.A).

TECHNICAL NOTE: If the sample is measured in an open container and readings do not stabilize within several minutes, the cause may be ${\rm CO_2}$ degassing—use a closed system to measure the sample. Filter the conductivity sample if the settling of clay particles appears to interfere with the stability of the readings.

TROUBLESHOOTING 6.3.4

Contact the instrument manufacturer if the actions suggested in table 6.3–4 fail to resolve the problem.

- ▶ If available, use a commercial, electronic calibrator to check the function of conductivity instruments.
- ► Check the voltage of batteries. Always have good batteries in instruments and carry spares.

Table 6.3–4. Troubleshooting guide for conductivity measurement [HCl, hydrochloric acid; °C, degrees Celsius]

Symptom	Possible cause and corrective action
Will not calibrate to standards	 Standards may be old or contaminated—use fresh standards. Electrodes dirty—clean with a detergent solution, then with 5 percent HCl. Before using any acid solution to remove resistant residues, check manufacturer's guidelines. Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. Weak batteries—replace. Temperature compensation incorrect—ensure that thermometer is operating properly and is calibrated. Sensor constant incorrect—replace sensor.
Erratic instrument readings	 Loose or defective connections—tighten or replace. Broken cables—repair or replace. Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. Rapid changes in water temperature—measure in situ. Outgassing of ground-water sample—use a downhole instrument; if unavailable, use a flowthrough chamber. Broken sensor—replace.
Instrument requires frequent recalibration	Temperature compensator not working—measure conductivity of a solution. Place solution in a water bath and raise solution temperature to about 20°C. Measure conductivity again, allowing sufficient time for temperature of conductivity sensor to equilibrate to temperature of solution. If the two values differ by 5 percent or more, replace conductivity sensor.

REPORTING 6.3.5

Report routine conductivity measurements to three significant figures, whole numbers only, in microsiemens per centimeter at 25°C.

- ► Record the accuracy range of the instrument system in the data base, if possible, and always report it with published values.
- ► Enter field-determined conductivity measurements on the NWQL Analytical Services Request form using the correct parameter code.

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USE OF MULTIPARAMETER 6.8 INSTRUMENTS FOR ROUTINE FIELD MEASUREMENTS

By Jacob Gibs, Franceska D. Wilde, and Heather A. Heckathorn

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USE OF MULTIPARAMETER 6.8 INSTRUMENTS FOR ROUTINE FIELD MEASUREMENTS

By Jacob Gibs, Franceska D. Wilde, and Heather A. Heckathorn

The miniaturization of sensors and other technological advances in electronics have resulted in water-quality instruments that house multiple sensors capable of simultaneous readings for various field measurements in environmental waters. With the use of these multiparameter instruments, field measurements can be determined with considerable reduction in the field work that generally is required when using multiple single-parameter instruments (table 6.8–1). This section addresses the short-term or discrete-measurement use of portable multiparameter instruments. Refer to Wagner and others (2006) for long-term or continuous-monitor deployment in surface water.

MULTIPARAMETER INSTRUMENT: An electronic instrument that contains sensors (each specific to the measurement of a given physical, chemical, or biological property) that are bundled in a single housing (a sonde) and deployed in environmental waters.

¹The term "field measurement(s)" is synonymous in this report with the terms field properties and field parameters. USGS field measurements include, for example, water temperature, pH, specific electrical conductance, turbidity, oxidation-reduction potential, barometric pressure, and calculations such as salinity and percent of dissolved oxygen in milligrams per liter. The term "field parameter" commonly is used in the environmental literature.

Table 6.8–1. Advantages and limitations of multiparameter instruments for field use

Advantages	Limitations
Efficiency is increased. Instruments are easy to clean, calibrate, and deploy. The time required to collect discrete samples for determining field properties is minimized. The time needed to measure and record multiple field properties is reduced. In situ measurement is likely to be more accurate and precise than measurements made in samples removed from their source. Instruments can store data, either in a display device or to internal memory. Instruments may be capable of long-term deployment.	Repair of sensors while working onsite often is not possible. Sensor replacement in the field may be unwieldy or not possible. Sensors must be replaced in a clean, dry environment. Backup field instruments (single parameter or multiparameter) are recommended to prevent data loss and extended field time. Purchase, repair, and replacement costs for multiparameter instruments are higher than for single-parameter instruments.

Quality assurance. To ensure the quality of the data collected, this section of NFM 6 describes standard operating procedures and recommendations that have been developed for routine U.S. Geological Survey (USGS) field studies. The instrument manufacturer is, however, the primary source of information about the maintenance and use of a specific instrument. The protocols and recommendations described in this section are meant to complement and enhance the manufacturer's guidelines, providing the level of quality assurance for which USGS data are held accountable.²

 $^{^2}$ USGS personnel should discuss any discrepancies between the protocols and recommendations described in this manual and the instructions provided by the instrument manufacturer with their water-quality specialists or with the USGS Office of Water Quality.

EQUIPMENT AND SUPPLIES 6.8.1

Multiparameter instruments are available for long- or short-term deployment at a stream, lake, reservoir, ground-water well, or other environmental setting, and their sondes³ are suitable for water that is fresh, brackish, saline, or polluted. Sensor housings (the sonde) of multiparameter instruments generally are available in a range of diameters from about 4 inches (in.) (10 centimeters (cm)) to less than 2 in. (5.1 cm). Small-diameter sondes may be used for downhole measurements in wells and may have more limited sensor capability than the larger diameter sonde. Depending on the manufacturer, some instruments can store instantaneous or continuous measurements to internal or external memory in a format compatible with a hand-held display, personal digital assistant (PDA), or laptop computer.

Advances in technology and design are expanding the sensor³ capabilities of multiparameter instruments and are improving instrument utility. The configuration and sensors that are available for multiparameter instruments can vary considerably among manufacturers. The procedures required for the maintenance, calibration, and use of these instruments also can change over time as a result of the technological changes being implemented; such information generally is available from the manufacturer, either online or as a manual or other document. **Users must stay current as to how their instrument operates and is maintained.**

- ► Sensors for the determination of water temperature, specific electrical conductance (SC), pH, dissolved-oxygen concentration (DO)⁴, and turbidity commonly are bundled in sondes used for USGS water-quality studies, as these measurements are routine for much USGS work.
- ► Sensors that determine oxidation-reduction potential (ORP or redox) and barometric pressure, and that calculate salinity, also are commonly included in the sonde.

³The term sensor, which is used in this report, is synonymous with the term "probe" that is common in the environmental literature. For multiparameter measurements, the sensors are bundled in a submersible sonde.

⁴DO is calculated as the percent of dissolved-oxygen concentration at saturation.

- ► For some instruments, sensors are available to measure fluorescence,⁵ water depth, and velocity. In some cases, specific-ion electrodes (for example, nitrate, ammonia, ammonium, and chloride) can be incorporated in a sonde. Use of sensors to measure cholorphyll and concentrations of specific nutrient species are becoming more common in USGS work. Some instruments include global positioning systems.
- When making field measurements in surface water, the sondes commonly are immersed in situ (directly within the water body). As an alternative to in situ deployment, a flowthough cell containing the sonde can be set up above land surface, to which sample water is pumped. The flowthrough cell commonly is used to monitor field measurements for ground-water investigations and for calibration of the sensors.

The types and number of sensors that can be bundled in a given sonde depend on the instrument model and manufacturer. When selecting a sensor, consult the manufacturer's recommendations and specifications for the instrument, taking into consideration the environmental conditions to be encountered, the data-quality objectives of the study, and the specific benefit of a particular sensor technology that might be applicable to the anticipated field conditions. The manufacturer is the most knowledgeable source of information for a given instrument. Consult the manufacturer's maintenance instructions for each instrument model before using the instrument.

Table 6.8–2 lists the equipment specifications and calibration solutions required when determining field-measurement values using a multiparameter instrument. The ancillary supplies needed for measuring field properties using multiparameter instruments (table 6.8–3) are the same or similar to those required for the calibration and maintenance of single-parameter instruments, and are discussed in greater detail in the individual field-measurement sections (NFM 6.1 through 6.7) of Chapter 6.

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⁵Fluorescence sensors indicate different algal pigment concentrations; see NFM 7.4 for additional information.

Table 6.8–2. Specifications and calibration solutions for multiparameter instruments

[\pm , plus or minus; -, minus; +, plus; °C, degrees Celsius; mV, millivolt; >, greater than; SC, specific electrical conductance; μ S/cm, microsiemens per centimeter at 25°C; DO, dissolved oxygen; mg/L, milligrams per liter; ORP, oxidation-reduction (redox) potential; NIST, National Institute of Standards and Technology; L, liter; \le , less than or equal to; μ m, micrometer; mL, milliliter; MSDS, Material Safety Data Sheet; SDVB, styrene-divinylbenzene beads; TDS, total dissolved solids; NFM, *National Field Manual for the Collection of Water-Quality Data*; USGS, U.S. Geological Survey.]

Item ¹	Description ²
Instrument (sensor) specifications:	Visual display - digital readout.
pH and millivolt	pH sensor - range of at least 2 to 12, preferably 0 to 14, pH units. Accuracy, ±0.2 pH units. Millivolt readout - accuracy, ±1.0 mV.
Temperature	Temperature sensor - thermistor range, at least -5 to +45°C. Accuracy, ±0.2°C.
SC	SC sensor - temperature compensating. Accuracy, the greater of 0.5±0.5 percent of reading or ±2 μS/cm.
DO	 DO polarographic sensor (amperometric method) - range from 0.05 to 20 mg/L. Accuracy, the greater of ±2 percent of reading or ±0.2 mg/L. DO optical sensor (luminescent-sensor method) - range from 0.05 to 20 mg/L. Accuracy, the greater of ±1 percent of reading or ±0.1 mg/L.
Turbidity	Turbidity sensor ³ - range and accuracy depend on the instrument type, manufacturer, and field conditions (see NFM 6.7). Choice of instrument will depend on application. Most multiparameter-instrument turbidity sensors use a monochrome light source with a spectral output typically near infrared (780 to 900 nanometers), usually a light-emitting diode. Note: Instrument should include a calibration cup specifically designed by the manufacturer, if available.
ORP ³	ORP sensors - accuracy, ±20 mV. For guidance on Eh measurements using the platinum electrode, refer to NFM 6, section 6.5 and the manufacturer's instructions.
Air pressure	Select instruments that incorporate an altimeter/barometer (measures to the nearest 1 millimeter).
Other sensors ³	Check the text for this section and the manufacturer's instructions for the availability of other sensors.

Table 6.8–2. Specifications and calibration solutions for multiparameter instruments — *continued*

ltem ¹	Description ²
Sensor-calibration	(Keep the respective MSDS guidance on hand in the laboratory and
solutions:	in the field. Dispose of hazardous waste according to regulations,
	using a licensed disposal company.)
pH buffers	Standard buffers are pH 4, 7, and 10. Temperature-correction chart(s)
	supplied by the buffer manufacturer or distributor are required.
SC standards	Use the SC standard(s) recommended by the manufacturer for
	calibration. NOTE: The manufacturer might require a proprietary
	calibration solution. For field verification of the calibration, select
	additional standard(s) that bracket the expected or known sample
	SC. Do not dilute a concentrated standard to prepare a standard of
	lower conductivity.
DO standard	Zero DO calibration solution. Dissolve 1 gram of sodium sulfite and
	a few crystals of cobalt chloride ⁴ in 1 liter of deionized water
	(prepared during the week of use). Cobalt chloride is toxic; check
OPP + 1 1	the MSDS for safe handling. ZoBell's solution ⁵
ORP standard	
	- This solution contains cyanide and may be harmful if absorbed through skin, inhaled, or swallowed. Check the MSDS for safe
	handling.
	- Use a dedicated hazardous waste disposal container for ZoBell's
	solution. Do not pour ZoBell's solution down the sink drain or
	onto the ground. Do not mix with acids or combustible
	materials.
Turbidity	Turbidity standard solutions with various ranges are available
standard	commercially. Most sensor manufacturers recommend either
	formazin-based or SDVB-polymer standards for calibrating their
	turbidity sensors. Do not use gels or solids for calibrating
	instruments (see sections 6.8.2 and NFM 6.7).
	 Turbidity-free water (deionized water filtered through a ≤0.2-µm membrane filter).
	- Formazin stock suspension can be obtained commercially or
	prepared in-house from hydrazine sulfate and
	hexamethylenetetramine (safety precautions for handling these
	chemicals are described in NFM 6.7, section 6.7.2)

¹Modify this list to meet the specific needs of the field effort and the specific requirements for the multiparameter instrument to be used.

²The accuracy specification provided in this table has been generalized, based on a survey of three or more manufacturers with instruments in common use among USGS field studies. Consult the manufacturer's operators' manual for the level of accuracy for a specific instrument.

³The turbidity sensor commonly is required or recommended for use (section 6.7). ORP sensors are less commonly used for USGS studies; see the description in section 6.5. Follow the manufacturer's guidance for use of the salinity or TDS option, and for other ion-selective sensors (for example, for nitrogen species and chlorophyll).

⁴Prepare fresh zero DO solution for each use. CAUTION: Use of cobalt chloride is recommended in Standard Methods (American Public Health Association, 2005); however, this is a toxic substance that must be handled with care and disposed of in accordance with prevailing regulations. If possible, prepare a zero-DO solution without using cobalt chloride.

⁵Alternatives to Zobell's are being investigated (January 2008).

EQUIPMENT TRANSPORT 6.8.1.A

Transport the multiparameter instrument in a case that is designed to protect this equipment.

- ► To avoid damaging the sensitive and expensive fieldmeasurement sensors, keep either the sensor guard or transportation/calibration cup installed. Some manufacturers specify adding a small amount of water to the transportation/calibration cup for transport between field sites; follow the manufacturer's recommendations.
- ▶ When packing the instrument for transport, use a case provided by the manufacturer; alternatively, obtain a suitable case, such as a PelicanTM case, Otter[®] box⁶, or a tool box, and modify it as needed.
 - Cases must be padded to absorb shock, using material that does not absorb water.
 - Pelican and Otter boxes are airtight; the case needs to be vented if using sensors that have a flexible or semipermeable membrane.
 - A white or light-colored case should be used to help deflect solar heating of the sonde.

INSTRUMENT MAINTENANCE 6.8.1.B AND STORAGE

Each instrument requires its own (dedicated) log book that accompanies the instrument, in which permanent records of instrument calibrations, bench checks, sensor replacements, general maintenance, and repairs are logged. The following recommendations pertain to maintenance of the multiparameter instrument that is deployed over discrete or short (attended) time intervals. For maintenance of instruments intended for long-term or unattended instrument deployment, refer to Wagner and others (2006) and the instructions provided by the manufacturer.

⁶Examples of transport cases can be found at www.otterbox.com or www.pelican.com (accessed 5/22/2007).

▶ Sensor and sonde care and maintenance:

- Rinse the sensors immediately after each use with deionized water (DIW).
- If the multiparameter instrument (handheld display and sensors-containing sonde) is particularly dirty or will be stored for longer than one day, clean it with a mild, nonphosphate detergent solution using a small, nonabrasive brush or cotton swab or cloth, followed by a thorough water rinse.
- Avoid using organic solvents or other corrosive solutions to clean the sensors.
- O-rings used for some types of dissolved-oxygen sensors are not very robust; inspect such O-rings before each DO measurement and replace if damaged.
- Do not coat the sonde or sensors with protective or anti-fouling paint, except as specifically instructed by the manufacturer.
- Manufacturers may have instructions specific to their sensors—check the manufacturer's operating manual for each instrument that will be in use.

Wiper and wiper-brush maintenance:

- Inspect the wiper pad and (or) wiper brush for dirt, deterioration, and damage after each use of the sonde. (Not all instruments have a wiper or wiper-brush mechanism.)
- Check wiper pads for wear, excessive discoloration, and particle accumulation, and change the pads as needed.
 Check that the wiper arm is parking properly. Follow the manufacturer's guidance for conditions requiring changing the pads and for wiper maintenance.
- A soft toothbrush can be used to clean wiper-brush bristles. Rinse with fresh tap water or DIW.
- Wiper-brush bristles should be kept moist at the start of the operation to prevent them from drying. If the bristles have dried, soak them in DIW and manually loosen them before deploying the sonde.

▶ General care of multiparameter instruments:

- Do not leave instruments in vehicles for long periods of time during extremes in temperature.
- At least once a year inspect cables for damage, and electronic connectors and sensor ports for corrosion.
- Inspect and clean the bulkhead O-rings and grease them with silicone lubricant annually, at a minimum. Replace any damaged O-rings.
- Store cables in a plastic container only after they are clean, dry, and neatly coiled (no tighter than 6-inchdiameter coils). Use protective plugs when cable connectors are not in use. When in use, protect cables from abrasion or unnecessary tension.
- Make sure that the instrument is running on software and firmware that is up-to-date. Check for updates from the manufacturer every 6 months or more frequently and follow the download or other installation instructions.

► General storage recommendations for multiparameter instruments and instrument cases:

- For short-term storage, some sensors need a small amount of the storage solution added to the protective (transport) cap or calibration cup; check the manufacturer's instructions.
- For long-term storage (longer than several weeks), remove the internal batteries; however, be sure to check the instrument manual for guidance before removing all of the batteries.
- Store multiparameter instruments in a carrying case or plastic container with foam cushioning (for shock protection). Keep the instrument and case out of direct sunlight and protected against extremely hot or cold temperatures.
- Insert a sensor-port plug into any vacant sensor port to prevent damage to the vacant port during maintenance, operation, or storage.

Table 6.8–3. General supplies related to field-measurement activities

[DO, dissolved oxygen; mL, milliliter; L, liter; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; ASTM, ASTM International Company; NFM, National Field Manual for the Collection of Water-Quality Data; USGS, U.S. Geological Survey]

ltem ¹	Information
Flowthrough cell	Standard flowthrough cell, obtained from the manufacturer of the instrument. (Commonly used for ground water or other water pumped from the water source to the airtight cell for measurement of field properties.)
Extra sensors and meters	Single-parameter meters and sensors or a multiparameter sonde (as a field backup). Refer to equipment lists and descriptions and instructions provided in NFM 6, sections 6.1 through 6.7.
Membrane- replacement kit for amperometric DO	Membrane-replacement kit (includes membranes or screw-on membrane caps, O-rings, filling solution).
Calibration (laboratory) thermometer	Liquid-in-glass or electronic-thermistor thermometer, either NIST-certified or manufacturer-certified as NIST-traceable. (See NFM 6, section 6.1 for USGS standard specifications.)
Field thermometer	Non-mercury liquid-in-glass or thermistor thermometer that has been office-laboratory certified against a properly certified calibration thermometer. (See NFM 6, section 6.1 for USGS standard specifications.)
Turbidity container and flasks	Bottle for turbidity-free water, cleaned and rinsed three times with filtered water before starting each field trip. Volumetric flask, Class A, 100 mL or 500 mL, if dilution of stock solutions is necessary (see section 6.8.2).
Carrying case	Protective case, vented, white or other reflective color, to hold the multiparameter instrument during transport and storage.
Holding stand ²	A stand to support the multiparameter sonde during calibration.
Log book(s) ³	One log book per instrument (multiparameter and single- parameter), for recording instrument calibrations, maintenance, and repairs. Log book travels with the instrument.
Flasks, beakers, and other measurement vessels	Insulated flask or beaker and additional polyethylene or Teflon® preferable beakers for temperature check or other field needs. Assorted sizes, 50 to 150 mL. Beakers must be clean but not acid rinsed.
Deionized water (DIW)	1 L of DIW with a maximum conductivity of 1 μS/cm (ASTM Type 1) for rinsing sensors.
Paper tissues	Laboratory grades (for example, lint free and (for turbidity) extra lint free Kimwipes [®]), soft, disposable.

Table 6.8–3. General supplies related to field-measurement activities — *continued*

Item ¹	Information
Dispenser (squeeze) bottles	Polyethylene to contain DIW; for rinsing instruments and instrument sensors.
Disposable gloves	Laboratory gloves, disposable, non-powdered and of a material suitable to contact anticipated chemical solutions and environmental waters or wastewater. Keep a supply on hand in the field vehicle.
Brushes for equipment cleaning	Brushes of various sizes, but generally small and soft to prevent scratching the sensor(s) or other surfaces.
Minnow bucket with tether, mesh bag, or equivalent	Used to contain fresh sample water into which tightly capped calibration solutions are immersed for thermal equilibration with the temperature of the sample water before being used for sensor calibration.
Antistatic spray or polish	Used on the digital display screen of a multiparameter instrument.
Cleaning solution	1 L of nonphosphate laboratory detergent (see NFM 3 for solution-concentration guidelines).
Batteries and/or battery pack(s)	Check that batteries are fully charged; bring spares.
Safety equipment	Select safety equipment appropriate for the field effort conditions, such as gloves, eye protection, face mask, apron, chemical spill kit, first-aid kit.
Waste-disposal containers	Appropriate for safe containment of regulated (hazardous or toxic) substances and dedicated to use for the respective waste material (examples: ZoBell's solution, methanol, and acid and turbidity calibration solutions).

 $^{^{1}\}mathrm{Modify}$ this list to meet the specific needs of the field effort.

²USGS personnel may check for the availability of instrument stands (HIF # 6103032 or #6103035) at the USGS Hydrologic Instrumentation Facility.

³Bound log books with water-resistant pages are available to USGS personnel through the USGS One Stop Shopping store.

6.8.2 CALIBRATION

Multiparameter instruments must be tested and the sensors calibrated before each field use. With some exceptions (for example, turbidity calibration), calibrations are performed in the field in preparation for making measurements.

When visiting more than one site for field measurements, the sensors and sonde housing must be cleaned and then the sensor calibration verified for each site. Field calibration should be completed in an area sheltered from wind, dust, and temperature fluctuations. Consult the manufacturer's guidelines before beginning the calibration process and contact the manufacturer's technical support if problems or questions arise.

Ensure that the sensors are properly installed in the sonde. Before beginning the calibration process, check the power source; only use batteries that indicate a full charge.

- ▶ Most multiparameter instruments perform best if allowed to warm up for at least 10 minutes after being turned on, or according to the manufacturer's recommendation.
- ► The following order is recommended for performing calibration or accuracy checks in the field:
 - 1. **Temperature** (using a thermometer that has been calibrated and office-certified, as described in NFM 6.1)
 - 2. **Specific electrical conductance (SC)** (note that the value of the SC standard solution changes by more than 3 percent when the temperature is less than (<) 6°C or greater than (>) 40°C; do not calibrate with standards <6°C or >40°C.
 - 3. **Dissolved oxygen (DO)** (amperometric or luminescent-sensor methods using polarographic or optical sensors, respectively)
 - 4. **pH** (be sure to check and adjust for the buffer pH value at the buffer temperature)
 - 5. Oxidation-reduction potential (ORP)
 - 6. **Turbidity** (most manufacturers recommend that the turbidity calibration be performed in a laboratory or other stable environment)
 - 7. Ion-selective electrodes, followed by chlorophyll-fluorescence and other sensors.

- ► Complete the calibration field form during calibration (Appendix 6.8–A). Accurate calibration records must be maintained and entered into the appropriate instrument log book at the time of calibration.⁷
 - Keep a hard copy of the field form in the field or site folder. These records contain vital information that can be referenced if technical or legal questions arise. Interpretation of data analyses or data quality may depend on the documentation regarding instrument performance and the calibration solutions and the methods used, in addition to the results recorded. This record should be checked and verified by a second or third party.
 - The field form documents that a sensor has met the dataquality objectives of the study and that the calibration was performed according to the required standard operating procedures. Lot numbers and expiration dates of calibration solutions are recorded on the electronic or paper field form (Appendix 6.8–A).
 - The instrument log book is the archival document for recording details chronologically, including calibrations, maintenance specific to the sensors, and general repairs. Log book entries should be recorded using black or blue ballpoint ink, preferably on water-resistant paper with the pages consecutively numbered and bound to deter page removal. To ensure the legal viability of the log-book record, a page never should be removed and a single line should be drawn through any erroneous information or data and initialed. (USGS personnel can obtain log books through One Stop Shopping).
- ► Clean the instrument onsite after each use to reduce the potential for site and sample cross contamination and loss of calibration.

Reagents used for calibration may be hazardous to health and require special handling. Review the MSDS for the reagent of concern. Keep the safety sheets handy.

⁷For USGS studies, the worksheet is included in the electronic (PCFF) and paper national surface-water and ground-water water-quality field-notes forms. Meter-calibration log books are available to USGS personnel through One Stop Shopping.

6.8.2.A STANDARD USGS CALIBRATION PROCEDURES FOR MULTIPARAMETER INSTRUMENTS

The results of sensor calibrations are recorded on a field form at the time of calibration (Appendix 6.8–A provides an example of a field form for recording calibrations and field measurements). In addition, a historical record of calibrations for each sensor used in a given multiparameter instrument must be kept in an instrument log book that accompanies the instrument to the field. This log book also is used to document maintenance, repairs, and sensor replacements for the instrument

When calibrating multiparameter-instrument sensors:

- 1. **Follow the manufacturer's instructions** for the instrument model and sensors being used.
 - Become familiar with the operation and setup of the handheld or other display hardware and software. Make sure that the batteries are fully charged, or install fresh batteries.
 - Ensure that the instrument has been set for the appropriate measurement unit, if this option is available.
 - Ensure that the instrument has been warmed up for the amount of time recommended by the manufacturer.
- 2. Bring calibration solutions (calibrants) to the temperature of the sample source, to the degree possible. Note there are exceptions to this protocol for SC and turbidity, as described below. To allow equilibration of the calibration solutions with ambient sample-water temperature, calibrant containers can be partially immersed in the stream being sampled, or in a bucket to which the ground water being sampled is pumped. Great care must be taken to prevent water from getting close to the top of the calibrant container and contaminating the calibrant.

Note 3/8/2012: Calibration requirements for field sensors are under review.

⁸For calibration of sensors for turbidity and specific electrical conductance, check with the manufacturer for guidance.

- Calibrate the instrument in a temperature-stable environment, out of the wind and direct sunlight.
- Use the calibration cup that comes with the instrument for calibration, unless otherwise instructed by the manufacturer. If a calibration cup is not available, follow the manufacturer's alternative recommendations.
- Use the recommended volume of calibrant when filling the calibration cup. The calibrant must cover the temperature sensor, as most sensors require temperature compensation.
- Be careful not to overtighten the calibration cup. This is especially important for DO calibration. Many calibration cups have vents that allow their equilibration with ambient pressure.
- For SC, do not equilibrate the temperature of the standards to that of the sample source if source temperature is less than 6°C or greater than 40°C, because the value of the SC calibration standard changes significantly (by more than 3 percent) as a function of temperature at these temperature extremes. In such situations, perform the SC calibration inside a room or vehicle in which the ambient temperature of the standards is maintained at a temperature >6°C and < 40°C.
- For turbidity, calibrations should be performed in an environment that is protected from wind and thermal fluctuations.
- 3. Rinse sensors thoroughly three times with deionized water after use of each calibrant, followed by three rinses with the next calibrant to be used.
 - To avoid dilution of calibration solutions, gently shake excess rinse water from sensors.
 - Use a lint-free laboratory tissue (for example, Kimwipes[®]) to absorb water droplets without touching or wiping the sensor surface; never touch or wipe the transparent surfaces associated with luminescent DO, pH, and turbidity sensors.
- 4. Calibrate the SC and DO sensors before calibrating the pH sensor. This helps prevent contamination of the SC sensor from pH buffer solutions (pH buffers have much higher conductivities than most environmental waters).
- 5. **Periodic removal and cleaning of sensors** may be needed for any multiparameter sonde that is deployed for long-term monitoring. The time interval between cleanings will depend on site conditions and study requirements.

Bring calibration solutions (standards and buffers) to the ambient temperature of the environmental sample to the degree possible.

6.8.2.B SENSOR-SPECIFIC CALIBRATION TIPS

The following guidelines comprise standard USGS procedures.

- ► Check sensor ports to be sure that either the ports have a properly installed sensor or that the empty ports are sealed. Sensors from which data are not being collected routinely can be removed from the sonde for safe storage, provided that the sensor is not necessary for the measurements of interest and provided that the empty port is sealed according to the manufacturer's instructions. The temperature sensor should not be removed. All electrical connections must be clean, dry, waterproof, and protected from dust.
- ► Clean sensors after each use and keep them maintained and stored according to the manufacturer's instructions.
 - Before calibrating and using an instrument in the field, inspect the sensors to be sure that they are clean and are not damaged.
 - Periodic cleaning may be needed for any instrument that is deployed for continuous monitoring (see Wagner and others, 2006).

Temperature (revised, 3/8/2012)

Check to ensure the accuracy of the temperature sensor at least every 3 months if the multiparameter instrument is in frequent use. The accuracy of pH and other field measurements depends on the accuracy of the temperature measurement.

- Verify the accuracy of the temperature sensor against a certified NIST-traceable digital or liquid-in-glass thermometer following the guidelines provided in NFM 6.1 (annual laboratory verification and biannual field checks are mandatory for USGS studies).
 *Note, 3/8/2012: NFM 6.1 calibrations guidelines are under review. For the calibration check, the NIST thermometer and sonde thermistor should be as close together as possible without touching. For field verification, use a non-mercury thermometer that has been certified as accurate within the past 6 months and is tagged as such by the verifier. When making the field check, record the temperature readings of both the multiparameter instrument and the NIST-traceable thermometer in the instrument log book.
 - If the difference between the readings does not fall within the manufacturer-specified accuracy, return the instrument to the manufacturer for repair or replacement.
 - See NFM 6.1 for a description of the annual and biannual calibration protocol for liquid-in-glass and digital thermometers, which also require calibration checks. *See Note above.
- 2. Make sure that the temperature sensor is completely submerged.
- 3. Allow at least 1 minute for temperature equilibration and stabilization before recording the temperature value and proceeding with the other measurements.

Specific Electrical Conductance (SC) (see NFM 6.3, section 6.3.2)

- 1. Most multiparameter instruments use a one-point calibration to calibrate the SC sensor. Use a standard having the conductivity recommended by the instrument manufacturer; otherwise, select a standard that is close in conductivity to that of the environmental water.
 - Rinse the calibration cup and sonde using a small amount of standard. **Repeat this two more times** and then fill the cup with the recommended volume of standard.
 - The sensor should be completely submerged in the standard (if a hole exists in the side of the sensor, it must be covered by the standard). Low fluid level can cause an erroneous calibration or may result in an error message on the instrument display.

- The presence of air bubbles in SC electrodes will cause erroneous readings and incorrect calibration.
- Although most SC sensors are shielded from effects caused by proximity to transmission lines and to alternating-current (AC) electrical outlets and radio-frequency noise sources, be aware of the possibility of this interference and check with the instrument manufacturer.
- 2. Wait for readings to stabilize (approximately 30 seconds under normal conditions) before adjusting and saving the calibration point.
 - The USGS reports SC in units of microsiemens per centimeter (μS/cm). The default SC setting on many multiparameter instruments often is in units of millisiemens per centimeter (mS/cm). Either change the setting to μS/cm (if this option is available) or measure in mS/cm and then convert to μS/cm (multiply mS/cm by 1,000). To fulfill USGS data protocols, record the SC value in μS/cm on paper or electronic (PCFF) field forms.
 - Do not override a calibration error message without troubleshooting and correcting the cause of the error. For example, check the fluid level and check for air bubbles in the sensor.
- 3. To verify that the accuracy of the SC sensor is within the range of the conductivities to be measured:
 - Ensure the linearity of response of the SC sensor at low-conductivity values and check the zero response of the dry sensor in air (Wagner and others, 2006).
 - Select two standards ("check standards") that bracket the expected SC range of your water as closely as possible; a third standard that is at or close to the actual ambient conductivity helps to pinpoint the accuracy of the sensor. Equilibrate the temperature of the standard to that of the water body, unless the water temperature is < 6°C or > 40°C (use of this protocol can depend also on instrument software consult the manufacturer's guidance). Follow the same procedure as for an actual calibration, but do not lock in or adjust these readings—this is an accuracy check, not a calibration point.

Handle conductivity standards in a manner so as to prevent their dilution or contamination.

- Do not use expired standards.
- Do not reuse standard or pour used standard back into the bottle.

Dissolved Oxygen (DO) (see also NFM 6.2, section 6.2.1.B)

Two sensor options are available for the DO measurement when using multiparameter instruments: the polarographic (or Clark cell) sensor or the luminescent (optical) sensor. Referring to NFM 6.2 on DO measurement methods, the polarographic-sensor option corresponds to the amperometric method, and the optical-sensor option corresponds to the luminescent-sensor method.

General comments:

- Follow the manufacturer's guidelines for care, proper setup, and calibration of the DO sensor for the instrument in use. For either sensor type, most manufacturers recommend that the sensor be allowed to equilibrate to the temperature of the air-saturated water or water-vapor-saturated air for at least 15 minutes before calibration.
- Before calibrating for 100-percent saturation of DO, loosen the calibration cup. (It should contain less than 1/8 in. (~0.32 cm) of water, or as recommended by the manufacturer.)
- Remove any water droplets from the thermistor or the DO membrane without wiping the membrane. Water droplets on these surfaces can cause a temperature compensation error in the DO calibration.
- Store and transport the sonde in a padded, vented, white (or light-colored) case to make DO calibration checks quicker and reduce
 the chance of DO sensor drift (since the instrument is in a more
 temperature-stable environment and can be calibrated within the
 cooler).
- Calibrate the DO sensor on the morning of the field day and check the calibration at each measurement station. Enter the barometric pressure (see NFM 6.2 for an explanation of corrected and uncorrected values).

TECHNICAL NOTE: Check the manufacturer's instructions regarding the need to recalibrate amperometric-instrument sensors with changes in altitude. For some instruments, the DO sensor should be recalibrated at each site at which there is a change of approximately 900 ft (~ 300 m) in altitude. Luminescent sensors tend to keep calibration over extended time periods; however, verification of sensor performance with appreciable altitude change is recommended to quality assure and document sensor performance. To convert inches (in.) of mercury (Hg) to millimeters (mm), multiply inches by 25.4.

- The calibration procedure depends on the type of DO sensor being used. Note the type of sensor being used—amperometric or optical (luminescent)—and follow the appropriate instructions provided by the manufacturer and as described below. Allow the sensor to equilibrate to the temperature of the solution for at least 15 minutes or as recommended by the manufacturer.
- Always perform a 100-percent saturation calibration before beginning the zero DO calibration.

Amperometric method for DO measurement (polarographic or Clark-cell sensor):

Instrument makes and models can vary considerably; always refer to the manufacturer's instructions for the instrument that is in use. To prevent water damage to the sonde's internal parts, maintain the O-rings and sealing surfaces on the sonde as directed by the manufacturer. Be aware that extreme temperatures and instrument vibrations may cause the DO sensor to drift out of calibration on a day when a series of measurements is made.

- 1. Inspect the DO sensor anodes and cathodes—if they are not bright and shiny, recondition them as instructed by the manufacturer.
- 2. Install a new membrane or membrane cap of the desired membrane thickness. If not using the membrane cap, the membrane should be tightly stretched, and have no bubbles, wrinkles, or tears. Replace any worn or stretched (loose) O-rings.
 - Membrane replacement should take place 24 hours before use (USGS standard procedure). Manufacturer guidance generally specifies membrane replacement at least 3 to 4 hours before use (M. Lizotte, YSI and Bruce Wilcox, Hach Environmental, written communs., May 2007).

- A tight-fitting O-ring is critical to good sensor performance.
- Run or power up the newly membraned sensor for 15 minutes.
- Do not allow electrolyte solution to wet the sensor or sonde connector or other O-ring sealed areas. Electrolyte solution is highly conductive and will short out electrical connections.
- 3. A wet towel can facilitate the water-saturated air calibration of the DO sensor as follows: wrap the sensor guard with a white towel wetted in field temperature water, forming an enclosed moist environment around the instrument sensor guard and sonde body. Allow time for the air inside the sensor guard and wet towel to become saturated with water vapor (10 to 15 minutes).
- 4. Rinse the DO sensor thoroughly, at least three times, with DIW or tap water after being calibrated in the zero-percent solution, to avoid cross contamination and faulty readings. Inadequate rinsing will cause negatively biased readings.

Luminescent-sensor method for DO measurement (optical sensor):

Great care is required when calibrating optical DO sensors in the field. Optical DO sensors (like polarographic sensors) can be calibrated in either water vapor-saturated air or in air-saturated water (see NFM 6.2). The air-saturated water method is recommended for calibrating optical sensors. Temperature equilibration of the sensor with the calibration solution must be achieved before proceeding with the calibration; follow the manufacturer's instructions.

- 1. To create an air-saturated water bath, one method is to fill a 5-gallon pail with tap water and aerate the water using a mid-sized aquarium air pump with air stone. Check the manufacturer's recommendations. Some manufacturers have developed their own bath aeration system to help avoid effects from variance of temperature and hydrostatic pressure on the calibration (R. Mooney, In-Situ Inc., written commun., May 2007).
 - The air-saturated water method is faster and guarantees temperature equilibration of the optical DO sensor and calibration medium.
 - If the water bath is kept air-saturated and ready to use, calibration time can be reduced, as there is no need to wait for a calibration cup or wet towel to saturate the air.

- 2. Aerate the water for at least 1 hour prior to use.
- 3. When measuring in low DO environments or after replacing a luminescent-sensor membrane, a two-point DO calibration and (or) a zero DO check is needed or required.
 - If the sensor is equipped with a wiper, remove the wiper before starting the calibration (see the warning in step 5 below).
 - Calibrate the saturated and zero DO levels following each manufacturer's specific instructions.
 - To prepare a zero DO calibration solution, dissolve 1 gram of sodium sulfite and a few crystals of cobalt chloride in 1 liter of DIW (prepare this solution during the week of use). Check the Material Safety Data Sheet (MSDS) for handling of cobalt chloride, which is a toxic substance.
- 4. Observe the readings for DO; when there is no appreciable change for approximately 30 seconds, lock in or adjust the reading.
- 5. After calibrating the sensor with the zero-percent solution, take extra care in rinsing the sensor thoroughly to remove any residue of the solution. Inadequate rinsing will cause negatively biased DO readings and can result in cross contamination, possibly causing faulty SC or pH readings. The three-time tapwater or DIW rinse recommended for the amperometric-instrument sensor may not be sufficient. One manufacturer recommends rinsing the sensor under running tap water for at least 10 minutes.

WARNING: On optical sensors equipped with wipers, remove the wiper before beginning the zero-DO calibration to prevent the wiper from soaking up sodium sulfite and thus contaminating the membrane when the wiper is activated.

pH (see also NFM 6.4, section 6.4.2)

- 1. **The pH measurement requires a two-point calibration.** Select the pH 7 buffer plus a second pH buffer (for example, pH 4 or pH 10) that brackets the expected range of sample pH.
 - Use historical pH data for the sampling site, if available, to select the correct buffers.

- After performing the calibration, a calibration check with a third buffer can be useful if the pH range is unknown or if sites with differing range in pH value will be measured.
- Do not use expired buffers. Discard decanted buffer after one use—do not reuse buffers or pour decanted buffer back into the original container.
- 2. Bring the buffers as close as possible to the ambient temperature of the water being sampled.
- 3. Normally the sensor is calibrated first against the pH 7 buffer; however, this may differ among manufacturers.
- 4. Rinse the sensors and calibration cup, first with DIW and then with the buffer.
 - a. Before using the first buffer, rinse the pH and temperature sensors and the calibration cup three times with the first buffer.
 - b. Fill the calibration cup with enough buffer to completely cover the temperature and pH sensors.
- 5. Allow time for the pH and temperature sensors to equilibrate to the temperature of the buffer.
- 6. Record the temperature reading after it has stabilized. The pH value is temperature dependent. Use the chart provided by the buffer manufacturer to determine the true pH value for the buffer at that temperature. You will need to adjust the calibration reading to that value. NOTE: Buffers from different manufacturers can yield somewhat different pH values for a given temperature.
- 7. Follow the manufacturer's instructions for calibration with the first buffer.
 - a. Record the temperature, pH, and millivolt (if available) readings before and after calibration with the first buffer.
 - b. If your instrument does not display the percent slope, then calculate and record the slope of the pH sensor.

EXAMPLE: The acceptable tolerance for the pH 4 buffer is 180±50 mV; for the pH 7 buffer, 0±50 mV; and for the pH 10 buffer, -180±50 mV. If a value of +3 mV were recorded for the pH 7 buffer and -177 mV were recorded for the pH 10 buffer, the slope would be 180 mV. The acceptable range for the slope is from 165 to 180 mV.

- 8. Repeat steps 4, 5, 6, and 7 using the second buffer.
- 9. If a third buffer will be used to check the calibration range of the sensor, follow the same general procedures described above for the first and second buffers, but do not lock in a calibration. The instrument reading should be within ±0.2 pH units of the theoretical pH value at the buffer temperature.

Oxidation-Reduction Potential (ORP or Eh) (see also NFM 6.5, section 6.5.2)

- 1. The pH sensor must be calibrated and working properly before calibrating the ORP sensor, if the instrument uses a combination pH-ORP electrode.
 - For most multiparameter instruments, the ORP electrode usually is combined with pH electrodes in one sensor body in order to utilize a common reference electrode (usually the silver/silver-chloride electrode).
 - Recommended calibration procedures differ among instrument manufacturers. Follow the manufacturer's recommendations for calibration of the specific instrument and electrodes being used.
- 2. A one-point calibration at a known temperature generally is used to calibrate the ORP sensor. The ORP measurement should stabilize within 1 to 3 minutes.
 - Table 6.8–4 shows the true readings in millivolts for ZoBell's solution as a function of temperature for the platinum/silver-silver chloride paired electrodes. These values must be converted to a standard hydrogen reference electrode when the field measurements are reported in the USGS National Water Information System (NWIS) QWDATA database. See NFM 6.5 for more detailed information about ORP sensors, data conversion to the standard hydrogen reference electrode, and use of ZoBell's solution.
 - The calibration values should be within a tolerance of ±5 millivolts of the values listed in table 6.8–4.
 - ZoBell's solution is toxic; handle with care. 9
- 3. Calibration can be affected by static electricity. Avoid touching the sensors during calibration and measurement.

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⁹Alternatives to ZoBell's solution are being investigated (January 2008).

- 4. The ORP sensors of some manufacturers must be oriented near the vertical ±45 degrees for proper operation. Be thoroughly familiar with the manufacturer's instructions before using the instrument.
- 5. Follow proper procedures for handling and disposal of ZoBell's solution and keep an MSDS for ZoBell's solution with the ORP equipment. Minimize the volume of ZoBell's solution being used and store the spent solution in a separate, dedicated container.

Table 6.8–4. Voltage of ZoBell's solution as a function of temperature for the platinum/silver-silver chloride paired electrodes

[°C, degrees Celsius; mV, millivolts]

Temperature, in °C	ZoBell's solution, ¹ in mV
-5	270.0
0	263.5
5	257.0
10	250.5
15	244.0
20	237.5
25	231.0
30	224.5
35	218.0
40	211.5
45	205.0
50	198.5

¹This table is provided as a courtesy by YSI (M. Lizotte, written commun., February 2006). See table 6.5–3 in NFM 6.5 for a chart showing the Eh of ZoBell's solution as a function of temperature.

ZoBell's solution is a toxic solution and considered a hazardous waste. Check with a chemical-substances safety officer and the MSDS for safe handling information and proper and legal disposal of spent ZoBell's solution.

Turbidity (see also NFM 6.7, section 6.7.2)

The methods and standards used for turbidity sensor calibration should be those that are recommended by the instrument manufacturer for the specific instrument type and model, using NFM 6.7 as a guide for USGS work.

Calibration of the turbidity sensor is highly sensitive to environmental fluctuations and should be performed away from wind, sunlight, and temperature fluctuations. (Most manufacturers recommend that the turbidity calibration be performed in a laboratory or other stable environment before departing for the field site. To some extent this is dependent upon the calibrant being used; for example, formazin use is confined to a laboratory environment. USGS protocol stipulates that calibration of the turbidity sensor be verified at each field site. Refer to NFM 6.7 for a detailed explanation.)

- ▶ Calibrants are not necessarily interchangeable. Serious calibration errors can result from using the wrong standards. Three types, or levels, of standard turbidity solutions (calibrants) are used to calibrate and (or) verify the accuracy of turbidity sensors (section 6.7.2). Use only those calibrants that are prescribed for the sensor by the instrument manufacturer. Refer to NFM 6.7 for detailed information on turbidity calibrants and for turbidity units of measurement as operationally assigned according to instrument type by the USGS. ¹⁰ The following terminology, taken from ASTM Method D6855, is used by the USGS to distinguish among classes of turbidity standards (C.W. Anderson, U.S. Geological Survey, written commun., December 2006; ASTM International, 2003):
 - Reference standard: 4000 NTU formazin solution, obtained commercially or prepared in-house ("from scratch").
 - Calibration standard: Diluted scratch formazin, StablCal[®] or styrene-divinylbenzene (SDVB) polymer.
 - Verification standard: Gels, solids, or diluted SDVB or StablCal.

¹⁰The guidelines for reporting turbidity units described in NFM 6.7 were developed jointly by the USGS, ASTM International, and participating instrument manufacturers.

- ▶ Diluting a reference standard for turbidity calibration can result in erroneous data and, in general, is not recommended.
 - Precise laboratory technique is essential for dilutions and should be performed only by experienced personnel. If not handled carefully, the dilutions can become unstable and particle suspension may be lost.
 - Discard a diluted scratch formazin calibration standard within 24 hours of preparation.
- ► The quality of the turbidity measurement is dependent on the type of standard (that is, on the particulate matter contained in the suspension) that is used to prepare instrument calibration curves.
 - Turbidity-free water, used as a zero-turbidity standard and for the preparation of standard solutions, dilutions, and equipment rinsing, is prepared as described in NFM 6.7.
 - Formazin-based calibration standards are freshly prepared by diluting a 4,000 NTU reference standard, using the dilution formula provided in NFM 6.7. Because the dilution process is subject to preparation errors, document that a calibration standard was used and report it as "calibration standard, prepared by dilution of a 4,000 NTU standard." A calibration standard must be prepared on the day of use and be discarded on the same day.
 - Record the source of the 4,000 NTU reference standard.
 The 4,000 NTU standard has a shelf life not to exceed 1 year.
 - o The diluted scratch formazin (calibration standard) has a shelf life of less than 24 hours.
 - o Do not use expired standards (American Public Health Association, 2005, Method 2130B, p. 2–9 to 2–11).
 - Do not dilute SDVB polymer or StablCal standard for use as a calibration standard. Although a diluted polymersuspension (less than 10:1) sometimes is used as a verification or calibration check (verification standard), this is not recommended by the USGS and should not be used for USGS studies.
 - Store the verification standards out of sunlight and in PVC bottles.
 - Handle verification standards carefully to maintain the stability of the suspension.

► Check the turbidity standards for expiration before performing a dilution, calibration, or calibration verification. Note that higher range formazin standards tend to settle and thus are less stable than lower range formazin standards.

The following summary of turbidity sensor calibration does not replace the more detailed information to be found throughout NFM 6.7, and specifically in section 6.7.2.

- 1. If the sonde includes a wiper brush and (or) pad for cleaning the DO, pH, and SC sensors, this brush must be removed before calibrating the turbidity sensor. If the wiper occupies a sensor port, be sure to plug the open port before starting the calibration.
- Perform the turbidity-sensor calibration in a protected environment, away from wind and thermal fluctuations.
 Standard USGS procedure is to calibrate sensors onsite, but in a location in which stable environmental conditions can be maintained.
 - Prevent disturbance to the standard solutions that might result in forming bubbles, and prevent exposure of these standards to direct sunlight.
 - Verify calibration of the turbidity sensor in an environment in which stable readings can be obtained.
 - If the calibration is performed in a laboratory just before departing for the field site, use a verification standard onsite to check the sensor calibration.
- 3. Use only the recommended calibration standards for actual calibration of the sensors. A verification standard may be used to check the calibration in the field.
- 4. Use the manufacturer-supplied calibration (or storage) cup with a non-reflective endcap.
 - Do not use plastic beakers or containers when working with sensors that use infrared light; clear plastics can reflect the infrared light beam and cause errors.
 - Clear glassware may be used with the sensor guard installed on the sonde.
 - Do not use small-diameter or small-volume containers (for example, 35-mm film-storage containers) for this purpose.

5. Inspect the instrument carefully.

- a. Check the instrument—ensure that all submerged parts of the multiparameter instrument are clean before beginning turbidity calibration. Sediment or other particulates from the sonde, wiper, or other parts can contaminate the standard, leading to an incorrect calibration and measurement.
- b. Check the optical ports—the optical surface of the turbidity sensor must be clean and free of bubbles, fingerprints, scratches, or other interferences.
- c. Check the wiper—if your turbidity sensor has a wiper with a pad or brush, inspect the condition of the pad/brush and replace it if necessary. Check that the wiper is parking properly and is operational.
- d. If the sensor is without a mechanical wiper (for example, during discrete sampling), take extra care to maintain a clean, bubble- and solid-material-free optical face. To remove bubbles from the optical face during calibration or field measurement, agitate the sonde by moving it in a vertical or circular motion.
- 6. Check the manufacturer's instructions for the minimum distance between the sensor face and the bottom of the calibration chamber, before and during the calibration process. Take care to avoid interference from the bottom of the calibration vessel.
- 7. Note that if the sensor is equipped with a wiper (or brush), the wiper (or brush) needs to be activated immediately before the calibration data are acquired.
- 8. When verifying the turbidity-sensor calibration, a three-point check is recommended before deciding to adjust the calibration.
 - If the sensor readings exceed the established calibration criteria for project data-quality objectives (for example, the greater of ±5 percent of the measured value or 0.5 turbidity units) during the inspection process, the sensor requires calibration.
 - If instrument calibration allows only a two-step process, use two calibration standards that cover the expected turbidity range and check for linearity using a third midpoint standard. If the instrument calibration requires only turbidity-free water and one calibration standard, select a midpoint standard to check for linearity.

TECHNICAL NOTE: The range of standards recommended for verification of turbidity-sensor calibration varies, depending on the manufacturer and the linearity of the instrument being used.

- 9. Perform multipoint calibrations in the order of increasing turbidity.
 - a. First rinse the calibration cup, turbidity sensor (and sensor guard) three times, each time using a small amount of zero-turbidity solution.
 - b. Using the zero-turbidity solution, carefully fill the calibration cup along the inside surface, so as to avoid aerating the solution. Set the multiparameter instrument on top of the calibration cup (do not engage the threads). Verify that there are no air bubbles on the sensor face; then run the wiper (if present) at least once before accepting the first calibration point. Record the first calibration point. Use 2 Formazin Nephelometric Units (FNU) as the low-end calibration point.

TECHNICAL NOTE: Consult the instrument manufacturer if the accuracy and precision of measurements below 2 FNU are important for the study, as calibration procedures within the 0 to 2 FNU range can differ depending on the instrument. Some manufacturers advise that instruments can be better calibrated to 2 or to 10 FNU than to 0 FNU

- c. Before using the next standard, re-rinse the calibration cup, sensor guard (if present), and sensor three times with the zero-turbidity solution. Repeat this rinse between each new standard.
- d. To assess the actual performance of the instrument near the detection limit, periodically check using standards in the 1 to 5 turbidity-unit (low-level) range.
- e. Calibrate at the second point, again removing air bubbles and wiping the sonde or sensor at least once before accepting the value.

- f. Monitor each output carefully to ensure that turbidity readings are stable before confirming the calibration value. Report the measurements in the proper units, as specified in NFM 6.7, table 6.7–4.
- g. Never override a calibration-error message without fully troubleshooting the cause of the problem. Calibration-error messages usually indicate that a problem exists that will result in incorrect field readings.
- 10. While in the field, check instrument performance periodically using either a calibration standard (StablCal, SDVB polymer, or diluted scratch formazin) or a verification standard (gels, solids, or diluted SDVB or StablCal) and turbidity-free water.

TECHNICAL NOTE: Field experience is the best guide as to how often the turbidity sensor will benefit from recalibration. The need for recalibration depends on the condition of the optical windows, which in turn depends on the environment in which the instrument is deployed. Instruments deployed in biologically active environments, for example, require frequent cleaning and calibration checks. Periodic checks of the sensor against calibrants can be beneficial for indicating how well the sensor is holding its calibration.

WARNING: Contamination of the zero turbidity standard (from inadequately cleaned equipment) often is the cause of negative turbidity readings in clear environmental waters. Contact the instrument manufacturer for recommendations if negative turbidity readings cannot be eliminated.

6.8.3 MEASUREMENT

The field-measurement procedures implemented depend on the type of water body for which the chemical and physical properties are being determined, onsite characteristics and conditions at the time of measurement, and on the study objectives and data-quality requirements of the project. Refer to the respective sections of this chapter for detailed information regarding field measurement of temperature, specific electrical conductance, dissolved-oxygen concentration, pH, oxidation-reduction potential, and turbidity.

- ▶ Record a description of site conditions and any anomalies at the time of sampling.
- ► Allow time for the readings on the display to stabilize within the criteria shown on table 6.8–5.
- ▶ Record all required and targeted field measurements on the appropriate paper or electronic field forms, laboratory analytical request forms, project log books, chain-of-custody logs, and other documentation that might be required for the study (Appendix 6.8–A). Note on the appropriate forms any onsite conditions that could have affected the quality of the data.

Table 6.8–5. Standard criteria for stabilization of common multiparameter-instrument sensors

[\pm , plus or minus; °C, degrees Celsius; %, percent; \leq , less than or equal to; μ S/cm, microsiemens per centimeter; >, greater than; mg/L, milligrams per liter; FNU, formazin nephelometric units]

Sensor	Standard sensor stabilization criteria (Note that the actual accuracy of the sensor varies, depending on sensor model and manufacturer)
Temperature (thermistor)	± 0.2°C
Specific electrical conductance (SC)	± 5% for SC ≤100 μS/cm, or ± 3% for SC >100 μS/cm
Dissolved oxygen (polarographic or optical)	\pm 0.2 mg/L to \pm 0.3 mg/L
рН	± 0.1 to 0.2 pH unit; if drifting persists or if measuring low-conductivity waters (≤75 μS/cm), allow ± 0.3 pH units
Turbidity	± 0.5 FNU or 5% of the measured value, whichever is greater, for turbidity 100 FNU; or 10% of the measured value, for turbidity >100 FNU

SURFACE WATER 6.8.3.A

Field measurements commonly are monitored within a cross section of the surface-water body to (a) help determine how well mixed the stream is, and consequently the sampling method to be used (NFM 4.1), and (b) determine the field-property values of the water body at the selected site. In situ use of a multiparameter instrument is the most efficient means of obtaining such data.

- Many instruments include a pressure transducer that produces a value for water depth or level. For instruments without pressure transducers, the approximate depth of the sonde as it is lowered through a transect can be noted by placing incremental marks along the instrument cable or be connected to a pressure transducer. Depending on site conditions, the sonde might need to be weighted (consult the manufacturer).
- ▶ Wait a minimum of 60 seconds for the sensors to reach thermal equilibrium with the water temperature at each new location. Some instruments require a longer equilibration time; check the manufacturer's recommendations.
- At each measuring point, allow the field-measurement values on the instrument display to stabilize within an established criterion before recording final field measurements (table 6.8–5).
 - Field-measurement values generally are considered stable if the variability among three or more consecutive readings, spaced some number of minutes apart, conforms to the designated criteria. See NFM 6.0 for a discussion on sensor-stabilization criteria.
 - After making multiple measurements across a stream transect, return to the original measurement location within the transect and make a second measurement at that location, to check for measurement stability. Repeat the transect measurements if the original measurement is not replicated within the stabilization criterion shown on table 6.8–5.
 - When aggregating the data from a cross section, document the median of the cross-sectional data for each field measurement.
- ▶ Biological growth or debris in the water can foul sensors, which will adversely affect sensor readings. If field conditions and quality-assurance protocols allow, adjust the spacing of the measurement intervals along the cross section or transect in order to avoid areas that will result in having to stop and clean algae, sediment, or debris from the sensors.

6.8.3.B GROUND WATER (revised 3/8/2012)

The stability of field-measurement values is monitored toward the end of well purging to help indicate when the water being withdrawn represents fresh formation water and when sample collection for other analytes should begin (NFM 4.2). The final field measurement typically is recorded after three or more well volumes have been purged and stability criteria have been met.

If the purpose of sampling is to obtain field measurements only, these data can be obtained in situ by deploying the sensor or multiparameter sonde downhole, followed by a submersible pump to draw water upward. If water-quality samples will be collected, pumping the water from the well to and through a flowthrough cell that contains the sonde or sensors is another efficient method for collecting field-measurement data without having to remove and redeploy sampling instruments. Flowthrough cells are supplied by the manufacturers of the multiparameter instruments.

- ➤ Connect all sampling-pump discharge-tubing fittings securely so that atmospheric oxygen does not enter the flowthrough cell of the multiparameter instrument, as this can affect the accuracy and quality of the measurements.
- ▶ Shield the flowthrough cell from direct sunlight to minimize changes in the temperature of the ground-water sample as it is withdrawn; changes in temperature also can affect the accuracy of the pH, ORP, and DO measurements, with respect to their ambient ground-water values, and incident light can affect turbidity readings.
- ▶ Wait a minimum of 60 seconds for the sensors to equilibrate to ambient ground-water conditions before monitoring field-measurement values. Some instruments require a longer equilibration time; check the manufacturer's recommendations.
 - Allow the value(s) on the instrument display to stabilize before recording a final field-measurement value (table 6.8–5).

- Field-measurement values generally are considered stable if, while purging the last of three well volumes of water, the variability among three or more consecutive readings spaced at least 3 to 5 minutes apart conforms to the designated criteria. See NFM 6.0, section 6.0.1 for a discussion on sensor-stabilization criteria and problems. See NFM 4.2.3 for detailed information about well purging.
- Good field judgment and experience are required to make a final determination when readings keep drifting or if what the values represent is in question. Such problems should be documented and advice (if needed) should be sought from a senior technician.

Field-measurement sensors must first be allowed to equilibrate to the ambient temperature of the water body being sampled or monitored. This can take from 60 seconds to more than 30 minutes, depending on the instrument and the start and final temperature range. Ensure that all field-measurement readings have stabilized before recording the final field measurement values.

6.8.3.C MEASUREMENT TIPS

Measurement accuracy depends on the adequacy of the calibration procedures used, and many of the precautions described in section 6.8.2 on calibration also apply when measuring the field properties of environmental waters. The following tips can enhance the quality of the field measurement and address some common onsite practices or issues.

- ► Equipment use: Each instrument must be tested and the sensors calibrated before use.
 - Apply the same precautions for measurement as were recommended for calibration.
 - Avoid faulty readings by cleaning calibration residues and dirt from sensors before use.
 - Instruments may be sensitive to static electricity. Keep the instrument at least 3 ft (about 1 m) away from objects that are not electrically grounded.
- ▶ Sensor-sample equilibration: Allow a minimum of 60 seconds for an instrument to warm up and the sensors to reach thermal equilibrium with the water temperature before recording field measurements. Some instruments require a longer equilibration time (up to 30 minutes); check the manufacturer's recommendations.
- ▶ Measurement accuracy: If the water matrix or other condition triggers a concern regarding the accuracy or replication of the measurement, check the sensor calibration and document any changes in the sensor response after sampling or completing a set of field measurements. This record will help to determine deterioration or malfunction of one or more of the sensors. A calibration check of the DO sensor is recommended as a routine practice, especially if the measurement was made in a suboxic environmental water.
- ▶ pH and ORP (see NFM 6.4, section 6.4.3, and NFM 6.5, section 6.5.3, respectively):
 - Check the slope of the pH electrode before use to verify that the electrode is working properly (the slope is determined as part of the calibration process; see section 6.8.2.B and NFM 6.4 for pH calibration tips).

- Record changes in ambient air or water temperature while onsite, as temperature affects pH and ORP readings.
- Depending on the sensor type and manufacture, pH or ORP sensors may or may not be designed for horizontal or near horizontal placement during measurement; check manufacturer's instructions (Hach pH sensors, for example, do allow for horizontal placement).
- ORP field values that are determined with a silver/silver chloride reference electrode must be converted to standard hydrogen electrode (SHE) values. See NFM 6.5 for calculation instructions.

► **Turbidity** (see NFM 6.7, section 6.7.3):

- Cover the flowthrough cell with aluminum foil to avoid potential bias to the readings from ambient light.
- Inspect the sensor body to ensure that no bubbles are on the optical surface before beginning measurement.
- If using a flowthrough cell, ensure that no bubbles are entrained in the sample water. The presence of bubbles will result in a high bias to readings.
- For sensors with wipers, follow the manufacturer's instructions for how to verify that the wiper arm is operating correctly.
- Instrument precision often decreases at turbidities less than 2 turbidity units—consult the manufacturer's specification for the expected accuracy of the measurement. Some instruments have the capability of processing low-turbidity data to improve reproducibility. Check whether the instrument has a user-adjustable turbidity data-filter option. If working in low-turbidity water, review the guidance in NFM 6.7 for selection of the appropriate multiparameter (or single-parameter) instrument type.

▶ Dissolved oxygen (see NFM 6.2, section 6.2.1):

— Table 6.8–6 provides general guidelines for use of the amperometric (polarographic or Clark cell) and luminescent (optical) sensors. Use of the luminescent-sensor method may be more practical for dissolved-oxygen measurement in the field, depending on site conditions.

- For surface-water measurements, selection of the DO amperometric or luminescent sensor should be based on flow regime and stratification of the water body.
- For an amperometric (polarographic sensor or Clark cell) measurement, some manufacturers recommend transporting the sonde with the sensor guard (instead of the storage/calibration cup) installed, keeping the sonde wrapped in the wet light-colored towel used for calibration. To reduce evaporation in hot weather, place the entire sonde and wet towel into a perforated plastic bag (that is kept unsealed). The wrapped sonde can be transported in a bucket or cooler.
 - Allow the amperometric instrument to warm up after turning on the display. The DO output should read saturation for the barometric pressure determined for the site.
 - Allow the polarographic sensor to equilibrate to the temperature of the stream, lake, or ground water.
 - For low-velocity water, follow the manufacturer's instructions when using an amperometric instrument.
 - Use the stirrer for the DO sensor that is provided or recommended by the manufacturer. Alternatively, use the luminescent-sensor method, which is not flow dependent.
 - If the instrument has no stirrer, move the sonde up and down (or side to side in shallow water) at the rate recommended by the manufacturer. (A stirrer is preferable to manually induced flow, especially under stratified conditions at the thermocline of a surfacewater body).
 - Flow dependence is diminished when using a "rapidpulse sensor;" however, some flow over the membrane is needed. Check the manufacturer's instructions.
- To verify the accuracy of the amperometric measurement, rinse the sensors and check the DO calibration by rewrapping it in the wet white towel. The instrument display should return to its saturation set point (±2 percent) within a few minutes. Record any post-measurement calibration check in the field notes.

Table 6.8–6. General guidelines for use of amperometric and luminescent dissolved-oxygen sensors on multiparameter instruments

A mnoromotrio concer			
Amperometric sensor (polarographic or Clark cell) ¹	Luminescent sensor (optical) ¹		
Inspect the sonde and sensor for damage, improper installation, or excessive buildup of biofouling matter. Follow the manufacturer's recommendations for cleaning and calibration.	Inspect the sonde and sensor for damage, improper installation, or excessive buildup of biofouling matter. Follow the manufacturer's recommendations for cleaning and calibration. The maintenance and use of optical dissolved-oxygen sensors are highly dependent on the		
Inspect the membrane for damage or improper installation (the average replacement interval is 2 to 4	technology used by the specific manufacturer. Follow the instructions specified by the manufacturer.		
weeks). Inspect the membrane for biofouling. Replace the membrane if biofouling is evident. Avoid contact of the membrane and	Example A – YSI "ROX" optical sensor. This sensor should not be left exposed to air for 2 hours or more or otherwise allowed to dry out. Store the sensor wet to avoid drift or having to rehydrate the sensor.		
sensor with acids, bases, and organic solvents. Replace the potassium chloride (KCl) solution once a month or sooner if performance degrades, and when replacing the sensor. Inspect O-rings periodically and replace as needed or per the manufacturer's recommendation.	Example B – Hydrolab "LDO" optical sensor: This sensor should not be left exposed to air and allowed to dry out. The sensor needs to be stored in liquid with its cap on. If the sensor is in a dry environment for several hours it may need to be soaked for up to 5 days before use. The sensor drifts slightly during hydration and must be fully hydrated before being calibrated. Example C – In-Situ "RDO" optical sensor. This sensor can be exposed to ambient air for extended periods, can be stored dry, and does not require a hydration period before deployment.		
For short-term storage, keep the DO sensor immersed in a calibration cup with enough water to keep electrolyte from evaporating.	Check the manufacturer's instructions for short-term and long-term sensor storage, as requirements can differ substantially among manufacturers.		
Anode and cathode maintenance: The silver anode can be contaminated and might be the cause of poor sensor performance: clean according to the manufacturer's recommendation. The gold cathode must be bright. Follow the manufacturer's recommendations for cleaning.	Sensors with wipers require manufacturer-specific maintenance procedures: • Use only the wiper recommended by the manufacturer for the sensor in use. • Inspect the wiper pad periodically for wear and tear, and biofouling. • Change the wiper before each long-term deployment, or as recommended by the manufacturer.		

¹Refer to Section 6.2.1 for detailed information on amperometric and luminescent-sensor methods for measuring dissolved-oxygen concentrations.

6.8.4 TROUBLESHOOTING

Multiparameter instruments that perform poorly can be tested and the cause can be identified. The complexity of the series of tests increases with the number of sensors in the sonde. The troubleshooting tests should be performed in a prescribed order that depends on the type of sensors in use and potential for sensor contamination. General troubleshooting tips are provided below in table 6.8–7. More detailed guidance is available from the manufacturer. **Consult the manufacturer's user manual for the specific instrument being used.**

- ► If the display shows a warning message, do not use the sensor until the error has been identified and corrected.
- ► Sensor ports on the instrument body should be dry before replacing sensors. Use compressed air, methanol, or isopropyl alcohol to dry the ports. When using methanol or isopropyl alcohol, gently shake off the excess liquid from the port and allow sufficient time for the liquid to evaporate.

WARNING: Alcohol or other solvents can damage certain types of plastics and can destroy the sensing surface of the optical DO sensor.

CAUTION: Avoid skin contact with, and fume inhalation of, potentially hazardous equipment-cleaning solutions such as methanol and isopropyl alcohol. If such substances will be used, wear a face mask and protective clothing. If possible, replace sensors under a fume hood.

Table 6.8–7. Troubleshooting tips for use of multiparameter instruments

[DO, dissolved oxygen; NIST, National Institute of Standards and Technology; SC, specific electrical conductance; ORP, oxidation-reduction (redox) potential; Cl, chloride; NH₄, ammonium; NO₃, nitrate; NTU, nephelometric turbidity unit]

Symptom	Possible cause(s), corrective actions, and tips	
Erratic or jumpy readings	 May be caused by loose connections or sensitivity to the electrical capacitance of your body and to static electricity: avoid touching the sonde housing and try to keep a distance of about 1 meter from the sonde. 	
Display does not turn on	 Check that the batteries are installed properly and are fully charged. Battery performance decreases with deceasing temperature. Batteries that charge at room temperature may not perform well when the temperature approaches freezing. Carry spare batteries. 	
The display does not show readings; the readings seem to be wrong	 Check that the readings are displayed in the appropriate units. Inspect all connectors for moisture, dirt, damage, or a loose connection. Clean as recommended by the manufacturer. Disconnect and reconnect and recalibrate the sensors. When replacing sensors, the waterproof and dustproof properties of the instrument must be maintained or instrument performance will degrade. 	
Data on the display appear scrambled	 Check for computer speed and software and hardware compatibility. Check for a damaged cable. Check that the correct units are displayed. If data remain scrambled, consult the manufacturer or authorized service center. 	
Initial drifting of the readings	 Increase the time for sensors to equilibrate to the water temperature. Check that the sensors are appropriately submerged and (if necessary for the instrument) that they are at the appropriate inclination from the horizontal. 	
Dissolved-oxygen reading is unstable or inaccurate	 Check that the sensor has been calibrated to the true onsite barometric pressure or altitude; recalibrate the sensor at the proper barometric pressure and, to the extent possible, with calibrants brought to sample temperature. Amperometric DO method: Inspect the membrane for a puncture, bubbles, or improper installation. Verify the integrity of the membrane, electrolyte solution, and O-ring by checking the reading against a zero-DO solution. Rinse the sonde thoroughly. 	
Temperature reading is unstable or inaccurate	 Check for water in the connector; dry the connector and reinstall the sensor. Check the accuracy of the reading with an NIST-traceable thermometer and have it replaced if necessary. Usually, only the manufacturer can replace a faulty thermistor. 	
Reading is unstable or inaccurate for SC, pH, ORP, turbidity, CI, NH ₄ , or NO ₃	 Examine the sensor for dirt or damage. Clean dirty sensors according to the manufacturer's instructions. Replace damaged sensors and recalibrate. Ensure that the temperature reading is accurate by allowing sufficient time for the temperature sensor to equilibrate to the water temperature. Check that the calibration solutions used for SC, pH, and ORP were not expired or subject to contamination. Recalibrate the sensor(s), first bringing the calibration solutions as close to the ambient temperature of the sample as is practical, given ambient field conditions. Check pH reference junction: if dry, follow manufacturer's instructions for soaking the sensor in tap water or buffer solution until readings stabilize. Alternatively, replace the junction. Check the sensor connector for water; dry the connector and reinstall the sensor. If the ZoBell check fails, was temperature dependence of the ZoBell solution accounted for? The SC sensor must be fully immersed for proper calibration and sample measurement. There must be no bubbles in the cell. The turbidity sensor wiper must be clean, activated, and rotating properly. Check that expired turbidity calibrants were not used, including any diluted 4000-NTU formazin standard (which must be used within 24 hours of preparation). 	

6.8.5 REPORTING

USGS personnel are instructed to record all field-measurement values on electronic or paper field forms, and to complete the field-measurement fields on Analytical Services Request forms of the USGS National Water Quality Laboratory or other laboratory at which samples will be analyzed. Field-measurement entries should be checked by a second party and compared for accuracy and consistency with those entered into NWIS.

Table 6.8–8. USGS guidelines for reporting field-measurement values

[\pm , plus or minus; o C, degrees Celsius; μ S/cm, microsiemens per centimeter; >, greater than; mg/L, milligrams per liter; mV, millivolt; SHE, standard hydrogen electrode; FNU, formazin nephelometric units; ppt, parts per trillion; psu, practical salinity units calculated from specific electrical conductance at 25 degrees Celsius]

Field measurement ¹	USGS reporting convention for the National Water Information System (NWIS) ²	Unit
Temperature	±0.1°C, depending on instrument accuracy and precision	°C
Specific conductance	Three significant figures to the nearest whole number	μS/cm at 25°C
Dissolved oxygen (DO)	Nearest 0.1 mg/L (for the amperometric or luminescent-sensor method) Nearest 0.01 mg/L (for the spectrophotometric/Rhodazine-D™ method) Report ">20 mg/L" for a DO measurement that exceeds 20 mg/L	mg/L
pН	Nearest 0.1 unit for most applications. Can be reported at 0.05 pH unit, depending on accuracy and precision of the calibrated sensor	pH, in standard units
Oxidation- reduction potential	Nearest 1 mV, calculated relative to the SHE (do not report raw data) and the temperature of the sample at the time of measurement	mV
Turbidity	Range: 0 to 10 to the nearest 0.1 FNU 10 to 100 to the nearest 1 FNU >100 to the nearest 10 FNU	FNU ³
Salinity	<1 to 10, to the nearest 0.1 ppt or psu 10 to 100, to the nearest 1 ppt or psu	ppt or psu

¹Information is based on manufacturers' specifications for the following multiparameter systems: Hydrolab Quanta and DataSonde 5 and 5X, DS5; YSI 6600; In-Situ Troll 9500; and Eureka Manta.

² It is USGS practice to enter values into NWIS that have more significant figures than are the standard for data publication. The NWIS databases produce the values that are rounded correctly, which are then reported in publications. This practice eliminates investigator mistakes when reporting rounded values. NWIS data must be input with the correct parameter and method codes, which can be found by accessing QWDATA.

³ Most multiparameter instruments used for USGS turbidity measurement contain single-beam infrared wavelength turbidity sensors and are reported in FNU. Check the Excel spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls to determine the appropriate turbidity unit of measure and NFM 6.7 for detailed information on turbidity measurement and instrumentation.

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6.8.7 ACKNOWLEDGMENTS

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APPENDIX 6.8-A

Example of a USGS field form for recording sensor calibrations and field measurements

NOTE: USGS personnel are advised to use the latest available version of this and other field forms.

Novembe	er 2006	METER C	ALIBR	ATIONS/	FIELD M	EASURE	EMENTS STN NO
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Date:		lim	e:				
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		percent or ± 0.5]
		Thermometer/The					± °C BANK VERTICAL AVG/MEDIAN OF POINTS
							: °C Method code Remark Qualifier
rieiu ke	auings #1	#2	#0	#4	#3	WIEDIAN	:C Method code Remark Qualifier
pH Mete	r make/model _			S/N	E	lectrode No	Type: GEL LIQUID OTHER
Sample:	FILTERED UN	IFLTERED (CHURN SPLITT	ER SINGLE	POINT AT	FT DEEP	VERTICAL AVG. OF POINTS CONE SPLITTER
pH BUFFER	BUFFER TEMP	THEO- RETICAL pH FROM TABLE	pH BEFORE ADJ.	pH AFTER ADJ.	SLOPE	MILLI- VOLTS	TEMPERATURE CORRECTION FACTORS FOR BUFFERS APPLIED? Y N BUFFER LOT NUMBERS:
pH 7							рн 7:
pH 7							pH:
pH 7		1					СНЕСК РН:
pH							BUFFER EXPIRATION DATES:
рH	1	1					рн 7:
рH	1	1					pH:
CHECK							CHECK pH:
pH							Calibration Criteria: ± 0.1 pH units
Field Re	adings #1	#2	#3	#4 #5	MEDIAN	:Uni	ts Method codeRemark Qualifier
CDECLE	CONDUCT	ANCE Meter	MANA PARA PARA PARA PARA PARA PARA PARA P				Sensor Type: DP FLOW-THRU OTHER
			_				•
Sample. C	HURN SPLITTER	SINGLE POINT AT		EEP VERTICAL	4VG. OF	_POINTS CON	AUTO TEMP COMPENSATED METER
Std Valu		SC Before	SC After		itd t No.	Std typ	IVIANUAL I EMP COMPENSATED METER
μ-1		Adj.	Adj.			(KCI; Na	CORRECTION FACTOR APPLIED? Y N
							CORRECTION FACTOR=
							Calibratica Calerina LE 9/ fra CC 4400 C/
							Calibration Criteria: ± 5 % for SC ≤100 µS/ cm or 3% for SC >100 µS/cm
Field rea	dings #1	#2#		#5			n Method code Remark Qualifier
DISSOLV	ED OXYGEN	N Meter MAKE/M					
		ic Luminescent				_	
					Water Air C	alibration Chaml	ber in Air Winkler Titration Other
Sample:	SINGLE POINT A	ATft DEE	P VERTICA	AL AVG. OF	POINTS BO	D BOTTLE OT	
WATER	BAROMETRI				DO	Zero DO Check	cmg/lL Adj. tomg/L Date:
TEMP °C	PRESSURE mm Hg	READING mg/L	CORR. FACTOR	BEFORE ADJ.	AFTER ADJ.	Zero DO Solutio	on Date Thermister Check? Y N Date
						Membrane Cha	inged? N Y Date: Time:
						Barometer Calil	brated? N Y Date: Time:
Calibration	Criteria: ± 0.2 r	mg/L				Battery Check:	REDLINE RANGE
Field rea	dings #1	#2	_#3#	4#5	MEDIAN	mg/l	L Method codeRemark Qualifier

Appendix 6.8–A. Example of a USGS field form for recording sensor calibrations and field measurements. (USGS personnel should use the latest available version of this and other field forms.)

Attachment C.2: Example Chain of Custody Forms (blank)



Weck Laboratories, Inc.

CHAIN OF CUSTODY RECORD

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				E / TIME	RECEIVED	RECEIVED BY						Pres Evide	eived On erved ence Sea ainer Att	als Pres	ent	Y / N Y / N Y / N Y / N	WW = V RW = R	rinking Water Vaste Water ain Water round Water
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CHAIN OF CUSTODY RECORD

Client:			Project Name/Number:		Analysis												
Address					Project Mgr.		1										
					P.O. #		1										
Phone N	umber:				Sampled By (signature)												
Date	Time	Comp.	Grab	Matrix	Sample ID	Volume/ Number											Comments
							-										
Relinquis	od Byry				Dat	e: Time:	Dolin	quica	d By: _{(s}	·	,						Date: Time:
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Attachment C.3: Dry Weather Outfall Screening Field Data Sheet (Example)

OUTFALL RECONNAISSANCE INVENTORY/ SAMPLE COLLECTION FIELD SHEET

pН

Ammonia

Section 1: Backg	ground Data											
Subwatershed:				Outfall ID:								
Today's date:				Time (Military):								
Investigators:				Form completed by	·:							
Temperature (°F):		Rainfa	all (in.): Last 24 hours:	Last 48 hours:								
Latitutde:		Longitude:		GPS Unit:		GPS LMK #:	:					
Camera:				Photo #s:								
Land Use in Drainaş	ge Area (Check all tha	t apply):										
☐ Industrial				☐ Open Space								
Ultra-Urban Resi	sidential			☐ Institutional								
☐ Suburban Reside	ential			Other:								
☐ Commercial				Known Industries:								
Notes (e.g, origin o												
LOCATION	MATE	RIAL	SHA	APE	DIMENSIC	ONS (IN.)	SUBMERGED					
	☐ RCP	□СМР	☐ Circular	Single	Diameter/Dimen	isions:	In Water:					
	☐ PVC	☐ HDPE	☐ Eliptical	☐ Double			☐ No ☐ Partially					
Closed Pipe	☐ Steel		☐ Box	☐ Triple			Fully					
	Other:		Other:	Other:			With Sediment: No Partially Fully					
☐ Open drainage	☐ Concrete ☐ Earthen ☐ rip-rap		☐ Trapezoid ☐ Parabolic ☐ Other:		Depth: Top Width: Bottom Width: _							
	Other:											
☐ In-Stream	(applicable wh	nen collecting	samples)									
Flow Present?	☐ Yes	☐ No	If No, Ski	ip to Section 5								
Flow Description (If present)	☐ Trickle	☐ Moderate	e Substantial									
Section 3: Quant	titative Characte	rization										
			FIELD DATA FOR FI	LOWING OUTFALLS	;							
PAR	RAMETER		RESULT		UNIT	EC	QUIPMENT					
□Flow #1	Volume				Liter		Bottle					
	Time to fill		_		Sec							
	Flow depth				In	T	ape measure					
□Flow #2	Flow width		, ,,,		Ft, In	Tape measure						
	Measured length		, ,,,		Ft, In	Tape measure						
	Time of travel				S	- :	Stop watch					
Ter	mperature				°F	Т	hermometer					

pH Units

mg/L

Test strip/Probe

Test strip

Outfall Reconnaissance Inventory Field Sheet

Section 4: Physical Indicators for Flowing Outfalls Only Are Any Physical Indicators Present in the flow?
Yes □ No (If No, Skip to Section 5) CHECK if INDICATOR DESCRIPTION **RELATIVE SEVERITY INDEX (1-3) Present** ☐ Rancid/sour ☐ Petroleum/gas Sewage ☐ 3 – Noticeable from a Odor ☐ 1 – Faint ☐ 2 – Easily detected distance Sulfide Other: Clear Brown ☐ Gray ☐ Yellow ☐ 2 – Clearly visible in ☐ 3 – Clearly visible in ☐ 1 – Faint colors in Color outfall flow sample bottle sample bottle Green Orange Red Other: See severity ☐ 1 – Slight cloudiness \square 2 – Cloudy \square 3 – Opaque Turbidity \square 2 – Some; indications 3 - Some; origin clear Floatables Sewage (Toilet Paper, etc.) ☐ Suds (e.g., obvious oil ☐ 1 – Few/slight; origin of origin (e.g., -Does Not Include not obvious possible suds or oil sheen, suds, or floating Other: Petroleum (oil sheen) Trash!! sheen) sanitary materials) Section 5: Physical Indicators for Both Flowing and Non-Flowing Outfalls Are physical indicators that are not related to flow present? ☐ Yes ☐ No (If No, Skip to Section 6) DESCRIPTION **INDICATOR CHECK if Present COMMENTS** Spalling, Cracking or Chipping Peeling Paint Outfall Damage Corrosion П Other: Deposits/Stains ☐ Oily ☐ Flow Line ☐ Paint Excessive ☐ Inhibited Abnormal Vegetation \square Colors Odors O ☐ Floatables ☐ Oil Sheen Poor pool quality ☐ Excessive Algae ☐ Suds Other: ☐ Brown Orange Green Other: Pipe benthic growth **Section 6: Overall Outfall Characterization** Suspect (one or more indicators with a severity of 3) Potential (presence of two or more indicators) Obvious Unlikely **Section 7: Data Collection** Sample for the lab? Yes ☐ No ☐ Pool If yes, collected from: ☐ Flow

Caulk dam

Section 8: Any Non-Illicit Discharge Concerns (e.g., trash or needed infrastructure repairs)?

☐ Yes

□ No

Intermittent flow trap set?

Peninsula CIMP Appendix D California Environmental Data Exchange Network (CEDEN) Spreadsheet Formats for Data Management and Reporting of Analytical Data and Field Measurements

				dCode	Φ			pth											
Code	eDate	tCode	ctionTime	tionMethod	eTypeCod	ate	tionDepth	CollectionDe	isDate	xName	dName	eName	ionName	ame	plicate		alCode		Φ.
atior	mpl	ojec	ollect	ollect	mple	Replicat	ollecti	bBa	alys	atrixl	tho	al yt	actic	UnitNa	bRe	sult	sQu	7	. Coo
Š	S COLOR	E L COOR	Ö	ŭ	Sa	Re	Ö	Labe	A	Ž	<u> </u>	A A	Ē		La	Res	Re	<u> </u>	전 8
	•	RWB7_Trend_2009 RWB7_Trend_2009	16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1 1		cm WPCL_L-024-226-09_BS559_S_PAH cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00 25/Aug/2009 00:00		EPA 8270M EPA 8270M	Acenaphthene Acenaphthene-d10(Surrogate)	Total Total	ng/g dw % recovery	1 1 83		ND =	0.789 0.5	
723NROTWM	28/Apr/2009	RWB7_Trend_2009	16:55	Sed_Grab	Integrated	1	2	cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Acenaphthylene	Total	ng/g dw	1		ND	0.789	0.789 SC
	•		16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH cm MPSL-DFG_2009Dig14_S_TM	16/Sep/2009 00:00 22/Sep/2009 00:00		EPA 8081BM EPA 200.8	Aldrin Aluminum	Total Total	ng/g dw mg/Kg dw	1 1 45		ND =	0.716 220	
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Anthracene	Total	ng/g dw	1		ND	0.789	
			16:55	Sed_Grab	Integrated	1		cm MPSL-DFG_2009Dig14_S_TM	22/Sep/2009 00:00		EPA 200.8	Arsenic	Total	mg/Kg dw	1 6.3		=	0.1	
	•		16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00 25/Aug/2009 00:00		EPA 8270M EPA 8270M	Benz(a)anthracene Benz(a)anthracene-d12(Surrogate)	Total Total	ng/g dw % recovery	1 0.8 1 13		=	0.789 0.5	
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00	sediment	EPA 8270M	Benzo(a)pyrene	Total	ng/g dw	1 0.9		=	0.789	,
			16:55 16:55	Sed_Grab Sed Grab	Integrated Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00 25/Aug/2009 00:00		EPA 8270M EPA 8270M	Benzo(b)fluoranthene Benzo(e)pyrene	Total Total	ng/g dw ng/g dw	1 2.2 1 1.4		=	0.789	0.789 SC 0.789 SC
			16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Benzo(g,h,i)perylene	Total	ng/g dw	1 2.2		=	0.789	
			16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Benzo(g,h,i)perylene-d12(Surrogate)	Total	% recovery	1 77		=	0.5	
			16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1 1		cm WPCL_L-024-226-09_BS559_S_PAH cm WPCL_L-222-226-09_S_PYD-PYN	25/Aug/2009 00:00 12/Jun/2009 00:00		EPA 8270M EPA 8081BM	Benzo(k)fluoranthene Bifenthrin	Total Total	ng/g dw ng/g dw	1		ND ND	0.789 0.25	
723NROTWM	28/Apr/2009	RWB7_Trend_2009	16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00	sediment	EPA 8270M	Biphenyl	Total	ng/g dw	1		ND	0.789	,
	•		16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1 1	_	cm WPCL_L-024-226-09_BS559_S_PAH cm MPSL-DFG 2009Dig14 S TM	25/Aug/2009 00:00 22/Sep/2009 00:00		EPA 8270M EPA 200.8	Biphenyl-d10(Surrogate) Cadmium	Total Total	% recovery mg/Kg dw	1 10 1 0.3		=	0.5 0.03	
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00		EPA 8081BM	Chlordane, cis-	Total	ng/tg dw	1		ND	0.716	
			16:55	Sed_Grab	Integrated	1	2	cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00		EPA 8081BM	Chlorousifes	Total	ng/g dw	1		ND	0.716	
	•		16:55 16:55	Sed_Grab Sed Grab	Integrated Integrated	1		cm WPCL_L-222-226-09_S_OP cm WPCL_L-222-226-09_S_OP	12/Jun/2009 00:00 12/Jun/2009 00:00		EPA 8141AM EPA 8141AM	Chlorpyrifos Chlorpyrifos methyl	Total Total	ng/g dw ng/g dw	1		ND ND	5 25	10 None 50 None
723NROTWM	28/Apr/2009	RWB7_Trend_2009	16:55	Sed_Grab	Integrated	1	2	cm MPSL-DFG_2009Dig14_S_TM	22/Sep/2009 00:00	sediment	EPA 200.8	Chromium	Total	mg/Kg dw	1 35		=	0.29	
			16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00 25/Aug/2009 00:00		EPA 8270M EPA 8270M	Chrysene Chrysenes, C1-	Total Total	ng/g dw ng/g dw	1 1.2 1 1.5		=	0.789	0.789 SC 0.789 HT,SC,SCR
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Chrysenes, C2-	Total	ng/g dw ng/g dw	1 1.5		=	0.789	
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Chrysenes, C3-	Total	ng/g dw	1 1.3		=		0.789 HT,SC,SCR
			16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm SCL_050609_GS cm SCL_050609_GS	06/May/2009 00:00 06/May/2009 00:00		Plumb, 1981, GS Plumb, 1981, GS	Clay Clay	Coarse 0.00195 to <0.0039 mm Fine <0.00098 mm	% %	1 6. ⁴ 1 15		=	0.01 0.01	
723NROTWM	28/Apr/2009	RWB7_Trend_2009	16:55	Sed_Grab	Integrated	1	2	cm SCL_050609_GS	06/May/2009 00:00	sediment	Plumb, 1981, GS	Clay	Medium 0.00098 to <0.00195 mm	%	1 6.3		=	0.01	
			16:55 16:55	Sed_Grab Sed Grab	Integrated Integrated	1		cm MPSL-DFG_2009Dig14_S_TM cm WPCL L-222-226-09 S PYD-PYN	22/Sep/2009 00:00 12/Jun/2009 00:00		EPA 200.8 EPA 8081BM	Copper Cyfluthrin, total	Total Total	mg/Kg dw ng/g dw	1 18 1		= ND	0.54	1.5 None 2 None
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-222-226-09_S_PYD-PYN	12/Jun/2009 00:00		EPA 8081BM	Cyhalothrin, lambda, total	Total	ng/g dw ng/g dw	1		ND	0.5	
			16:55	Sed_Grab	Integrated	1		cm WPCL_L-222-226-09_S_PYD-PYN	12/Jun/2009 00:00		EPA 8081BM	Cypermethrin, total	Total	ng/g dw	1		ND	1	2 None
		RWB7_Trend_2009 RWB7_Trend_2009	16:55 16:55	Sed_Grab Sed Grab	Integrated Integrated	1 1		cm WPCL_L-211-349-09_BS560_S_OCH cm WPCL L-211-349-09 BS560 S OCH	16/Sep/2009 00:00 16/Sep/2009 00:00		EPA 8081BM EPA 8081BM	Dacthal DBCE(Surrogate)	Total Total	ng/g dw % recovery	1 1.0 1 62		=	0.358 -88	
723NROTWM	28/Apr/2009	RWB7_Trend_2009	16:55	Sed_Grab	Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00		EPA 8081BM	DDD(o,p')	Total	ng/g dw	1 0.5		DNQ	0.358	
	•	RWB7_Trend_2009 RWB7_Trend_2009	16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00 16/Sep/2009 00:00		EPA 8081BM EPA 8081BM	DDD(p,p') DDD(p,p')(Surrogate)	Total Total	ng/g dw % recovery	1 0.7 1 84		DNQ =	0.358 -88	
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00		EPA 8081BM	DDE(o,p')	Total	ng/g dw			DNQ	0.358	
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00		EPA 8081BM	DDE(p,p')	Total	ng/g dw	1 18		=	0.716	
			16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00 16/Sep/2009 00:00		EPA 8081BM EPA 8081BM	DDMU(p,p') DDT(o,p')	Total Total	ng/g dw ng/g dw	1		ND ND	0.716 0.716	
			16:55	Sed_Grab	Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00		EPA 8081BM	DDT(p,p')	Total	ng/g dw	1 1.5		=	0.716	
	•		16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-222-226-09_S_PYD-PYN cm WPCL L-222-226-09 S OP	12/Jun/2009 00:00 12/Jun/2009 00:00		EPA 8081BM EPA 8141AM	Deltamethrin Diazinon	Total Total	ng/g dw ng/g dw	1		ND ND	1	2 None 10 None
			16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Dibenz(a,h)anthracene	Total	ng/g dw ng/g dw	1		ND	0.789	
723NROTWM	28/Apr/2009	RWB7_Trend_2009	16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00	sediment	EPA 8270M	Dibenzothiophene	Total	ng/g dw	1		ND		0.789 SC
	•	RWB7_Trend_2009 RWB7_Trend_2009	16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1 1		cm WPCL_L-024-226-09_BS559_S_PAH cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00 25/Aug/2009 00:00		EPA 8270M EPA 8270M	Dibenzothiophenes, C1- Dibenzothiophenes, C2-	Total Total	ng/g dw ng/g dw	1 0.8 1 2.8		=		0.789 HT,SC,SCR 0.789 HT,SC,SCR
			16:55	Sed_Grab	Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00		EPA 8270M	Dibenzothiophenes, C3-	Total	ng/g dw	1 3.6		=		0.789 HT,SC,SCR
			16:55	Sed_Grab	Integrated	1		cm WPCL_L-222-226-09_S_PYD-PYN	12/Jun/2009 00:00		EPA 8081BM	Dibutylchlorendate(Surrogate)	Total	% recovery	1 76		=	-88	
	•		16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-222-226-09_S_OP cm WPCL_L-211-349-09_BS560_S_OCH	12/Jun/2009 00:00 16/Sep/2009 00:00		EPA 8141AM EPA 8081BM	Dichlofenthion Dieldrin	Total Total	ng/g dw ng/g dw	1 1 1.2		ND =	25 0.358	
723NROTWM	28/Apr/2009	RWB7_Trend_2009	16:55	Sed_Grab	Integrated	1	2	cm WPCL_L-024-226-09_BS559_S_PAH	25/Aug/2009 00:00	sediment	EPA 8270M	Dimethylnaphthalene, 2,6-	Total	ng/g dw	1		ND	0.789	0.789 SC,VFDP
	•		16:55 16:55	Sed_Grab Sed_Grab	Integrated Integrated	1		cm WPCL_L-024-226-09_BS559_S_PAH cm WPCL_L-222-226-09_S_OP	25/Aug/2009 00:00 12/Jun/2009 00:00		EPA 8270M EPA 8141AM	Dimethylphenanthrene, 3,6- Dioxathion	Total Total	ng/g dw ng/g dw	1 1		ND ND	0.789 25	
	•		16:55	Sed_Grab	Integrated	1		cm WPCL_L-211-349-09_BS560_S_OCH	16/Sep/2009 00:00		EPA 8081BM	Endosulfan I	Total	ng/g dw	1		ND	0.716	

^{*}Fields shown are the minimum required fields for loading data into CEDEN.
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http://www.ceden.org/ceden_datatemplates.shtml#guidance

Toxicity

onCode pleDate sctCode sctionTime pleTypeCode icate	sctionDepth CollectionDepth aatch	ixName odName Duration	tment Centration Treatment ion Source Source yteName	tionName Analyte Point	an JDev atisticalMethod	ValueType ulatedValue calValue entEffect ffect
Sam Sam Stati Sam Stati Sam Sa	Solution 1	Meth Meth Orga	Prea Con Con Cox Nag	Frac	Mea Stati	Calo Calo Calo Calo Criti
EXAMPLE Probability	<u> </u>					0 0 0 12 0 1
205COY060 17/Jan/2012 SWB_SPoT_2012 9:45 Sed_Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Survival Non	e % Day 10 8	25.0 22.00 T-test 0.05	Probability 0.000 0.050 69.9 SL None
205COY060 17/Jan/2012 SWB_SPoT_2011 9:45 Sed_Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non	e mg/ind Day 10 7		Probability 0.007 0.050 26.08 SL None
541MERDEL 12/Jan/2012 SWB_SPoT_2013 14:10 Sed_Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Survival Non		4.0 7.40 T-test 0.05	•
541MERDEL 12/Jan/2012 SWB_SPoT_2011 14:10 Sed_Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non	o ,	0.125 0.04 T-test 0.05	
541MERECY 12/Jan/2012 SWB_SPoT_2011 15:30 Sed_Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Survival Non		0.000 0.00 T-test 0.05	
541MERECY 12/Jan/2012 SWB_SPoT_2011 15:30 Sed_Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non	o ,	-88 -88.00 T-test 0.05	
LABQA 14/Feb/2012 Not Applicable 0:00 Not Applicable CNEG 1			Temperature 15 Deg C 100 not applicable None Survival Non			Probability 0.500 0.050 0.00 NA None
LABQA 14/Feb/2012 Not Applicable 0:00 Not Applicable CNEG 1	-88 cm GC_SPOT11_15_15_S_Tox	sediment EPA 600/R-99-064 10 days Hyalella azteca	Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non	e mg/ind Day 10 8	0.128 0.03 T-test 0.05	Probability 0.500 0.050 0.00 NA None
EXAMPLE TST						
205COY060 17/Jan/2012 SWB SPoT 2012 9:45 Sed Grab Integrated 1	2 cm GC SPOT11 15 15 S Tox	sediment EPA 600/R-99-064 10 days Hyalella azteca	Temperature 15 Deg C 100 not applicable None Survival Non	e % Day 10 8	0.8 0.465 TST Welch Test 0.25	T Value 0.597 0.706 42.42 Fail None
205COY060 17/Jan/2012 SWB SPoT 2011 9:45 Sed Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non	•	0.095 0.009 TST Welch Test 0.25	T Value -0.165 0.703 26.08 Fail None
541MERDEL 12/Jan/2012 SWB SPoT 2011 14:10 Sed Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Survival Non	,	0.22 0.115 TST Welch Test 0.25	T Value -10.807 0.694 95.45 Fail None
541MERDEL 12/Jan/2012 SWB SPoT 2011 14:10 Sed_Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non		0.125 0.035 TST Welch Test 0.25	T Value 1.106 1.000 2.34 Pass None
541MERECY 12/Jan/2012 SWB SPoT 2011 15:30 Sed Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Survival Non	,	0.16 0.000 TST Welch Test 0.25	T Value -15.954 0.711 100.0 Fail None
541MERECY 12/Jan/2012 SWB SPoT 2011 15:30 Sed Grab Integrated 1			Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non	,	0.00 0.000 TST Welch Test 0.25	T Value -88 -88 100.0 NA None
LABQA 14/Feb/2012 Not Applicable 0:00 Not Applicable CNEG 1			Temperature 15 Deg C 100 not applicable None Survival Non	,	1.16 0.167 TST Welch Test 0.25	T Value 3.906 0.696 0.00 NA None
LABQA 14/Feb/2012 Not Applicable 0:00 Not Applicable CNEG 1			Temperature 15 Deg C 100 not applicable None Growth (wt/surv indiv) Non		0.13 0.029 TST Welch Test 0.25	T Value 2.511 0.696 0.00 NA None

^{*}Fields shown are the minimum required fields for loading data into CEDEN. The complete list of fields can be found through the CEDEN website: http://www.ceden.org/ceden_datatemplates.shtml#guidance

Field Measurements

itationCode	SampleDate	rojectCode	CollectionTime	CollectionMethodCode	Replicate	CollectionDepth	JnitCollectionDepth	MatrixName	MethodName	AnalyteName	FractionName	UnitName	Result	ResQualCode	QACode
()	0)	1			ш.				_						
723NRBDRY	28/Apr/2009	RWB7_Trend_2009	15:15	Field	1	0.1	 m	samplewater	FieldMeasure	Oxygen, Dissolved	None	mg/L	6.17	=	None
		RWB7_Trend_2009 RWB7_Trend_2009			1					Oxygen, Dissolved Oxygen, Saturation	None None	•	6.17 72.6	= =	None None
723NRBDRY	28/Apr/2009		15:15	Field	1 1 1	0.1	m	samplewater		Oxygen, Saturation		%			
723NRBDRY 723NRBDRY	28/Apr/2009 28/Apr/2009	RWB7_Trend_2009	15:15 15:15	Field Field	1 1 1 1	0.1 0.1	m m	samplewater samplewater	FieldMeasure	Oxygen, Saturation pH	None	% none	72.6	=	None
723NRBDRY 723NRBDRY 723NRBDRY	28/Apr/2009 28/Apr/2009 28/Apr/2009	RWB7_Trend_2009 RWB7_Trend_2009	15:15 15:15 15:15	Field Field Field	1 1 1 1 1	0.1 0.1 0.1	m m m	samplewater samplewater samplewater	FieldMeasure FieldMeasure FieldMeasure	Oxygen, Saturation pH	None None None	% none	72.6 7.48	=	None None
723NRBDRY 723NRBDRY 723NRBDRY 723NRBDRY	28/Apr/2009 28/Apr/2009 28/Apr/2009 28/Apr/2009	RWB7_Trend_2009 RWB7_Trend_2009 RWB7_Trend_2009	15:15 15:15 15:15 15:15	Field Field Field Field	1 1 1 1 1 1	0.1 0.1 0.1	m m m m	samplewater samplewater samplewater samplewater	FieldMeasure FieldMeasure FieldMeasure	Oxygen, Saturation pH Salinity SpecificConductivity	None None None	% none ppt	72.6 7.48 3.20	= = =	None None None

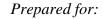
^{*}Fields shown are the minimum required fields for loading data into CEDEN.

The complete list of fields can be found through the CEDEN website:

http://www.ceden.org/ceden_datatemplates.shtml#guidance

D - 3

Peninsula CIMP Appendix E City of Rolling Hills Non-Stormwater Screening and Monitoring Program





2 Portuguese Bend Road Rolling Hills, CA 90274

City of Rolling Hills

Non-Storm Water Screening and Monitoring Program

Prepared by:



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Attachment A: Screening Locations

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1. INTRODUCTION

The 2012 Municipal Separate Storm Sewer System (MS4) Permit¹ (Permit) requires the City of Rolling Hills (City) to develop a Monitoring and Reporting Program (MRP) to accomplish the following primary objectives:

- 1. Assess the chemical, physical, and biological impacts of discharges from the MS4 on receiving waters.
- 2. Assess compliance with receiving water limitations (RWLs) and water quality-based effluent limitations (WQBELs) established to implement Total Maximum Daily Load (TMDL) wet-weather and dry-weather waste load allocations (WLAs).
- 3. Characterize pollutant loads in MS4 discharges.
- 4. Identify sources of pollutants in MS4 discharges.
- 5. Measure and improve the effectiveness of pollutant controls implemented under the Permit.

To achieve these objectives in a cost efficient and effective manner, the Permit allows Permittees to coordinate monitoring efforts on a watershed or subwatershed basis by developing a Coordinated Integrated Monitoring Program (CIMP). Although the City has decided not to participate in the development of an enhanced watershed management program (EWMP), the City submitted a letter of intent to the Los Angeles Regional Water Quality Control Board (Regional Board) on June 27, 2013 stating the City's intent to collaborate with the Palos Verdes Peninsula agencies² to develop a CIMP in accordance with the requirements of the Permit (Peninsula CIMP).

County Flood Control District.

¹ Order No. R4-2012-0175 NPDES Permit No. CAS004001 Waste Discharge Requirements for Municipal Separate Storm Sewer System (MS4) Discharges within the Coastal Watersheds of Los Angeles County, except those Discharges Originating from the City of Long Beach MS4.

² The Palos Verdes Peninsula agencies include the City of Rolling Hills, City of Rancho Palos Verdes, City of Palos Verdes Estates, City of Rolling Hills Estates, County of Los Angeles, and the Los Angeles



Because the City has chosen not to participate in an EWMP, they are required to develop an integrated monitoring plan addressing any monitoring requirements that will not be addressed by the Peninsula CIMP (i.e., those monitoring requirements which they intend to implement individually), per Attachment E, Part IV.C.2 of the Permit.

This report has been drafted to serve as the individual integrated monitoring plan for the City. As discussed in the August 22, 2013 meeting between the City and Regional Board, this integrated monitoring plan includes the following:

- 1. Non-storm water screening and monitoring plan, including the information identified in Part VII.A and IX of Attachment E of the Permit; and
- 2. A description and documentation of all ongoing TMDL compliance monitoring conducted by the City individually or in coordination with other agencies and confirmation that the TMDL compliance monitoring will continue uninterrupted during the development and approval of the CIMP.

All other MS4 Permit monitoring requirements will be addressed by the City's participation in the Peninsula CIMP, which was submitted to the Regional Board on June 27, 2014 and the City's participation in the Coordinated Compliance Monitoring Plan for the Greater Los Angeles Harbor Waters Toxic Pollutants TMDL monitoring which is also incorporated by reference in the Peninsula CIMP. A December 5, 2013 letter from the Regional Board to the City confirms the Regional Board's agreement with this approach.

2. NON-STORM WATER SCREENING AND MONITORING

This Non-Storm water Screening and Monitoring program provides a detailed approach to screening and identifying significant non-storm water discharges from the City of Rolling Hills to address Permit requirements in Attachment E Part IX A through F. The Peninsula CIMP is referenced to address how any significant non-storm water discharges that cannot be eliminated will be monitored to address the non-storm water monitoring requirements in Permit Attachment E Part IX G and H.

2.1 Background

The City of Rolling Hills is a uniquely developed community, being composed entirely of low-density, single family residential homes on large lots and lacking a continuous improved storm drain system throughout the City. The City is by design a low density, low impact, rural residential community with primary drainage conveyed via natural canyons. Roadways are narrow with soft shoulders (no curb-and-gutter). Dry weather



flows and small rainfall events are infiltrated within the natural soft-bottom canyons which serve as the primary drainage system. Storm water from private property drains into these largely undisturbed, heavily vegetated, soft-bottom canyons.

This lack of a developed storm drain system within the City, coupled with the particular attention given to the monitoring of "major outfalls" in the Permit, means that the City's Non-Storm Water Outfall Monitoring Program must be adapted to this unique situation. The City will therefore focus non-storm water screening efforts on the natural canyons that serve as the primary drainage network in the City. The term "outfall," as used by the Permit and applied to the City, will refer to the selected screening/monitoring locations within the City's canyons that are described in this plan.

The City's Non-Storm Water Outfall Screening and Monitoring Program integrated with the Peninsula CIMP has been prepared to meet the specific objectives outlined in Part IX.A of Attachment E of the Permit:

- 1. To identify non-exempt non-storm water discharges or conditionally exempt non-storm water discharges³ from the City's canyons, so that such discharges may be eliminated or effectively controlled in accordance with City's illicit connection/illicit discharge (IC/ID) program; and
- 2. To assess whether such non-storm water discharges are causing or contributing to exceedances of applicable receiving water limits to be evaluated through implementation of Section 2 of the Peninsula CIMP.

2.2 <u>Canyon Screening and Identifying Canyons with Significant Non-Storm Water Discharges</u>

The MS4 Permit requires Permittees to "identify MS4 outfalls with significant non-storm water discharges" within their jurisdiction. To accomplish this, the City will conduct a field screening of pre-determined "major canyons" to visually observe whether non-storm water discharges are present in significant amounts. "Major canyons" are defined as canyons within the City which drain at least 50 acres⁴ of land within the City's jurisdiction. Canyons which are known to contain natural flows on a

³ These discharges are defined in Section III.A of the Permit and have been codified in Chapter 8.32 of the City's Municipal Code.

⁴ Attachment A of the Permit similarly uses a drainage area of 50 acres as the threshold to define a major outfall.



regular basis (e.g., canyons fed by a perennial spring), as determined by historic observations and review of the USGS National Hydrograph Dataset, will not be screened directly as part of the non-storm water monitoring program; however, the results of screening in the other canyons will be used to consider whether similar non-storm water discharges could also discharge to the canyons with natural flow and will be investigated through the City's Illicit Discharge Elimination Program and results received from dry weather receiving water monitoring through the Peninsula CIMP. These canyons known to contain natural flows include Sepulveda Canyon, George F. Canyon, Bent Springs Canyon, and Klondike Canyon.

Five major canyons have been identified for screening within the City: Aqua Magna Canyon (including Johns Canyon), Blackwater Canyon, Purple Canyon, Paintbrush Canyon, and an unnamed canyon near the southeast corner of the City (hereinafter called "Unnamed Canyon 1"). Aqua Magna Canyon and Blackwater Canyon are within the Machado Lake Watershed; Purple Canyon is within the Greater LA Harbor Watershed; and Paintbrush Canyon and Unnamed Canyon 1 is within the Santa Monica Bay Watershed. These major canyons are shown on Figure 1.

These five canyons will be screened four times during dry weather spaced out over a twelve-month period. The first two screening events will occur within the 2014-15 reporting year, with the goal of conducting the first screening event in late summer/early fall of 2014 prior to the rainy season, then conducting the second screening in early spring following two months of dry weather subsequent to the rainy season. Two additional screenings will be conducted during early summer and late summer prior to the onset of the 2015-16 rainy season. An example schedule thus described could be achieved with screenings in: September 2014, May 2015, July 2015, and September 2015.

Screening will be conducted at specific locations near the downstream end of each major canyon. Screening locations for each canyon have been selected based on a desktop evaluation and general familiarity with the City's terrain. Factors considered in selection included accessibility/safety, proximity to City boundary, and ability to adequately observe the presence/absence of flows. These screening locations are shown on Figure 1; photos and brief descriptions of these locations are provided in Attachment A. It is important to note that these locations may be altered if it is determined by field personnel that adequate observations cannot be made safely. In such cases, field personnel will note the reason for the alteration as well as the new location selected. If necessary, new locations will be considered outside of the City's boundary farther towards the bottom of canyons, with reasonable attempts being made to get as near to the City boundary as possible.



For each screened major canyon, field personnel will determine if significant non-storm water discharges are present. Attachment E of the Permit provides examples of various characteristics that may be used to determine if discharges are considered significant. Due to the uniqueness of the City's storm water infrastructure, observed measurable flows that are not known to be naturally occurring will be defined as significant non-storm water discharges for the sake of this screening.

If, after four dry weather screenings, no significant non-storm water discharges are present at a particular monitoring location, no further action is necessary under this Plan.

A field data sheet (Attachment B) will be completed by field personnel at each screening location to assist in the development of an inventory of the screened canyons.

2.3 Inventory of Monitored Canyons

An inventory of the screened canyons will be developed following the screening, identifying those canyons with observed significant non-storm water discharges and those requiring no further assessment (Part IX.D of Attachment E of the Permit). For canyons requiring no further assessment, the inventory will include the justification of this determination (e.g., the canyon does not have observed measurable flow).

To gather necessary information of each major canyon to be used in the City's inventory, a field data sheet will be filled out for each major canyon. A blank field data sheet has been provided in Attachment B, which includes the minimum attributes listed in Part IX.D.2 of Attachment E.

Collected data will be incorporated into an electronic inventory which the City will maintain. Updates to the inventory will occur at least once a year, as necessary.

2.4 Prioritization of Monitored Canyons

Part IX.E.1 of Attachment E of the Permit requires that identified outfalls with significant non-storm water discharges be prioritized according to the following:

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⁵ Measurable flows are defined as active flows that continue beyond the City boundary or line of sight (if upstream of the City boundary). Ponded water, wetted soil, or flows that dry up within the City's boundary are not considered significant discharges since they do not leave the City.



- a. Outfalls discharging directly to receiving waters with water quality based effluent limitations (WQBELs) or receiving water limitations in the TMDL provisions for which final compliance deadlines have passed.
- b. All major outfalls and other outfalls that discharge to a receiving water subject to a TMDL shall be prioritized according to TMDL compliance schedules.
- c. Outfalls for which monitoring data exist and indicate recurring exceedances of one or more of the Action Levels identified in Attachment G of the MS4 Permit.
- d. All other major outfalls identified to have significant non-storm water discharges.

Due to the limited number of major canyons within the City, such a prioritization is not necessary at this time. Additionally, based on current information, all major canyons in the City would qualify as "Priority b" if significant non-storm water discharges are observed.

Following the screening of the major canyons, a source identification schedule will be developed to ensure that source investigations are conducted on no less than 25% of the major canyons with significant non-storm water discharges by December 28, 2015, and 100% by December 28, 2016. Depending on the nature and origin of any significant sources that are identified, additional time may be required to fully identify and characterize the sources.

2.5 **Source Identification**

A source investigation is required for major canyons identified to have significant non-storm water discharges to ascertain the source(s) and point(s) of origin of the non-storm water discharge(s).

Due to the unique nature of the City and the lack of man-made storm water infrastructure, conducting source investigations within the major canyons of the City presents numerous challenges. As a result, the process the City will follow to conduct these source investigations will be a fluid one, changing as necessary based on the specifics of the observed discharge. In most cases, the procedure will be to walk the canyon under investigation, beginning at the downstream end and walking upstream to attempt to locate the source of flow. In some locations, canyon access is impossible due to characteristics such as steep grades or the presence of poison oak. In these instances, the City will attempt to gain safe access from other locations in the canyon, or at the very least observe the canyon from additional viewing points, in an attempt to identify



the source of discharge. In cases where private access is required, the City will obtain appropriate access permission before proceeding.

Significant non-storm water flows will be classified into one of these three categories:

- A. <u>Illicit discharges:</u> If the source is determined to be an illicit discharge, the City will follow procedures outlined in its Illicit Discharge Elimination Program and appropriate documentation will be made regarding the source.
- B. Authorized or conditionally exempt essential non-storm water discharges: If the source is determined to be authorized per Chapter 8.32 of the City's Municipal Code, the source will be documented in the inventory and photographs of the source will be archived. Such findings will be reported each year in the City's annual report. In order to identify potential non-storm water discharges authorized by an individual or general NPDES Permit, the City will consult the State's Stormwater Multiple Application and Report Tracking System (SMARTS) and will also seek assistance from Regional Board staff in identifying potential authorized discharges within the City not included in the SMARTS system.
- C. <u>Unknown sources:</u> If the source is unknown or is a conditionally exempt non-essential non-storm water discharge, the City will conduct monitoring consistent with Part IX.G of Attachment E of the Permit. The City will document the efforts undertaken to identify the source.

For cases where multiple sources are discovered within the same canyon, the City will attempt to quantify the relative contribution of each individual source, to the extent practicable. In the unlikely event that significant non-storm water discharges cannot be eliminated through the City's Illicit Discharge Elimination Program, and the discharges are not natural, authorized, or essential conditionally exempt discharges, then such discharges will be incorporated into the Peninsula CIMP non-storm water monitoring program.

2.6 Monitoring

If monitoring is required following the identification of significant non-storm water discharges, procedures for conducting monitoring consistent with those outlined in the Permit Attachment E, Section IX.G as described in Section 4.7 of the Peninsula CIMP will be followed. Such monitoring if required will be incorporated into the Peninsula CIMP Non-Stormwater Monitoring Program.



2.7 Reporting

The City will report the findings of this Non-Storm Water Screening and Monitoring Program in its annual report at the conclusion of the twelve months of screening and then annually as needed to report the results of Source Identification investigations. Included in the first annual report will be a spreadsheet database listing information accumulated through the screening for each location including but not limited to: receiving water, nearest receiving water monitoring station, drainage area tributary to the screening location in total and within Rolling Hills, dates of screening, etc. If any significant non-storm water discharges that cannot be eliminated are incorporated into the Peninsula CIMP non-storm water monitoring program, then reporting of that information will be included as part of the Peninsula CIMP annual report.

3. SUMMARY OF ONGOING TMDL COMPLIANCE MONITORING

On June 27, 2013 the City submitted a Letter of Intent to the Regional Board to participate in the development of a Coordinated Integrated Monitoring Program (CIMP) in collaboration with the Palos Verdes Peninsula watershed agencies. These agencies are part of Jurisdictional Group 7 with respect to the coordinated shoreline monitoring that currently exists under the Santa Monica Bay Beaches Bacteria TMDL. On December 5th 2013, the City received a letter from the Executive Officer confirming the City's participation in the Peninsula CIMP which was submitted on June 27, 2014 to meet the City's obligations for receiving water monitoring and storm water outfall monitoring. The following discussion summarizes ongoing TMDL compliance monitoring either conducted by the City individually or in coordination with other agencies that will continue until the Peninsula CIMP is approved. Upon approval of the Peninsula CIMP, these programs may be incorporated into the CIMP. Additional details for these programs can be found in the Peninsula CIMP.

3.1 Machado Lake Nutrient TMDL Monitoring for Palos Verdes Peninsula

The incorporated cities of the Palos Verdes Peninsula are conducting joint monitoring to meet the requirements of the *Machado Lake Eutrophic*, *Algae*, *Ammonia*, *and Odors* (*Nutrient*) *Total Maximum Daily Load* (TMDL) established by the Regional Board on May 1, 2008 (Resolution No. R08-006). This monitoring is being conducted in accordance with the *Palos Verdes Peninsula Coordinated Monitoring Plan* (CMP) approved by the Executive Officer of the Regional Board. Monitoring under the CMP began in August 2011. The first annual monitoring report with full analysis of the data was submitted by December 14, 2012, and the second report was submitted with the City's MS4 Permit Annual report by December 15, 2013.



3.2 Machado Lake Pesticides and PCBs Monitoring

The Executive Officer of the Regional Board conditionally approved the Palos Verdes Peninsula Coordinated Monitoring and Reporting Plan and Quality Assurance and Project Plan for the TMDL for Pesticides and PCBs in Machado Lake on August 2, 2013. The Peninsula Agencies' contractor conducting the Machado Lake Nutrient TMDL monitoring has been directed to expand the wet weather monitoring to include sampling and analysis of storm water-borne sediment for pesticides and PCBs in accordance with the approved plan. This was initiated during the 2013-14 reporting year; however, sufficient sediment was not collected from the single qualifying storm to conduct the pesticide and PCB analysis.

3.3 Santa Monica Bay Beaches Bacteria TMDL Monitoring

Monitoring under the Coordinated Shoreline Monitoring Plan in accordance with the Santa Monica Bay Beaches Bacteria TMDL is conducted on a weekly basis by the Sanitation Districts of Los Angeles County at nine shoreline monitoring locations along the Palos Verdes Peninsula (Jurisdictional Group 7). The data is reported directly to the Los Angeles Regional Water Quality Control Board such that annual monitoring reports are not currently being prepared by Jurisdictional Group 7.

Drainage from that portion of the City of Rolling Hills that drains toward the Santa Monica Bay is conveyed via natural soft bottom canyons (Klondike Canyon, Paint Brush Canyon, and several smaller unnamed canyons) across significant areas of open space for a distance of ½ mile to a mile before reaching improved storm drains operated by other agencies that outlet into Portuguese Bend. The shoreline monitoring location in Portuguese Bend, also known as SMB 7-5, is an open beach shoreline monitoring location on the Palos Verdes Peninsula that is considered to be an anti-degradation monitoring location, i.e., it has historically and continues to exhibit a lower rate of exceedances than the reference monitoring location at Leo Carillo Beach (reference beach). For a weekly sampling schedule, SMB 7-5 is allocated zero (0) single sample exceedances per year during summer dry weather (April 1 through October 31), one (1) exceedance per year during winter dry weather (November 1 through March 30), and one (1) exceedance per year during year-round wet weather (November 1 through October 31) of the indicator bacterial targets under the Santa Monica Bay Beaches Bacteria TMDL.

3.4 Machado Lake Trash TMDL Monitoring

The City of Rolling Hills has now completed a fourth year of monitoring in accordance with the Trash Monitoring and Reporting Plan and has submitted annual trash



monitoring reports along with its MS4 Permit Annual Report. Because the City of Rolling Hills does not have a storm drain system that is amenable to the installation of full capture devices, it has implemented a Trash Monitoring and Reporting Plan (TMRP) which includes a Minimum Frequency of Assessment and Collection Program (MFAC) in conjunction with Best Management Practices (BMPs) in order to achieve compliance with the Machado Lake Trash TMDL. The results obtained through implementation of the City's approved TMRP indicate an effective implementation of existing institutional and source controls such as weekly collection of trash (with additional pickup as needed) along roads and equestrian trails by the Rolling Hills Community Association (RHCA) maintenance crew, strict enforcement of litter laws, enforcement of ordinances requiring solid waste enclosures, and close oversight of the solid waste hauler. The collected data demonstrates that the City has reduced its generated trash by 100% from its baseline of 7,004 gallons of trash per year through its current BMP program.

3.5 Santa Monica Bay Debris TMDL Monitoring

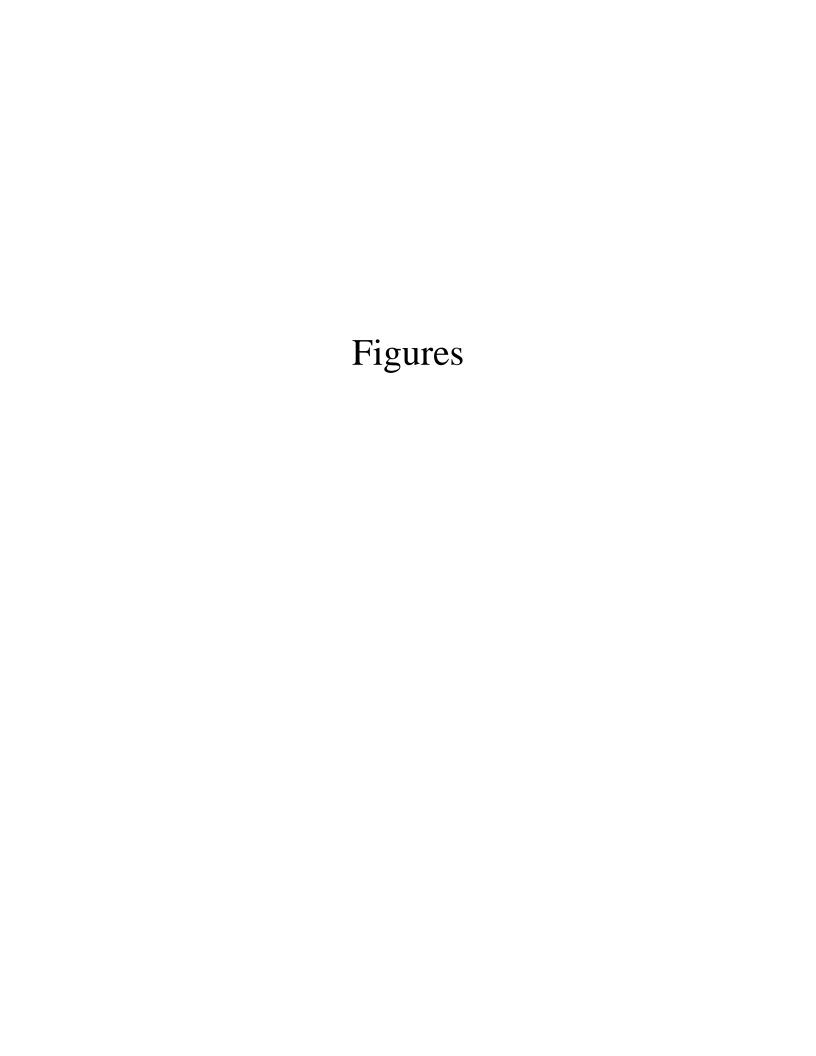
On September 3, 2013, the Executive Officer of the Regional Board approved the City of Rolling Hills' proposed approach to address the trash monitoring and reporting requirements for the Santa Monica Bay Nearshore and Offshore Debris TMDL. The City will utilize BMPs and institutional controls currently in effect to address the Machado Lake Trash TMDL which have demonstrated 100% reduction in the City's baseline trash generation rate. The City of Rolling Hills will utilize the Machado Lake Trash TMRP and resulting monitoring data to demonstrate compliance with the Santa Monica Bay Nearshore and Offshore Debris TMDL. A separate monitoring report is to be submitted by the City according to the implementation schedule for the Santa Monica Bay Nearshore and Offshore Debris TMDL using the data obtained from the Machado Lake TMRP.

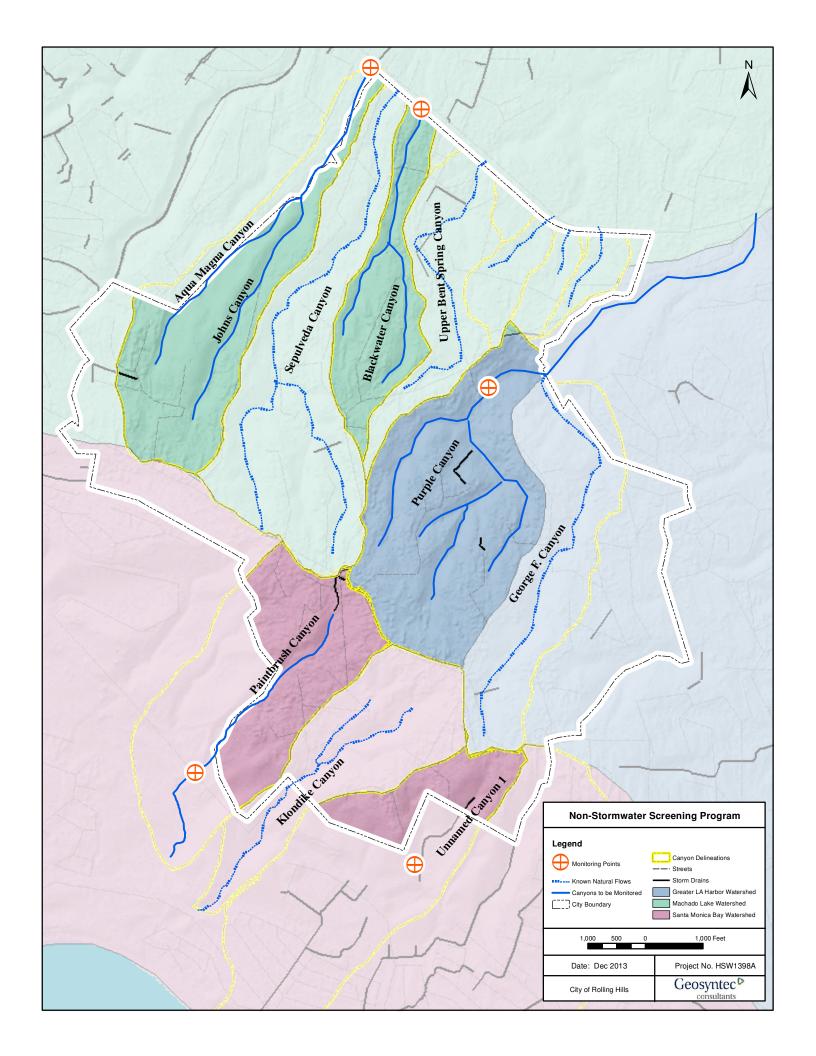
3.6 Greater Los Angeles Harbor Waters Toxic Pollutants TMDL Monitoring

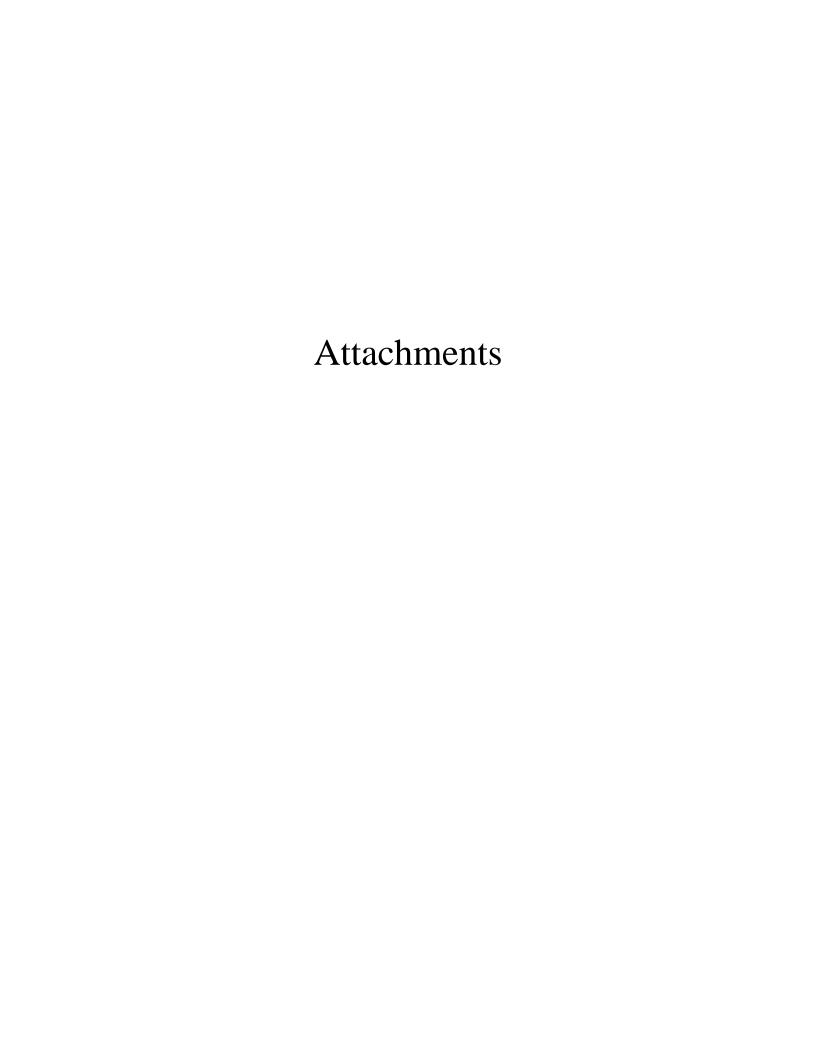
Receiving water monitoring in the Greater Los Angeles and Long Beach Harbors consistent with the TMDL for Toxic Pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbors is being conducted through a Coordinated Compliance Monitoring and Reporting Plan approved by the Executive Officer of the Regional Board on June 6, 2014. The City of Rolling Hills has entered into a Memorandum of Understanding (MOU) with the Los Angeles Gateway Integrated Regional Water Management Joint Powers Authority along with a group of other responsible agencies to implement the Coordinated Compliance Monitoring Plan



approved by the Executive Officer. Receiving water monitoring under the plan began in the summer of 2013 as part of the Bight regional monitoring program.







Attachment A: Screening Locations

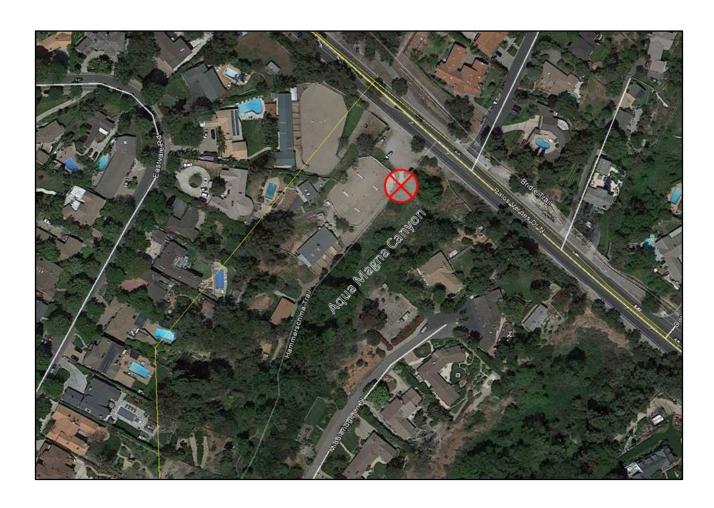


Non-Storm Water Screening and Monitoring Program Monitoring Locations

Monitoring Location ID: Agua Magna Canyon #1 Latitude: 33° 46' 45.8 N

Longitude: 118° 20' 54.5 W

Monitoring Location Description: Agua Magna Canyon intersects Palos Verdes Dr North, after which it continues underground until the botanic garden. Hammerschma Trail, which is outside the City boundaries, runs along the canyon until it merges with John's Canyon Trail. Monitoring will initially be conducted near the intersection of the canyon and Palos Verdes Dr North. The beginning of Hammerschma Trail provides a good view point to monitor the canyon. However, due to the possibility of contributions in this vicinity from outside the City boundaries, if flows are observed, Hammerschma Trail will be followed upstream to observe if the flows are in fact from the City.



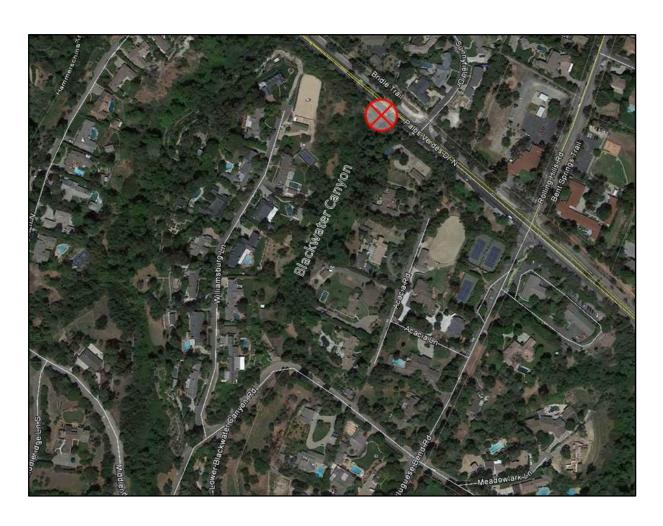


Non-Storm Water Screening and Monitoring Program Monitoring Locations

Monitoring Location ID: Blackwater Canyon #1 Latitude: 33° 46' 39.5 N

Longitude: 118° 20' 44.3 W

Monitoring Location Description: Like Agua Magna Canyon, Blackwater Canyon intersects Palos Verdes Dr North. Monitoring will initially be conducted at the intersection of the canyon and Palos Verdes Dr North. If observations cannot be made from Palos Verdes Dr North, Lower Blackwater Canyon Road provides another observation point upstream. From there, if flows are observed and need to be tracked, Blackwater Canyon Trail can be walked since it follows the canyon flow path.





Non-Storm Water Screening and Monitoring Program Monitoring Locations

Monitoring Location ID: Purple Canyon #1 Latitude: 33° 45' 46.6 N

Longitude: 118° 20' 34.5 W

Monitoring Location Description: Poppy Trail provides an optimal observation point to view Purple Canyon downstream of the confluence point, where multiple reaches of the canyon come together. If flows are observed, Lower Willow Springs Trail will allow for monitoring at the City border to determine if flows leave the City. Additionally, Sleepy Hollow Trail and Georgeff Trail provide access to track flow sources up Purple Canyon.



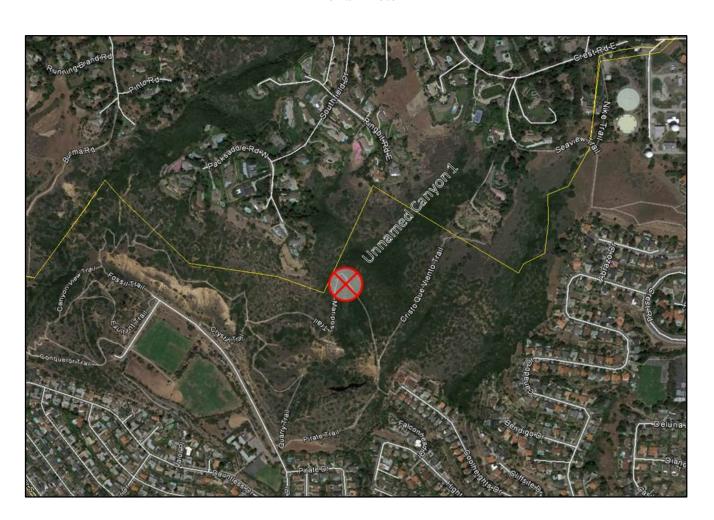


Non-Storm Water Screening and Monitoring Program Monitoring Locations

Monitoring Location ID: Unnamed Canyon 1 #1 Latitude: 33° 44' 33.3 N

Longitude: 118° 20' 43.6 W

Monitoring Location Description: Unnamed Canyon 1 is located near the southeast corner of the City boundary. The canyon is difficult to reach from the City, but can be accessed from hiking trails to the south. In particular, Mariposa Trail provides access to a point near the bottom of the canyon. The canyon is likely too steep to hike for source tracking purposes, so if such tracking is required, this will most likely be done on the various residential roads in the vicinity.



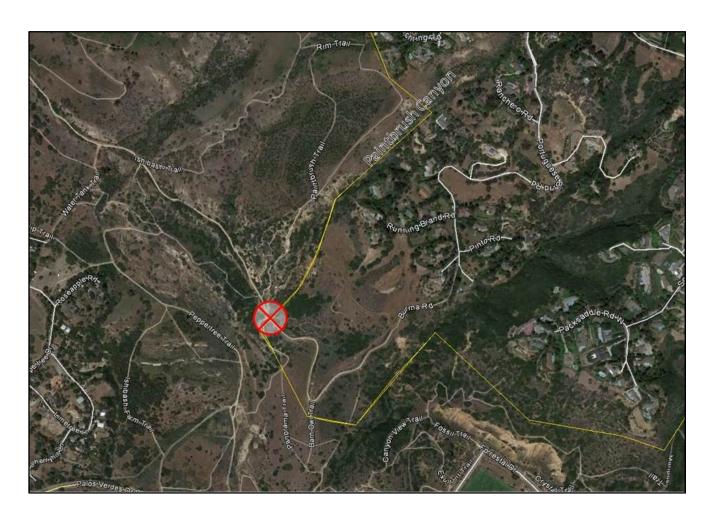


Non-Storm Water Screening and Monitoring Program Monitoring Locations

Monitoring Location ID: Paintbrush Canyon #1 Latitude: 33° 44' 44.4 N

Longitude: 118° 21' 30.5 W

Monitoring Location Description: Like Unnamed Canyon 1, Paintbrush Canyon is a challenge to assess from the City. However, a variety of trails near the outlet of the canyon make for easy access from the downstream end. In particular, Burma Road crosses the canyon's mouth immediately downstream of the City boundary. This road can be accessed on foot from a variety of trails (e.g., Panorama Trail). A trailhead is located off of Palos Verdes Dr South.



Attachment B:

Field Data Sheet



Non-Storm Water Screening and Monitoring Program

Field Data Sheet

	Page of
Inspector:	Date:
Monitoring Location:	Arrival Time:
Nearest accessible street address:	
Downstream Receiving Water:	Nearest Receiving Water Monitoring Site:
☐ Santa Monica Bay	
☐ Machado Lake	
☐ Los Angeles Harbor	
Sky: Stormy, Overcast, Partial clouds, Haze, Fog, Clear	Wind: Calm, Light breeze, Strong breeze, Windy, Gusty
Non-Storm Water Discharge Observed? Yes / No	If no discharge was there:
Approximate Depth of Flow:	_ □ Wetted soil
Approximate Width of Flow:	_ Donding
Approximate Flow Rate:	feet
Sources of Non-Storm Water Discharge Observa	ble? Yes / No
If Yes, Provide Description:	
Other Noticeable Characteristics of Flow (circ	le those that apply):
Odor: None, Musty, Sewage, Rotten	Egg, Sour milk, Fishy, Other:
Color: None, Yellow, Brown, Grey,	Green, Red, Other:
Clarity: Clear, Cloudy, Opaque, Susp	pended solids, Other:
Floatable/Settleable Solids: None, Oil s Food, Paper, Plastic, Grease, Hydrop	sheen, Foam, Animal waste, Green waste, hytes, Trash, Other:
Weeds: None, Normal, Excessive, No	ote:
Biology: None, Algae bloom, Larvae, Hydrophytes, Blue-green algae, Other:	Crawfish, Frogs, Fish, Waterfowl,

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Peninsula CIMP Appendix F LACFCD Background Information

Appendix F Los Angeles County Flood Control District Background Information

LACFCD Background Information

In 1915, the Los Angeles County Flood Control Act established the LACFCD and empowered it to manage flood risk and conserve stormwater for groundwater recharge. In coordination with the United States Army Corps of Engineers the LACFCD developed and constructed a comprehensive system that provides for the regulation and control of flood waters through the use of reservoirs and flood channels. The system also controls debris, collects surface storm water from streets, and replenishes groundwater with storm water and imported and recycled waters. The LACFCD covers the 2,753 square-mile portion of Los Angeles County south of the east-west projection of Avenue S, excluding Catalina Island. It is a special district governed by the County of Los Angeles Board of Supervisors, and its functions are carried out by the Los Angeles County Department of Public Works. The LACFCD service area is shown in **Figure F-1.**

Unlike cities and counties, the LACFCD does not own or operate any municipal sanitary sewer systems, public streets, roads, or highways. The LACFCD operates and maintains storm drains and other appurtenant drainage infrastructure within its service area. The LACFCD has no planning, zoning, development permitting, or other land use authority within its service area. The permittees that have such land use authority are responsible under the Permit for inspecting and controlling pollutants from industrial and commercial facilities, development projects, and development construction sites. (Permit, Part II.E, p. 17.)

The MS4 Permit language clarifies the unique role of the LACFCD in storm water management programs: "[g]iven the LACFCD's limited land use authority, it is appropriate for the LACFCD to have a separate and uniquely-tailored storm water management program. Accordingly, the storm water management program minimum control measures imposed on the LACFCD in Part VI.D of this Order differ in some ways from the minimum control measures imposed on other Permittees. Namely, aside from its own properties and facilities, the LACFCD is not subject to the Industrial/Commercial Facilities Program, the Planning and Land Development Program, and the Development Construction Program. However, as a discharger of storm and non-storm water, the LACFCD remains subject to the Public Information and Participation Program and the Illicit Connections and Illicit Discharges Elimination Program. Further, as the owner and operator of certain properties, facilities and infrastructure, the LACFCD remains subject to requirements of a Public Agency Activities Program." (Permit, Part II.F, p. 18.)

Consistent with the role and responsibilities of the LACFCD under the Permit, the [E]WMPs and CIMPs reflect the opportunities that are available for the LACFCD to collaborate with permittees having land use authority over the subject watershed area. In some instances, the opportunities are minimal, however the LACFCD remains responsible for compliance with certain aspects of the MS4 permit as discussed above.

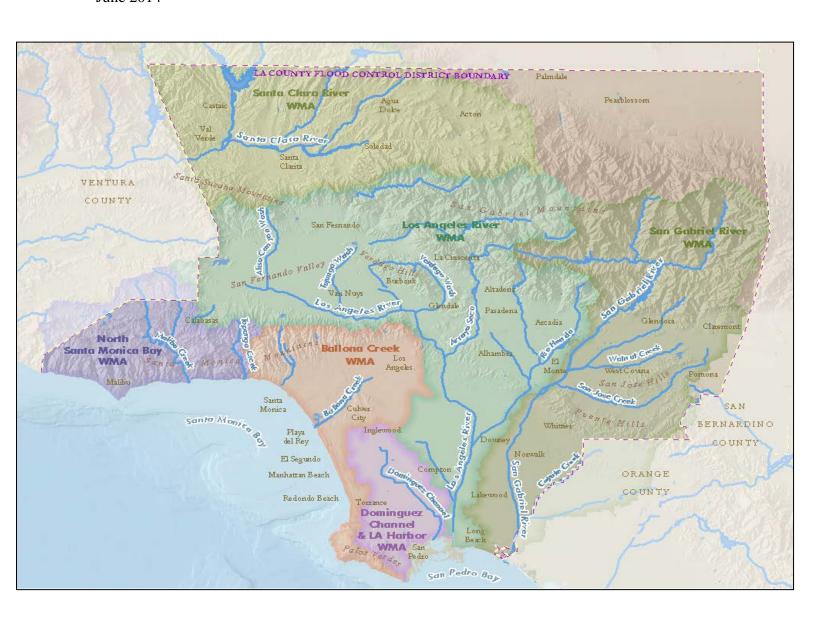


Figure F-1 Los Angeles County Flood Control District Service Area

Peninsula CIMP Appendix G
Coordinated Compliance Monitoring and
Reporting Plan Incorporating Quality
Assurance Project Plan Components for
Greater LA and LB Harbor Waters

COORDINATED COMPLIANCE MONITORING AND REPORTING PLAN

INCORPORATING QUALITY ASSURANCE PROJECT PLAN COMPONENTS

GREATER LOS ANGELES AND LONG BEACH HARBOR WATERS

Prepared for

California Department of Transportation

Cities of Bellflower, Lakewood, Long Beach, Los Angeles, Paramount, Rancho Palos Verdes,

Rolling Hills, Rolling Hills Estates, and Signal Hill

Los Angeles County

Los Angeles County Flood Control District

Ports of Long Beach and Los Angeles

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TITLE AND APPROVAL SHEETS (ELEMENT A1)

Coordinated Compliance, Monitoring, and Reporting Plan incorporating Quality Assurance Project Plan Components related the Greater Los Angeles and Long Beach Harbor Waters

Approval sheets are included in the PQAPP.

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LIST OF ACRONYMS AND ABBREVIATIONS

ADR Automated Data Review

Bight Program Southern California Bight Regional Monitoring Program

BRI Benthic Response Index

CA LRM California Logistic Regression Model

Caltrans California Department of Transportation

CCMRP Coordinated Compliance, Monitoring, and Reporting Plan

CDFW California Department of Fish and Wildlife

cm centimeter

COC chain-of-custody

COPC contaminant of potential concern

CSI Chemical Score Index

CTR California Toxics Rule

CWA Clean Water Act

DGPS Differential Global Positioning System

DO dissolved oxygen

DQO Data Quality Objectives

eCOC electronic chain-of-custody

EDD Electronic Data Deliverable

EDL estimated detection limit

ELAP Environmental Laboratory Accreditation Program

ERL effects range low

ERM effects range median

FCEC Fish Contamination Education Collaborative

FCG fish contamination goals

Greater Harbor Waters Greater Los Angeles and Long Beach Harbor Waters (including

Consolidated Slip)

Harbor Toxics TMDL Total Maximum Daily Load for Toxic Pollutants in Dominguez

Channel and Greater Los Angeles and Long Beach Harbor

Waters

HDPE high density polyethylene

IBI Index of Biotic Integrity

IDL Interactive Data Language

ITP Incidental Take Permit

LA load allocation

LOD limit of detection

LOE lines of evidence

MBC Applied Environmental Sciences

MDL method detection limit

MEC MEC Analytical

MLLW mean lower low water

MLOE multiple lines of evidence

mm millimeter

MPSL-DFG Marine Pollution Studies Laboratory – Department of Fish and

Game

MRL method reporting limit

MS4 Municipal Separate Storm Sewer Systems

NAD83 North American Datum 1983

NLAP National Environmental Laboratory Accreditation Program

NOAA National Oceanic and Atmospheric Administration

NPDES National Pollutant Discharge Elimination System

OEHHA Office of Environmental Health Hazard Assessment

Order Waste Discharge Requirements for Municipal Separate Storm

Sewer Systems Discharges within the Coastal Watersheds of Los Angeles County, Except Those Discharges Originating from the

City of Long Beach MS4

PAH polycyclic aromatic hydrocarbon

PCB polychlorinated biphenyl

PQAPP Programmatic Quality Assurance Project Plan

PTFE polytetrafluoroethylene

QA quality assurance

QAPP Quality Assurance Project Plan

QC quality control

RBI Relative Benthic Index

RIVPACS River Invertebrate Prediction and Classification System

RMC Regional Monitoring Coalition

RWQCB Los Angeles Regional Water Quality Control Board

SAIC Science Applications International Corporation

SAP Sampling and Analysis Plan

SCAMIT Southern California Association of Marine Invertebrate

Taxonomists

SCB Southern California Bight

SCCWRP Southern California Coastal Water Research Project

SOP Standard Operating Procedure

SQO Sediment Quality Objective

SQV sediment quality value

SRM standard reference materials

SWAMP Surface Water Ambient Monitoring Program

SWI sediment-water interface

T/E threatened or endangered

TIE Toxicity Identification Evaluation

TIWRP Terminal Island Water Reclamation Plant

TMDL total maximum daily load

TOC total organic carbon
TSS total suspended solid

USEPA U.S. Environmental Protection Agency

WLA

waste load allocation

FORWARD/DOCUMENT ORGANIZATION

The Coordinated Compliance, Monitoring, and Reporting Plan (CCMRP) is developed to be consistent with other California state and regional monitoring programs, as well as other plans developed to support the *Total Maximum Daily Load for Toxic Pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters* (Harbor Toxics TMDL). These programs, including California's Surface Water Ambient Monitoring Program (SWAMP), California's Sediment Quality Objectives (SQO), and the Southern California Bight Regional Monitoring Program (Bight Program), as well as a supplemental Programmatic Quality Assurance Project Plan (PQAPP), are described in greater detail below, and provide the foundation for work to be undertaken as part of this CCMRP.

Surface Water Ambient Monitoring Program

SWAMP is a coordinated, statewide umbrella program that integrates water quality monitoring performed under the State Water Regional Control Board and Regional Water Quality Control Boards, as well as other agencies, dischargers, and private groups. SWAMP provides a consistent approach to sampling, data analysis, quality assurance, and data management. Detailed methods and procedures outlined by SWAMP promote statewide data comparability and will be widely utilized in monitoring conducted for the Harbor Toxics TMDL program.

Sediment Quality Objectives Program

The SQO program provides guidance for the application of the *Water Quality Control Plan for Enclosed Bays and Estuaries – Part I Sediment Quality* (SWRCB 2009). SQOs have been developed for contaminants of concern in bays and estuaries in California based on an approach that incorporates multiple lines of evidence (MLOE; Bay et al. 2009). These MLOE include sediment chemistry, sediment toxicity, and benthic community composition. Further information is provided below. This CCMRP calls for the use of the SQO program to aid implementation of the Harbor Toxics TMDL program.

Sediment Chemistry Line of Evidence

The chemistry line of evidence (LOE) requires chemical analysis of a suite of constituents. Two indices are used to interpret the results: the California Logistic Regression Model (CA LRM) and the Chemical Score Index (CSI). Results produced by these indices are subsequently used to produce a single score representing the chemistry LOE.

Sediment Toxicity Line of Evidence

The toxicity LOE requires two toxicity tests: acute amphipod survival and a sub-lethal test (i.e., bivalve embryo development). The results of each test are compared to classification ranges (nontoxic, low toxicity, moderate toxicity, or high toxicity) and assigned a corresponding score. The two test scores are integrated to produce a single score for the toxicity LOE.

Benthic Community Line of Evidence

The benthic community LOE is comprised of enumerating and identifying organisms to species level (when possible) and evaluating results based on four indices: the Index of Biotic Integrity (IBI), the Relative Benthic Index (RBI), the Benthic Response Index (BRI), and the River Invertebrate Prediction and Classification System (RIVPACS). The four indices are weighted together to provide an overall score for the benthic community LOE.

Integration of Multiple Lines of Evidence

First, integration of MLOEs aids in determining two broad effects categories. The chemistry and toxicity LOEs are evaluated together to determine the potential for chemically-mediated effects; likewise, the toxicity and benthic community LOEs are combined to determine the severity of biological effects. Finally, integration of the two effects categories results in an overall station assessment in which the station is placed into one of six impact categories (unimpacted, likely unimpacted, possibly impacted, likely impacted, clearly impacted, or inconclusive).

Southern California Bight Regional Monitoring Program

The Southern California Bight (SCB) is the approximate 400 miles of coastline from Point Conception in Santa Barbara County to Cabo Colnett in Ensenada, Mexico. The Southern California Coastal Water Research Project (SCCWRP) coordinates an extensive monitoring program within the SCB approximately every 5 years. The Bight program began in 1994 and data gathered during monitoring events has allowed for long-term tracking of benthic communities, fisheries, water quality, sediment chemistry and toxicity, and the general health of the SCB over time. This complex program incorporates multiple agencies and organizations, and, as such, a series of guidance documents for field data collection, laboratory analyses, quality assurance, and data management have been created for each monitoring event. The most recent monitoring event occurred in 2008, and associated guidance is referenced and utilized in this CCMRP.

Programmatic Quality Assurance Project Plan

A PQAPP (Anchor QEA 2013) was developed to ensure high quality data collection as part of compliance monitoring and special studies required by and in support of the Harbor Toxics TMDL. The PQAPP includes the following key elements that focus on analytical methods and data generated during a project:

- Program management
- Field sampling data quality objectives
- Laboratory data quality objectives
- Data review, verification, and validation

Coordinated Compliance Monitoring and Reporting Plan

The PQAPP was not intended to adhere to all recommended elements of the SWAMP QAPP guidance document. This document, the CCMRP, and any other Sampling and Analysis Plans developed to support Harbor Toxics TMDL-related studies, incorporates all relevant PQAPP elements (e.g., *presented in italicized text throughout this document*) in addition to supplemental information specific to each study in order to develop a single, all-inclusive, monitoring plan compatible with SWAMP QAPP requirements.

The required elements of a SWAMP QAPP and their corresponding location in this CCMRP are listed in Table 1.

Table A SWAMP QAPP Elements and Corresponding CCMRP Sections

SWAMP QAPP			
Element	Element Title		
А	PROJECT MANAGEMENT		
A1	Title and Approval Sheet (s)	i	
A2	Table of Contents	ii	
A3	Distribution List	i	
A4	Project/Task Organization	2	
A5	Problem Definition/Background	1	
A6	Project/Task Description	3	
A7	Quality Objectives and Criteria	8	
A8	Special Training/Certifications	9	
A9	Documentation and Records	10	
В	DATA GENERATION AND ACQUISITION		
B01	Sampling Process Design (Sampling Design and Logistics)	4	
B02	Sampling (sample collection) Methods	5	
B03	Sample Handling and Custody	6	
B04	Analytical Methods and Field Measurements	7	
B05	Quality Control	11	
B06	Instrument/Equipment Testing, Inspection, and Maintenance	12	
B07	Instrument/Equipment Calibration and Frequency	13	
B08	Inspection/Acceptance for supplies and Consumables	14	
B09	Non-direct Measurements	15	
B10	Data Management	16	
С	ASSESSMENT AND OVERSIGHT		
C1	Assessments and Response Actions	17	
C2	Reports to Management	18	
D	DATA VALIDATION AND USABILITY		
D1	Data Review, Verification, and Validation	19	
D2	Verification and Validation Methods		
D3	Reconciliation with User Requirements	21	

EXECUTIVE SUMMARY

On March 23, 2012, the *Total Maximum Daily Load for Toxic Pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters* (Harbor Toxics TMDL) became effective and was promulgated to protect and restore fish tissue, water, and sediment quality in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters (including Consolidated Slip; Greater Harbor Waters) by remediating contaminated sediment and controlling the sediment loading and accumulation of contaminated sediment in the harbor.

Each named responsible party is required to conduct compliance monitoring activities; however, the Harbor Toxics TMDL encourages collaboration and coordination of monitoring efforts. This document is the Coordinated Compliance, Monitoring, and Reporting Plan (CCMRP) for the Greater Harbor Waters. Because the Greater Los Angeles and Long Beach Harbor Responsible Parties recommend a coordinated monitoring effort, all monitoring efforts are proposed to be located in receiving waters at a point that suitably represents the combined discharge of cooperating parties.

Compliance Monitoring Program

The monitoring program consists of the collection of water and sediment samples at a total of 22 stations (Table ES-1; Figure ES-1) and the collection of fish tissue samples within four waterbodies (Table ES-1; Figure ES-2). To maintain consistency and to take advantage of coordinated sampling efforts with other regional monitoring programs, sample collection methods will adhere to Bight or Surface Water Ambient Monitoring Program (SWAMP) monitoring protocols (BCEC 2008; and CDFG 2001).

Table ES-1
Station Locations

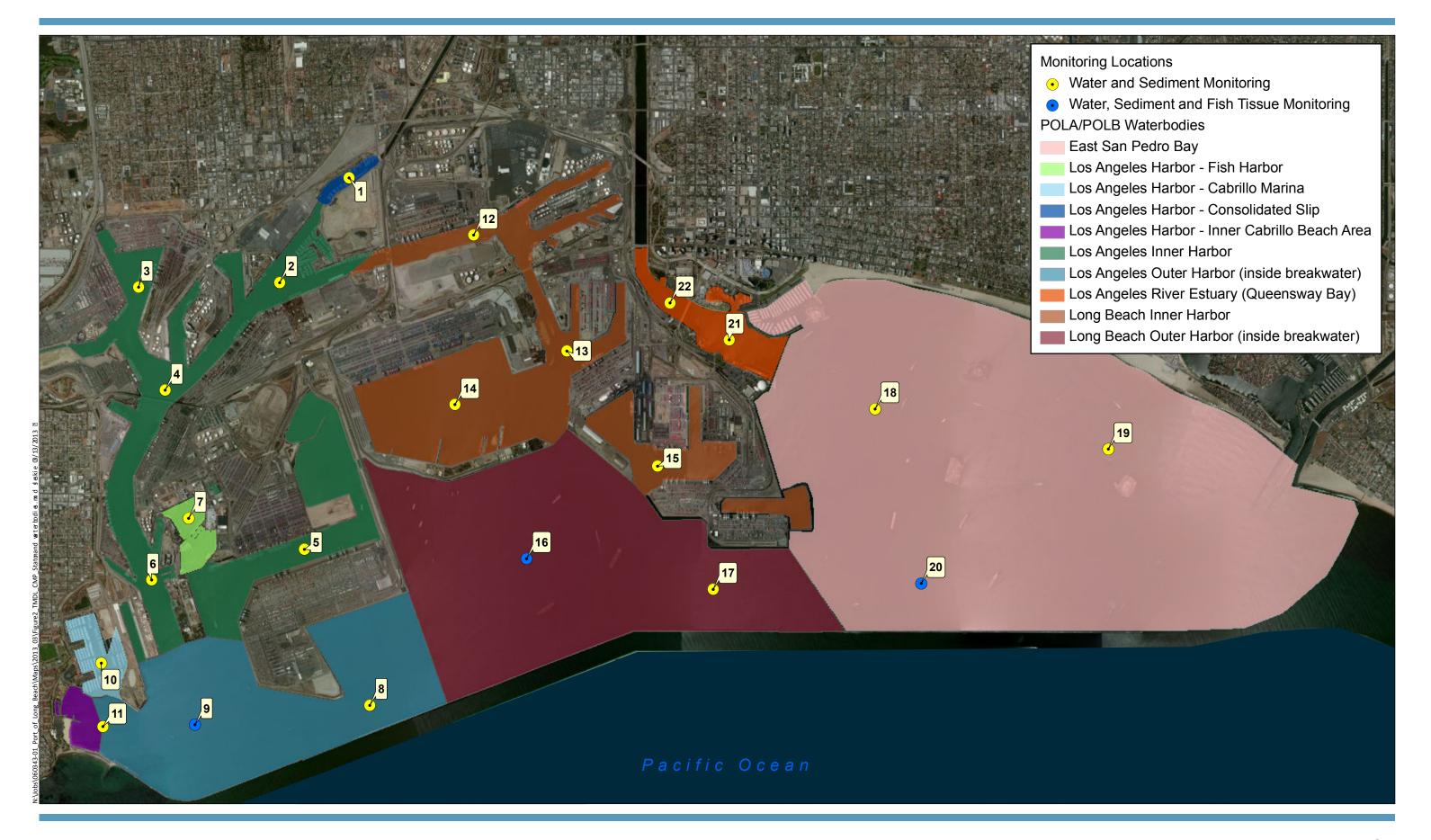
Waterbody Name	Station ID	Latitude (Decimal Degrees) WGS84	Longitude (Decimal Degrees) WGS84	Station Location
Consolidated Slip ¹	1	33.77484789	-118.2453739	Center of Consolidated Slip
	2	33.76489964	-118.2520890	East Turning Basin
	3	33.76228823	-118.2740995	Center of the Port of Los Angeles West Basin
Los Angeles Inner	4	33.75184257	-118.2709906	Main Turning Basin north of Vincent Thomas Bridge
Harbor	5	33.73244349	-118.2513428	Between Pier 300 and Pier 400
	6	33.72572842	-118.2714880	Main Channel south of Port O'Call
Fish Harbor	7	33.73580102	-118.2672600	Center of inner portion of Fish Harbor
	8	33.71466100	-118.2423894	Los Angeles Outer Harbor between Pier 400 and middle breakwater
Los Angeles Outer Harbor ¹	9	33.71204959	-118.2634051	Los Angeles Outer Harbor between the southern end of the reservation point and the San Pedro breakwater
Cabrillo Marina	10	33.71938642	-118.2790736	Center of West Channel
Inner Cabrillo Beach	11	33.71180088	-118.2810632	Center of Inner Cabrillo Beach
	12	33.76726235	-118.2335604	Cerritos Channel between the Heim Bridge and the Turning Basin
Long Beach Inner	13	33.75383222	-118.2163996	Back Channel between Turning Basin and West Basin
Harbor	14	33.74898245	-118.2308246	Center of West Basin
	15	33.74214303	-118.1994876	Center of Southeast Basin
Long Beach Outer	16	33.73144867	-118.2210007	Center of Long Beach Outer Harbor
Harbor ¹	17	33.72759372	-118.1860575	Between the southern end of Pier J and the Queens Gate
	18	33.75383222	-118.1813321	Northwest of San Pedro Bay near Los Angeles River Estuary
San Pedro Bay ¹	19	33.73667149	-118.1315908	East of San Pedro Bay
	20	33.72547972	-118.1573319	South of San Pedro Bay inside breakwater

Waterbody Name	Station ID	Latitude (Decimal Degrees) WGS84	Longitude (Decimal Degrees) WGS84	Station Location
Los Angeles River	21	33.75644363	-118.1933943	Los Angeles River Estuary Queensway Bay
Estuary	22	33.76101300	-118.2021110	Los Angeles River Estuary

Notes:

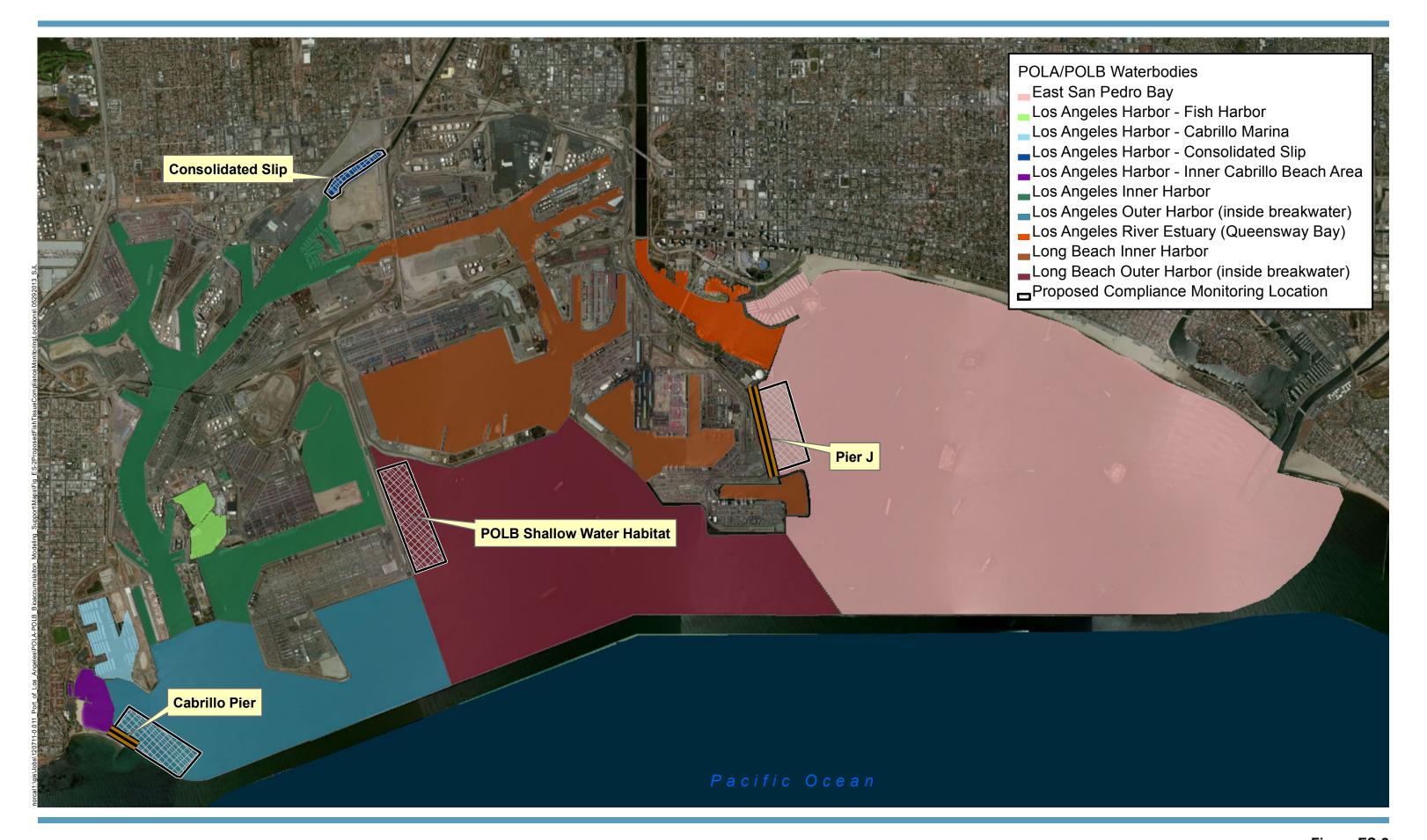
WGS84 = World Geodetic System 1984

¹ Fish tissue samples will be collected within four waterbodies: Consolidated Slip, Los Angeles Harbor, Long Beach Harbor, and San Pedro Bay, from popular fishing areas, or areas with habitat or structure that may attract fish. Specific fish tissue sampling locations will be determined at the time of the sampling event using guidelines outlined in Section 4.2.3.













Water

In situ water quality will be measured and water samples will be collected three times annually, two during wet weather events and one during a dry weather event at each of the 22 stations. The first large storm of the season will be targeted as one of the two wet weather events and will have a predicted rainfall of at least 0.25 inch (0.64 centimeter) with a 70 percent probability of rainfall at least 24 hours prior to the event start time. In situ measurements include temperature, dissolved oxygen, pH and salinity. Water samples will be collected and submitted for the following parameters:

- Total suspended solids (TSS)
- Dissolved and total metals
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene)
- Polychlorinated biphenyl (PCB) congeners

Flow will not be measured in receiving waters, because mixing and other hydrodynamic factors will confound the flow measurements.

Sediment

Sediment monitoring will be performed twice every 5 years at each of the 22 stations. Surface sediment grabs will be collected and submitted for chemistry, toxicity, and benthic community analyses in accordance with Sediment Quality Objectives (SQO) Part I sediment triad assessment. Sediment chemistry analyses will include the following parameters:

- Total organic carbon (TOC)
- Grain size
- Metals
- Polycyclic aromatic hydrocarbons (PAHs)
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene)
- PCB congeners

SQO sediment line of evidence (LOE) toxicity analyses will include an acute amphipod¹ survival test and the chronic, sub-lethal sediment-water interface (SWI) test using the bivalve, *Mytilus galloprovincialis*. Benthic community analyses will be conducted and benthic community condition will be measured using four indices: 1) IBI, 2) RBI, 3) BRI, and 4) RIVPACS.

Tissue

Fish tissue samples will be collected once every 2 years at only four stations: one in Consolidated Slip, one each in Los Angeles Outer Harbor and Long Beach Outer Harbor Outer Los Angeles and Long Beach Harbors, and one in (eastern) San Pedro Bay. Composite samples of three fish species (white croaker [Genyonemus lineatus], California halibut [Paralichthys californicus], and shiner surfperch [Cymatogaster aggregate]) will be collected at all stations, with the exception of Consolidated Slip; only white croaker will be collected at this station. Fish tissue samples will be submitted for the following parameters:

- Percent lipids
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene)
- PCB congeners

¹ Acceptable test species in accordance with SQO guidance (Bay et al. 2009) include *Eohaustorius estuarius*, *Leptocheirus plumulosus*, or *Rhepoxynius abronius*.

Coordinated Compliance Monitoring and Reporting Plan Greater Los Angeles and Long Beach Harbor Waters

1 PROBLEM DEFINITION AND BACKGROUND (ELEMENT A5)

1.1 Introduction

The *Total Maximum Daily Load for Toxic Pollutants in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters* (Harbor Toxics TMDL) became effective on March 23, 2012. The requirements of the Harbor Toxics TMDL are specified in Attachment A to Resolution No. R11-008, Amendment to the Water Quality Control Plan – Los Angeles Region (RWQCB 2011). The Harbor Toxics TMDL was promulgated to protect and restore fish tissue, water and sediment quality in Dominguez Channel and Greater Los Angeles and Long Beach Harbor Waters (including Consolidated Slip; Greater Harbor Waters).

1.2 Background

Section 303 (d)(1)(A) of the Clean Water Act (CWA) requires states to identify waterbodies within its boundaries for which effluent limitations are not stringent enough to implement water quality standards applicable to those waters. This list of impaired waterbodies is commonly referred to as the Section 303(d) list. Subsequently, in accordance with Section 303 (d)(1)(C), states are required to develop a total maximum daily load (TMDL) for pollutants not meeting the effluent limitations and at a level necessary to implement the established water quality standards. A TMDL represents the maximum amount of a pollutant a waterbody can receive and still meet water quality standards.

The 2010 California 303(d) List of Water Quality Limited Segments identified Los Angeles Harbor—including Inner Cabrillo Beach, Cabrillo Marina, Consolidated Slip, Fish Harbor, Inner Harbor, Outer Harbor, San Pedro Bay, and Los Angeles River Estuary—as water segments where standards are not met and a TMDL is required. One or more pollutants or endpoints for each waterbody were listed as the cause of impairment for these waterbodies that comprise the Greater Harbor Waters (Table 1).

1.3 Harbor Toxics Total Maximum Daily Load

To protect marine life and minimize human health risks due to the consumption of fish, the Harbor Toxics TMDL includes annual contaminant limits in surface sediment, stormwater effluent, and fish tissues in the Greater Harbor Waters. These limits are defined as target

loads or concentrations for compliance with the Harbor Toxics TMDL. The intent of a TMDL is to: 1) determine the quantity of contaminants a system can assimilate while protecting water quality; 2) determine all inputs of contaminants to the system and linkages of inputs to impairments; and 3) allocate reductions to each source to bring the waterbody into compliance with established criteria for the protection of beneficial uses related to water quality.

1.3.1 Numeric Targets

Applicable water quality objectives for the Harbor Toxics TMDL are narrative objectives for chemical constituents, bioaccumulation, and toxicity in the Basin Plan and the numeric water quality criteria promulgated in 40 CFR section 131.38 (the California Toxics Rule [CTR]). In addition, sediment condition objectives were determined using sediment quality guidelines and the State Water Quality Control Plan for Enclosed Bays and Estuaries – Part 1 Sediment Quality (Sediment Quality Objectives [SQO] Part 1).

Water targets were determined by the Basin Plan and the CTR.

Sediment targets were determined by the narrative standards of the Basin Plan, the SQO, and sediment quality guidelines recommend in Long et al. (1998) and MacDonald et al. (2000). The Harbor Toxics TMDL anticipates that revisions to specific sediment quality targets may be determined by development of site-specific sediment quality values (SQV).

Fish tissue targets were determined from Fish Contaminant Goals and Advisory Tissue Levels for Common Contaminants in California Sport Fish: chlordane, DDTs, dieldrin, methylmercury, polychlorinated biphenyls (PCBs), selenium, and toxaphene, developed by Office of Environmental Health Hazard Assessment (OEHHA; 2008) to assist agencies in developing fish tissue-based criteria for pollution mitigation or elimination and to protect humans from consumption of contaminated fish.

1.3.2 Interim and Final Waste Load Allocations and Load Allocations

Final waste load allocations (WLAs) are assigned to stormwater dischargers (i.e., MS4, California Department of Transportation [Caltrans], general construction, and general industrial dischargers) and other National Pollutant Discharge Elimination System (NPDES) dischargers. Final load allocations (LAs) are assigned to direct atmospheric deposition and bed sediments in both wet and dry weather. Mass-based allocations have been set where sufficient data were available to calculate mass-based allocations; otherwise, concentration-based allocations have been set.

The following interim and final allocations are listed in Attachment A to Resolution No. R11-008, Amendment to the Water Quality Control Plan – Los Angeles Region (RWQCB 2011):

- Interim concentration-based allocation for sediment in Dominguez Channel Estuary and Greater Harbor Waters
- Final concentration-based WLAs for receiving water in Dominguez Channel Estuary and Greater Harbor Waters
- Final mass-based WLAs and LAs for Dominguez Channel Estuary and Greater Harbor Waters
- Final concentration-based sediment WLAs for metals in Dominguez Channel Estuary, Consolidated Slip, and Fish Harbor
- Final mass-based WLAs and LAs for bioaccumulative compounds in fish tissue for Dominguez Channel Estuary and Greater Harbor Waters

1.4 Compliance Measures

The Harbor Toxics TMDL set WLAs in the Greater Harbor waterbodies limit sediment bound pollutant loadings from upstream and on-land sources. In addition, the Harbor Toxics TMDL set LAs in the Greater Harbor waterbodies to limit concentrations in bedded sediments believed to impact marine benthos (direct effects) and fish tissue (indirect effects). Mass based limits for chemical constituents are provided in Table 2 and Table 3.

Water quality currently meets water quality objectives for beneficial use. However, monitoring is required to confirm no degradation is occurring. Water column concentrations will be compared to CTR values.

Compliance with sediments may be demonstrated via any one of three different means:

- Final sediment allocations, as presented in Attachment A to Resolution No. R11-008, Amendment to the Water Quality Control Plan – Los Angeles Region (RWQCB 2011), are met.
- 2. The qualitative sediment condition of Unimpacted or Likely Unimpacted via the interpretation and integration of MLOE as defined in the SQO Part 1, is met, with the exception of chromium, which is not included in the SQO Part 1.
- 3. Sediment numeric targets are met in bed sediments over a 3-year averaging period.

Compliance with the fish tissues may be demonstrated via any of four different means:

- 1. Fish tissue targets are met in species resident to the Harbor Toxics TMDL waterbodies.
- 2. Final sediment allocations, as presented in Attachment A to Resolution No. R11-008, Amendment to the Water Quality Control Plan Los Angeles Region (RWQCB 2011), are met.
- 3. Sediment numeric targets to protect fish tissue are met in bed sediment over a 3-year averaging period.
- 4. Demonstrate that the sediment quality condition protective of fish tissue is achieved per the Statewide Enclosed Bays and Estuaries Plan, as amended to address contaminants in resident finfish and wildlife.

1.5 Reporting Requirements

The Harbor Toxics TMDL identifies specific reporting requirements for compliance. The Coordinated Compliance, Monitoring, and Reporting Plan (CCMRP) will be provided to the Los Angeles Regional Water Quality Control Board's (RWQCB's) Executive Officer for approval within 20 months after the effective date of the Harbor Toxics TMDL. A data summary report will be submitted to the RWQCB within 15 months after monitoring starts and annually thereafter. The Harbor Toxics TMDL further specifies that monitoring and

reporting plans shall include a requirement that the responsible parties report compliance and non-compliance with WLA and LAs as part of annual reports submitted to the RWQCB. The evaluation of compliance with WLAs is not applicable to a receiving water monitoring program and will be included in MS4 programs. The Harbor Toxics TMDL permits multiple means for demonstrating compliance with sediment and fish tissue TMDLs. Therefore, the report will include the following data summaries:

- Water quality compared to applicable water quality criteria (e.g., CTR values)
- Sediment quality compared to effects range low (ERL), effects range median (ERM), sediment associated fish contamination goals (FCG) values, and a qualitative sediment condition defined by the Statewide Enclosed Bays and Estuaries Plan
- Fish tissue concentrations compared to FCG values

1.6 Programmatic Quality Assurance Project Plan

The Programmatic Quality Assurance Project Plan (PQAPP; Anchor QEA 2013) was developed to ensure high quality data collection as part of compliance monitoring and special studies required by and in support of the Harbor Toxics TMDL. The PQAPP includes the following key elements that focus on analytical methods and data generated during a project:

- Program Management. This section identifies the specific roles and responsibilities of
 data collectors and data managers and describes the process through which field and
 analytical data will be processed, reduced, and stored in an EQuIS database by the
 managing consultant.
- Field Sampling Data Quality Objectives. This section includes detailed information on field collection requirements including sample processing, sample handling, sample identification, sample custody and shipping requirements, field quality control (QC) sample requirements with associated performance criteria, field records, and field electronic data deliverable (EDD) requirements.
- Laboratory Data Quality Objectives. This section includes detailed information on analytical methods, analyte lists and reporting limits, laboratory QC sample requirements with associated performance criteria and corrective actions, laboratory record requirements, and laboratory EDD requirements.
- **Data Review, Verification, and Validation**. This section outlines the procedures used to ensure the project data quality objectives are met.

The PQAPP was designed to be programmatic in nature and not targeted at one study, given the plans for both compliance monitoring and a variety of other Harbor Toxics TMDLrelated sampling and analysis activities over the next 5 years. Consequently, while the PQAPP complies with SWAMP protocols and is SWAMP compatible, it is not written in the format of a SWAMP Quality Assurance Project Plan (QAPP). In addition, it does not include all elements of SWAMP QAPP (SWRCB 2008) guidance. This format was not possible because not all special studies have been designed or contractors determined. Instead, the PQAPP states that elements of the SWAMP QAPP guidance document relating to projectspecific field collection requirements should be included in the CCMRP or any subsequent Sampling and Analysis Plans (SAPs) developed to support Harbor Toxics TMDL-related studies. The benefit of the programmatic approach outlined in the PQAPP is that there will be a uniform data collection and management program for all Harbor Toxics TMDL-related studies that provides high quality data and efficiencies due to standardization of sample collection, nomenclature, analysis, data review/validation, processing, storage, management, and seamless data export to the Regional Monitoring Coalition (RMC) and State databases, regardless of study type or contractors performing the work.

This CCMRP has been designed accordingly to incorporate relevant PQAPP elements in addition to supplemental information specific to the compliance monitoring program in order to develop a single, all-inclusive, monitoring plan compatible with SWAMP QAPP requirements.

1.7 Coordinated Compliance and Monitoring Reporting Plan

The Harbor Toxics TMDL requires monitoring activities by the responsible parties in three waterbody areas:

- 1. Dominguez Channel, Torrance Lateral, and Dominguez Channel Estuary
- 2. Greater Los Angeles and Long Beach Harbor Waters (including Consolidated Slip)
- 3. Los Angeles River and San Gabriel River

The CCMRP outlines the monitoring activities to be conducted by the cooperating parties for the Greater Harbor Waters. To be consistent with and potentially collaborate with other regional monitoring programs, the sample collection methods prescribed within this CCMRP are to be conducted in accordance with methods established for use during Bight or SWAMP compatible programs. Compliance monitoring and reporting activities must also be conducted in accordance with the PQAPP developed for the Harbor Waters Toxics TMDL to ensure usability and provide benefit with other Harbor Waters Toxics TMDL related programs and studies.

1.8 Objectives

The goal of this document is to develop an approach to Harbor Toxics TMDL required compliance monitoring and reporting elements that will be approved by the RWQCB and considers all aspects of sample collection and handling, analysis, data evaluation, validation and management, quality assurance/quality control, and reporting.

This document fulfills the Harbor Toxics TMDL requirement for the development of a Compliance Monitoring and Reporting Plan that incorporates all elements of SWAMP compatible QAPPs.

1.9 Integration with Other Monitoring Programs

In 2012, the RWQCB adopted Order No. R4-2012-0175 (NPDES Permit No. CAS004001), Waste Discharge Requirements for Municipal Separate Storm Sewer Systems (MS4) Discharges within the Coastal Watersheds of Los Angeles County, Except Those Discharges Originating from the City of Long Beach MS4 (Order). The Order includes requirements that are consistent with and implement WLAs and monitoring requirements that are assigned to discharges from the Los Angeles County MS4 for established TMDLs. Each individual named Permittee of the Order is responsible for discharges from the MS4 for which they are owners and/or operators. For comingled discharges, compliance is determined from the group of Permittees. Individual Permittees are responsible for the determination of compliance with effluent limits.

The provisions included within the Order allow for coordination of integrated monitoring programs for the alignment and efficient implementation of monitoring requirements with Harbor Toxics TMDL monitoring requirements. For example, the Order specifies that receiving water monitoring will be conducted at Harbor Toxics TMDL compliance monitoring stations. However, it should be emphasized that participation in the RMC for the Greater Harbor Waters does not supersede the requirements of the Order, and each RMC responsible party is individually responsible for ensuring requirements of the Order are met.

2 PROJECT TASK AND ORGANIZATION (ELEMENT A4)

2.1 Responsible Parties

The Harbor Toxics TMDL names the following responsible parties for the Greater Harbor Waters:

- Greater Harbor Waters MS4 Permittees
 - Caltrans
 - City of Bellflower
 - City of Lakewood
 - City of Long Beach
 - City of Los Angeles
 - City of Paramount
 - City of Signal Hill
 - City of Rolling Hills
 - City of Rolling Hills Estates
 - Rancho Palos Verdes
 - Los Angeles County
 - Los Angeles County Flood Control District
- City of Long Beach (including the Port of Long Beach)
- City of Los Angeles (including the Port Los Angeles)
- California State Lands Commission
- Individual and General Stormwater Permit Enrollees
- Other Non-Stormwater Permittees, including City of Los Angeles' Terminal Island Water Reclamation Plant (TIWRP)

The Los Angeles River Estuary responsible parties subgroup includes the following entities:

- Caltrans
- City of Long Beach
- City of Los Angeles
- City of Signal Hill
- Los Angeles County
- Los Angeles County Flood Control District

The Consolidated Slip responsible parties subgroup includes the following entities:

- City of Los Angeles
- Los Angeles County
- Los Angeles County Flood Control District

The Harbor Toxics TMDL encourages collaboration and coordination of monitoring efforts amongst the responsible parties to avoid duplication and reduce associated monitoring costs.

2.2 Roles and Responsibilities

The specific roles and responsibilities of project managers, data managers, and laboratory project managers are shown on Figure 1. A list of names and responsible parties and their respective roles will be provided to the RMC in letter format. The list will be updated as necessary during the course of the project.

2.2.1 Project Managers

The RMC's project managers will be responsible for project administration and will serve as the lead contacts for Harbor Toxics TMDL compliance monitoring and related special studies. The RMC project managers will also serve as the point of contact between the RMC and the consulting team and will manage all project activities.

The managing consultant's Harbor Toxics TMDL study project manager will be responsible for:

- Managing the overall Harbor Toxics TMDL program
- Ensuring the project and the RMC's objectives are met throughout the conduct of project activities
- Coordinating internal communications with the RMC, the RMC contractors, managing consultant's data manager and quality assurance (QA) manager
- Overseeing all project deliverables
- Performing the administrative tasks needed to ensure timely and successful completion of the Harbor Toxics TMDL program studies
- Resolution of project concerns or conflicts related to technical matters

For each compliance monitoring event or special study, the RMC will select a contractor to be the special study/monitoring study project manager. This project manager will be identified in the SAP prepared prior to conducting the study. The monitoring/special study project manager will be responsible for:

- Providing oversight, overall special study project management, and progress reports
- Communicating with the TMDL study project manager and the RMC
- Organizing field staff
- Coordinating with subcontract laboratories
- Scheduling sampling days
- Installing and maintaining field sampling equipment, sample handling and transport, data transmittal in accordance with the PQAPP and CCMRP, and study reporting

2.2.2 Field Coordinator

For each compliance monitoring event or special study, a field coordinator will be identified in the SAP prepared by the contractor awarded the work. The field coordinator for each sampling program will be responsible for day-to-day technical and quality assurance and quality control (QA/QC) oversight. The field coordinator will ensure that appropriate protocols for sample collection, preservation, and holding times are observed, and will submit environmental samples to selected laboratories for chemical and physical analyses. The field coordinator will also be responsible for submitting the finalized field data to the QA manager in a pre-determined format, as discussed in Section 16.1 of this CCMRP.

2.2.3 Laboratory Project Managers

The laboratory manager of any laboratory testing samples for the RMC will oversee all laboratory operations associated with the receipt of the environmental samples, chemical and physical analyses, and laboratory report preparation for this project. The laboratory manager will review all laboratory reports and prepare case narratives describing any anomalies and exceptions that occurred during analysis.

The analytical testing laboratories will be responsible for the following:

 Delivering sample confirmation receipt notifications to the field coordinator and QA manager (by submittal to the TMDL Study project manager)

- Performing the analytical methods described in this CCMRP
- Following documentation, custody, and sample logbook procedures
- Ensuring that personnel engaged in preparation and analysis tasks have appropriate, documented training
- Meeting all reporting and QA/QC requirements
- Delivering electronic data files as specified in Section 16
- Meeting turnaround times for deliverables

2.2.4 Data Managers

The managing consultant's QA manager will provide QA oversight for field sampling and laboratory programs associated with the Harbor Toxics TMDL study, ensuring that samples are collected and documented appropriately, coordinating with selected analytical laboratories, ensuring data quality, overseeing data validation, and supervising project QA coordination.

The managing consultant will compile field observations and analytical data from laboratories into a database, review the data for completeness and consistency, append the database with qualifiers assigned by the data validator, and ensure that the data obtained is in a format suitable for inclusion in the appropriate databases and delivery to various agencies.

The managing consultant's designated data validator will be responsible for verifying and validating all analytical data and submitting assigned data qualifiers to the database manager.

3 PROJECT TASK DESCRIPTION (ELEMENT A6)

3.1 Summary of Monitoring Plan

The project area is a dynamic system. First and foremost, the project area contains the busiest container Port complex in the United States (Journal of Commerce 2012). The project area is defined by numerous channels, slips, and marinas throughout the Inner Harbors and relatively open water in the Outer Harbors. Three major rivers and drainage channels, the Los Angeles River, Dominguez Channel, and San Gabriel River, discharge to the project area. Storm events are infrequent, but during the winter month's stormwater discharges from surrounding watersheds are substantial. Therefore, natural variability, both temporal and spatial, must be considered when designing and evaluating a monitoring program. This monitoring program is appropriately designed to address these concerns by conducting frequently recurring monitoring events during both summer and winter seasons and at multiple stations throughout the project area.

The monitoring program consists of the collection of water, sediment, and tissue samples. Water will be collected during multiple events, both dry and wet weather, annually. Sediment samples will be collected every 2 to 3 years to assess sediment quality per SQO Part 1 (Bay et al. 2009). Fish tissue samples will be collected biennially.

3.2 Project Schedule

Compliance Monitoring and Reporting Plans will be submitted 20 months after the effective date of the Harbor Toxics TMDL for RWQCB Executive Officer approval. Monitoring will begin six months after the monitoring plan is approved by the Executive Officer and continue annually until the Executive Officer has determined no additional monitoring is necessary (i.e., compliance has been achieved) or an amended program is appropriate. Annual monitoring reports will be submitted. A summary of the field schedule projected on a 10-year recurring timeline is presented in Table 4. Adaptions will be made as necessary through the course of the project.

3.3 Deliverables

The PQAPP, along with this document, the CCMRP, are the first deliverables to the RWQCB. Once approved and monitoring is initiated, monitoring reports will be submitted to the RWQCB annually. The first report is due 15 months after monitoring begins, and subsequent reports will be submitted annually thereafter. A schedule of reports due to the RWQCB is presented in Table 5.

Annual monitoring reports will include a description of monitoring activities conducted for a given year, a summary table of water, sediment, and tissue analytical results, a data validation report, a summary of any deviations from the proposed sampling program, and associated quality assurance/quality control issues, including any action/response activities. As prescribed, the annual monitoring reports will provide a statement assessing whether or not monitoring results indicate compliance or non-compliance with waste load and load allocations.

4 SAMPLING PROCESS AND DESIGN (ELEMENT B01)

4.1 Station Locations

The station locations for water and sediment sample collections are presented on Figure 2. A total of 22 stations are included in the compliance monitoring program. These stations are consistent with the Harbor Toxics TMDL Basin Plan Amendment (RWQCB and USEPA 2011) monitoring requirements and descriptions. Because the Greater Los Angeles and Long Beach Harbors Responsible Parties propose a coordinated monitoring effort, stations were located in receiving waters at a point that suitably represents the combined discharge of cooperating parties. Detailed station location information is presented in Table 6. Fish tissue sample collections will take place within four waterbodies: Consolidated Slip, Los Angeles Outer Harbor, Long Beach Outer Harbor, and (eastern) San Pedro Bay (Figure 3). Precise station locations are not provided in this CCMRP. Instead, guidelines for station locations within the four waterbodies are provided in Section 4.1.1, which will be used to identify specific sampling locations prior to each sampling event.

In years when sampling for the sediment quality component of the compliance monitoring program aligns with the Southern California Bight Regional Monitoring Program (Bight Program), station locations may be modified in order to meet the Bight Program's requirement that station locations representing different strata (bay, port, marina, and estuary) be selected randomly. Therefore, Bight Program stations that are located within the same waterbody segment (e.g., turning basin, channel) as the Harbor Toxics TMDL-specified station locations will be considered representative of the Harbor Toxics TMDL-specified station location. If a Bight Program station is not located within the same waterbody segment, then the Harbor Toxics TMDL-specified station location will be sampled.

Prior to each sediment sampling event, it is anticipated correspondence with the RWQCB will be required to confirm the location of sediment sampling stations for two reasons:

1. The Bight Program randomly selects stations locations, and confirmation with the RWQCB regarding whether a Bight Program station is representative of a Harbor Toxics TMDL-specified station will be required.

2. In non-Bight Program years, sediment stations may be altered from the Harbor Toxics TMDL-specified locations listed in Table 4 to address the need for confirmation of Bight Program or other program SQO results.

4.1.1 Fish Tissue

In accordance with the requirements of the Harbor Toxics TMDL (RWQCB 2011), fish tissue monitoring must be conducted in the following four waterbodies: Consolidated Slip, Port of Angeles, Port of Long Beach, and (Eastern) San Pedro Bay (Figure 3). The proposed target sampling areas were designed to address two concerns raised by stakeholders during the public review period for this TMDL: 1) popular fishing areas for local anglers; and 2) known contaminated sites. To address the stakeholder concerns about popular fishing areas three proposed target sampling areas will be monitored: 1) Cabrillo Pier in Los Angeles Outer Harbor; 2) Pier J in Eastern San Pedro Bay; and 3) Outer Long Beach Harbor shallow water habitat. Cabrillo Pier and Pier J are well-known, popular fishing spots for local anglers, according to the Fish Contamination Education Collaborative (FCEC), a regional educational outreach program whose purpose is to protect vulnerable populations from the risks associated with fish consumption (FCEC 2013). Due to its popularity, Cabrillo Pier was also included in the 1992 regional seafood consumption study (SCCWRP and MBC 1994). There are no public fishing piers in Outer Long Beach Harbor; however, the Outer Long Beach Harbor shallow water habitat located east of Pier 400 is recommended for fish collection due to the higher diversity and abundance of benthic organisms and fishes in this area, as compared to those in the deep water habitat of the Outer Long Beach Harbor waterbody (SAIC 2010). In addition, this area has been recommended by experienced anglers for the collection of the target fish species listed in Section 5.3.1 (Kenny Nielson, personal communication). To address the stakeholder concerns about known contaminated sites, Consolidated Slip, specified as a target fish sampling location in the Harbor Toxics TMDL, will be monitored.

This CCMRP does not specify exact locations (i.e., geographic coordinates) for fish collection by trawling or other methods. Instead, guidelines have been established that allow for some flexibility in selecting the most appropriate fish collection area within each waterbody to improve the chances for success of the fish monitoring program.

Specifically, the following guidelines will be followed for the collection of fish within the four waterbodies specified in the TMDL:

- 1. Fish collection should be targeted as close to the following four areas as practicable, while accounting for limitations in the sampling vessel due to size and draft, and the type of equipment (e.g., trawl and seine) necessary for fish collection:
 - Cabrillo Pier (Los Angeles Outer Harbor)
 - Long Beach Outer Harbor breakwater (inside), midway between Angel's Gate and Queen's Gate
 - Pier J ([Eastern] San Pedro Bay)
 - Consolidated Slip
- 2. Every effort should be taken to ensure than any particular trawl track (or alternative fish sampling technique) occurs within the proposed target sampling areas. However, it is recognized that numerous factors (e.g., safe navigation around vessels and structures, wind, currents, and presence or absence of targeted fish species) may require the collection of fish outside the boundaries of the target sampling areas.
- 3. If extensive efforts have been made and insufficient fish have been caught at the target locations, all available resources, such as fish finders or echosounders, should be used to find an alternative sampling location that is as close to the original sampling location as practicable, and still within the waterbody specified in the Harbor Toxics TMDL (i.e., Los Angeles Outer Harbor, Long Beach Outer Harbor, [Eastern] San Pedro Bay, and Consolidated Slip). The field crew will note the reasons for relocation in the field log and fish collection efforts will be attempted at the secondary location.

It is recognized that fish tissue sampling will also be important in waterbodies other than those prescribed by the TMDL (e.g., Fish Harbor, Inner Los Angeles Harbor, Inner Long Beach Harbor) to better understand the linkages between sediment contaminants and fish tissue contaminant concentrations in these waterbodies and throughout the entire Harbor. Fish tissue sampling in waterbodies not specified in the TMDL will be conducted as part of special studies that will be designed to address sediment-fish linkages, characterize the food web structure of the target fish species, support the development of a site-specific Harbor bioaccumulation model, and, ultimately, determine compliance with the TMDL.

4.2 Field Sampling Parameters

A summary of water, sediment, and fish tissue data to be collected at each station is presented in Table 7. A schedule for data collection and the type and number of samples by matrix to be collected over the 20-year project is provided in Table 4.

4.2.1 Water

Water samples will be collected at each of the 22 Harbor Toxics TMDL-specified station locations (or approved, alternative Bight Program locations). Water quality measurements and samples will be collected at three depths during wet and dry weather events (surface, mid-water column, and bottom). Surface samples are defined as those collected between 0 and 1 meter below the water surface. Mid-water column sample depths will be based on overall water depth and are to be determined in the field. Bottom surface samples are defined as those collected within 1 meter above the mudline.

Actual locations will be within 15 meters of the proposed sampling station. If a station cannot be sampled, the sampling site will be moved to a location within 100 meters horizontal distance from the original site, staying within plus or minus 10 percent of the depth of the original station.

4.2.2 Sediment

Surface sediment samples will be collected at each of the 22 Harbor Toxics TMDL-specified station locations (or approved, alternative Bight Program locations). Actual locations will be within 15 meter of the proposed sampling station. If a station cannot be sampled, the sampling site will be moved to a location within 100 meter horizontal distance from the original site, staying within plus or minus 10 percent of the depth of the original station.

4.2.3 Targeted Species

The Harbor Toxics TMDL requires the collection of three different fish species: white croaker (*Genyonemus lineatus*), a sport fish, and a prey fish. White croaker was likely selected as a target species for the TMDL compliance monitoring program for numerous reasons. A regional fish consumption study (SCCWRP and MBC 1994) demonstrated that white croaker was caught off Cabrillo Pier and the Cabrillo Beach Boat Ramp in Los

Angeles/Long Beach Harbor and consumed by some recreational anglers. The health advisory and safe eating guidelines developed by OEHHA (2009) suggest that white croaker caught from Ventura to San Mateo Point should not be eaten (regardless of age or gender); these guidelines are based on elevated concentrations of PCBs and DDTs in croaker fillets, which have historically been above fish consumption advisory tissue levels. White croaker is found in nearshore habitats and is a bottom-dwelling species that primarily feeds on benthic organisms including polychaetes and clams. Consequently, it is likely that white croaker is indirectly exposed to sediment contaminants through the consumption of benthic organisms (Moore 1999). This species is also a preferred target species for monitoring because they are abundant throughout Los Angeles/Long Beach Harbor and easy to catch, as demonstrated by the Biological Baseline studies conducted in 1988, 2000, and 2008 (MEC 1988, 2002; SAIC 2010).

The selection of a sport fish species for compliance monitoring was based on similar rationale as to what is described above for white croaker. For the selection of sport fish, the following considerations were evaluated:

- The sport fish selected should be one that is fished in the Harbor and consumed, based on the Southern California Coastal Water Research Project (SCCWRP) and MBC Applied Environmental Sciences regional fish consumption survey (SCCWRP and MBC 1994).
- The sport fish selected should be one for which there is a fish consumption advisory (OEHHA 2009), or the sport fish selected should be one that has been shown to have elevated concentrations of PCBs and DDTs in muscle tissue.
- The sport fish selected should be abundant in the Los Angeles/Long Beach Harbor.

Based on these considerations, California halibut (*Paralichthys californicus*) was selected as the sport fish for the monitoring program. The SCCWRP and MBC (1994) fish consumption survey demonstrated that this species was caught and consumed by anglers in Los Angeles/Long Beach Harbor (i.e., Cabrillo Pier and Cabrillo Beach Boat Ramp). OEHHA (2009) recommends reduced servings of halibut caught in the Los Angeles/Long Beach Harbor region, and concentrations of PCBs and DDTs have been elevated in some halibut caught within the harbor. Biological baseline studies in 2000 and 2008 demonstrated that California halibut is abundant throughout the Harbor (MEC 2002; SAIC 2010). In addition, this species has been selected because it is being studied as part of other TMDL-related

special studies being conducted to support Phase II and III TMDL implementation efforts. Specifically, a fish movement study using both white croaker and California halibut will be initiated in June 2013 to understand the movement of these species and their exposure to Harbor sediments. Halibut was chosen over other fish species for the fish movement study because juveniles and adults caught in the Harbor have large body cavities and adequate body size and are sturdy enough to be used in a fish movement (i.e., tracking) study, which involves the use of electronic fish tagging devices. While species such as barred sand bass and queenfish meet the considerations for monitoring, they are not appropriate for use in the fish movement study (i.e., barred sand bass caught in the Harbor are typically too small for tagging and queenfish body cavities are too small for tagging). Consequently, the use of California halibut in the monitoring program will maximize the usefulness of fish tissue data collected as part of both TMDL programs.

A similar selection process was used to determine the most appropriate prey fish for TMDL monitoring. For the selection of prey fish, the following considerations were evaluated:

- The prey fish selected should be a species that is a prey item or a representative prey item of white croaker and the sport fish selected for monitoring.
- The prey fish selected should be one for which there is a fish consumption advisory (OEHHA 2009) or the prey fish selected should be one that has been shown to have elevated concentrations of PCBs and DDTs.
- The prey fish selected should be one that is abundant in the Los Angeles/Long Beach Harbor. The size of abundant prey fishes should also be considered.

Based on these considerations, shiner surfperch (*Cymatogaster aggregate*) was selected as the prey fish for the monitoring program. In California, white croaker has been shown to consume small fishes (e.g., anchovies) in addition to a wide variety of other organisms, such as worms, shrimps, crabs, squid, clams, and other items, living or dead (CDFG 2001, 2002). In contrast to white croaker, the California halibut diet is primarily composed of small fishes. Halibut have been shown to prey upon Pacific sardines (*Sardinops sagax caerulea*), white croaker, Northern anchovy (*Engraulis mordax*), atherinids (e.g., topsmelt [*Atherinops affinis*]) and surfperches (including shiner surfperch [*Cymatogaster aggregate*] and walleye surfperch [*Hyperprosopon argenteum*]), in addition to some invertebrates (Allen 1990; CDFG 2002; CDFW 2013a). Two of the prey fishes listed above are on OEHHA's list for reduced consumption or no consumption (OEHHA 2009): surfperches and topsmelt,

respectively. Both surfperches and topsmelt have been shown to be abundant prey fishes in the Los Angeles/Long Beach Harbor (SAIC 2010). However, the most abundant size classes of shiner surfperch (4 to 6 centimeters [cm]) were smaller than those of topsmelt (6 to 8 cm; SAIC 2010). Consequently, shiner surfperch are selected as the prey fish for the monitoring program because the most abundant white croaker size classes in the Los Angeles/Long Beach Harbor (16 to 20 cm) more likely to prey upon the smaller shiner surfperch than the larger topsmelt due to the ease of catching smaller prey fish. In addition, shiner surfperch is representative of important prey fish because their diets are similar to topsmelt; both species have been shown to feed on zooplankton, algae, amphipods, polychaetes, and gastropods (Odenweller 1975; Sempier 2013; UC 2013).

4.3 Sample Frequency

The proposed frequency for water, sediment, and tissue monitoring events is presented in Table 4.

4.3.1 Water

Water samples will be collected during two wet weather events and one dry weather event each year. The wet weather events will be targeted 24 hours after a storm event occurring between October 1 and April 30. This 24-hour period provides time for Permittees to monitor storm water outfalls and allows runoff from the watershed to reach the receiving waters. In addition, for health and safety purposes, allowing 24 hours to pass before launching vessels and conducting sampling improves the likelihood of sampling in less dangerous conditions than those present at the start of a storm. The first storm of the season will be targeted. The first storm is defined as having a predicted rainfall of at least 0.25 inch (0.64 cm) and a 70 percent probability of rainfall at least 24 hours prior to the event start time. Defining a storm event as having a predicted rainfall of at least 0.25 inch (0.64 cm) is consistent with the Los Angeles County Department of Public Works trigger for monitoring mass emission stations of 0.25 inch (0.64 cm) rainfall received within a 24-hour period. Constraining the first storm event of a season to be greater than 0.25 inch (0.64 cm) may preclude characterizing contaminants of potential concern (COPCs) if a larger storm does not occur until late in the season. For example, a study funded by Caltrans (Stenstrom and Kayhanian 2005) revealed that concentrations of COPCs declined as the wet season progressed. One additional wet weather event occurring in the same season will be sampled.

Depending on the seasonal forecast (e.g., drought vs. wet years), this wet weather event will consist of a storm that produces at least 0.1 inch (0.25 cm) of precipitation per day and separated by an antecedent dry period (less than 0.1 inch [0.25 cm] of rain per day) of at least 72 hours, but consideration will be given to monitor larger storm events (0.5 inch [1.28 cm] or greater) if forecasted. The dry weather event may be conducted any time of the year but only after an antecedent dry period of at least 72 hours has passed since the last rainfall event. Although unlikely, the lack of storm events, especially during drought years, may constrain the ability to successfully monitor wet weather.

4.3.2 Sediment

SQO Part 1 (sediment triad sampling) will be performed twice every 5 years. Sediment will be sampled in Year 1 and Year 4, and this cycle will repeat every 5 years. This schedule guarantees no single sediment sampling event is greater than 3 years from the previous effort, and maximizes the number of paired sampling events with biennial fish tissue sampling efforts. The schedule outlined in Table 4 illustrates this approach. The proposed sediment sampling approach will be conducted in the same years as the Southern California Regional Bight Monitoring Program, assuming that program maintains the current frequency of once every 5 years.

In accordance with the *Sediment Quality Assessment Draft Technical Support Manual* (Bay et al. 2009), sediment triad sampling will be conducted between July 1 and September 30. Benthic assemblages change with season, light, and temperature. The *Sediment Quality Assessment Draft Technical Support Manual* recommends sampling during a specific time of year for consistency and comparability of data (Bay et al. 2009). The greatest organism abundances and diversities are typically observed in the summer months. Due to the increased data available in summer months, this timeframe was selected to provide the best representation of benthic community health. No other time or resource constraints are anticipated for the collection of sediment samples.

4.3.3 Fish Tissue

Fish tissue samples will be collected once every 2 years. In accordance with the Bight Field Operations Manual (BCEC 2008), fish tissue collection efforts will be conducted between July 1 and September 30. Fish are more robust in the summer, as their food is more abundant during this time. Thus, they have the potential to bioaccumulate more contaminants during the summer. This timeframe was selected as a conservative approach to provide data reflective of the maximum levels of bioaccumulatives present in fish tissues for the given sampling year. No other time or resource constraints are anticipated for the collection of fish tissue samples.

4.4 Station and Sample Identification

Each station identification code will be unique and be maintained throughout the duration of compliance monitoring activities. The station identification codes are consistent with the station numbers listed in Sediment Chemistry Monitoring Requirements table of the Harbor Toxics TMDL Basin Plan Amendment (RWQCB and USEPA 2011).

Each sample will have an adhesive plastic or waterproof paper label affixed to the container and will be labeled at the time of collection. The following information will be recorded on the container label at the time of collection:

- Project name
- Sample identifier (sample identification code)
- Date and time of sample collection
- Preservative type (if applicable)
- Analysis to be performed

The sample nomenclature should include the identifiers listed below. A catalogue of identification codes is provided in Table 8. The identification codes shown below should be used when applicable; however, sample identification code requirements for special studies are not yet defined and consequently, minor modifications to the recommended identification codes will be acceptable in these cases.

- Waterbody or site as shown in Table 8
- Media or sampling method code

- Station number
- Organism common name, if applicable
- Depth interval (in metric units), if applicable
- Date of collection
- Indication of field duplicate (i.e., add 1000 to station number)

For equipment rinsate blank or field blank samples, "EB" or "FB" will be used, respectively, in place of the waterbody or site and station number. The date of sample collection will be added to end in YYYYMMDD format.

For fish tissue samples, no station number will be used. Because one station will be selected in each of the four required waterbodies, the waterbody code will be sufficient to identify fish tissue samples.

Sample nomenclature for water and sediment samples is shown on Figure 4, using the following example: a surface sediment grab at 0-5 cm, station number 09 from Outer Harbor – Los Angeles on July 31, 2013 would be written as:

OA-SS-09-0-5-20130731

Sample nomenclature for tissue samples is shown on Figure 5, using the following example: a white croaker, fish fillet skin off, from Outer Harbor – Long Beach on July 31, 2013 would be written as:

OB-FF-WC-20130731

Sample nomenclature for field duplicates is shown on Figure 6, using the following example: a water sample collected at 2 meters, station number 09 from Outer Harbor – Los Angeles on July 31, 2013, that is a field duplicate would be written as:

OA-RW-1009-2-20130731

Sample nomenclature for equipment blanks is shown on Figure 7, using the following example: *an equipment blank of the decontaminated sample processing equipment after sample collection* on July 31, 2013 would be written as:

EB-20130731

4.5 Critical Information

Supplemental information relating to the different types of data to be collected and whether that data is considered informational or critical to the project is provided in Table 9. In general, visual observations are informational and all other data is critical.

5 SAMPLE COLLECTION (ELEMENT B02)

Methods adhere to Bight and SWAMP protocols. A list of field standard operating procedures (SOPs) is presented in Table 10; SOPs are provided in Appendix A. Additional information regarding samplers and sample processing for each matrix is provided in Table 11. Specific information regarding chemical constituents to be analyzed, sample containers and volumes, holding times, temperatures, and preservatives is presented in Table 12.

5.1 Water

Water quality monitoring consists of in situ measurements and the collection of water samples for chemical analyses.

5.1.1 In Situ Measurements

For each sampling event and at each station, water depth and in situ² water quality parameters (temperature, dissolved oxygen [DO], pH, and salinity) will be collected. Water quality parameters and water depth will be recorded on a field data sheet.

The water depth at each station should be recorded using a probe or lead line. Water quality will be measured in situ at the station by immersing a multi-parameter instrument³ into the water at the same location where the water sample is collected. The instrument must equilibrate for at least one minute before collecting temperature, pH, conductivity and/or salinity measurements and at least 90 seconds before collecting DO measurements. Because DO takes the longest to stabilize, record this parameter after temperature, pH, and salinity. See the SWAMP SOP for additional details on the collection of field parameters (MPSL-DFG 2007). Methods are also summarized in the SOP: In situ Water Quality Monitoring (Appendix A). Water quality measurements will be collected at three depths during wet and dry weather events (surface, mid-water column, and bottom).

Water quality parameter measurements may be taken in the laboratory immediately following sample collection, if auto samplers are used for sample collection or if weather conditions are unsuitable for field measurements.

³ A multi-parameter instrument is preferred; however multiple specific water quality parameter meters may also be used.

The Harbor Toxics TMDL states that flow also be included as a parameter to be measured. At the point of a stormwater or dry weather discharge, it is appropriate to measure for flow. In these cases, flow measurements (i.e., the volume of water discharged per unit of time from a specific discharge point) may be used to calculate suspended sediment and pollutant loadings to a receiving waterbody. In contrast, at stations within a receiving waterbody, it is not appropriate to measure flow for two primary reasons:

- Tidal and wind currents (in bays and estuaries) or flows originating from upstream sources (in rivers and channels) will cause inaccurate flow measurements of the discharge after it mixes with receiving water.
- Mixing of the discharge with receiving water prevents calculations of loadings
 (i.e., the pollutant concentration multiplied by flow measurement) because the
 discharge and its suspended sediment and pollutant load is immediately diluted in the
 receiving water.

This CCMRP proposes to sample at locations within receiving waters. As such, flow will not be measured, because mixing and other hydrodynamic factors will confound the flow measurements and loading calculations.

5.1.2 Grab Samples

Water samples will be collected from the same three depths as the in situ water quality measurements. Grab samples (i.e., instantaneous, not time or flow-weighted composites) for total suspended solids (TSS) will be taken at all three depths during wet and dry weather events. Grab samples for analytical chemistry will be taken only from the surface sample. Water samples will be collected with a grab sampler (e.g., Niskin or Van Dorn) that has been decontaminated prior to sample collection at each station. Sampling methods will generally conform to U.S. Environmental Protection Agency's (USEPA's) clean sampling methodology described in the SWAMP SOP (MPSL-DFG 2007). Methods are also summarized in the SOP: Grab Water Sampling (Appendix A).

Sample processing and handling for water chemistry will be conducted in accordance with guidance developed in the Quality Assurance Management Plan for the State of California's SWAMP (Pucket 2002). Aliquots for TSS, metals, organochlorine pesticides, and PCBs will

be taken directly from the grab sampler into appropriate containers or bottles (Table 12). Water samples will be preserved, depending on the type of analysis, in the field in order to meet specified holding time (Table 12). Water samples will be stored at <4°C until delivery to the appropriate analytical laboratory.

5.2 Sediment

Surface sediment samples will be collected at each station. Multiple grab samples may be required at each station in order to provide sufficient sediment volumes to complete all analyses required for the SQO Part 1 assessment (Bay et al. 2009). Sediment grabs will be evaluated for acceptance as outlined in the Bight Field Operations Manual, Section VIII (BCEC 2008).

Surface sediment grab samples procedures will be collected using a Van Veen sampler, or similar sampling device as appropriate for the type of sediment sample being collected, as described in the Bight Field Operations Manual, Section VIII (BCEC 2008) and summarized in the SOP: Surface Sediment Grab Sampling (Appendix A).

Sediment sample processing and handling for purposes of sediment chemical analyses, sediment toxicity, and benthic community assessment in support of the SQOs Part 1 assessment will be performed in accordance with procedures specified in the Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009) and the Bight Field Operations Manual (BCEC 2008). Methods are also included in SOPs: Sediment Chemistry Sample Processing, Sediment Toxicity Sample Processing, and Benthic Infauna Processing (Appendix A). Recommended conditions for sampling containers and sample handling and storage are listed in Table 12. Sediment samples for chemistry and toxicity analyses will be stored at <4°C until delivery to the appropriate analytical laboratory. Benthic infauna samples will be stored in 10 percent buffered formalin in the short term and then subsequently transferred to 70 percent ethanol (or equivalent) for long term storage.

5.3 Fish Tissue

Fish tissue samples will be collected and analyzed for chemical contaminants of concern. Sampling, processing, and testing methods will be carried out in accordance with Bight

protocols (BCEC 2008, 2009). Methods are summarized in SOPs: Fish Collection and Fish Processing (Appendix A). Necessary permits (e.g., scientific collection, incidental take) will be secured prior to fish collection. Applications and procedures for permits can be found online at the California Department of Fish and Wildlife (CDFW) website (2013b).

CDFW code section 1002 and Title 14 sections 650 and 670.7 requires a Scientific Collecting Permit to take, collect, capture, mark, or salvage, for scientific purposes, fish and invertebrates. CDFW section 2081(b) requires an Incidental Take Permit (ITP) for any species listed as threatened or endangered (T/E). Although, none of the targeted species for this study are T/E species, it is possible that T/E species will be accidentally caught as by catch. An ITP is required for T/E species that are caught or handled in any way, even if they are returned to the ocean.

In addition, the permit holders must notify the local CDFW office prior to collection and submit a report of the animals taken under the permits within 30 days of the expiration date of the permits. More information is available on CDFW's website (2013a).

5.3.1 Fish Collection and Processing

Composite samples of three fish species (white croaker, California halibut, and shiner surfperch) will be collected at all stations, with the exception of Consolidated Slip; only white croaker will be collected at this station. White croaker is the only species being sampled in Consolidated Slip for the following reasons:

- White croaker is more abundant in this subarea and easier to catch than California halibut or shiner perch as demonstrated in the Ports' Biological Baseline Survey from 2008 (SAIC 2010).
- The Consolidated Slip area is small and consequently has limited space available for targeted fish collection of uncommon species such as California halibut and shiner perch.
- Based on historical data, white croaker represent the fish with the highest concentrations of PCBs and other organics, and therefore, croaker is indicative of the highest human health exposure levels in relation to seafood consumption from this subarea.

When possible, fish will be collected using a semi-balloon, 7.6-meter headrope otter trawl following the methods in the Bight Field Operations Manual (BCEC 2008). If other methods need to be employed in the case an otter trawl is not feasible (e.g., lampara net, beach seine, fish trap, or hook and line), SWAMP methods will be used (MPSL-DFG 2001). SOPs for fish collection are provided in Appendix A.

Once the catch is onboard the vessel, the targeted species will be identified and separated for subsequent processing. At each station, 12 individuals of each fish species will be collected for further processing. There is currently no legal size limit for white croaker. An ocean fish contaminant survey was performed from 2002 to 2004 (NOAA 2007). In part, this survey sought to generate information on contaminants of concern for fish caught for sustenance in Southern California. Collection of white croaker for the Harbor Toxics TMDL study should be consistent with this survey, which recommended a minimum length of 160 millimeters (mm; total length). Collection of California halibut of legal size limit is preferred. The current regulations specify at least 22 inches (or 559 mm; total length) for California halibut (FGC 2012). Collection of adult shiner surfperch (i.e., second year age-class with a target length of 88 mm [Odenweller 1975]) is preferred. Additional individuals of the three target species and non-target species will be returned to the ocean as soon as possible to minimize loss. It should be noted that field personnel may encounter by catch that are potentially harmful while sorting for targeted species. The Bight Field Operations Manual (BCEC 2008) and Fish Collection SOPs in Appendix A provide information on the safe handling of these organisms.

Each targeted fish kept will be tagged with a unique identification number and then measured for total length, fork length, and weight and examined for gross pathology in accordance with guidance established in the Bight Field Operations Manual (BCEC 2008). Three composite samples per species per station will be created. A composite sample will be comprised of four individuals; therefore, a total of 12 individuals per station are required. If more than 12 specimens are caught, then the 12 individuals best and most closely distributed about the 75th percentile of the length distribution of all individuals will be used for the composites. The selected 12 individual fish will then be arranged by size and the smallest four fish, the middle four fish, and the largest four fish within a species will be grouped for each composite to satisfy the 75 percent rule (the smallest individual in a composite is no less

than 75 percent of the total length of the largest individual in a composite; USEPA 2000). This may permit data evaluation based on size class, if necessary. Skin-off fillets will be used for white croaker, California halibut, and shiner surfperch to be consistent with the *2002* – *2004 Southern California Coastal Marine Fish Contaminants Survey* (NOAA 2007). Dissection and compositing methods will be performed in the analytical laboratory in accordance with USEPA guidance (USEPA 2000).

Fish tissue will be analyzed for chemical parameters. Processing and preservation will be performed in accordance with the methods described in the Bight Field Operations Manual and Bioaccumulation Workplan (BCEC 2008, 2009). Fish will be processed in the field according to the steps below.

- Sacrifice fish and leave whole body intact.
- Blot fish dry and pack each fish in aluminum foil (shiny side out).
- Place each packed fish in a labeled, food grade, resalable plastic bag and store on ice.
- Ship overnight to the analytical laboratory on wet or blue ice. If samples are held more than 24 hours, pack on dry ice.

Chain-of-custody forms will be maintained. Tissue compositing will be conducted by the analytical laboratory. Recommended conditions for sampling containers, sample handling and storage are listed in Table 12.

5.4 Field Equipment Decontamination Procedures

Sample containers, instruments, working surfaces, technician protective gear, and other items that may come into contact with sample material must meet high standards of cleanliness. All equipment and instruments used that are in direct contact with various media collected for chemical analysis must be made of glass, stainless steel, high-density polyethylene (HDPE) or polytetrafluoroethylene (PTFE) and will be cleaned prior to each day's use and between sampling or compositing events. The decontamination procedure is as follows:

- 1. Pre-wash rinse with tap or site water.
- 2. Wash with solution of warm tap water or site water and $Alconox^{TM}$ soap.
- 3. *Rinse with tap or site water.*

- 4. Rinse thoroughly with organic-free water.
- 5. Cover (no contact) all decontaminated items with aluminum foil.
- 6. Store in a clean, closed container for next use.

Disposable gloves will be discarded after processing each station and replaced prior to handling decontaminated instruments or work surfaces.

Water quality probes will be rinsed three times with distilled water prior to collecting measurements at each station.

5.5 Waste Disposal

All disposable sampling materials and personal protective equipment used in sample processing, such as disposable coveralls, gloves, and paper towels, will be placed in heavyweight garbage bags or other appropriate containers. Disposable supplies will be removed from the site by sampling personnel and placed in a normal refuse container for disposal as solid waste. Waste disposal procedures for specific media are as follows.

5.5.1 Water

Excess water from the sampler will be returned to the collection site, prior to moving to the next sampling location.

5.5.2 Sediment

Any incidental sediment remaining after sampling will be washed overboard at the collection site, prior to moving to the next sampling location. Any sediment spilled on the deck of the sampling vessel will be washed into surface waters at the collection site after sampling.

5.5.3 Fish Tissue

After target fish have been collected, the remaining catch should be returned to the sea. Dead specimens should be discarded offshore, outside the breakwater, to avoid spoiling of nearshore areas (i.e., harbors and bays).

5.6 Sampling Platform and Equipment

The subcontractor will provide the sampling vessel and all equipment necessary for safe operation during sampling. The vessel shall conform to U.S. Coast Guard safety standards. The vessel should be equipped with the proper equipment for the safe deployment and retrieval of sampling gear, such as an A-frame and/or davit with an associated electrical or hydraulic winch system. An A-frame should be used for the deployment of fish sampling (e.g., trawl) gear. An A-frame or davit may also be used for the deployment of water quality and sediment sampling gear. In addition, the vessel should have sufficient deck space for sample processing and water pumps available to aid in sample processing and cleaning of the deck and equipment between stations. A list of equipment and support facilities that may be necessary to conduct sampling is provided in Table 13. Subcontractors are responsible for providing a complete list of equipment and support facilities to be used for sampling.

5.7 Positioning and Vertical Controls

On-vessel navigation and positioning will be accomplished using a differential global positioning system (DGPS). The navigation system will be used to guide the vessel to pre-determined core sampling locations, with an accuracy of plus or minus 10 feet. The vessel will maintain position using a three-point anchoring system. The coordinates of the actual sampling locations will be reported in latitude and longitude in degrees, decimal, and minutes (to three decimal places). Positions will be relative to the North American Datum 1983 (NAD83).

Upon locating the sampling location, station depth will be measured using an onboard, calibrated fathometer or a leadline. The mudline elevation relative to mean lower low water (MLLW) datum will be determined by adding the tidal elevation to the measured depth. In the Port of Los Angeles, the Los Angeles, California, tide gauge (Station ID 9410660) will be referenced. In the Port of Long Beach and San Pedro Bay, the Long Beach Terminal Island tide gauge (Station ID 9410680) will be referenced. Vertical elevations will be reported to the nearest 0.1 foot relative to MLLW.

6 SAMPLE HANDLING AND CUSTODY (ELEMENT B03)

6.1 Sample Shipping

All samples will be shipped or hand delivered to the analytical laboratory no later than the day after collection. Samples collected on Friday may be held until the following Monday for shipment provided that this delay does not jeopardize any hold time requirements. Specific sample shipping procedures are as follows:

- Each cooler or container containing the samples for analysis will be shipped via overnight delivery to the laboratory. In the event that Saturday delivery is required, the field coordinator will contact the analytical laboratory before 3 p.m. on Friday to ensure that the laboratory is aware of the number of containers shipped and the airbill tracking numbers for those containers. Following each shipment, the field coordinator will call the laboratory and verify that the shipment from the day before has been received and is in good condition.
- Coolant ice will be sealed in separate double plastic bags and placed in the shipping containers.
- Individual sample containers will be placed in a sealable plastic bag, packed to prevent breakage, and transported in a sealed ice chest or other suitable container.
- Glass jars will be separated in the shipping container by shock-absorbent material (e.g., bubble wrap) to prevent breakage.
- The shipping containers will be clearly labeled with sufficient information (name of project, time and date container was sealed, person sealing the container, and consultant's office name and address) to enable positive identification.
- The shipping waybill number will be documented on all COC forms accompanying the samples.
- A sealed envelope containing COC forms will be enclosed in a plastic bag and taped to the inside lid of the cooler.
- A minimum of two signed and dated custody seals will be placed on adjacent sides of each cooler prior to shipping.
- Each cooler will be wrapped securely with strapping tape, labeled "Glass Fragile" and "This End Up," and will be clearly labeled with the laboratory's shipping address and the consultant's return address.

Upon transfer of sample possession to the analytical laboratory, the persons transferring custody of the sample container will sign the COC form. Upon receipt of samples at the laboratory, the custody seals will be broken, and the receiver will record the condition of the samples on a sample receipt form. COC forms will be used internally in the laboratory to track sample handling and final disposition.

6.2 Chain-of-Custody Procedures

Samples are considered to be in one's custody if they are: 1) in the custodian's possession or view; 2) in a secured location (under lock) with restricted access; or 3) in a container that is secured with an official seal(s) so that the sample cannot be reached without breaking the seal(s).

Chain-of-custody (COC) procedures will be followed for all samples throughout the collection, handling, and analysis process. The principal document used to track possession and transfer of samples is the COC form. Each sample will be represented on a COC form the day it is collected. All manual data entries will be made using an indelible ink pen. Corrections will be made by drawing a single line through the error, writing in the correct information, then dating and initialing the change. Blank lines and spaces on the COC form will be lined out, dated, and initialed by the individual maintaining custody. Electronic COC (eCOC) forms will be emailed directly to the laboratory and QA manager.

A COC form will accompany each container of samples to the analytical laboratories. Each person in custody of samples will sign the COC form and ensure the samples are not left unattended unless properly secured. Copies of all COC forms will be retained in the project files.

7 FIELD MEASUREMENTS AND ANALYTICAL METHODS (ELEMENT B04)

Field SOPs for field measurements are listed in Table 14 and included in Appendix A. Field instruments are presented in Table 15. Water, sediment, and tissue analytical chemistry will be performed by a laboratory certified by the California Environmental Laboratory Accreditation Program (ELAP) and/or National Environmental Laboratory Accreditation Program (NELAP) on contract with Ports of Long Beach and Los Angeles. Sample containers and preservatives, as appropriate, will be provided by the analytical laboratory. The laboratory will maintain documentation certifying the cleanliness of bottles and the purity of preservatives provided. A summary of the major chemical constituents to be analyzed is presented in Table 16. A complete list of analytes by matrix is included in Tables 17, 18, and 19.

7.1 Water

In situ water quality field measurements will be made for the following parameters:

- pH
- Temperature
- DO
- Salinity

Water quality will be measured in situ at the station location by immersing a water quality sonde into the water at the same location where the water sample is collected. See Appendix A and the SWAMP SOP for additional details on the collection of field parameters (MPSL-DFG 2007).

Water samples will be analyzed for the following:

- TSS
- Dissolved and total metals
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene)
- PCBs

Table 17 lists the specific compounds to be analyzed and details the analytical methods and target reporting limits. Sample volumes and preservation techniques for required analyses are included in Table 12. The sample volume needed may vary due to the analytical methods and reporting limit capabilities of the laboratory.

7.2 Sediment Triad Sampling

7.2.1 Chemistry

Sediment chemistry is one of three essential lines of evidence (LOE) required for the SQO Part 1 (sediment triad assessment), which helps determines the type of chemical exposure and its potential for producing adverse biological effects. Determination of the chemistry LOE is comprised of two main components: 1) measurement of a suite of constituents and 2) interpretation of the results using two indices of chemical exposure: CA CLR and chemical score index (CSI; Bay et al. 2009).

Sediment samples will be analyzed for the following:

- Total organic carbon (TOC)
- Grain size
- Metals
- Polycyclic aromatic hydrocarbons (PAHs)
- Organochlorine pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene)
- PCB congeners

Specific compounds to be analyzed and analytical methods and target reporting limits are provided in Table 18. Sample volumes and preservation techniques for required analyses are presented in Table 12. Sediment chemical analyses will be conducted in accordance with Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009). The sample volume needed may vary due to the analytical methods and reporting limit capabilities of the laboratory.

7.2.2 Toxicity

Sediment toxicity is the second essential LOE for conducting a SQO Part 1 assessment. Toxicity tests will be conducted in accordance with Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009). Methods are summarized in the SOP: Sediment Toxicity Testing (Appendix A). Two sediment toxicity tests, including an acute amphipod survival and a chronic, sub-lethal test are required for the assessment (Bay et al. 2009). For consistency and comparability with the Bight program and over time, the *Eohaustorius* estuarius amphipod toxicity test should be used for compliance monitoring. E. estuarius has been historically used during Bight Monitoring in the Los Angeles and Long Beach Harbors in 1998, 2003, and 2008 (SCCWRP 2003, 2007; Nautilus 2009) and Ports of Long Beach and Los Angeles' Biological Baseline Monitoring in 2008 (SAIC 2010). The continued use of this species as part of future monitoring events will allow for the greatest data comparability over time. However, due to the intolerance of *E. estuarius* for sediment with a high percent of clay, alternative species accepted by the SQO guidance (e.g., *Leptocheirus plumulosus*) should be considered in areas expected to have a high percent of fines. In addition, if healthy *E. estuarius* organisms are not available during the required sampling period, then Rhepoxynius abronius may be an acceptable species for toxicity testing. It is unlikely, due to holding time restraints, that grain size data will be available from the analytical laboratory prior to species determination for toxicity testing. As such, species determinations should be made via best professional judgment based on the physical appearance and texture of test sediments and availability of test organisms at the time of sample collection. The field manager and toxicity laboratory manager should work together to identify the grain size and appropriate test species for each test sediment. It is not uncommon to use two different species within the same study to accommodate testing sediments of differing grain size.

The chronic, sublethal toxicity test that should be conducted as part of an SQO assessment in the Los Angeles/Long Beach Harbor Complex is the mussel (*Mytilus galloprovincialis*) sediment-water interface test. Recent Bight monitoring in 2008 employed the sediment-water interface (SWI) test and, continued use of this test will provide the best data comparability between previous and future sampling events. In accordance with the original intent of the SWI test design (Anderson et al. 1996), *M. galloprovincialis* larvae should be exposed to intact cores. In contrast, homogenized sediment was used in the Bight 2008 testing program. The use of intact cores instead of homogenized sediment will reduce the

potential for confounding effects of ammonia and sulfides found in deeper sediment, while still testing for the toxic effects of chemicals fluxing from sediment to overlying water. A description of these toxicity test methods specified under the SQO policy is provided in Chapter 4 of the Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009). Specifically, Chapter 4 provides guidance on sample preparation, organism acclimation, test methods, QA/QC procedures, and data analysis and interpretation (Bay et al. 2009).

7.2.3 Benthic Community

The third essential LOE for sediment quality assessment is the composition of the benthic community. The benthic LOE is a direct measure of the effect that sediment contaminant exposure has on the benthic biota of California's bays and estuaries. Determination of the benthic LOE is based on four measures of benthic community condition: 1) Index of Biotic Integrity (IBI), 2) Relative Benthic Index (RBI), 3) Benthic Response Index (BRI), and 4) River Invertebrate Prediction and Classification System (RIVPACS; Bay et al. 2009). Benthic community analyses will be conducted in accordance with Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009). Chapter 5 of the Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009) details recommended laboratory procedures for the processing of benthic infauna samples and subsequent data analysis necessary for the SQO Part 1 assessment. Methods are included in the SOP: Benthic Infauna Community Analysis (Appendix A).

7.3 Sediment Quality Objective Assessment

The SQO assessment incorporates the MLOE described above (chemistry, toxicity, and benthic community) to develop final station assessments. SQO assessment should be conducted in accordance with the Water Quality Control Plan (SWRCB and CalEPA 2009) and the Technical Support Manual (Bay et al. 2009). The calculation of the toxicity LOE is straightforward, as described in the Technical Support Manual. Consequently, only supplemental guidance is provided here for the chemistry and benthic LOEs.

7.3.1 Chemistry Line of Evidence

Calculation of the chemistry LOE should follow methods described in the Water Quality Control Plan (SWRCB and CalEPA 2009) and the Technical Support Manual (Bay et al. 2009). Specific attention should be given to guidance on the summing of total high molecular weight PAHs, low molecular weight PAHs, total PCBs, and total DDTs; guidance on using the specific chemical constituents in each class to sum, managing non-detects, and applying a multiplication factor as part of the total PCB concentration estimate should be strictly followed.

For individual analytes with a non-detect result, an estimated concentration represented by half the detection limit should be consistently used. Using this method will ensure consistency across all monitoring events. This stipulation does not apply to non-detect results used in a sum (as previously described). While there are other ways that non-detects can be estimated (i.e., non-detect equals detection limit), the recommended method is in agreement with the Technical Support Manual (Bay et al. 2009).

Calculations may be performed using various tools, including a calculator, Microsoft Excel®, or programming languages (i.e., Interactive Data Language [IDL]). SCCWRP has also developed a data integration tool in Microsoft Excel® (Data Integration Tool v5.4) for calculating each LOE and the final MLOE. The current version is available on the Sediment Quality Assessment Tools page of the SCCWRP website (SCCWRP 2009). It should be noted that this tool is currently under revision.

7.3.2 Benthic Line of Evidence

Calculation of the benthic LOE should follow methods described in the Water Quality Control Plan (SWRCB and CalEPA 2009) and the Technical Support Manual (Bay et al. 2009). As part of this calculation, data should be prepared and benthic indices calculated in accordance with this manual. The preparation of data for benthic indices calculations is a critical step that has significant impacts on the results and SQO outcome. The Technical Support Manual (Bay et al. 2009) describes most key steps required to prepare data prior to benthic indices calculations. In addition, the Technical Support Manual states that data

should be prepared by identifying each taxon to the appropriate level "in keeping with the benthic macrofauna species list for the relevant habitat."

While a seemingly uncomplicated task, to address this data requirement in full, the following steps should be taken to ensure consistency with SCCWRP data assessment tools, as it will allow for the most comprehensive quality control:

- Species collected from within the Los Angeles/Long Beach Harbor Complex should be compared to the "Benthic Lookup" worksheet found within the Data Integration Tool v5.4 Excel file (SCCRWP 2008). Species should be matched to corresponding names within this species list, and if no corresponding species exists, species should be matched to the next lowest taxonomic level (genus, family, order, class, or phylum). Species may be identified to the nearest taxonomic level using the Southern California Association of Marine Invertebrate Taxonomists (SCAMIT) Taxonomic Toolbox available at http://www.scamit.org/taxontools/.
- Species not matching a corresponding species or the next lowest taxonomic level should be checked to ascertain that the species name is the most recently accepted name for that organism. For example, *Caesia perpinguis* (Hinds 1844) should be recorded as *Nassarius perpinguis*. The most recently accepted species names may be checked at the following website:
 - http://www.bily.com/pnwsc/web-content/Articles/Name%20Changes%20 from%20the%20Lights%20Manual.html.
- If benthic species or taxon does not match any taxon provided in the Benthic Lookup worksheet, they should be excluded from benthic indices calculations entirely (i.e., their names should be removed from the species listed at that station), until revision of the Data Integration Tool v5.4 is complete, which will allow for the ability to include some species that may not be on the list, but are in fact marine benthic invertebrates.
- Upon conversion of species names to the lowest taxonomic level, duplicate, triplicate, or more taxon results should be compiled into one taxon result with one corresponding abundance. For example, if the abundance data show two organisms identified as *Lineus bilineatus* (which can be converted to the family Lineidae, as it is the lowest matching taxonomic level) and four organisms identified as Lineidae, then

- there should be one line item for Lineidae with a total of six organisms (Ranasinghe 2010).
- Within the Benthic Lookup worksheet found within the Data Integration Tool v5.4 Excel file, there is a species level column that indicates whether or not a species should be dropped. SCCWRP states that "when present, 'Drop' in this column indicates that abundances of this taxon are included in index calculations, but it is not included for counting numbers of taxa because lower taxonomic level entries in this taxon are also present" (SCCWRP 2008). It is critical that programming language or user-designed spreadsheets used to calculate benthic indices incorporate this "drop" instruction.

The supplemental data preparation steps previously described must be followed such that QC checks can be conducted on the numerical results of the indices using the SCCWRP Data Integration Tool v5.4, assuming initial indices calculations were performed using a programming language such as IDL, SAS® software, or separate Excel file. In addition, if species names are not matched to the Benthic Lookup worksheet when they should be, the match between observed and expected species could be reduced, which would affect the RIVPACS score and could also have an impact on the result of other benthic indices due the inclusion of total number of taxa or subclasses of taxa (i.e., molluscs) in the calculation of these indices. If species names are included in the data analyses when they do not match the species list, the scores of the benthic indices could be impacted, which could potentially affect the benthic LOE outcome.

7.3.3 Quality Control of Chemistry and Benthic Lines of Evidence Data Assessment

A minimum of 10 percent of any data entry performed prior to data assessment should be assessed as part of the QC program. If major issues are found, then 100 percent of data entry conducted should be reviewed. If LOE calculations are done using an alternative method to the SCCWRP data integration tool, data from 10 percent of the samples (minimum of five samples) should be entered into the data integration tool and results of each individual LOE (i.e., CSI, the California Logistic Regression Model [CA LRM], RIVPACS, and IBI.) for each sample should be compared to results using alternative methods. If the data integration tool

is the primary method used for the calculation, then 10 percent of the data should be checked using a calculator or alternative method. If major issues are found with indices calculations, then 100 percent of indices calculations should be reviewed. Results of the QC checks should be presented as part of a QA/QC report attached to any SQO assessments conducted.

7.4 Fish Tissue

The laboratory will receive 12 whole fish per station per species. Three composites of four fish will be used for analysis. Individual fish will be sexed before processing. White croaker, California halibut, and shiner surfperch will be filleted, and skin-off muscle fillets will be analyzed. Fish tissue samples will be analyzed for the following:

- Percent lipids
- Organochlorine Pesticides (including DDT and its derivatives, chlordane compounds, dieldrin, and toxaphene)
- PCB congeners

Specific compounds to be analyzed and analytical methods and target reporting limits are provided in Table 19. Sample volumes and preservation techniques for required analyses are included in Table 12.

7.5 Analyte Lists, Analytical Methods, and Reporting Limits

Analyte lists and target reporting limits for water, sediment, and fish tissue are identified in Tables 17, 18, and 19, respectively. Analytical methods and target detection limits were selected to comply with SWAMP guidance (SWRCB 2008). The analyte list for sediments includes the recommended chemical analytes needed to calculate the chemistry exposure line of evidence for application of the California sediment quality assessment framework (SWRCB 2009).

The laboratory should report detected compounds down to the MDL, if applicable. Laboratories should also provide the instrument verified limit of detection (LOD) for each analyte in the lab report and EDD. Reported values between the MDL and method reporting limit (MRL) should be qualified with a "J." Non-detects should be reported at the lowest calibration level (typically the MRL) or LOD, whichever is lower. In some cases, non-detects may be reported at the MDL.

7.6 Laboratory Turn Around Times

Turnaround times for laboratory analyses are presented in Table 20.

8 QUALITY OBJECTIVES AND CRITERIA (ELEMENT A7)

8.1 Field Measurements

Guidance for data quality objectives (DQOs) for field measurements is derived from the SWAMP guidance for water parameters (SWRCB 2008) and from Bight Field Operations Manual for fish tissue parameters (BCEC 2008). Quality objectives for parameters that will be measured in the field, including in situ water quality and fish measurements are presented in Table 21. A description of sediment grab quality objectives and criteria are located in Bight Field Operations Manual on pages 24 – 25 (2008).

Field measurements will be made in triplicate on five percent of the measurements. Each result will be recorded along with the average of the three results, the difference between the largest and smallest result, and the percent difference between the largest and smallest result. The percent difference will be calculated as follows:

Percent difference = 100*(largest-smallest)/average

Triplicate measurements, the average of the results, and percent difference will be recorded on the field data sheet. The percent difference, as appropriate, will be compared against the precision criteria established for field measurements in Table 21. If precision does not meet the established criteria the equipment should be inspected to ensure that it is working properly. Re-calibrate equipment if necessary and then repeat the triplicate measurements process until DQOs are achieved.

8.2 Laboratory Analyses

It is critical to ensure that the data collected are of acceptable quality so that the project objectives for each special study or monitoring program sampling are achievable. Guidance for laboratory DQOs is derived from the SWAMP guidance (SWRCB 2008). The quality of the laboratory data are assessed by precision, accuracy, representativeness, comparability, completeness, and sensitivity.

The definitions for the data quality indicators are as follows:

- Precision is the ability of an analytical method or instrument to reproduce its own measurement. It is a measure of the variability, or random error, in sampling, sample handling, and laboratory analysis.
- Accuracy is a measure of the closeness of an individual measurement (or an average of multiple measurements) to the true or expected value.
- Representativeness expresses the degree to which data accurately and precisely
 represent an environmental condition. Examples of how representativeness will be
 assessed and controlled for include generating analyte lists from known contaminants
 of concern, field observations made during sample collection, and analytical methods
 evaluated during data validation.
- Comparability expresses the confidence with which one dataset can be evaluated in relation to another dataset. For this program, comparability of data will be established through the use of standard analytical methodologies and reporting formats, and of common traceable calibration and reference materials.
- Completeness is a measure of the amount of data that is determined to be valid in proportion to the amount of data collected.
- Sensitivity is related to the instrument calibration low level standard, method detection limits (MDLs), and/or estimated detection limits (EDLs). For each study, analytical methods will be selected to achieve reporting limits that comply with, or are close to, target detection limits.

Chemistry laboratory data quality objectives are presented in Table 22. Sediment toxicity and benthic community data quality objectives are provided in Table 23.

9 SPECIAL TRAINING AND CERTIFICATIONS (ELEMENT A8)

For sample preparation tasks, field crews will be trained in standardized sample collection requirements so that the samples collected and the data generated from the samples are consistent among field crews. The field coordinator must ensure that all field crew members are fully trained in the collection and processing of sediment, surface water, tissues, decontamination protocols, and sample transport and COC procedures.

Supplemental information related to field sampling and laboratory analyses is provided in Table 24. All field personnel are responsible for complying with quality assurance/quality control requirements that pertain to their organizational and technical function. Each field staff member must have a combination of experience and education to adequately demonstrate a specific knowledge of their particular function. Analytical laboratories must be certified by the California ELAP and/or NELAP for the analyses they are responsible for performing.

10 DOCUMENTATION AND RECORDS (ELEMENT A9)

Document requirements for field records and laboratory reports are provided in Section 16 – Data Management. Each project team member (field coordinator, QA manager, etc.) is responsible for documenting all necessary project information and should maintain files for individual tasks. Upon completion of each sampling event, project team members must provide electronic copies of such files to the Harbor Toxics TMDL project manager. Electronic documents will be maintained by the managing consultant and RMC.

11 QUALITY CONTROL (ELEMENT B05)

Procedures and formulas for calculating quality control results can be found in the SWAMP Manual (SWRCB 2008). Section 8 describes what should be done if control limits are exceeded and how corrective actions will be assessed and documented. Precision and bias are also discussed in Section 8. This section identifies quality control activities, including blanks, spikes, and duplicates and provides a definition of the various QA/QC related terms.

11.1 Field Quality Assurance/Quality Control Samples

Field QA/QC samples will be collected along with environmental samples. Field QA/QC samples are useful in identifying possible problems resulting from sample collection or sample processing in the field. The collection of field QA/QC samples will follow SWAMP guidance and may include field (homogenization) duplicates, rinsate (equipment) blanks, and/or field blanks (SWRCB 2008). Rinsate blanks will be collected by pouring distilled water into a decontaminated grab sampler and poured into an appropriate bottle. Field blanks are required whenever samples for trace metals analysis are being collected. The field blank will be prepared by pouring distilled water for its original container into a sample bottle while in the field; this sample will be analyzed for metals. The field duplicate will be collected and analyzed in the same manner as the original sample immediately following the collection of the original sample. Field QA/QC sample frequencies and performance criteria are presented in Table 25.

11.2 Laboratory Quality Assurance/Quality Control

Additional sample volume will be collected to ensure that the laboratory has sufficient sample volume to run the program-required analytical QA/QC samples for analysis, as specified in Table 26.

11.2.1 Laboratory Quality Control Definitions

Laboratory QA/QC definitions are identified in Table 27.

12 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE (ELEMENT B06)

This section describes procedures for testing, inspection, and maintenance of field and laboratory equipment. A summary is provided in Table 28.

12.1 Field Instruments/Equipment

The field coordinator or designee will maintain inventories of field instruments and equipment and will be responsible for the preparation, documentation, and implementation of preventative maintenance. The frequency and types of maintenance will be based on the manufacturer's recommendations and/or previous experience with the equipment. The frequency of maintenance is dependent on the type and stability of the equipment, the methods used, the intended use of the equipment, and the recommendations of the manufacturer. Detailed information regarding the calibration and frequency of equipment calibration is provided in specific manufacturer's instruction manuals.

The field coordinator or designee will also be responsible for navigation and will confirm proper operation of the navigation equipment daily. This verification may consist of internal diagnostics or visiting a location with known coordinates to confirm the coordinates indicated by the navigation system. The samplers will be inspected daily for any mechanical problems. Any problems will be noted in the field logbook and corrected prior to continuing sampling operations.

12.2 Laboratory Instruments/Equipment

The selected laboratories will maintain an inventory of instruments and equipment and the frequency of maintenance will be based on the manufacturer's recommendations and/or previous experience with the equipment.

Selected laboratories will have a preventative maintenance program, as detailed in their QA Plans, organized to maintain proper instrument and equipment performance, and to prevent instrument and equipment failure during use. The program considers instrumentation, equipment, and parts that are subject to wear, deterioration, or other changes in operational characteristics, the availability of spare parts, and the frequency at which maintenance is

required. Any equipment that has been overloaded, mishandled, shown to give suspect results, determined to be defective will be taken out of service, or tagged with the discrepancy note, will be stored in a designated area until the equipment has been repaired. After repair, the equipment will be tested to ensure that it is in proper operational condition. The QA manager will be promptly notified in writing if defective equipment casts doubt on the validity of analytical data. The QA manager will also be notified immediately regarding any delays due to instrument malfunctions that could impact holding times. Selected laboratories will be responsible for the preparation, documentation, and implementation of the preventative maintenance program. All maintenance records will be checked according to the schedule on an annual basis and recorded by the responsible individual. A laboratory QA/QC manager or designee shall be responsible for verifying compliance.

13 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY (ELEMENT B07)

Proper calibration of equipment and instrumentation is an integral part of the process that provides quality data. Instrumentation and equipment used to generate data must be calibrated at a frequency that ensures sufficient and consistent accuracy and reproducibility.

13.1 Field Equipment

Field equipment will be calibrated prior to the sampling event according to manufacturer's recommendations using manufacturer's standards. A calibration check will be performed at the beginning of each day. The equipment, calibration, and maintenance information will be documented in the instrument calibration log. The frequency of calibration is dependent on the type and stability of the equipment, the methods used the intended use of the equipment, and the recommendations of the manufacturer. Detailed information regarding the calibration and frequency of equipment calibration is provided in specific manufacturer's instruction manuals. Equipment that fails calibration will be recalibrated prior to use. Supplemental information is provided in Table 29.

13.2 Analytical Laboratory Equipment

As part of their QC program, selected laboratories will perform two types of calibrations. A periodic calibration is performed at prescribed intervals for relevant instruments and laboratory equipment (i.e., balances, drying ovens, refrigerators, and thermometers), and operational calibrations are performed daily, at a specified frequency, or prior to analysis (i.e., initial calibrations) according to method requirements. Calibration procedures and frequency are discussed in the laboratory QA Plan. Calibrations are discussed in the laboratory SOPs for analyses.

The laboratory QA/QC manager will be responsible for ensuring that the laboratory instrumentation is calibrated in accordance with specifications. Implementation of the calibration program shall be the responsibility of the respective laboratory manager. Recognized procedures (USEPA, ASTM, or manufacturer's instructions) shall be used when available.

Physical standards (i.e., weights or certified thermometers) shall be traceable to nationally recognized standards such as the National Institute of Standards and Technology (NIST). Chemical reference standards shall be NIST standard reference materials (SRMs) or vendor-certified materials traceable to these standards.

The calibration requirements for each method and respective corrective actions shall be accessible, either in the laboratory SOPs or the laboratory's QA Plan for each instrument or analytical method in use. An instrument that fails calibration will be recalibrated prior to use. All calibrations shall be preserved on electronic media.

14 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES (ELEMENT B08)

14.1 Field

Equipment and supplies purchased for use in field sampling will be inspected for damage as they are received. Confirmation that sample bottles are laboratory-certified clean will be made when received.

14.2 Analytical Laboratories

Equipment and supplies purchased for use in analytical laboratories will be inspected for damage as they are received. Supplies purchased from outside sources must be of adequate quality to sustain confidence in the laboratory's test. If no independent quality assurance of outside supplies is available, the laboratory will first perform tests with the new supplies to be sure they comply with specified requirements.

15 NON-DIRECT MEASUREMENTS (ELEMENT B09)

Measurements of tide are being provided by the National Oceanic and Atmospheric Administration (NOAA 2013). When in the Port of Los Angeles, use Los Angeles, California, tide gauge 9410660. When in Port of Long Beach or San Pedro Bay, use Long Beach Terminal Island tide gauge 9410680. Tide predictions are assumed to be accurate. No other non-direct measurements are anticipated for this project.

16 DATA MANAGEMENT (ELEMENT B10)

16.1 Overview of Data Management Process

Data will be stored in a customizable database program called EQuisS (version 5, EarthSoft 2013), maintained by the managing consultant. After each field event, field data will be imported into the EQuIS database either by direct import using a custom field application export or manual submittal of a field EDD containing information from field collection logs (Figure 8). Field data collection and management options are described below, along with field EDD requirements. Water quality data will be exported into an EDD format compatible with the 2012 NPDES MS4 permit (RWQCB 2012), specifically the Southern California Storm Water Monitoring Coalition's Standardized Data Transfer Formats, or any subsequently revised RWQCB required format. These field data will undergo quality control checks such as sample identification code review, transcription error review, and completeness verification. Independent of the field data, laboratory data will be submitted to the QA manager in specified PDF and EDD formats. This data will undergo verification and validation using Automated Data Review (ADR) software and then will be uploaded into the EQuIS database with the applied final validation qualifiers. These two datasets will be linked in the database to retain corresponding field data for each sample. Data will be exported from EQuIS in custom formats to meet agency database requirements.

16.2 Field Records

All collected field samples will be documented using a custom field application or field collection logs that will be manually converted to a field EDD prior to data submittal. Additionally, the field coordinator or designee will keep a daily record of significant events, observations, and measurements on a daily log. Entries for each day will begin on a new page. The person recording information must enter the date and time and initial each entry. In general, sufficient information will be recorded during sampling so that reconstruction of the event can occur without relying on the memory of the field personnel. The daily log will contain the following information, at a minimum:

- Project name
- Field personnel on site
- Site visitors
- Weather conditions

- Field observations
- Maps and/or drawings
- Date and time sample collected
- Sampling method and description of activities
- Identification or serial numbers of instruments or equipment used
- Deviations from the PQAPP, CCMRP, and SAP
- Conferences associated with field sampling activities

After each field event, field data will be imported into the EQuIS database either by direct import using a custom field application export or manual submittal of a field EDD containing information from field collection logs. The field data collection and management options are described below along with field EDD requirements.

16.2.1 Water

Refer to SWAMP SOP (MPSL-DFG 2007) for standardized language for taking notes. Upon arrival at a sampling site, record visual observations on the appearance of the water and other information related to water quality and water use. A field data sheet will be completed for each water sample collection location. The field form should indicate sample time and where the sample was collected within the water column (i.e., surface, mid-depth, or bottom). Required data for field EDDs is included as Appendix B.

At a minimum each field data sheet will include the name of personnel, date, time, location coordinates (measured by DGPS), weather (e.g., heavy rains, cold front, very dry, very wet), wind speed and direction (see Beaufort Scale as presented in MPSL-DFG 2007), collection depth, physical description of the water sample (e.g., suspended of floating material, color, odor, or sheen), biological activity (e.g., presence of fish, birds, macrophytes, phytoplankton), description of in-water activities (e.g., recreational boating, active discharges), and the water quality parameter measurements. If the water quality conditions are exceptionally poor, note that standards are not met in the observations, (e.g., dissolved oxygen is below state criteria).

Continuous water quality monitoring data collected will be saved in raw format on the field laptop and also saved to a dedicated project file currently maintained by the managing consultant. After completion of each sampling event, data will be transferred to the RMC.

16.2.2 Sediment

A surface sediment collection form will be completed for each grab sediment sample. Required data for field EDDs is included as Appendix B. In addition to standard entries of personnel, date, and time, the form will include information regarding station coordinates, grab sampler penetration, and physical characteristics of the sediment, such as texture, color, odor, and sheen.

A representative grab sample from each location will be photographed. Project, sample identification number, attempt number (if more than one attempt), and sample date and time will be labeled on a white board and included in each photograph.

16.2.3 Fish Tissue

Several datasheets will be utilized in association with fish tissue collection at each location. Required data for field EDDs is included as Appendix B. Data should be collected to include general trawl information and individual fish data, including length, weight, and gross pathology.

16.3 Field Data Option 1: Custom Field Application

Electronic Field EDDs can be generated from a custom field application that provides electronic data entry forms for field information and generates field collection logs, sample labels, and eCOCs. A custom field application improves data quality by minimizing handwritten errors through the use of required data entry elements and controlled, unique identifiers for locations, samples, and analytical test requests. In addition, it promotes efficiency in the field and provides eCOCs for laboratory sample check-in and for loading field information to the managing consultant's data management system, further reducing transcription errors. When a custom field application is used in place of field collection logs, all information and generated forms are backed up to removable storage devices and should be emailed to the QA manager at the end of each field day for data security. The same

elements required for the field logs described in Section 16.4 would be captured in the custom field application. To use this application, the field coordinator should coordinate with the QA manager.

16.4 Field Data Option 2: Field Collection Logs

All field sample collection information will be recorded on field collection logs maintained by the field coordinator, or designee, for each activity. Key information should be recorded for each sample such as sample station, station coordinates, sample identification code, and sample matrix. The information recorded during sample collection should fulfill the requirements of the Field EDD described in Section 16.5.

Notes will be taken in indelible, waterproof blue or black ink. Errors will be corrected by crossing out with a single line, dating, and initialing. Each field collection log will be marked with the project name, number, and date. The field logs will be will be scanned at the end of each field day and emailed to the special study/monitoring study project manager.

16.5 Field Electronic Data Deliverable Requirements

Field data collection, including observations, field measurements, and sample generation, will be facilitated by submittal of a Field EDD generated from the custom field application or field collection logs. Field data must be submitted to the managing consultant. It is imperative that the field sample data match field forms and the COC forms. The Field EDD template (Excel workbook format) will be provided by the QA manager upon request. Required, conditional, and optional fields will be identified in the Field EDD template along with defined valid values. Required fields must be filled out prior to submittal of field data. Conditional fields are required for specific matrices, collection methods, or if a field QC sample is collected. Optional fields may be populated at the field coordinator's discretion. Columns may be left blank but should not be deleted. Any questions with regards to filling out the Field EDD should be directed to the QA manager.

16.6 Laboratory Record Requirements

Analytical data records (bookmarked PDF and EDD formats) will be generated by the laboratory and submitted to the managing consultant upon completion. If the files are too

large to be emailed, a notification email with download instructions can be sent to the managing consultant. The data package level will depend on the sampling event. The field coordinator or QA manager will identify the required data package level on the COC.

The analytical laboratory will be required to report the following, where applicable:

- Case Narrative. This summary will discuss problems encountered during any aspect of analysis, if any. It should discuss, but is not be limited to, QC issues, sample shipment, sample storage, and analytical difficulties. Any problems encountered, actual or perceived, and their resolutions will be documented in as much detail as appropriate. Analytical QC samples that exceed project performance criteria and/or lab performance criteria should also be discussed in the case narrative.
- COC Records. Legible copies of the COC forms will be provided as part of the data package. This documentation will include the time of receipt and condition of each sample received by the laboratory. Additional internal tracking of sample custody by the laboratory will also be documented on a sample receipt form. The form must include all sample shipping container temperatures measured at the time of sample receipt.
- Sample Results. The data package will summarize the results for each sample analyzed. The summary will include the following information when applicable:
 - Field sample identification code and corresponding laboratory identification code
 - Sample matrix
 - Date and time of sample extraction
 - Date and time of analysis
 - Final concentration volumes and dilution factors
 - Instrument and analyst identification
 - MRLs and MDLs accounting for sample-specific factors (e.g., dilution and total solids)
 - Analytical results with reporting units identified
 - Data qualifiers and their definitions
 - Raw data including instrument printouts, chromatograms, and bench sheets (required for full data packages)

- QA/QC Summaries. Contract Laboratory Program (CLP)-like form summaries should be generated for all required laboratory QC components and samples (e.g., method blanks, instrument daily tunes, surrogate spikes, internal standards, laboratory control samples). These summaries should include spike volumes, parent sample concentrations, percent recoveries, relative percent differences, area counts, and laboratory control limits as applicable. For full data packages, the associated raw data files should be included.
- Instrument Calibration Data. CLP-like form summaries of calibration data (i.e., initial calibration, initial calibration verification, and continuing calibration verification) should be included in all data packages. For full data packages, the associated raw data files should be included.

All instrument data shall be fully restorable at the laboratory from electronic backup. Laboratories will be required to maintain all records relevant to project analyses for a minimum of 5 years.

16.7 Laboratory Electronic Deliverable Requirements

EDDs will be submitted by the lab in the ADR format. ADR software is a tool used to streamline data validation by automatically evaluating the laboratory QC samples to the performance criteria established in this CCMRP. A1 and A3 files will be required. Specifications and valid values can be found in Appendix C. An ADR electronic QAPP will be developed and distributed to the laboratories as required prior to project implementation. Updates to the specifications, valid values, and electronic QAPPs will occur over time and will be distributed to the laboratories when they become available.

17 ASSESSMENT AND RESPONSE ACTIONS (ELEMENT C1)

The following sections describe the types of assessments that may be conducted for this project and how these assessments will be reported to project management.

17.1 Assessments and Response Actions

Laboratory and field performance audits consist of on-site reviews of QA systems and equipment for sampling, calibration, and measurement. The field coordinator is responsible for assessment of field activities and has the authority to issue a stop work order on sample collection. The Harbor Toxics TMDL study project manager or designee provides additional oversight on all field and laboratory activities and consequently may also issue a stop work order on sample collection if warranted. Laboratory audits are not anticipated to be conducted as part of this study; however, all laboratory audit reports will be made available to the project QA manager upon request. The laboratory is required to have written procedures addressing internal QA/QC (i.e., QA Plan), which will be reviewed by the project QA manager to ensure compliance with the project SAP. The laboratory must ensure that personnel engaged in sampling and analysis tasks have appropriate training. As part of the audit process, the laboratory will provide written details of any and all method modifications planned for consultant's review. Laboratory non-conformances will be documented and submitted to the QA manager for review. All non-conformances will be discussed in the final data report.

17.2 Corrective Actions

The following sections identify the responsibilities of key project team members and actions to be taken in the event of an error, problem, or nonconformance to protocols identified in this document.

17.2.1 Field Activities

The field coordinators will be responsible for correcting equipment malfunctions during the field sampling effort. The project QA manager will be responsible for resolving situations identified by the field coordinators that may result in noncompliance with this SAP. All corrective measures will be immediately documented in the field logbook.

17.2.2 Laboratory

The laboratory is required to comply with their SOPs. The laboratory manager will be responsible for ensuring that appropriate corrective actions are initiated as required for conformance with this CCMRP. All laboratory personnel will be responsible for reporting problems that may compromise the quality of the data.

The laboratory project manager will be notified immediately if any QC sample grossly exceeds the laboratory in-house control limits. The analyst will identify and correct the anomaly before continuing with the sample analysis. If the anomaly cannot be corrected, the laboratory manager will document the corrective action taken in a memorandum submitted to the QA manager within 5 days of the initial notification. A narrative describing the anomaly, the steps taken to identify and correct the anomaly, and the treatment of the relevant sample batch (i.e., recalculation, reanalysis, and re-extraction) will be submitted with the data package.

18 REPORTS TO MANAGEMENT (ELEMENT C2)

QA reports to management will include verbal status reports, written reports on field sampling activities and laboratory processes, data validation reports, and final project reports. These reports shall be the responsibility of the Harbor Toxics TMDL study project manager.

Progress reports will be prepared by the field coordinators and delivered to the Harbor Toxics TMDL study Project manager following each sampling event. These progress reports will contain final versions (peer reviewed) of field logs, field notebooks, COCs, observations, etc.

19 DATA REVIEW, VERIFICATION, AND VALIDATION (ELEMENT D1)

During the validation process, analytical data will be electronically and/or manually evaluated for method and laboratory QC compliance, and their validity and applicability for program purposes will be determined.

Based on the findings of the validation process, data validation qualifiers may be assigned. The validated project data, including qualifiers, will be entered into the project database, thus enabling this information to be retained or retrieved, as needed.

20 VERIFICATION AND VALIDATION METHODS (ELEMENT D2)

Data verification includes a review for completeness and accuracy by the field coordinator and laboratory manager; review by the data managers for outliers and omissions; and the use of performance criteria to identify laboratory quality control sample outliers. For this program, completeness checks (target analyte lists, etc.), holding time compliance and laboratory QC sample performance evaluations (method blank detections, surrogate recoveries, laboratory control sample recoveries, etc.) will be conducted with ADR software. ADR will generate a report of all results that are outside of the performance criteria presented in this CCMRP. Data validation will then be conducted by the data validator and consists of accepting, rejecting, or applying qualifiers to data based on the ADR verification findings, analytical method criteria, NFG data validation guidance (USEPA 1999, 2004, 2005, 2008), and professional judgment. A data validation report will be generated to document qualifications applied to data. All validated data will be entered into the EQuIS database, and a final data file will be exported. Verification of the database export against the PDF data report will be performed by the QA manager or designee. Any errors found in the data file export will be corrected in the database and reviewed for systemic reporting errors. Once all discrepancies are resolved, the database will be established.

All laboratory data will receive a Stage 2A validation (USEPA 2009). The recommended QC checks identified in a Stage 2A validation are as follows:

- Completeness
- Holding times
- Requested methods were performed
- MRL/EDL project requirements were met
- Sample-related QC data were analyzed at the required frequencies
- QC performance criteria were met for the following:
 - Laboratory control samples
 - Matrix spike/matrix spike duplicate
 - Standard reference material
 - Surrogate recoveries
 - Method blanks
- Field QC samples

The project QA manager will be responsible for the final review of all data generated from analyses of samples.

21 RECONCILIATION WITH USER REQUIREMENTS (ELEMENT D3)

The QA manager will review data at the completion of each task to determine if DQOs have been met. If data do not meet the project's specifications, the QA manager will review the errors and determine if the problem is due to calibration/maintenance, sampling techniques, or other factors and will suggest corrective action, if appropriate. It is expected that the problem would be able to be corrected by retraining, revision of techniques, or replacement of supplies/equipment; if not, the DQOs will be reviewed for feasibility. If specific DQOs are not achievable, the QA manager will recommend appropriate modifications. If matrix interference is suspected to have attributed to the exceedance, adequate laboratory documentation must be presented to demonstrate that instrument performance and/or laboratory technique did not bias the result. In cases where the DQOs have been exceeded and corrective actions did not resolve the outlier, data will be qualified per USEPA National Functional Guidelines (USEPA 1999, 2004, 2005, 2008). In these instances, the usability of the data will be determined by the extent of the exceedance. Rejected data will be assigned an "R" qualifier and will not be used for any purposes.

22 SEDIMENT QUALITY OBJECTIVES PART 1 – STRESSOR INVESTIGATIONS

The SQO Part 1 assessment process categorizes sediment quality and associated benthic health based on MLOE; however, it does not identify the cause of impacts, if present, to the benthic community. For stations that do not meet the SQO for aquatic life (i.e., for stations categorized as Possibly Impacted, Likely Impacted, or Clearly Impacted), the SQO Part 1 Technical Guidance recommends additional investigations in order to identify the cause of sediment impacts (Bay et al. 2009). Table 30 provides a summary of possible outcomes from the integration of three LOEs (sediment chemistry, sediment toxicity, and benthic community).

The Harbor Toxics TMDL mandates, "if moderate toxicity as defined in the SQO Part 1 is observed, results shall be highlighted in annual reports and further analysis and evaluation to determine causes and remedies shall be required in accordance with the EO approved monitoring plan." This CCMRP recommends a modified approach to stressor investigations. Stressor investigations will be conducted if the SQO Part 1 station assessment results in a final category of Likely Impacted or Clearly Impacted. Stressor investigations may be considered if the SQO Part 1 station assessment results in a final category of Possibly Impacted. This recommendation is predicated on three points:

- Compliance with the Harbor Toxics TMDL may be demonstrated by meeting (i.e., final station assessment is Unimpacted or Likely Unimpacted) the SQO Part 1
- Stations may be categorized as Unimpacted or Likely Unimpacted even if moderate toxicity is observed
- Stations may be categorized as Possibly Impacted of Likely Impacted even if no or low toxicity is observed

Attainment of the Harbor Toxics TMDL is the ultimate goal. Stressor investigation studies, as recommended in the SQO Part 1 Technical Guidance (Bay et al. 2009), will more effectively benefit the objectives of the Harbor Toxics TMDL when the SQO Part 1 assessment is not met; rather than when it has been met but moderate toxicity is still observed.

The SQO Part 1 Technical Guidance (Bay et al. 2009) recommends a phased approach to stressor identification, including:

- Confirmation that pollutants are indeed the basis for the impact determine that the benthic community is not impaired due to confounding factors such as physical disturbance or non-pollutant constituents
- Establishment of what specific chemical(s) is the cause of impact using either statistical analyses, laboratory toxicity identification evaluations (TIEs), or bioavailability analyses, determine the specific chemical(s) causing impairment; then, confirm initial results
- **Identification of the source of the chemical(s)** conduct additional field investigations to determine source of contaminants causing impairment

In the event sediment quality is categorized as impaired in accordance with SQO Part I, the results will be evaluated to determine the feasibility and scale of a stressor identification study. For example, instead of conducting a separate stressor identification study for each station, it may be more effective to conduct a single stressor identification study for a region if multiple stations located in relative proximity exhibited similar impairments. A site-specific monitoring and reporting plan (separate from this document) will be developed and submitted for approval prior to commencement of investigations. Site-specific monitoring and report plans will address each phase of a stressor identification study (Bay et al. 2009) and will include the following components:

- **Sample Methodology** when, where, why, and how confirmatory samples will be collected and analyzed
- Quality Assurance/Quality Control methodology to ensure samples are collected, analyzed and evaluated according to the Harbor Toxics TMDL program established standards

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TABLES

Table 1
Sediment Quality 303(d) Listings for Harbor Waters

	Pollutants Requiring TMDL	
Waterbody	(Sediment and/or Tissue)	Other Requirements
-	Tissue: Chlordane, Dieldrin, DDT, PCBs,	·
Los Angeles/Long Beach Inner Harbor	Toxaphene	Toxicity, benthic community effects
	Sediment: Metals (Copper, Zinc), Benzo(a)pyrene,	
	Chrysene	
Los Angeles/Long Beach Outer Harbor	Tissue: Chlordane, Dieldrin, DDT, PCBs,	Toxicity
	Toxaphene	
	Sediment: None	
Los Angeles Harbor – Inner Cabrillo Beach	Tissue: Chlordane, Dieldrin, DDT, PCBs,	None
	Toxaphene	
	Sediment: Metals	
Los Angeles Harbor – Cabrillo Marina	Tissue: Chlordane, Dieldrin, DDT, PCBs,	None
	Toxaphene	
	Sediment: Benzo(a)pyrene, Pyrene	
Los Angeles Harbor – Fish Harbor	Tissue: Chlordane, Dieldrin, DDT, PCBs,	Toxicity
	Toxaphene	
	Sediment: Metals (Copper, Lead, Mercury, Zinc),	
	Chlordane, DDT, PCBs, PAHs (Benzo[a]pyrene,	
	Phenanthrene, Benzo[a]anthracene, Chrysene,	
	Pyrene, Dibenzo[a,h]anthracene)	
Consolidated Slip	Tissue: Chlordane, Dieldrin, DDT, PCBs,	Toxicity, benthic community effects
	Toxaphene	
	Sediment: Metals (Cadmium, Copper, Chromium,	
	Lead, Zinc, Mercury), Chlordane, DDT, PCBs, PAHs	
	(Benzo[a]pyrene, 2-methyl-napthalene,	
	Phenanthrene, Benzo[a]anthracene, Chrysene,	
	Pyrene)	
San Pedro Bay	Tissue: Chlordane, Dieldrin, DDT, PCBs,	Toxicity
	Toxaphene	
	Sediment: Metals, Chlordane, PAHs, DDT	
Los Angeles River	Tissue: None	Toxicity
Estuary	Sediment: Metals, Chlordane, DDT, PCBs	

Note:

Bold pollutants are required by the Harbor Toxics TMDL.

Table 2
Final, Mass-Based TMDLs and Allocations for Metals, PAHs, DDT, and PCBs

				Total	Total	Total
	Total Cu	Total Pb	Total Zn	PAHs	DDT	PCBs
Waterbody/Source	(kg/year)	(kg/year)	(kg/year)	(kg/year)	(g/year)	(g/year)
Consolidated Slip - TMDL	12.1	16.6	53.3	1.43	0.56	1.14
Inner Harbor - TMDL	76.7	105.3	338.3	9.1	3.56	7.22
Outer Harbor - TMDL	81.6	112.1	360.1	9.7	3.79	7.68
Fish Harbor - TMDL	1.04	1.43	4.59	0.123	0.048	0.098
Cabrillo Marina - TMDL	1.32	1.81	5.8	0.156	0.061	0.124
Inner Cabrillo Beach - TMDL		-		-	0.04	0.09
San Pedro Bay - TMDL	648	890	2858	76.6	30.1	61.0
LA River Estuary - TMDL	735	1009	3242	86.9	34.1	69.2

Notes: kg = kilogram g = gram

Table 3
Final Concentration-Based Sediment WLAs for Metals in Consolidated Slip and Fish Harbor

Concentration-based Sediment WLAs (mg/kg dry sediment)											
Cadmium	Chromium	Mercury									
1.2	81	0.15									

Mercury applies to both Consolidated Slip and Fish Harbor; cadmium and chromium applies to Consolidated Slip only.

Table 4
10-Year Recurring Schedule

		10-Year Schedule Recurring Schedule																																											
			[2013]	/202	23		[2014]	/202	4		202	15/2025 2016			2016/2026			2017/2027			2018/2028			2019/2029				2020/2030				2021/2031				2022/2032									
Task	Frequency	W	Sp	Su	F	W	Sp	Su	F	W	S	p 9	Su	F	W	Sp	Su	F	W	S	9	Su	F	W	Sp	Su	F	W	/ Sp	Su	J F	\	V S	ìр	Su	F	W	Sp	Su	F	W	Sp	9	Su	F
Water Quality Monitoring	Annually: 2 wet (♦), 1 dry (♦)	•		•	•	•		•	•	•			•	•	•		•	•	•			•	•	•		•	•	•	•	•	•		•		•	•	•		•	•	•			•	•
Sediment Sampling (SQO)	two per 5 years			•													•									•													•						
Fish Tissue Sampling	Biennially							•									•									•									*									•	
Reporting	Annually			[] ◆				•					•				•				•	•				•				•	•				•				•					•	

Wet weather monitoring occurs between October 1 and April 30. For illustrative purposes, wet weather monitoring is shown to occur in winter and fall. Wet weather monitoring may occur during April (spring), and it is likely two wet weather events may occur in the same season. Similarly for dry weather, it may occur during May or June (spring).

The wet weather season and the reporting schedule are not the same. Annual reports may not include all wet weather monitoring events for a given wet season.

Water quality monitoring includes in situ monitoring (pH, dissolved oxygen, temperature, and salinity) and water sampling for subsequent chemical analyses.

Sediment sampling includes collect grab samples for chemical and toxicological analyses and benthic infauna community analysis.

Fish tissue sampling includes compositing fish tissue/species for chemical analyses.

[] = Indicates no sampling to be conducted in bracketed year. For example, Winter 2013 does not require a wet weather sampling event; however, Winter 2023 will require a wet weather sampling event.

- ♦ = dry weather
- = wet weather
- ◆ = Sediment quality evaluations conducted in coordination with Bight Program years.

F = Fall (October 1 – December 31)

Sp = Spring (April 1 – June 30)

SQO = sediment quality objectives

Su = Summer (July 1 – September 30)

W = Winter (January 1 – March 31)

Table 5
Deliverables Schedule

Type of Report	Frequency	Project Delivery Date(s)	Person(s) Responsible for Report Preparation	Report Recipients
PQAPP	Once	March 2013		
CCMRP	Once	March 2013	Field Project	
Draft Monitoring Reports	Annually	March 15	Manager and Program Manager	Los Angeles Regional Board
Final Monitoring Reports	Annually	April 15	Trogram Manager	

Table 6
Station Locations

	Station	Latitude (Decimal Degrees)	Longitude (Decimal	
Waterbody Name	ID	WGS84	Degrees)	Station Location
Consolidated Slip ¹	1	33.77484789	-118.2453739	Center of Consolidated Slip
	2	33.76489964	-118.2520890	East Turning Basin
	3	33.76228823	-118.2740995	Center of the POLA West Basin
Los Angeles Inner Harbor	4	33.75184257	-118.2709906	Main Turning Basin north of Vincent Thomas Bridge
narbor	5	33.73244349	-118.2513428	Between Pier 300 and Pier 400
	6	33.72572842	-118.2714880	Main Channel south of Port O'Call
Fish Harbor	7	33.73580102	-118.2672600	Center of inner portion of Fish Harbor
Las Avaralas Ovitari	8	33.71466100	-118.2423894	Los Angeles Outer Harbor between Pier 400 and middle breakwater
Los Angeles Outer Harbor ¹	9	33.71204959	-118.2634051	Los Angeles Outer Harbor between the southern end of the reservation point and the San Pedro breakwater
Cabrillo Marina	10	33.71938642	-118.2790736	Center of West Channel
Inner Cabrillo Beach	11	33.71180088	-118.2810632	Center of Inner Cabrillo Beach
	12	33.76726235	-118.2335604	Cerritos Channel between the Heim Bridge and the Turning Basin
Long Beach Inner	13	33.75383222	-118.2163996	Back Channel between Turning Basin and West Basin
Harbor	14	33.74898245	-118.2308246	Center of West Basin
	15	33.74214303	-118.1994876	Center of Southeast Basin
Long Beach Outer	16	33.73144867	-118.2210007	Center of Long Beach Outer Harbor
Harbor ¹	17	33.72759372	-118.1860575	Between the southern end of Pier J and the Queens Gate
	18	33.75383222	-118.1813321	Northwest of San Pedro Bay near Los Angeles River Estuary
San Pedro Bay ¹	19	33.73667149	-118.1315908	East of San Pedro Bay
	20	33.72547972	-118.1573319	South of San Pedro Bay inside breakwater
Los Angeles River	21	33.75644363	-118.1933943	Los Angeles River Estuary Queensway Bay
Estuary	22	33.76101300	-118.2021110	Los Angeles River Estuary

Note: 1 Fish tissue samples will be collected within four waterbodies: Consolidated Slip, Los Angeles Harbor, Long Beach Harbor, and San Pedro Bay from popular fishing areas or areas with habitat or structure that may attract fish. Specific fish tissue sampling locations will be determined at the time of the sampling event using guidelines outlined in Section 4.2.3.

Table 7
Collection of Data Parameters by Station

Matrix	Depth	рН	Salinity	DO	Temp.	TSS	Analytical Chemistry	Toxicity	Benthic Infauna
	Surface	Х	Х	Х	Х	Х	X ³		
Water ¹	Mid-depth	Х	Х	Х	Х	Х	-		
	Bottom	Х	Х	Х	Х	Х	-		
Sediment	Surface						X ⁴	х	Х
Fish Tissue ²	Variable						X ⁵		

TSS = total suspended solids

- 1 In situ water quality parameters include pH, salinity, dissolved oxygen, and temperature. Grab water samples will be collected for TSS (at all three depths) and chemical constituents (at the surface only).
- 2 Fish tissue will be collected via trawling, beach seine, etc. over a specific area rather than a point station.
- 3 Constituents to be measured in water samples include dissolved and total metals, pesticides, and PCBs. A complete list is provided in Table 17.
- 4 Constituents to be measured in sediment samples include TOC, grain size, metals, PAHs, organochlorine pesticides, and PCBs. A complete list is provided in Table 18.
- 5 Constituents to be measured in tissue samples includes lipids, organochlorine pesticides, and PCBs. A complete list is provided in Table 19.

Table 8
Sample Nomenclature

						Org	anism							
Waterbody or Other Area	Codes	Station	Number ¹	Media Codes		Scientific Name	Common Name	Code	Organism or Num	r Composite nber	Dep	oth	Date of (Collection
Outer Harbor- LB	OA	1	01	Receiving Water	RW	Genyonemus lineatus	White Croaker	WC	1 or C1	01 or C1	0-1 m	0-1	1-Jul-13	20130701
Outer Harbor- LB	ОВ			Surface Sediment	SS	Paralichthys californicus	California Halibut	СН			15-60 cm	15-60		
Inner Harbor - LA	IA			Fish Fillet skin off (muscle)	FF	Cymatogaster aggregata	Shiner Surfperch	SS						
Inner Harbor - LB	IB			Field Blank	FB									
Consolidated Slip	CS			Equipment Rinsate Blank	EB									
Fish Harbor	FH													
Cabrillo Marina	CM													
Cabrillo Beach	СВ													
San Pedro Bay	SP													
Dominguez Channel	DC													
Cabrillo Pier	СР													

Water and Sediment Sample IDs include: waterbody/station number/media code/depth/date.

Tissue Sample IDs include: waterbody/station number/media code/organism name/organism or composite number/date.

1 When collecting a field duplicate, add '1000' to the station number.

Table 9
Informational vs. Critical Data

Type of Data	Are Data Informational or Critical?
Visual observations (weather, fish anomalies, photographs, etc.)	Informational
Physical station measurements (water depth, tide, etc.)	Informational
Water samples	Critical
In situ water quality measurements	Critical
Sediment samples	Critical
Fish tissue samples	Critical
Fish measurements (lengths, weights, etc.)	Informational

Table 10 Field Standard Operating Procedures

Field SOP	Number	Date	Regulatory Citation	Corresponding CCMRP Section
Grab Water Sampling	MPSL-DFG Procedure Number 1.0	10/15/2007	SWAMP (MPSL-DFG 2007)	5.1.2
In situ water quality monitoring	MPSL-DFG Procedure Number 1.0	10/15/2007	SWAMP (MPSL-DFG 2007)	5.1.1
Surface Sediment Grab Sampling	Pgs. 22-25	7/2008	Bight Field Operations Manual (2008)	5.2
Sediment Chemistry Sample Processing	Pgs. 22-25	7/2008	Bight Field Operations Manual (2008)	5.2
Sediment Toxicity Sample Processing	Pg. 32	7/2008	Bight Field Operations Manual (2008)	5.2
Sediment Toxicity Testing	Chapter 4	5/2009	SQO Draft Technical Support Manual (Bay et al. 2009)	7.2.2
Benthic Infauna Processing	Pgs. 26-28	7/2008	Bight Field Operations Manual (2008)	5.2
Benthic Infauna Community Analysis	Chapter 5	5/2009	SQO Draft Technical Support Manual (Bay et al. 2009)	7.2.3
Fish Collection (otter trawl nets)	Pgs. 33-38	7/2008	Bight Field Operations Manual (2008)	5.3
Fish Collection (all other methods)	MPSL-DFG Method Number 102	7/20/01	SWAMP (MPSL-DFG 2007)	5.3
Fish Processing	Pgs. 44-46; Pg. 7 (Section C3)	7/2008	Bight Field Operations Manual (2008); Bight Bioaccumulation Workplan (2009)	5.3

Table 11 Sampling Methods and Processing

Sample Matrix	Sampler	Sample Processing
Water	Grab sampler (e.g., Van Dorn or niskin bottle)	None
In situ water quality measurements	Multi-parameter water quality sonde equipped with probes for temperature, dissolved oxygen, pH, and salinity	None
Sediment	Van Veen	Chemistry: homogenize Toxicity: none Benthic infauna: sieve
Fish Tissue	Otter trawl or lampara net, beach seine, fish trap, or hook and line	Composite

More sampling equipment may be added by contractors as needed.

Table 12
Sample Containers and Holding Conditions

Parameter Waters	Sample Size	Container Size and Type	Holding Time	Preservative
Total suspended solids	1 L	1-L HDPE	7 days	Cool ≤6°C
Total suspended solids	1.	TENDIE	48 hours until preservation	Cool ≤6°C
Total metals	100 mL	250 mL HDPE	6 months to analysis	Ambient; HNO3 to pH<2
			Field filter; 48 hours until preservation	Cool ≤6°C
Dissolved metals	100 mL	250 mL HDPE	6 months to analysis	Ambient; HNO ₃ to pH<2 after filtration
Organochlorine pesticides	1 to 2 L	2 X 1-L amber glass	14 days to extraction	Cool ≤6°C; pH 5-9
pesticides		giass	40 days after extraction	Cool ≤6°C
PCB Congeners	1 to 2 L	2 X 1-L amber glass	None ²	Cool ≤6°C
Sediments	•			
Bulk density	50 g	4-oz glass	None established	Ambient
Specific gravity	100 g	16-oz glass	None established	Ambient
Total solids	10 g	8-oz glass	14 days	Cool ≤6°C
Grain size	300 g	16-oz plastic	6 months	Cool ≤6°C
DOC in porewater	1- 2 L sediment ¹	2 X 1-L amber glass	48 hours for extraction, filtration and preservation; 28 days to analysis	HCl or H2SO4 to pH<2 after filtration; Cool ≤6°C and dark
			28 days	Cool ≤6°C
ТОС	10 g	4-oz glass	1 year, if frozen within 28 days of collection	Freeze -20°C
			6 months	None
Total metals and Mercury	100 g	4-oz glass	1 year; samples must be extracted within 14 days of thawing	Freeze -20°C ³
			14 days to extraction	Cool ≤6°C
PAHs/ Organochlorine pesticides	500 g	Two 8-oz glass	1 year to extraction; samples must be extracted within 14 days of thawing	Freeze -20°C
			40 days after extraction	Cool ≤6°C
PCB Congeners	500 g	Two 8-oz glass	None ¹	Cool ≤6°C Freeze -20°C

Parameter	Sample Size	Container Size and Type	Holding Time	Preservative
Tissues				
Lipids	200 g	Split taken from sample for chemistry analyses	1 year	Freeze -20°C
			14 days to extraction	Cool ≤6°C
Organochlorine pesticides	200 g	Polyethylene bags or 8-oz glass	1 year to extraction; samples must be extracted within 14 days of thawing	Freeze -20°C
			40 days after extraction	Cool ≤6°C
		Polyethylene	2	Cool ≤6°C
PCB Congeners	200 g	bags or 8-oz glass	None ²	Freeze -20°C

Some criteria may differ from SWAMP guidance; however are consistent with analytical method criteria.

Recommendations are intended as guidance only. The selection of sample container and amount of sample required may vary per contracted laboratory sampling requirements.

- 1 Volume of sediment collected must be sufficient to produce a minimum of 40mL of porewater.
- 2 PCB hold time was removed in SW-846, Chapter 4, Revision 4, February 2007 for aqueous and solid samples stored cool ≤6°C.
- 3 Mercury will be analyzed prior to freezing.
- 4 POC solids are analyzed for TOC by USEPA 9060. The volume of water collected must be sufficient to produce a minimum of 10g of suspended sediment. Water may be field filtered.

°C = degrees Celsius

DDT = dichlorodiphenyltrichloroethane

DOC = dissolved organic carbon

g = gram

HDPE = high-density polyethylene

L = liter

mL = milliliter

oz = ounce

PAH = polycyclic aromatic hydrocarbon

PCB = polychlorinated biphenyl

POC = particulate organic carbon

SWAMP = California Surface Water Ambient Monitoring

Program

TOC = total organic carbon

USEPA = U.S. Environmental Protection

Agency

VOA = volatile organic analysis

Table 13
Equipment and Support Facilities Needed

Equipment/Support Facility	Provided By
General	
Sampling platform	Subcontractor
Water	
Water quality sonde	Subcontractor
Water sampler	Subcontractor
Sediment	
Sediment sampler	Subcontractor
Fish	
Fish collection gear (trawl nets,	Subcontractor
beach seine, fish traps, hook/line)	Subcontractor
Scales	Subcontractor
Other ¹	

1 Other equipment/support facilities needed to be provided by subcontractors.

Table 14
Field Measurement SOPs

Field Measurement			
SOPs	Number	Date	Regulatory Citation
In situ Water Quality Monitoring	MPSL-DFG Procedure Number 1.0	10/15/2007	SWAMP (MPSL- DFG 2007)
Fish Processing	Pgs. 40-42	7/2008	Bight Field Operations Manual (2008)

Table 15
Field Instruments

Instrument	Unit	Major Attribute ¹
Water quality sonde – temperature probe	°C	
Water quality sonde – dissolved oxygen		
probe	mg/L	
Water quality sonde – pH probe	units	
Water quality sonde – salinity probe	ppt	
Scales	g	
Other ²		

°C = degrees Celsius

mg = milligram

L = liter

g = grams

ppt = parts per thousand

- 1 Major attributes to be provided by subcontractors
- 2 Other instruments to be determined by subcontractors

Table 16
Parameters to be Monitored and Corresponding Analytical Methods

Parameter	Analytical Method	Notes
Water		
TSS	USEPA 160.2/SM 2540D	
Metals – total and dissolved	USEPA 6010A/6020/200.8/1640	
Mercury – total and dissolved	USEPA 7471A/USEPA 245.7	
Organochlorine pesticides	USEPA 8081A/USEPA 625	
PCB Congeners	USEPA 8270C (SIM or TQ)/USEPA 625	
Sediment		
TOC	USEPA 9060A/SM 5310B	
Grain Size	ASTM D442/SM 2560	
Total solids	USEPA 160.3/SM 2540B	
Metals	USEPA 6010B/USEPA 6020	
Mercury	USEPA 7471A/USEPA 245.7/USEPA 1631	
PAHs	USEPA 8270C/USEPA 8270D SIM	
Organochlorine Pesticides	USEPA 8081A/USEPA 8270C	
PCB Congeners	USEPA 8270C (SIM or TQ)/USEPA 625	
Toxicity – Acute	10-day amphipod survival	Bay et al. 2009
Toxicity- Chronic	28-day juvenile polychaete growth and survival or	Bay et al. 2009
	2-day bivalve embryo development	
Benthic Infauna	Sorting, taxonomic analysis	Bay et al. 2009
Fish Tissue		
Percent Lipids	NOAA 1993A	Gravimetric
Organochlorine Pesticides	USEPA 8081/USEPA8270C	
PCB Congeners	USEPA 8270C/USEPA 8270D	

Table 17
Water Parameters, Analytical Methods, and RLs

Parameter ¹	Analytical Method ²	Target RL ³
Conventionals (mg/L)	-	
Total Suspended Solids	SM 2540 D	2
Seawater (and Freshwater) Total and Dissolved Meta	als (μg/L)	
Cadmium	USEPA 6010A/6020/200.8/1640	0.01
Chromium	USEPA 6010A/6020/200.8/1640	0.1
Copper	USEPA 6010A/6020/200.8/1640	0.01
Lead	USEPA 6010A/6020/200.8/1640	0.01
Mercury	USEPA 7470A/245.7/1631	0.0002
Zinc	USEPA 6010A/6020/200.8/1640	0.10
PCB Congeners (ng/L) ⁴ - Low Resolution Analytical M	ethods	
CL3-PCB-18	USEPA 8270C (SIM or TQ)/625	0.1
CL3-PCB-28	USEPA 8270C (SIM or TQ)/625	0.1
CL3-PCB-37	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-44	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-49	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-52	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-66	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-70	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-74	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-77	USEPA 8270C (SIM or TQ)/625	0.1
CL4-PCB-81	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-87	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-99	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-101	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-105	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-110	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-114	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-118	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-119	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-123	USEPA 8270C (SIM or TQ)/625	0.1
CL5-PCB-126	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-128	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-138	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-149	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-151	USEPA 8270C (SIM or TQ)/625	0.1

Parameter ¹	Analytical Method ²	Target RL ³
CL6-PCB-153	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-156	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-157	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-158	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-167	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-168	USEPA 8270C (SIM or TQ)/625	0.1
CL6-PCB-169	USEPA 8270C (SIM or TQ)/625	0.1
CL7-PCB-170	USEPA 8270C (SIM or TQ)/625	0.1
CL7-PCB-177	USEPA 8270C (SIM or TQ)/625	0.1
CL7-PCB-180	USEPA 8270C (SIM or TQ)/625	0.1
CL7-PCB-183	USEPA 8270C (SIM or TQ)/625	0.1
CL7-PCB-187	USEPA 8270C (SIM or TQ)/625	0.1
CL7-PCB-189	USEPA 8270C (SIM or TQ)/625	0.1
CL8-PCB-194	USEPA 8270C (SIM or TQ)/625	0.1
CL8-PCB-201	USEPA 8270C (SIM or TQ)/625	0.1
CL9-PCB-206	USEPA 8270C (SIM or TQ)/625	0.1
Chlorinated Pesticides (ng/L)	-	
alpha-Chlordane (cis-chlordane)	USEPA 8081A/625	0.50
gamma-Chlordane (trans-chlordane)	USEPA 8081A/625	0.50
Oxychlordane	USEPA 8081A/625	0.50
cis-Nonachlor	USEPA 8081A/625	0.50
trans-Nonachlor	USEPA 8081A/625	0.50
Total chlordane ⁵	USEPA 8081A/625	
2,4'-DDD	USEPA 8081A/625	0.50
2,4'-DDE	USEPA 8081A/625	0.50
2,4'-DDT	USEPA 8081A/625	0.50
4,4'-DDD	USEPA 8081A/625	0.50
4,4'-DDE	USEPA 8081A/625	0.50
4,4'-DDT	USEPA 8081A/625	0.50
Dieldrin	USEPA 8081A/625	0.10
Toxaphene	USEPA 8081A/625	2.0

High volume alternative sampling techniques may be used to achieve lower reporting limits for these analyses.

- 1 Specific analytes used for each study conducted for the RMC may vary by waterbody, according to the listings.
- 2 Laboratories may use different versions of recommended methods (i.e. USEPA 8270C) as long as the QA/QC elements identified in this CCMRP are met.
- 3 Matrix interference and/or dilutions due to non-target analytes may increase target reporting limits. The method detection limit (MDL) should be at least three times lower than the reporting limit (40 CFR 136) but will vary per instrument by MDL study. Detected data between the MDL and the RL will be reported and flagged by the lab as estimated. Non-detected data may be reported at the MDL.
- 4 PCB co-elutions will vary by instrument and column, and may increase reporting limits for some congeners.
- 5 Total chlordane is calculated using the following compounds: alpha-chlordane, gamma-chlordane, oxychlordane, cis-nonachlor, and trans-nonachlor.

μg/L = microgram per liter

ng/L = nanogram per liter

CCMRP = Coordinated Compliance Monitoring and Reporting Plan

CFR = Code of Federal Regulations

DDT = dichlorodiphenyltrichloroethane

DDD = dichlorodiphenyldichloroethane

DDE = dichlorodiphenyldichloroethylene

MDL = method detection limit

QA/QC = quality assurance/quality control

RL = reporting limit

SIM = selected ion monitoring

SM = standard method

TMDL = total maximum daily load

PCB = polychlorinated biphenyl

TBD = to be determined

-- = no RL available

Table 18
Sediment Parameters, Analytical Methods, and RLs

Parameter ^{1,2}	Analytical Method ³	Target RL ⁴
Conventional Parameters		
Total solids (% wet weight)	SM 2540B/USEPA 160.3	0.1
Grain size (% retained)	ASTM D442/SM 2560	1%
		0.01%
Total organic carbon (%)	SM 5310B/USEPA 9060A	OC
Metals (μg/g or mg/kg)		
Cadmium	USEPA 6010B/6020	0.01
Chromium	USEPA 6010B/6020	0.1
Copper	USEPA 6010B/6020	0.01
Lead	USEPA 6010B/6020	0.01
	USEPA	
Mercury	6010B/6020/7471A/245.7/1631	0.03
Zinc	USEPA 6010B/6020	0.10
Polycyclic Aromatic Hydrocarbons (ng/g or μg/kg)		
Acenaphthene	USEPA 8270C/8270D - SIM	20
Anthracene	USEPA 8270C/8270D - SIM	20
Biphenyl	USEPA 8270C/8270D - SIM	20
Naphthalene	USEPA 8270C/8270D - SIM	20
2,6-Dimethylnaphthalene	USEPA 8270C/8270D - SIM	20
Fluorene	USEPA 8270C/8270D - SIM	20
1-Methylnaphthalene	USEPA 8270C/8270D - SIM	20
2-Methylnaphthalene	USEPA 8270C/8270D - SIM	20
1-Methylphenanthrene	USEPA 8270C/8270D - SIM	20
Phenanthrene	USEPA 8270C/8270D - SIM	20
Benz[a]anthracene	USEPA 8270C/8270D - SIM	20
Benzo[a]pyrene	USEPA 8270C/8270D - SIM	20
Benzo(e)pyrene	USEPA 8270C/8270D - SIM	20
Chrysene	USEPA 8270C/8270D - SIM	20
Dibenz[a,h]anthracene	USEPA 8270C/8270D - SIM	20
Fluoranthene	USEPA 8270C/8270D - SIM	20
Perylene	USEPA 8270C/8270D - SIM	20
Pyrene	USEPA 8270C/8270D - SIM	20
Organochlorine Pesticides (ng/g or μg/kg) - Low Reso	olution Analytical Methods	
Total Chlordane ⁵	USEPA 8081A/8270C	
alpha-Chlordane (cis-chlordane)	USEPA 8081A/8270C	0.5
gamma-Chlordane (trans-chlordane)	USEPA 8081A/8270C	0.5
Oxychlordane	USEPA 8081A/8270C	0.5
cis-Nonachlor	USEPA 8081A/8270C	0.5

Parameter ^{1,2}	Analytical Method ³	Target RL ⁴
trans-Nonachlor	USEPA 8081A/8270C	0.5
Dieldrin ⁶	USEPA 8081A/8270C	0.02
Toxaphene ⁶	USEPA 8081A/8270C	0.10
2,4'-DDD	USEPA 8081A/8270C	0.5
2,4'-DDE	USEPA 8081A/8270C	0.5
2,4'-DDT	USEPA 8081A/8270C	0.5
4,4'-DDD	USEPA 8081A/8270C	0.5
4,4'-DDE	USEPA 8081A/8270C	0.5
4,4'-DDT	USEPA 8081A/8270C	0.5
PCB Congeners (ng/g or μg/kg) ⁷ - Low Resolution Analy	rtical Methods	
CL3-PCB-18	USEPA 8270C /8270D-SIM	0.2
CL3-PCB-37	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-44	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-49	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-52	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-66	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-70	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-74	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-77	USEPA 8270C/8270D-SIM	0.2
CL4-PCB-81	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-87	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-99	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-101	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-105	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-110	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-114	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-118	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-119	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-123	USEPA 8270C/8270D-SIM	0.2
CL5-PCB-126	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-128	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-138	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-149	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-151	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-153	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-156	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-157	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-158	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-167	USEPA 8270C/8270D-SIM	0.2

Parameter ^{1,2}	Analytical Method ³	Target RL ⁴
CL6-PCB-168	USEPA 8270C/8270D-SIM	0.2
CL6-PCB-169	USEPA 8270C/8270D-SIM	0.2
CL7-PCB-170	USEPA 8270C/8270D-SIM	0.2
CL7-PCB-177	USEPA 8270C/8270D-SIM	0.2
CL7-PCB-180	USEPA 8270C/8270D-SIM	0.2
CL7-PCB-183	USEPA 8270C/8270D-SIM	0.2
CL7-PCB-187	USEPA 8270C/8270D-SIM	0.2
CL7-PCB-189	USEPA 8270C/8270D-SIM	0.2
CL8-PCB-194	USEPA 8270C/8270D-SIM	0.2
CL8-PCB-201	USEPA 8270C/8270D-SIM	0.2
CL9-PCB-206	USEPA 8270C/8270D-SIM	0.2

- 1 Specific analytes used for each study conducted for the Ports may vary by waterbody, according to the listings.
- 2 Units in dry weight unless otherwise noted. Specific analytes used for each study conducted for the Ports may vary by waterbody, according to the listings.
- 3 Laboratories may use different versions of recommended methods (i.e. USEPA 8270C) as long as the QA/QC elements identified in this CCMRP are met.
- 4 Matrix interference, total solid concentrations and/or dilutions due to non-target analytes may increase target reporting limits. The method detection limit (MDL) should be at least three times lower than the reporting limit (40 CFR 136) but will vary per instrument by MDL study.
- 5 Total chlordane is calculated using the following compounds: alpha-chlordane, gamma-chlordane, oxychlordane, cis-nonachlor, and trans-nonachlor.
- 6 TMDL sediment target for this compound is currently below achievable laboratory reporting limits. Results should be reported to the EDL/MDL.
- 7 PCB co-elutions will vary by instrument and column, and may increase reporting limits for some congeners. $\mu g/g = microgram per gram$

CCMRP = coordinated compliance monitoring and reporting plan

CFR = code of federal regulations

DDT = dichlorodiphenyltrichloroethane

DDD = dichlorodiphenyldichloroethane

DDE = dichlorodiphenyldichloroethylene

EDL = estimated detection limit

MDL = method detection limit

mg/kg = milligrams per kilogram

ng/g = nanogram per gram

OC = organic carbon

PCB = polychlorinated biphenyl

QA/QC = quality assurance/quality control

RL = reporting limit

SIM = selected ion monitoring

SM = standard method

TMDL = total maximum daily load

USEPA = U.S. Environmental Protection Agency

Table 19
Fish Tissue Parameters, Analytical Methods, and RLs

Parameter ¹	Analytical Method ²	Target RLs ³
Conventionals (%)	<u> </u>	1
Lipids	NOAA 1993a/Gravimetric	0.5
Organochlorine Pesticides (ng/g or µg/kg wet weight) - Low Resolution Analytical Methods	
Total Chlordane ⁴	USEPA 8081A/8270C	
alpha-Chlordane (cis-chlordane)	USEPA 8081A/8270C	4.0
gamma-Chlordane (trans-chlordane)	USEPA 8081A/8270C	4.0
Oxychlordane	USEPA 8081A/8270C	2.0
cis-Nonachlor	USEPA 8081A/8270C	4.0
trans-Nonachlor	USEPA 8081A/8270C	2.0
Dieldrin ⁵	USEPA 8081A/8270C	0.46
Toxaphene ⁵	USEPA 8081A/8270C	6.1
2,4'-DDD	USEPA 8081A/8270C	4.0
2,4'-DDE	USEPA 8081A/8270C	4.0
2,4'-DDT	USEPA 8081A/8270C	6.0
4,4'-DDD	USEPA 8081A/8270C	4.0
4,4'-DDE	USEPA 8081A/8270C	4.0
4,4'-DDT	USEPA 8081A/8270C	10.0
PCB Congeners ⁶ (ng/g wet weight) - Low Resolution	Analytical Methods	
CL3-PCB-18	USEPA 8270C/8270D	0.4
CL3-PCB-28	USEPA 8270C/8270D	0.4
CL3-PCB-37	USEPA 8270C/8270D	0.4
CL4-PCB-44	USEPA 8270C/8270D	0.4
CL4-PCB-49	USEPA 8270C/8270D	0.4
CL4-PCB-52	USEPA 8270C/8270D	0.4
CL4-PCB-66	USEPA 8270C/8270D	0.4
CL4-PCB-70	USEPA 8270C/8270D	0.4
CL4-PCB-74	USEPA 8270C/8270D	0.4
CL4-PCB-77	USEPA 8270C/8270D	0.4
CL4-PCB-81	USEPA 8270C/8270D	0.4
CL5-PCB-87	USEPA 8270C/8270D	0.4
CL5-PCB-99	USEPA 8270C/8270D	0.4
CL5-PCB-101	USEPA 8270C/8270D	0.4
CL5-PCB-105	USEPA 8270C/8270D	0.4
CL5-PCB-110	USEPA 8270C/8270D	0.4
CL5-PCB-114	USEPA 8270C/8270D	0.4
CL5-PCB-118	USEPA 8270C/8270D	0.4
CL5-PCB-119	USEPA 8270C/8270D	0.4
	·	-
CL5-PCB-123	USEPA 8270C/8270D	0.4

Parameter ¹	Analytical Method ²	Target RLs ³
CL5-PCB-126	USEPA 8270C/8270D	0.4
CL6-PCB-128	USEPA 8270C/8270D	0.4
CL6-PCB-138	USEPA 8270C/8270D	0.4
CL6-PCB-149	USEPA 8270C/8270D	0.4
CL6-PCB-151	USEPA 8270C/8270D	0.4
CL6-PCB-153	USEPA 8270C/8270D	0.4
CL6-PCB-156	USEPA 8270C/8270D	0.4
CL6-PCB-157	USEPA 8270C/8270D	0.4
CL6-PCB-158	USEPA 8270C/8270D	0.4
CL6-PCB-167	USEPA 8270C/8270D	0.4
CL6-PCB-168	USEPA 8270C/8270D	0.4
CL6-PCB-169	USEPA 8270C/8270D	0.4
CL7-PCB-170	USEPA 8270C/8270D	0.4
CL7-PCB-177	USEPA 8270C/8270D	0.4
CL7-PCB-180	USEPA 8270C/8270D	0.4
CL7-PCB-183	USEPA 8270C/8270D	0.4
CL7-PCB-187	USEPA 8270C/8270D	0.4
CL7-PCB-189	USEPA 8270C/8270D	20.0
CL8-PCB-194	USEPA 8270C/8270D	0.4
CL8-PCB-201	USEPA 8270C/8270D	0.4
CL9-PCB-206	USEPA 8270C/8270D	0.4

Data will be reported uncorrected for lipid content.

- 1 Specific analytes used for each study conducted for the RMC may vary by waterbody, according to the listings.
- 2 Laboratories may use different versions of recommended methods (i.e. USEPA 8270C) as long as the QA/QC elements identified in this CCMRP are met.
- 3 Matrix interference and/or dilutions due to non-target analytes may increase target reporting limits. The method detection limit (MDL) should be at least three times lower than the reporting limit (40 CFR 136) but will vary per instrument by MDL study.
- 4 Total chlordane is calculated using the following compounds: alpha-chlordane, gamma-chlordane, oxychlordane, cis-nonachlor, and trans-nonachlor.
- 5 TMDL tissue target for this compound is currently below achievable laboratory reporting limits. Results should be reported to the EDL/MDL.
- 6 PCB co-elutions will vary by instrument and column, and may increase reporting limits for some congeners.

CCMRP = Coordinated Compliance Monitoring and Reporting Plan

reporting rian

CFR = Code of Federal Regulations

DDT = dichlorodiphenyltrichloroethane

DDD = dichlorodiphenyldichloroethane

DDE = dichlorodiphenyldichloroethylene

ng/g = nanogram per gram

EDL = estimated detection limit

MDL = method detection limit

NOAA = National Oceanic and Atmospheric

Administration

QA/QC = quality assurance/quality control

RL = reporting limit

PCB = polychlorinated biphenyl

USEPA = U.S. Environmental Protection Agency

Table 20
Turnaround Times for Laboratory Analyses

Laboratory Analysis	Turnaround Time
Chemistry	Not to exceed 20 business days
Toxicity	Variable and will not have a duration greater than approved sediment holding times plus test duration
Benthic Infauna	Not to exceed 3 months

Table 21
DQOs for Field Measurements

					Target Reporting	
Group	Parameter	Accuracy	Precision	Recovery	Limits	Completeness
Water	Depth (m)	± 0.1 m	± 0.1 m	NA	NA	NA
Water	Temperature (°C)	± 0.5 °C	± 0.5 °C	NA	NA	NA
Water	рН	± 0.2 units	± 0.2 units	NA	NA	NA
Water	Dissolved oxygen	± 0.2 mg/L	5 percent	NA	NA	NA
Water	Salinity ¹ (ppt)	± 0.2 ppt	± 0.2 ppt	NA	NA	NA
Fish Tissue	Fish species identification	95 percent	NA	NA	NA	NA
Fish Tissue	Fish enumeration	90 percent	NA	NA	NA	NA
Fish Tissue	Fish lengths	90 percent	90 percent	NA	NA	NA
Fish Tissue	Fish weights	90 percent	Within 0.2 kg	NA	NA	NA

1 The value for salinity may be computed from specific conductance provided salinity is above 3 ppt based on previous observations at or near that location.

m = meter

mg/L = milligram per liter

°C = degrees Celsius

ppt = part per thousand

 μ S/cm = micro Siemens/cm

Table 22
Laboratory and Reporting Data Quality Objectives

Parameter	Precision ¹	Accuracy ²	Completeness ³			
Water						
Total suspended solids	± 25% RPD	N/A	90%			
Total and Dissolved Metals	± 25% RPD	75-125% R	90%			
PCB Congeners ⁴	± 25% RPD	50-150% R	90%			
Organochlorine Pesticides ⁴	± 25% RPD	50-150% R	90%			
Sediments						
Total solids	± 25% RPD	N/A	90%			
Grain size	± 25% RPD	N/A	90%			
Total organic carbon	± 25% RPD	80-120% R	90%			
Total Metals	± 25% RPD	75-125% R	90%			
Polycyclic aromatic hydrocarbons ⁴	± 25% RPD	50-150% R	90%			
Organochlorine pesticides ⁴	± 25% RPD	50-150% R	90%			
PCB Congeners ⁴	± 25% RPD	50-150% R	90%			
Tissues						
Lipids	± 25% RPD	N/A	90%			
Organochlorine pesticides ⁴	± 25% RPD	50-150% R	90%			
PCB Congeners ⁴	± 25% RPD	50-150% R	90%			

CRM = certified reference material

DDT = dichlorodiphenyltrichloroethane

PCB = polychlorinated biphenyl

R = recovery

RPD = relative percent difference

- 1 not applicable if native concentration of either sample is <RL.
- 2 Laboratory control sample, CRM's, and matrix spike/matrix spike duplicate percent recovery
- 3 Percent of each class of analytes that are not rejected after data validation conducted in accordance with the Technical Support Manual (Bay et al. 2009)
- 4 The accuracy goal is 70-130% R if certified reference material is used

Table 23

DQOs for Sediment Toxicity and Benthic Infauna Analyses

Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
	Meet all performance	Meet all performance			
Toxicity- Acute ¹	criteria in method	criteria in method relative to sample	NA	NA	90 percent
	reference toxicant	replication			
Toxicity- Chronic ¹	Meet all performance criteria in method relative to reference toxicant	Meet all performance criteria in method relative to sample replication	NA	NA	90 percent
Benthic Infauna - Sorting	95 percent	NA	NA	NA	NA
Benthic Infauna - Taxonomy	95 percent	± 5 percent	NA	NA	NA

1 DQOs follow procedures established in Bay et al. (2009)

Table 24
Specialized Personnel Training or Certification

Specialized Training Course Title or Description	Training Provider	Personnel Receiving Training/Organizational Affiliation	Location of Records and Certifications ¹
Education and/or Project Experience in Marine Biology/Ichthyology	Subcontractor	Individuals who will be performing fish identification onboard	NA
Experience using water and sediment grab samplers and in situ water quality probes; review of SOPs	Subcontractor	Individuals who will be collecting water and sediment samples	Signed copies of SOPs will reside with field datasheets
ELAP/NELAP Certification for laboratory analyses of water and sediment analyses	Subcontractor	Analytical laboratories	Server currently maintained by the managing consultant

1 If training records and/or certifications are on file elsewhere, then document their location in this column. If these training records and/or certifications do not exist or are not available, note this.

NA = Not applicable

ELAP = Environmental Laboratory Accreditation Program

NELAP = National Environmental Laboratory Accreditation Program

Table 25
Frequencies and Performance Criteria for Field Quality Assurance/Quality Control Sampling

Analysis Type	Field Duplicate	Field Duplicate Performance Criteria ^{1,2}	Field and Rinse Blank ³	Field and Rinse Performance Criteria ⁴	
Total solids	5% of total project	≤25%RPD if both result(s) are >5x RL.	NA	NA	
Total solius	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	NA	INA	
Lipids	5% of total project	≤25%RPD if both result(s) are >5x RL.	NA	NA	
Lipius	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	NA .	INA	
Grain size	5% of total project	≤25%RPD if both result(s) are >5x RL.	NA	NIA	
Grain Size	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	NA	NA	
Total suspended and dissolved	5% of total project	≤25%RPD if both result(s) are >5x RL.	NA	NIA	
solids	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	NA	NA	
Total and dissolved organic	5% of total project	≤25%RPD if both result(s) are >5x RL.	Not a method requirement;	<rl< td=""></rl<>	
carbon	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	task specific	\\L	
Total metals	5% of total project	≤25%RPD if both result(s) are >5x RL.	Not a method requirement;	<rl< td=""></rl<>	
Total metals	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	task specific	< KL	
Polycyclic aromatic	5% of total project	≤25%RPD if both result(s) are >5x RL.	Not a method requirement;	<rl< td=""></rl<>	
hydrocarbons	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	task specific	≺KL	
Pesticides	5% of total project	≤25%RPD if both result(s) are >5x RL.	Not a method requirement;	<rl< td=""></rl<>	
resticides	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	task specific	\KL	
DCD Congonors	5% of total project	≤25%RPD if both result(s) are >5x RL.	Not a method requirement;	∠DI	
PCB Congeners	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	task specific	<rl< td=""></rl<>	

- 1 Field duplicate RPD exceedances alone would not result in data qualification. Further evaluation into the sample collection procedures should be conducted.
- 2 This criteria is a slight deviation from SWAMP due to the ultra-low detection levels utilized for these studies.
- 3 If low level contamination could potentially bias results, field blanks and/or rinse (equipment) blanks should be collected.
- 4 The determination to qualify results based on field and/or rinse blank concentrations will be made by the QA Manager as part of the overall data usability assessment.

NA = not applicable

PCB = polychlorinated biphenyl

RL = reporting limit

RPD = relative percent difference

SWAMP = California Surface Water Ambient Monitoring Program

Table 26
Frequencies and Performance Criteria for Laboratory Quality Assurance/Quality Control Samples

Analysis Type	Initial Calibration ^{1,2}	Continuing Calibration Verification	LCS or SRM ³	Replicates	Matrix Spikes	Matrix Spike Duplicates	Method Blanks	Surrogate Spikes	Internal Standard
Total solids	Daily or each batch	N/A	N/A	1 per 20 samples	N/A	N/A	N/A	N/A	N/A
Lipids	Daily or each batch	N/A	N/A	1 per 20 samples	N/A	N/A	N/A	N/A	N/A
Grain size	Daily or each batch	N/A	N/A	1 per 20 samples	N/A	N/A	N/A	N/A	N/A
Total suspended and dissolved solids	Daily or each batch	N/A	N/A	1 per 20 samples	N/A	N/A	N/A	N/A	N/A
Total metals	Daily or each batch	Per 10 analytical runs	1 per 20 samples or 1 per batch	1 per 20 samples or 1 per batch	1 per 20 samples or 1 per batch	N/A	Each batch	N/A	Per method
PCB Congeners by low resolution method	As needed	Every 12 hours	1 per 20 samples or 1 per batch	N/A	1 per 20 samples or 1 per batch	1 per 20 samples or 1 per batch	Each batch	Every sample	Every sample
Polycyclic aromatic hydrocarbons	As needed	Every 12 hours	1 per 20 samples or 1 per batch	N/A	1 per 20 samples or 1 per batch	1 per 20 samples or 1 per batch	Each batch	Every sample	Every sample
Pesticides by low resolution method	As needed	Per 10 analytical runs	1 per 20 samples or 1 per batch	N/A	1 per 20 samples or 1 per batch	1 per 20 samples or 1 per batch	Each batch	Every sample	Every sample

Primary column is considered the column that contains the highest value with the least interference.

Values should have RPDs less than 40 percent or they are P flagged. ICALS = 20 percent or less and CCALS = 15 percent or less.

- 1 For physical tests, calibration and certification of drying ovens and weighing scales are conducted annually.
- 2 Calibrations should be conducted per analytical methods or instrument manufacturers specifications.
- 3 When a Standard Reference Material is not available, an LCS will be analyzed.

DDT = dichlorodiphenyltrichloroethane

LCS = Laboratory control sample

SRM = standard reference material

N/A = not applicable

PCB = polychlorinated biphenyl

Table 27
Laboratory Quality Assurance/Quality Control Definitions

Laboratory Quality Control	Definition
Calibration	A comparison of a measurement standard, instrument, or item with one having higher accuracy to detect, quantify, and record any inaccuracy or variation; the process by which an instrument setting is adjusted based on response to a standard to eliminate the inaccuracy.
Certified/Standard Reference Material	A substance whose property values are certified by a procedure that establishes its traceability and uncertainty at a stated level of confidence.
Continuing Calibration Verification	A periodic standard used to assess instrument drift between calibrations.
Internal Standard	Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.
Laboratory Replicate	Two or more representative portions taken from one homogeneous sample by the analyst and analyzed in the same testing facility.
Laboratory Control Sample	A specimen of known composition prepared using contaminant-free reagent water, or an inert solid, which is spiked with the analyte of interest at the midpoint of the calibration curve or at the level of concern, and then analyzed using the same preparation, reagents, and analytical methods employed for regular specimens and at the intervals set in the Quality Assurance Project Plan.
Matrix Spike	A test specimen prepared by adding a known concentration of the target analyte to a specified amount of a specific homogenized specimen where an estimate of the target concentration is available and subjected to the entire analytical protocol.
Matrix Spike Duplicate	A sample prepared simultaneously as a split with the matrix spike sample with each specimen being spiked with identical, known concentrations of targeted analyte.
Method Blank	A blank prepared to represent the sample matrix as closely as possible and analyzed exactly like the calibration standards, samples, and quality control (QC) samples. Results of method blanks provide an estimate of the within-batch variability of the blank response and an indication of bias introduced by the analytical procedure.
Sample Batch	Twenty or fewer field samples prepared and analyzed with a common set of quality assurance samples.
Surrogate	A pure substance with properties that mimics the analyte of interest (organics only) and which is unlikely to be found in environmental samples. It is added into a sample before sample preparation.

Table 28
Testing, Inspection, Maintenance of Sampling Equipment, and Analytical Instruments

Equipment/ Instrument	Maintenance, Testing, or Inspection Activities	Responsible	Frequency	SOP Reference
Grab water samplers	Inspect to ensure sampler ends close tightly to create seal, ensure sampler is rigged, deployed, retrieved properly	Subcontractor	With each use	SWAMP SOP (MPSL-DFG 2007)
Water quality sondes	Subcontractor		With each use	SWAMP SOP (MPSL-DFG 2007)
Sediment grab samplers	Inspect to ensure equipment is in good working order, properly rigged, deployed, retrieved	Subcontractor	With each use	Bight Field Operations Manual (2008)
Hook and line	Inspect to ensure equipment is in good working order	Subcontractor 1		SWAMP SOP (MPSL-DFG 2007)
Beach seines	Inspect for holes, ensure net is properly rigged, deployed, retrieved	Subcontractor	Daily	SWAMP SOP (MPSL-DFG 2007)
Fish traps	Inspect for holes, ensure trap is properly setup, deployed, and retrieved	Subcontractor	Daily	SWAMP SOP (MPSL-DFG 2007)
Trawl nets	Inspect for holes, ensure net is properly rigged, deployed, retrieved	Subcontractor	Daily	Bight Field Operations Manual (2008)
Scales	Ensure scales are calibrated and in good working order	Subcontractor	Daily	Manufacturer's recommendation

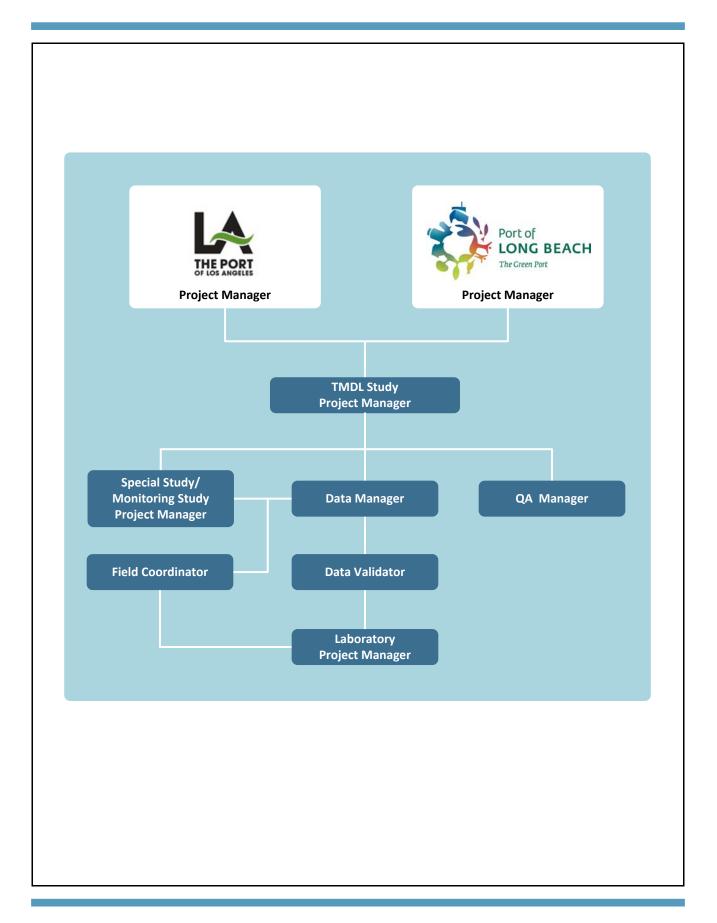
Table 29
Instrument/ Equipment Calibration and Frequency

Equipment/Instrument	SOP Reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
Water quality sonde	SWAMP	Calibrate each probe to manufacturer's specifications	Daily, more frequently if necessary	Subcontractor
Scales	Manufacturer's specifications	Calibration to known standard weights	Daily	Subcontractor

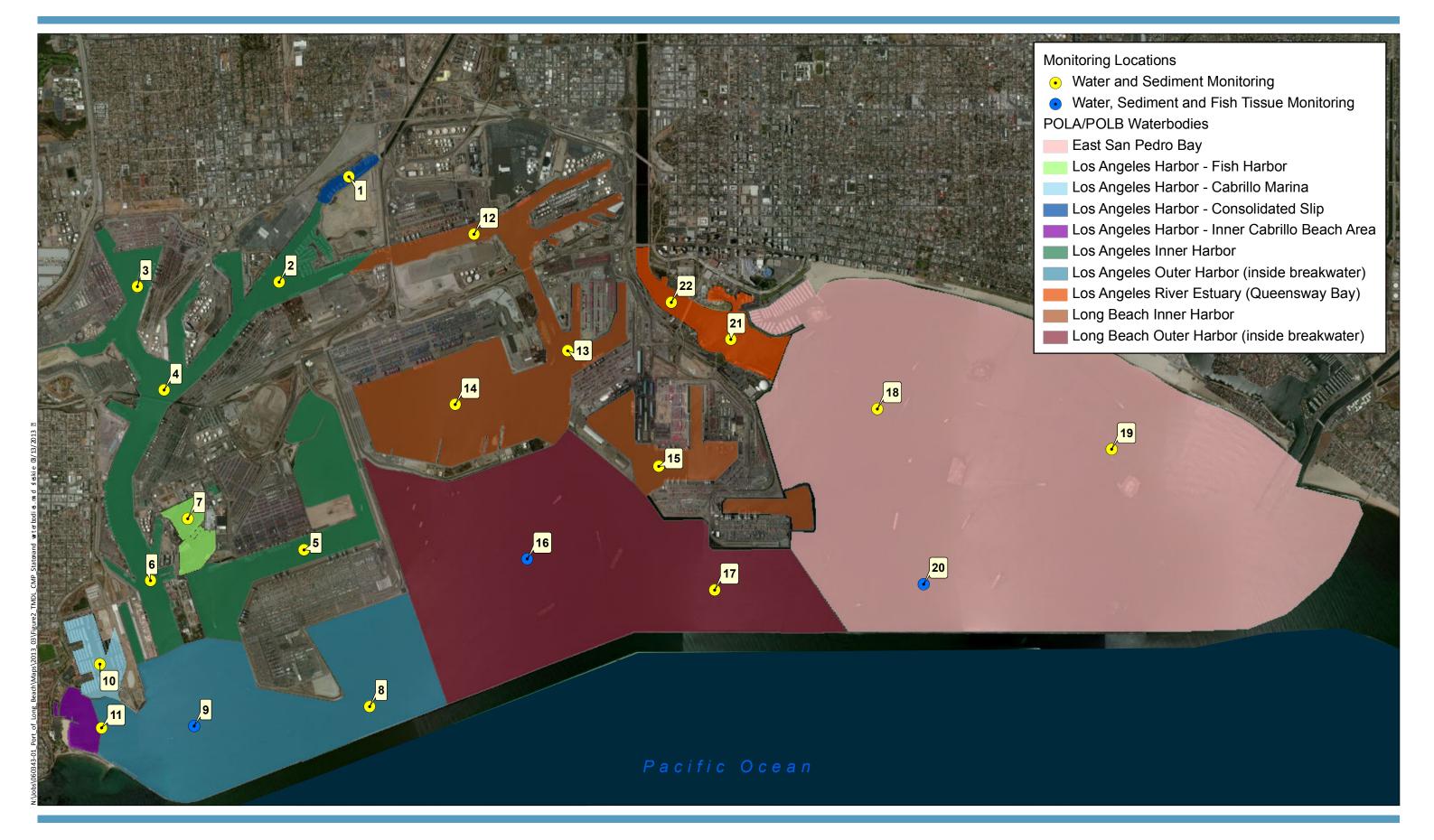
Table 30
Recommended Further Actions for Each of the Sediment Quality Categories

Category	Description	Recommended Actions
Unimpacted	No significant adverse impacts	None
Likely Unimpacted	Not expected to cause significantly adverse effects	None
Possibly Impacted	Adverse impacts may be present, but they are weak and/or uncertain	Continue to monitor site until enough information can determine if the site requires further investigation
Likely Impacted	Evidence of adverse impact	Follow on investigation:
Clearly Impacted	Clear and severe adverse impacts	 Conduct stressor ID study to confirm linkage to COC Conduct source ID study to determine management action
Inconclusive	Data are suspect or additional info required	Additional data required

FIGURES

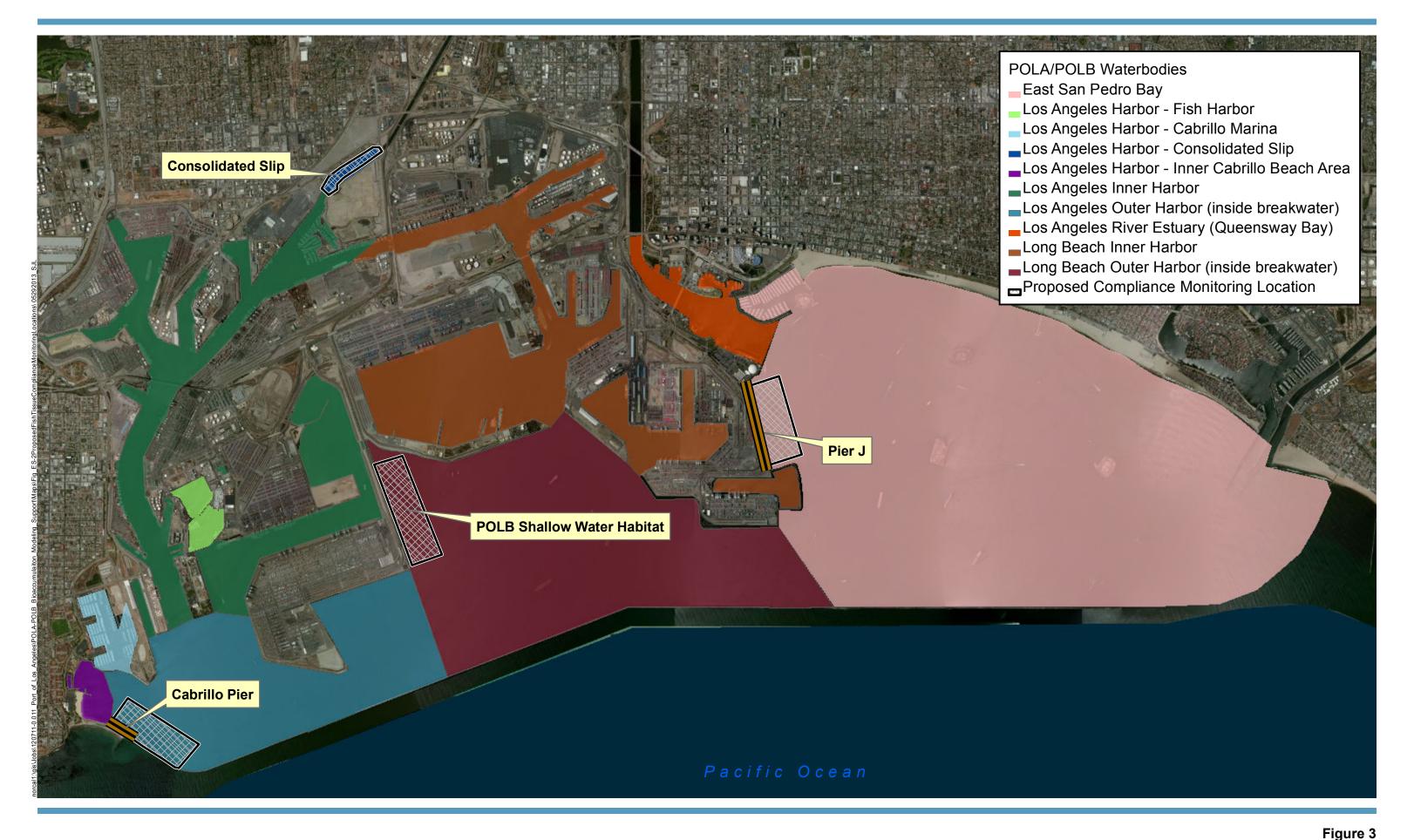






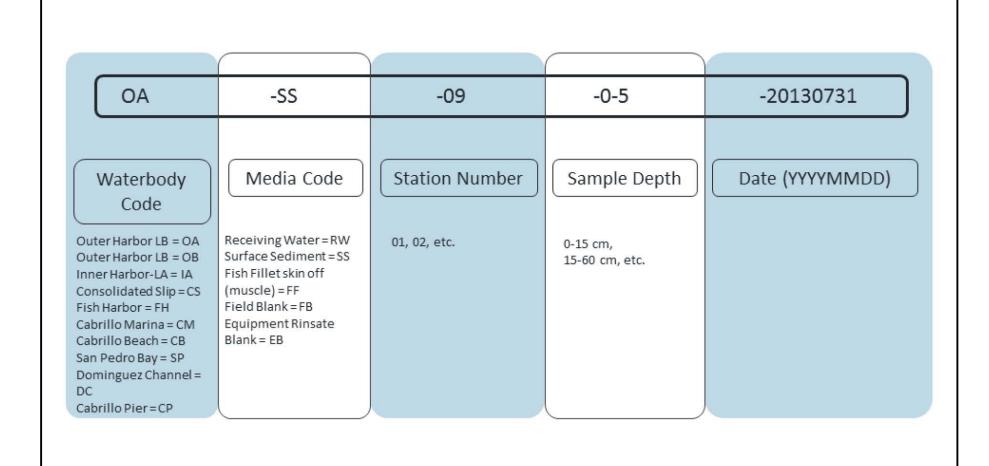




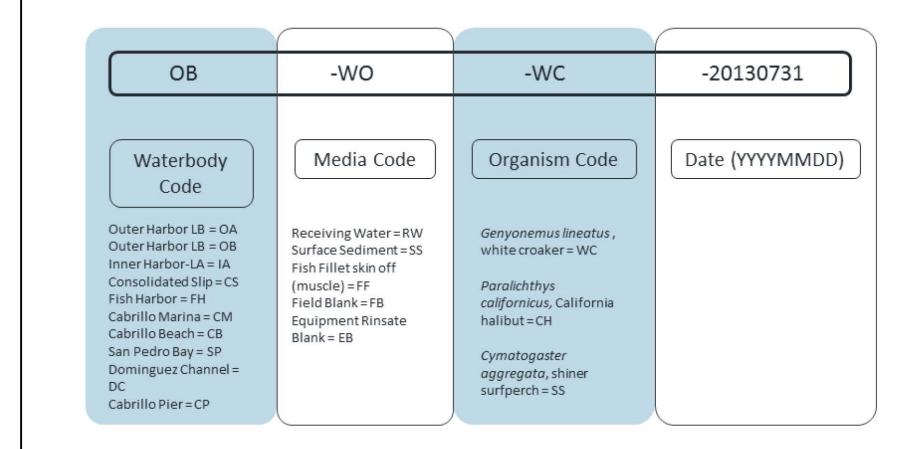








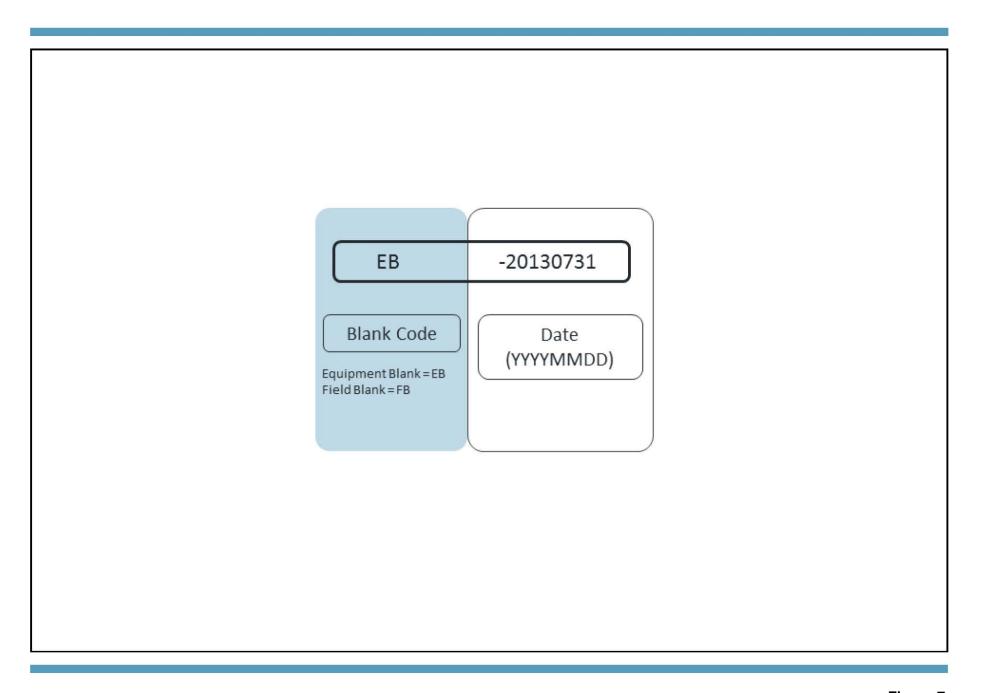


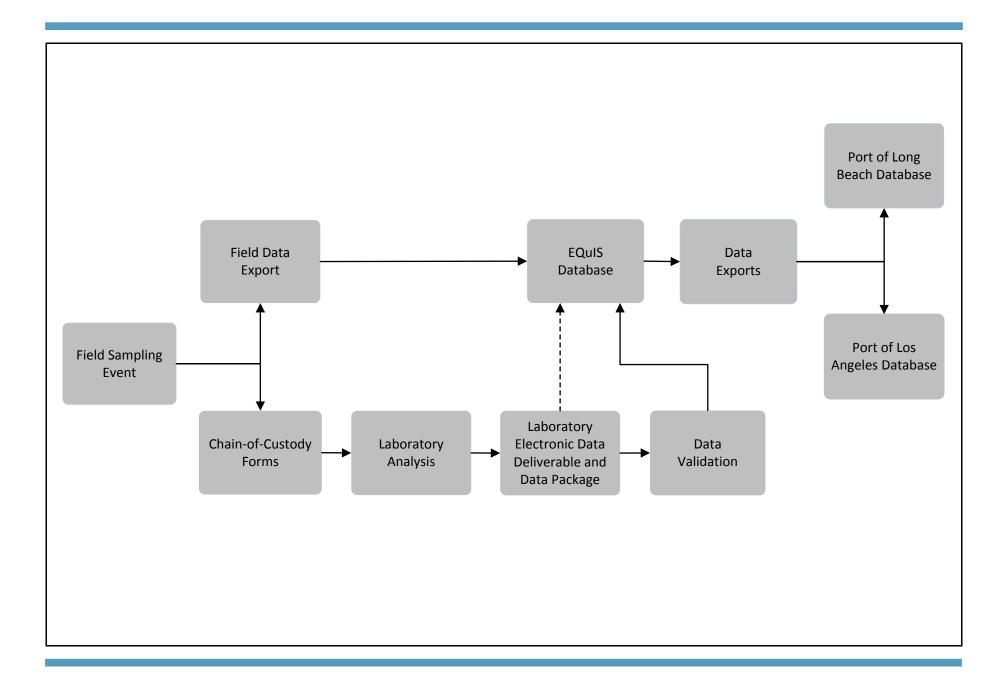




	DW	10	00	2	20120721
OA	-RW	-10	-09	-2	-20130731
Waterbody Code	Media Code	"10" indicates field duplicate	Station Number	Sample Depth	Date (YYYYMMDD)
Outer Harbor LB = OA Outer Harbor LB = OB Inner Harbor-LA = IA Consolidated Slip = CS Fish Harbor = FH Cabrillo Marina = CM Cabrillo Beach = CB San Pedro Bay = SP Dominguez Channel = DC Cabrillo Pier = CP	Receiving Water = RW Surface Sediment = SS Fish Fillet skin off (muscle) = FF Field Blank = FB Equipment Rinsate Blank = EB		01, 02, etc.	0-15 cm, 15-60 cm, etc.	









APPENDIX A STANDARD OPERATING PROCEDURES

STANDARD OPERATING PROCEDURE: GRAB WATER SAMPLING

Project Numl	oer:	Project Name:	
My signature		at I have read and understand t	
Date Date	Name (print)	Signature	Company
Date	wanie (print)	Signature	Company

1.1 Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for the collection of grab water samples using a Niskin, Van Dorn, or equivalent sampler. Grab water samples will be collected at locations described in the Coordinated Compliance Monitoring and Reporting Plan (CCMRP).

1.2 Purpose

The purpose of water sampling is to obtain data on water chemistry for contaminants of concern.

1.3 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and corresponding documents (i.e., CCMRP and Programmatic Quality Assurance Project Plan [PQAPP]). Field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.4 Procedures

Water samples will be collected from the same three depths as the in situ water quality measurements. Grab samples (i.e., instantaneous, not time- or flow-weighted composites) for total suspended solids (TSS) will be taken at all three depths during wet and dry weather events. Grab samples for analytical chemistry will be taken only from the surface sample (-3 feet below water surface). Water samples will be collected with a grab sampler (e.g., Niskin or Van Dorn) that has been decontaminated prior to sample collection at each station. Sampling methods will generally conform to U.S. Environmental Protection Agency's (USEPA's) clean sampling methodology described in the Surface Water Ambient Monitoring Program (SWAMP) SOP (MPSL-DFG 2007).

Sample processing and handling for water chemistry will be conducted in accordance with guidance developed in the Quality Assurance Management Plan for the State of California's SWAMP (California Department of Fish and Game, Pucket 2002). Aliquots for TSS, metals,

dichlorodiphenyltrichloroethane (DDT), and polychlorinated biphenyls (PCBs) will be taken directly from the grab sampler into appropriate containers or bottles (Table 1). Water samples will be preserved in the field, depending on the type of analysis, to meet specified holding times (Table 1). Water samples will be stored at less than 4 degrees Celsius (°C) until delivery to the appropriate analytical laboratory.

Table 1
Sample Containers and Holding Conditions

Parameter	Sample Size	Container Size and Type	Holding Time	Preservative
		Wa	ter	
Total suspended solids	1 L	1-L HDPE	7 days	Cool ≤6°C
Total Metals	100 mL	250 mL HDPE	48 hours until preservation	Cool ≤6°C
Total Metals	100 1111	230 IIIL IIDFL	6 months to analysis	Ambient; HNO₃ to pH<2
Dissolved metals	100 mL 250 m	250 mL HDPE	Field filter; 48 hours until preservation	Cool ≤6°C
Dissolved metals	100 1112	230 IIIL IIDI'L	6 months to analysis	Ambient; HNO₃ to pH<2 after filtration
		2 X 1-L amber	14 days to extraction	Cool ≤6°C; pH 5-9
DDT	DDT 1 to 2 L glass	40 days after extraction	Cool ≤6°C	
PCB Congeners	1 to 2 L	2 X 1-L amber glass	None ^b	Cool ≤6°C

Notes:

Some criteria may differ from SWAMP guidance but may be consistent with analytical method criteria. Recommendations are intended as guidance only. The selection of sample container and amount of samples required may vary per contracted laboratory sampling requirements.

°C = degrees Celsius

DDT = dichlorodiphenyltrichloroethane

HDPE = high-density polyethylene

L = liter

mL = milliliter

PCB = polychlorinated biphenyl

1.5 Quality Assurance/Quality Control

Quality control procedures will consist of following standard practices for the collection of water quality samples. Entries in the field forms and on sample container labels will be double checked by the field team staff to verify that the information is correct. It is the responsibility of the Field Team Leader to periodically check to ensure that water sampling procedures are in conformance with those stated in this SOP.

Field quality assurance/quality control samples to be collected are included in Table 2.

Table 2
Frequencies and Performance Criteria for Field Quality Assurance/Quality Control Sampling

Analysis Type	Field Duplicate	Field Duplicate Performance Criteria ^{1,2}	Field and Rinse Blank ³	Field and Rinse Performance Criteria ⁴
Total suspended and dissolved solids	5% of total project sample count	≤25%RPD if both result(s) are >5x RL. Difference ≤2x RL if result(s) are ≤5x RL.	NA	NA
Total and dissolved organic carbon	5% of total project sample count	≤25%RPD if both result(s) are >5x RL. Difference ≤2x RL if result(s) are ≤5x RL.	Not a method requirement. Task specific	<rl< td=""></rl<>
Total metals	5% of total project sample count	≤25%RPD if both result(s) are >5x RL. Difference ≤2x RL if result(s) are ≤5x RL.	Not a method requirement. Task specific	<rl< td=""></rl<>
DDT	5% of total project sample count	≤25%RPD if both result(s) are >5x RL. Difference ≤2x RL if result(s) are ≤5x RL.	Not a method requirement. Task specific	<rl< td=""></rl<>
PCB Congeners	5% of total project sample count	≤25%RPD if both result(s) are >5x RL. Difference ≤2x RL if result(s) are ≤5x RL.	Not a method requirement. Task specific	<rl< td=""></rl<>

Notes:

1 Field duplicate RPD exceedances alone would not result in data qualification. Further evaluation into the sample collection procedures should be conducted.

2 This criteria is a slight deviation from SWAMP due to the ultra-low detection levels utilized for these studies.

 ${\tt DDT = dichlorodiphenyltrichloroethane}$

NA = not applicable

PCB = polychlorinated biphenyl

RL = recording limit

RPD = relative percent difference

STANDARD OPERATING PROCEDURE: IN SITU WATER QUALITY MONITORING

Project Numl	oer:	Project Name:	
My signature		at I have read and understand t	
Date Date	Name (print)	Signature	Company
Date	wanie (print)	Signature	Company

1.1 Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for the collection of in situ water quality data using a multi-probe water quality instrument.

1.2 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and corresponding documents (i.e., Coordinated Compliance Monitoring and Reporting Program [CCMRP] and Programmatic Quality Assurance Project Plan [PQAPP]). Field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.3 Pre-Sampling Procedures

Prior to use in the field, the water quality instrument will be calibrated according to the manufacturer's recommendation. Calibration will be documented on a calibration log.

1.4 Procedure

For each sampling event and at each station, water depth and in situ water quality parameters (temperature, dissolved oxygen [DO], pH, and salinity) will be collected. Water quality parameters and water depth will be recorded on a field data sheet or in the field electronic data deliverable (EDD).

The water depth at each station will be recorded using a probe or lead line. Water quality will be measured in situ at the station by immersing a multi-parameter instrument into the water at the desired depths. The instrument must equilibrate for at least one minute before collecting temperature, pH, conductivity, or salinity measurements, and at least 90 seconds before collecting DO measurements. Because DO takes the longest to stabilize, this parameter will be recorded after temperature, pH, conductivity, or salinity. See the surface water ambient monitoring program (SWAMP) SOP for additional details on the collection of field parameters (MPSL-DFG 2007). Water quality measurements will be collected at three depths during wet and dry weather events (surface [-3 feet below], mid-water column [to be determined in the field], and bottom [3 feet above mudline]).

1.4.1 Observations

- Water appearance Record general appearance (e.g., color; unusual amount of suspended matter, debris, or foam)
- Water temperature
- pH (standard units)
- DO
- Conductivity/salinity
- Weather Record recent meteorological events that may have impacted water quality (e.g., heavy rains, cold front, very dry, very wet)
- Biological Activity Record excessive macrophyte, phytoplankton, or periphyton growth. The observation of water color and excessive algal growth is very important in explaining high chlorophyll a values. Also record other observations, such as presence of fish, birds, and spawning fish.

1.5 Quality Assurance/Quality Control

Guidance for data quality objectives (DQOs) for field measurements is derived from the SWAMP guidance for water parameters (SWRCB 2008). Quality objectives for parameters that will be measured in the field are presented in Table 1.

Field measurements will be made in triplicate on five percent of the measurements. Each result will be recorded along with the average of the three results, the difference between the largest and smallest result, and the percent difference between the largest and smallest result. The percent difference will be calculated as follows:

Percent difference = 100*(largest-smallest)/average

Triplicate measurements, the average of the results, and percent difference will be recorded on the field data sheet. The percent difference will be compared against the precision criteria established for field measurements in Table 1, as appropriate. If precision does not meet the established criteria, the equipment should be inspected to ensure that it is working properly. Equipment will be recalibrated, if necessary, and then the triplicate measurements process will be repeated until DQOs are achieved.

Table 1

DQOs for Field Measurements

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
Water	Depth (m)	± 0.1 m	± 0.1 m	NA	NA	NA
Water	Temperature (°C)	± 0.5 °C	± 0.5 °C	NA	NA	NA
Water	рН	± 0.2 units	± 0.2 units	NA	NA	NA
Water	Dissolved oxygen	± 0.2 mg/L	5 percent	NA	NA	NA
Water	Salinity ¹ (ppt)	± 0.2 ppt	± 0.2 ppt	NA	NA	NA

Notes:

1 The value for salinity may be computed from specific conductance provided salinity is above 3 ppt based on previous observations at or near that location.

°C = degrees Celsius

m = meter

mg/L = milligram per liter

NA = not applicable

ppt = parts per thousand

STANDARD OPERATING PROCEDURE: SURFACE SEDIMENT GRAB SAMPLING

	ber:	ROCEDURE ACKNOWLEDG	
,			
-		I have read and understand th	e procedures specified in this
	erating Procedure.		
Date	Name (print)	Signature	Company

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the collection of surface sediment samples using a Van Veen grab sampler (or similar). Surface sediment samples will be collected at locations described in the Coordinated Compliance Monitoring and Reporting Plan (CCMRP).

1.2 Purpose

The purpose of sediment sampling is to obtain data on localized community structure of infaunal invertebrate assemblages, sediment chemistry for contaminants of concern, and sediment toxicity.

1.3 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and corresponding documents (i.e., CCMRP and Programmatic Quality Assurance Project Plan [PQAPP]). Field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.4 General Procedures

The Field Team Leader is responsible for collecting all of the required information associated with each station occupation and each grab sampling event. While the field computer is the preferred method of collecting these data, paper data forms may be used. The required station occupation information includes the following:

- Station ID
- Date
- Vessel name
- System used for navigation
- Weather and sea conditions
- Latitude and longitude
- Depth
- Distance from station target location

1.5 Grab Sampling Procedures

Surface sediment samples will be collected at each station. Multiple grab samples will be required at each station to provide sufficient sediment volumes to complete all analyses required for the Sediment Quality Objectives (SQO) Part 1 assessment (Bay et al. 2009). The grabs will be numbered sequentially; grab numbers, visual observations, and the type of sample each grab was used for (e.g. benthic infauna, chemistry, or toxicity) will be recorded on datasheets. For benthic infauna processing, the entire grab sample will be processed. For grab samples used for chemistry and toxicity analyses, only the top 5 centimeters (cm) will be collected.

1.6 Deployment and Retrieval of the Grab Sampler

Prior to deployment, the grab sampler will be cocked with the safety key in place, then hoisted over the side of the vessel and the safety key removed. The grab sampler will be lowered at up to 2 meters per second (m/sec) until it is approximately 5 m above the bottom, then lowered at 1 m/sec to minimize the effects of bow wave disturbance of the surface sediment. In water depths greater than 300 m, the rate of deployment may have to be reduced to less than 1 m/sec to avoid "kiting" of the grab sampler or premature tripping in the water column. After bottom contact has been made (indicated by slack in the winch wire), the tension on the wire will slowly be increased, causing the lever arms to close the grab sampler. Once the grab sampler is back on board, the top doors will be opened for inspection.

While a radius limit of 100 m (200 m for island stratum) has been established for sampling, once sampling processes have begun, the Field Team Leader will ensure that the vessel remains in the same position with as much precision as conditions allow. Because analytical results from separate grab samples will be used to characterize the benthic community, contaminant load, and toxicity of the sediment, each successive grab must be collected as close as possible to the others.

1.7 Criteria for Acceptable Grab Samples

Sample acceptance criteria are shown in Figure 1. Upon retrieval of the grab sampler, the acceptability of the sample must be determined. Acceptability is based on two

characteristics: sample condition and depth of penetration. Sample condition will be judged using criteria for surface disturbance, leakage, canting, and washing.

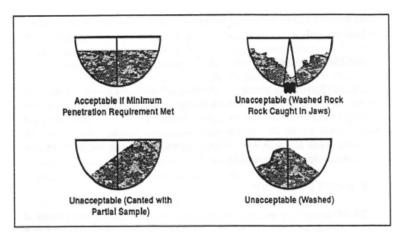


Figure 1. Examples of acceptable and unacceptable grab sample conditions.

A grab sample will be judged acceptable if the sediment has an even surface with minimal disturbance and little or no leakage of the overlying water (see Figure 1). Heavily canted samples will be unacceptable. Samples with a large amount of humping along the midline of the grab, which indicates washing of the sample during retrieval, will also be unacceptable. While some humping will be evident in samples taken from firm sediment where penetration has been poor, this can be due to the closing action of the grab and is not necessarily evidence of unacceptable washing.

If the sample condition is acceptable, the overlying water will be drained off and the depth of penetration will be determined by insertion of a plastic (rather than metal) ruler vertically along the grab midline and measuring to the nearest 0.5 cm. Sediment penetration depth must be at least 5 cm; however, penetration depths of 7 to more than 10 cm should be obtained in silt (fine sand to clay). In habitats where sediments are unusually soft, it may be necessary to remove the lead weights to prevent the grab sampler from toppling onto its side, deeming the sample unacceptable.

Extra caution should be taken to drain the overlying water from the grabs for chemistry and toxicity samples. It is recommended that a siphon be employed for these grab samples to

avoid disturbance and loss of the surface sediments. The overlying water in grabs intended for infaunal samples may be drained by slightly opening the jaws of the grab and allowing the water to run off, as long as all drained water is captured for screening with the sediments.

If both sample condition and penetration are acceptable in the first grab, sampling at the station will proceed. It is required that all of the grabs taken at a station be of similar sediment type and depth penetration.

If sampling success at a particular station is inconsistent, the site may be abandoned after a minimum of nine attempts. The reason for site abandonment must be documented. The station should be relocated within the radius limit and $\pm 10\%$ of the depth of the target site. If a station is relocated, the new coordinates should be recorded in the field computer or on a datasheet.

1.8 Sample Processing

Sediment sample processing and handling for purposes of sediment chemical analyses, sediment toxicity, and benthic infauna assessment in support of the SQOs Part 1 assessment will be performed in accordance with procedures specified in the Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009) and the Bight Field Operations Manual (BCEC 2008). The following information will be recorded for each grab:

- Time when the grab reaches the sediment surface
- Sediment composition (type)
- Sediment odor
- Sediment color
- Presence of shell hash (note if 50% or greater)
- Sample types produced from sediment grab

Methods for processing samples are described in the corresponding SOPs for each type of sample. Recommended conditions for sampling containers, sample handling, and storage are listed in Table 11 of the CCMRP.

1.9 Quality Assurance/Quality Control

It is the responsibility of the Field Team Leader to periodically check and ensure that the sampling procedures are in conformance with those stated in this SOP.

STANDARD OPERATING PROCEDURE: SEDIMENT CHEMISTRY SAMPLE PROCESSING

Project Num	ber:	Project Name:	
-			the procedures specified in this
	erating Procedure.		
Date	Name (print)	Signature	Company

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to processing of sediment grabs for chemical analyses. Surface sediment grab samples will be collected using a Van Veen sampler, or a similar sampling device, as appropriate for the type of sediment sample being collected, as is described in the Bight Field Operations Manual, Section VIII (BCEC 2008) and the corresponding SOP *Surface Sediment Grab Sampling*.

1.2 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and corresponding documents (i.e., Coordinated Compliance Monitoring and Recording Plan [CCMRP] and Programmatic Quality Assurance Project Plan [PQAPP]). Specialized training is not required for sample processing; however, field staff will be supervised by experienced staff.

1.3 Processing Sediment Samples for Chemical Analyses

Multiple grabs may be necessary to obtain sufficient sediment for chemical analyses. Sediment samples will be collected by scooping the top 5 centimeters (cm) of the undisturbed surface material with a stainless steel spoon into a stainless steel bowl. Sediment within 1 cm of the metal sides of the grab will be avoided to prevent sample contamination. Sediment will be homogenized and placed into sample containers (Table 1). Samples will be stored at 0 to 4 degrees Celsius. Equipment will be decontaminated prior to use at each station.

Table 1
Sample Containers and Holding Conditions

Parameter	Sample Size	Container Size and Type	Holding Time	Preservative		
	Sediment					
Total solids 10 g 8-oz glass 14 days Cool s						
Grain size	300 g	16-oz plastic	6 months	Cool ≤6°C		

Parameter	Sample Size	Container Size and Type	Holding Time	Preservative
			28 days	H ₂ SO ₄ ; pH < 2;Cool ≤6°C
Total organic	10 g	4-oz glass	1 year, if frozen within 28	
carbon	10 g	4-02 glass	days of collection	Freeze -20°C
			6 months	None
Total metals and	100 g 4-oz glass	A-oz glass	1 year; samples must be	
mercury		analyzed within 14 days of	Freeze -20°C ^c	
			thawing	
Polycyclic			14 days to extraction	Cool ≤6°C
aromatic		Two 8-oz	1 year to extraction;	
hydrocarbons/	500 g		samples must be extracted	Freeze -20°C
DDT and		glass	within 14 days of thawing	
derivatives			40 days after extraction	Cool ≤6°C
DCD compositions	E00 a	Two 8-oz	None ^a	Cool ≤6°C
PCB congeners	500 g	glass	Notie	Freeze -20°C

Notes:

Some criteria may differ from SWAMP guidance but are consistent with analytical method criteria. Recommendations are intended as guidance only. The selection of a sample container and the amount of sample required may vary per contracted laboratory sampling requirements.

a Volume of sediment collected must be sufficient to produce a minimum of 40mL of porewater.

DDT = dichlorodiphenyltrichloroethane

g = gram

oz = ounce

PCB = polychlorinated biphenyl

SWAMP = California Surface Water Ambient Monitoring Program

1.4 Quality Assurance/Quality Control

Quality control procedures will consist of following standard practices for the collection of water quality samples. Entries in the field forms and on sample container labels will be double checked by the field team staff to verify that the information is correct. It is the responsibility of the Field Team Leader to periodically check and ensure that sediment chemistry sample processing procedures are in conformance with those stated in this SOP.

Field quality assurance/quality control samples to be collected are included in Table 2.

[°]C = degrees Celsius

Table 2
Frequencies and Performance Criteria for Field Quality Assurance/Quality Control Sampling

Analysis Type	Field Duplicate	Field Duplicate Performance Criteria ^{1,2}	Field and Rinse Blank ³	Field and Rinse Performance Criteria ⁴
Takal salida	5% of total project	≤25% RPD if both result(s) are >5x RL.	NA	NA
Total solids	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	NA	INA
Continuing	5% of total project	≤25% RPD if both result(s) are >5x RL.	NA	NA
Grain size	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	NA	IVA
Particle size determination for	5% of total project	≤25% RPD if both result(s) are >5x RL.	NIA	N/A
suspended solids	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	NA	NA
5	5% of total project	≤25% RPD if both result(s) are >5x RL.	Not a method requirement.	4DI
Particulate organic carbon	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	Task specific	<rl< td=""></rl<>
Tatal matala	5% of total project	≤25% RPD if both result(s) are >5x RL.	Not a method requirement.	∠DI.
Total metals	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	Task specific	<rl< td=""></rl<>
Polycyclic aromatic	5% of total project	≤25% RPD if both result(s) are >5x RL.	Not a method requirement.	∠DI
hydrocarbons	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	Task specific	<rl< td=""></rl<>
557 11 : ::	5% of total project	≤25% RPD if both result(s) are >5x RL.	Not a method requirement.	₹DI
DDT and derivatives	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	Task specific	<rl< td=""></rl<>
DCD Communication	5% of total project	≤25% RPD if both result(s) are >5x RL.	Not a method requirement.	∠DI.
PCB Congeners	sample count	Difference ≤2x RL if result(s) are ≤5x RL.	Task specific	<rl< td=""></rl<>

Notes:

1 Field duplicate RPD exceedances alone would not result in data qualification. Further evaluation into the sample collection procedures should be conducted.

2 This criteria is a slight deviation from SWAMP due to the ultra-low detection levels utilized for these studies.

DDT = dichlorodiphenyltrichloroethane

NA = not applicable

PCB = polychlorinated biphenyl

RL = recording limit

RPD = relative percent difference

STANDARD OPERATING PROCEDURE: SEDIMENT TOXICITY SAMPLE PROCESSING

Project Number: P		Project Name:	Project Name:	
My signature below certifies that I have read and understand the procedures specified in this Standard Operating Procedure.				
Date	Name (print)	Signature	Company	
<u></u>				

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to processing of sediment grabs for toxicity analyses. Surface sediment grab sampling procedures will be collected using a Van Veen sampler or similar sampling device as appropriate for the type of sediment sample being collected, as described in the *Bight Field Operations Manual*, Section VIII (BCEC 2008) and the corresponding SOP *Surface Sediment Grab Sampling*.

1.2 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and the corresponding documents (i.e., Coordinated Compliance Monitoring and Reporting Plan [CCMRP] and Programmatic Quality Assurance Project Plan [PQAPP]). Specialized training is not required for sample processing; however, all field staff will be supervised by experienced staff.

1.3 Processing Sediment Samples for Toxicity Tests

Sediment will be collected for an acute amphipod toxicity test and the sediment-water interface (SWI) test. Multiple grabs may be necessary to obtain sufficient sediment for the amphipod test. Sediment samples will be collected by scooping the top 5 cm of the undisturbed surface material with a stainless steel spoon into a stainless steel bowl. Sediment within 1 cm of the metal sides of the grab will be avoided to prevent sample contamination. Sediment for the amphipod test will be homogenized and placed into double-lined, plastic sediment bags. Samples will be stored at 0 to 4 degrees Celsius.

The SWI test is used to assess toxicity of solid phase sediment samples using the embryo or larval stages of marine and estuarine invertebrates. This test is designed to be conducted on a relatively undisturbed core sample containing the upper 5 cm of sediment, which requires the use of the special sample processing methods described in the following paragraphs. Sediment will be collected from a grab sample with a polycarbonate core (7.5 cm inner diameter). This sub-sample must be the first sediment taken from an undisturbed grab. The core will be pressed 5 cm into the sediment, and a pre-cleaned acrylic plate or a gloved hand will be inserted under the bottom of the core to prevent loss of sample as the core is removed.

Core sub-sample integrity will be verified by the presence of sediment overlying water and the required depth of sediment. If an inordinate volume of sediment is lost, the sample will be discarded, and a new one will be collected. After the core is removed from the grab and deemed acceptable, it will be gently wiped of exterior sediment, and the bottom will be capped quickly with a polyethylene plastic cap (7.5 cm inner diameter). The top will then be capped, and both ends will be taped to the tube. Each core tube will be labeled with station identification, date, time, and replicate number. Core tubes will be stored upright at or less than 4 degrees Celsius. Care must be taken to minimize tilting, shaking, or vibrating cores during transport. Precautions should also be taken to prevent contamination of the core contents by water from melting ice during storage.

Equipment will be decontaminated prior to use at each station.

1.4 Quality Assurance/Quality Control

It is the responsibility of the Field Team Leader to periodically check and ensure that the sediment toxicity sample processing procedures are in conformance with those stated in this SOP.

STANDARD OPERATING PROCEDURE: SEDIMENT TOXICITY TESTING

1 STANDARD OPERATING PROCEDURE ACKNOWLEDGEMENT FORM				
Project N	umber:	Project Name:		
My signature below certifies that I have read and understand the procedures specified in this Standard Operating Procedure.				
Date	Name (print)	Signature	Company	

1.1 Scope and Application

This Standard Operating Procedure (SOP) provides a description of the sediment toxicity test methods specified under the draft Sediment Quality Objective (SQO; Bay et al. 2009) policy. It is intended to supplement published toxicity protocols by providing information on specific aspects of the methods that are used in many California monitoring programs so that future analyses will yield comparable and high-quality results.

1.2 Purpose

Sediment toxicity provides two types of information in this assessment: 1) the potential bioavailability of contaminants and 2) a measure of contaminant biological effects. Multiple toxicity tests are needed to assess toxicity because no single method exists that can capture the full spectrum of potential contaminant effects.

1.3 Procedures

Toxicity assessment under the SQO framework requires two types of tests: a short-term amphipod survival test and a sub-lethal test.

1.3.1 Species

The short term amphipod survival test will be performed with *Eohaustorius estuarius*, except for sediments with a high percent of fines, in which case *Leptocheirus plumulosus* will be used. The sub-lethal test will consist of the sediment-water interface test (SWI) with the bivalve, *Mytilus galloprovincialis*.

1.3.2 Sample Preparation

The amphipod survival tests should be started within one month of sample collection and SWI tests within 2 weeks of sample collection in order to minimize potential changes in toxicity due to storage. Samples should be tested as soon after collection as possible in order to minimize the potential for changes in sediment quality during storage.

Sediment for the amphipod survival tests should be homogenized and press-sieved in order to remove native animals that might be either predators or the same species as a test

organism. Press-sieving consists of forcing the sediment through a 2-millimeter mesh screen without adding water beyond that which is already naturally associated with the sample. Press-sieving is not applicable for the SWI test. Sediment within the core tubes collected in the field should not be disturbed.

1.3.3 Animal Acclimation

With respect to temperature and salinity, the test animals used in each method must be acclimated to test conditions within each laboratory prior to the start of testing. The acclimation period required for each species is variable.

1.3.4 Test Setup

Refer to U.S. Environmental Protection Agency (1994) and American Society for Testing and Materials (1996) methods for the amphipod survival test and Bight methods (Bay et al. 2009) for SWI test methods. Required test conditions are summarized in Table 1.

Table 1
Required Test Conditions for Sediment-Water Interface Test

	Amphipo	SWI Test	
Parameter	Eohaustorius estuarius	Leptocheirus plumulosus	Mytilus galloprovincialis
Temperature	15 ±1°C	25 ±1°C	15 ±1°C
Salinity	20 ±2 ppt	20 ±2 ppt	32 ±2 ppt
Luminance	500-1000 lux	500-1000 lux	500-1000 lux
Photoperiod	Continuous light	Continuous light	16:8 hours light:dark
Acclimation	2-10 days at test temperature and salinity	2-10 days at test temperature and salinity	2 days at test temperature and salinity; up to 4 weeks
Size and life stage	3 - 5 mm	2 - 4 mm, no mature animals	Newly fertilized eggs
Number of organisms/chamber	20	20	250
Number of replicates/treatment	5	5	4
Aeration	Enough to maintain 90% saturation	Enough to maintain 90% saturation	Enough to maintain 90% saturation
Feeding	None	None	None
Test duration	10 days	10 days	48 hours

	Amphipo	SWI Test	
Parameter	Eohaustorius estuarius	Leptocheirus plumulosus	Mytilus galloprovincialis
Took a seembalailibre	Mean control survival of	Mean control survival of	Mean control percent normal-
Test acceptability	≥90 and ≥80% survival	≥90 and ≥80% survival	alive of ≥80%; meet all water
criteria	in each replicate	in each replicate	quality limits
Grain size tolerance	0.6-100% sand	0-100% sand	0-100% sand
Ammonia tolerance	<60 (total, mg/L)	<60 (total, mg/L)	< 4 (total, mg/L)
Total sulfide tolerance	1.9 mg/L	Not available	< 0.09 (mg/L)

Notes:

°C = degrees Celsius

mg/L = milligrams per liter

mg = milligrams

ppt = parts per thousand

SWI = sediment-water interface (test)

The SWI test chambers should mimic the setup shown in Figure 1.

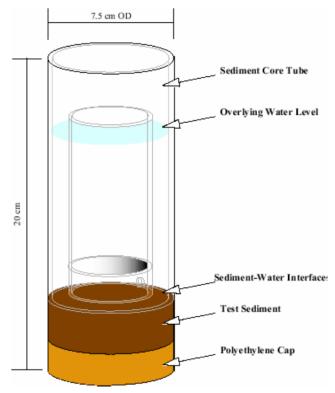


Figure 1
Sediment-water test chamber.

Sediment will be collected in polycarbonate core tubes (7.5 centimeters [cm] in diameter) with polyethylene caps. A sample will be collected at a depth of 5 cm. There must be at least 8 cm between the top of the sediment and the top of the core tube in order to allow room for the screen tube that will hold the embryos for the test. A minimum of four cores should be collected for toxicity testing from each station. At least one additional core should be collected for water quality measurements. Intact cores should be transported with overlying water from the sediment collection in place. Approximately 24 hours prior to test initiation, all but approximately 0.5 cm of the overlying water should be siphoned off and gently replaced with 300 milliliters of clean seawater. The core tubes will then be placed at 15 degrees Celsius with gentle aeration.

1.4 Personnel Qualifications

Laboratories will be accredited by California Environmental Laboratory Accreditation Program / National Environmental Laboratory Accreditation Program (ELAP/NELAP) for toxicological analyses. Laboratory personnel will be sufficiently trained and demonstrate proficiency in test methods.

1.5 Quality Assurance/Quality Control

A 10-day, water-only reference toxicant test using cadmium or ammonia should be performed simultaneously with each set of field samples tested. Whichever reference toxicant is chosen, each laboratory must establish a control chart consisting of at least three tests and no more than the 20 most recent tests.

The half maximal Effective Concentration (EC50) is the concentration of a toxicant that induces a response (i.e., percent mortality) that is halfway between the baseline and maximum possible effect. The EC50 for un-ionized ammonia or cadmium for each test performed should fall within two standard deviations of the mean of the previous tests on the control chart. A test falling outside two standard deviations should trigger a review of all data and test procedures to assure that the data are of good quality.

All test batches must include a negative control. The negative control should consist of sediment from the amphipod collection site or sediment with as little known contamination

as possible. The control also must have previously demonstrated that it meets test control acceptability requirements. If any of the chambers within a test exceed this ammonia concentration, 50% of the overlying water in all chambers within the experiment may be changed up to twice per day until all are below the target concentration. The mean control survival for each test batch must be 90% or greater. Individually, each control replicate must have at least 80% survival. In addition, water quality parameters must be within acceptable limits, and initial size ranges for the amphipods must be followed.

STANDARD OPERATING PROCEDURE: BENTHIC INFAUNA PROCESSING

STANDARD OPERATING PROCEDURE ACKNOWLEDGEMENT FORM				
Project Nur	mber:	Project Name:		
My signature below certifies that I have read and understand the procedures specified in this				
	perating Procedure.		1	
Date	Name (print)	Signature	Company	

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to processing of sediment grabs for benthic infauna community analyses. Surface sediment grab samples will be collected using a Van Veen sampler, or similar sampling device as appropriate for the type of sediment sample being collected, as described in the Bight Field Operations Manual, Section VIII (BCEC 2008) and the corresponding SOP *Surface Sediment Grab Sampling*.

1.2 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and the corresponding documents (i.e., Coordinated Compliance Monitoring and Reporting Plan [CCMRP], Programmatic Quality Assurance Project Plan [PQAPP]). Specialized training is not required for sample processing; however, field staff will be trained and supervised by experienced staff.

1.3 Benthic Infaunal Sample Processing

After the sample description has been completed, the entire sediment grab sample intended for biological analysis is washed from the sampler through a 1.0-millimeter (mm) screen or sieve. The use of a sediment-washing table is recommended, but not required. The table is useful because it provides a flat, smooth surface over which to spread and wash the sample, providing a means of gently breaking up the sediment before it runs off the end of the table into the screen box. The screen box must be equipped with stainless steel mesh with 1.0-mm openings. Wire diameter should be similar to that found in the U.S. Standard 1.00-mm Sieve (i.e., 0.58 mm). The surface area of the screen should be adequate to easily accept the sample without buildup. Raw water used to wash the samples is to be filtered to prevent the introduction of surface-water organisms. Thoroughly wash the sediment from the sampler and transfer it to a sediment-washing table (or a screen box, metal sieve, etc.) for screening. An alternative sieving method for small vessels without wash water would involve semi-submerging the sieve in seawater and swirling it in the water (taking care to prevent the loss of grab organisms and/or the introduction of surface water organisms) until the sediment washes away.

All the water drained from the sampler and used to wash the sampler must be captured and subsequently processed through screening. Typically, a tub (greater than 70-liter [L] capacity) is positioned under the grab. While washing the sample, control the water pressure to avoid damaging the organisms. Minimize direct application of water from the hose to the material and organisms collecting on the screen.

Once the sample has been washed through the screen, transfer the material (debris, coarse sediment, and organisms) retained on the screen to a sample container. Label the sample container with an external label containing the station name, sample type, date, and split number (e.g., 1 of 1, 2 of 3, etc.). An internal label bearing the same information should be placed inside the infaunal samples. This label can be written in pencil or indelible ink on 100% rag paper, poly paper, or other paper of a quality suitable for wet labels. The sample container must have a screw-cap closure and be sufficiently large to accommodate the sample material with a head space of at least 30% of the container volume. A sample may be split between two or more containers. However, each container must have external and internal labels (as described above) with the appropriate split number clearly marked. Field crews should have a broad range of sample container sizes available to them, with none less than a 16-ounce (0.47-L) capacity.

Gently remove the material retained on the screen, taking care to avoid damaging the organisms. The sample container should be filled to approximately 50% to 70% of capacity with screened material. After the bulk of material has been transferred to the container, closely examine the screen for any organisms caught in the mesh. Remove any organisms with forceps and add them to the sample container. Thoroughly wash the screen box and scrub the mesh before the next sample is screened.

All infaunal samples will be treated with a relaxant solution for approximately 30 minutes prior to fixation. Either an Epsom salts (MgSO₄) solution or a propylene phenoxytol solution (formulations below) may be used for this purpose. Relaxant solutions may be used as the diluent water for the fixative, or may be decanted after exposure and replaced with 10% buffered formalin. If it is used as diluent water, fill the sample container to 85% to 90% of its volume, close the container, and invert it several times to distribute the solution. Leave the sample in the relaxant. After 30 minutes, top off the container with enough sodium borate

buffered formaldehyde to achieve a 10% formalin solution. Close the container once again, and invert it several times to ensure mixing. Store the sample for return to the laboratory.

If the relaxant solution is not used as the diluent water, the relaxant must be removed from the sample container and replaced with 10% buffered formalin. After 30 minutes of treatment, decant the relaxant from the sample through a screen with a mesh size of 1.0 mm or less. Ensure that all organisms are removed from the screen and placed in the sample container. Fill the container with sodium borate buffered 10% formalin rather than undiluted formaldehyde, close the container, invert it several times, and store it for return to the laboratory.

Relaxant and fixative stock solution alternatives are as follows:

1) Epsom salts relaxant solution: 1.5 kilograms (kg) Epsom salts (MgSO₄ at 7H₂O)

per 20 L of freshwater

2) Propylene phenoxytol solution: 30 mL propylene phenoxytol to 20 L of seawater 3) Buffered formalin solution: 50 g sodium borate (Na₂B₄O₇) per 1 L of formalin

4) Buffered 10% formalin solution: 1 part buffered formalin to 9 parts fresh or salt

water

1.4 Quality Assurance/Quality Control

It is the responsibility of the Field Team Leader to periodically check and ensure that the sampling procedures are in conformance with those stated in this SOP.

STANDARD OPERATING PROCEDURE: BENTHIC INFAUNA COMMUNITY ANALYSIS

Project Number:		Project Name:		
My signature below certifies that I have read and understand the procedures specified in this				
Standard Op	erating Procedure.			
Date	Name (print)	Signature	Company	

1.1 Scope and Application

The goal of this Standard Operating Procedure (SOP) is to provide recommendations for laboratory processing, quality assurance (QA), quality control (QC), and data analysis procedures that are recommended for assessing the condition of soft bottom benthic macroinvertebrate communities of California's bays and estuaries. It is intended to supplement protocols presently used in California with regard to methods that meet the requirements of the sediment quality assessment framework contained in the draft Sediment Quality Objectives (SQO) policy.

Benthic infauna analyses will be conducted in accordance with Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009). Chapter 5 of the Sediment Quality Assessment Draft Technical Support Manual (Bay et al. 2009) details recommended laboratory procedures for the processing of benthic infauna samples and subsequent data analysis necessary for the SQO Part 1 assessment.

1.2 Personnel Qualifications

Personnel performing benthic sorting of organisms into major phyla will have sufficient training and experience to perform this task. Taxonomists will have a combination of education and experience to identify organisms to species level. The Quality Control/Quality Assurance (QA/QC) procedures described below shall be used to verify accuracy.

1.3 Procedures

Benthic infauna sample processing in the laboratory includes the following tasks.

1.3.1 Sample Preservation

Samples that are received from the field in formalin fixative must be washed and transferred to alcohol preservative. The removal of formalin is necessary for two reasons. Formaldehyde becomes increasingly acidic over time and prolonged exposure damages organisms with calcareous structures (e.g., shelled mollusks) which are often essential for accurate identifications. Secondly, formaldehyde is a noxious, potentially dangerous chemical. Replacing formaldehyde with ethanol makes subsequent sample handling safer.

Other benefits of the washing process are the removal of excess silt from mud balls and fecal pellets that may have broken down during fixation and, in some cases, the opportunity to separate most of the organisms in a sample from inorganic debris using an elutriation process (defined below).

Samples fixed in formalin in the field should remain in formalin fixative for at least 72 hours, but no sample should remain in fixative for longer than two weeks because formalin will decalcify mollusks and echinoderms. Benthic community samples should be preserved in a 70% ethanol solution. Denatured alcohol and dyes for staining organisms are not recommended. The alcohol preservative should be buffered with marble chips, especially if the ethanol is produced by industrial distillation rather than fermentation. Ethanol is commonly purchased as a 95% ethanol solution. To prepare 1 L of 70% ethanol solution, 263 ml of purified water (i.e., filtered and de-ionized by reverse osmosis) is added to 737 ml of 95% ethanol. If samples contain a high percent of crustaceans, it is recommended to substitute some water with glycerin (i.e., 70% ethanol, 25% purified water, 5% glycerin) to help maintain exoskeleton shape.

1.3.2 Sample Sorting

Organisms that were alive at time of collection are removed from the organic and inorganic residues (debris) that compose the sample. They are then sorted into broad taxonomic categories for analysis by taxonomists. Sorting must be accurate and complete to ensure the value of subsequent steps in the sample analysis process. Quality control procedures described in the following paragraphs are used to ensure that sorting accuracy and completeness meet data quality objectives.

Several sorting techniques are used for the removal of benthic organisms from sediment. Commonly, a small amount of sample is placed in a Petri dish, and each organism is systematically sorted and removed under a dissecting microscope using forceps. The elutriation or "floating" method is an effective technique when a sample is primarily coarse sand or highly organic. Inorganic material in the sample is separated from the lighter organic debris and organisms by the following elutriation process: After washing the formalin from the sample, spread the sample material out in a shallow pan or flat tray and

cover with water. Gently agitate the sample by hand to allow the lighter fraction of debris and organisms to separate from the heavier material. The densest material settles to the bottom while the less dense material, such as organic material, arthropods, and other soft-bodied organisms, becomes suspended. The solution is then poured through the sieve and sorted. The denser material (i.e., sand grains and mollusks) is covered with water, so that it is more easily sorted and removed under a dissecting microscope. The water containing the lighter material should be decanted through a sieve, repeating the process several times until no more material is observed in the decanted water. Then the material in the decanted water is collected into a small sample container, topped with preservative, and returned to the original sample container along with the balance of the sample material. The sample container should be filled with preservative and its lid tightly affixed. Both containers should be labeled properly with internal labels.

It is generally recommended that sorting be done in 70% ethanol, with care taken to ensure that the sample being sorted is always fully covered with alcohol. It is not uncommon for Ophiuroidea to be removed from the ethanol and air dried to assist with identification. Organisms removed from the sample are sorted into taxonomic groups for subsequent taxonomic analysis. Remove all individual organisms and fragments from the sample with the exception of nematodes, foraminifera, and planktonic species or life stages. All fragments, such as decapod chelae and legs, should be placed in their respective taxa groups. The number and identity of taxa groups composing the sorted sample, the number of containers used if sample is split, and the time (to the nearest one-half hour) required to sort the sample should be recorded on the sorting record form.

Aggregate the taxa groups into one or more sample containers. It is generally recommended that each sample container and taxa group be internally labeled with station name, sampling date and depth, and split number (if more than one container is used). Labels should be written in pencil or indelible ink on 100% rag paper, poly paper, or other paper suitable for permanent wet labels.

1.3.3 Taxonomic Analysis

The purpose of sorting into taxonomic groups is to facilitate taxonomic analysis by project taxonomists, with each group being analyzed by a single taxonomist. Therefore, the specifics of taxonomic groups may vary with the number of project taxonomists available and the details of their taxonomic expertise.

Organisms in samples are identified and counted, voucher specimens are prepared to document identifications, and taxonomic analysis accuracy may be evaluated by reanalyzing selected samples.

1.3.4 Data Analysis to Determine Benthic Invertebrate Community Condition

The composition of the benthic community constitutes an essential line of evidence (LOE) for sediment quality assessment. The Benthic LOE is a direct measure of the effect that sediment contaminant exposure has on the benthic biota of California's bays and estuaries. Determination of the Benthic LOE is based on four measures of benthic community condition: 1) the Index of Biotic Integrity (IBI), 2) the Relative Benthic Index (RBI), 3) the Benthic Response Index (BRI), and 4) the River Invertebrate Prediction and Classification System (RIVPACS). This chapter includes computational tools for calculating the Benthic LOE category and provides an example of the step-by-step process for its determination.

1.4 Quality Assurance/Quality Control (QA/QC)

Quality control of sorting is essential to ensure the value of all the subsequent steps in the sample analysis process. A standard sorting form is usually used for tracking the sample. It includes the name of the technician responsible, time required for sorting, comments, and re-sorting results. Re-sorting of samples is employed for QC purposes. It is a good practice to have, at a minimum, 10 to 20% of all samples re-sorted to monitor sorter performance.

There are two recommended approaches used for re-sorting: the aliquot sample method and the whole sample method. A laboratory may choose one of these two methods but, for consistency, a single method should be employed by a laboratory for all samples in a single project. The re-sort method used should be noted on the sorting form along with the re-sort results.

- Whole Sample Method. At least 10% of the samples processed by each sorter are completely re-sorted.
- **Aliquot Method**. A representative aliquot of at least 10% of the sample volume of every sample processed by each sorter is re-sorted.

Regardless of the method employed, an experienced sorter other than the original sorter conducts all re-sorting. Percent sorting efficiency is calculated as follows:

Whole Sample Method:

```
% Efficiency = 100 · [#Organisms sorted ÷ (#Organisms sorted + #Organisms from Re-sort)]
```

Aliquot Method:

```
% Efficiency = 100 · [#Organisms sorted ÷ (#Organisms sorted + #Organisms from Re-sort · %aliquot)]
```

If sorting efficiency is greater than 95% (i.e., no more than 5% of the organisms in the original sample are missed), then no further action is required. Sorting efficiencies below 95% initiate continuous monitoring of the underperforming technician. Failure to achieve 95% sorting efficiency initiates re-sorting of all samples previously sorted by that technician. Organisms found during re-sort should be included in the results from the sample. The calculated sorting efficiency is recorded on the sorting form for each sample that is re-sorted. The laboratory responsible for sorting should retain sample debris left after sorting until cleared for disposal. The debris should be properly labeled and preserved with 70% ethanol. Specific attention should be given to nomenclature rules because this information significantly affects the efficiency of the benthic indices calculations and QA/QC procedures. Species lists provided should be strictly adhered to, and the most up-to-date taxon names and exact spelling of taxon names based on the species lists should be used. Doing so will prevent miscounting of key organisms and erroneous benthic indices calculations.

STANDARD OPERATING PROCEDURE: FISH COLLECTION (OTTER TRAWL NETS)

1 STANDARD OPERATING PROCEDURE ACKNOWLEDGEMENT FORM				
Project Number:		Project Name:		
My signature below certifies that I have read and understand the procedures specified in this Standard Operating Procedure.				
Date	Name (print)	Signature	Company	

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the collection of targeted fish species via otter trawling. Fish tissue samples will be collected and analyzed for chemical contaminants of concern. Sampling, processing, and testing methods will be carried out in accordance with Bight protocols (BCEC 2008, 2009a). Necessary permits (e.g., scientific collection, incidental take) will be secured prior to fish collection.

Targeted species

- White croaker (*Genyonemus lineatus*)
- California halibut (*Paralichthys californicus*)
- Shiner surfperch (*Cymatogaster aggregata*)

1.2 Health and Safety Warnings

Use caution when sorting through the catch. Field personnel are likely to encounter a variety of organisms that are potentially harmful. California scorpionfish (Scorpaena guttata) have venomous fin spines that can cause severe pain. This species should be handled with leather gloves and/or pliers. Hot water, meat tenderizer, or ammonia should be applied to any puncture wound inflicted by this fish; heat is useful in breaking down the protein in the venom. Several species of rockfishes and the spotted ratfish (*Hydrolagus colliei*) also have mildly venomous spines that can cause a burning sensation. The round sting ray (*Urobatis halleri*), the California butterfly ray (*Gymnura marmorata*), and the bat ray (*Myliobatis* californica) all have venomous spines on their tails. The wound should be immersed in hot water to break down the protein in the venom. The Pacific electric ray (*Torpedo californica*) can emit a very strong electric shock. If you must handle this species, wear rubber gloves and hold it by the tail. Do not grasp the disk with both hands. Pacific angel sharks (Squatina californica), spiny dogfish (Squalus acanthias), spotted ratfish, Pacific electric rays, and California halibut (*Paralichthys californicus*) all have sharp teeth that can result in painful bites if they are not handled properly. Care must also be taken in handling the blueleg mantis shrimp (*Hemisquilla ensigera*). This species is capable of severely cutting a person with its raptorial appendages. Care should also be taken in handling any of the large crabs and octopi.

1.3 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and corresponding documents (i.e., Coordinated Compliance Monitoring and Reporting Plan [CCMRP] and Programmatic Quality Assurance Project Plan [PQAPP]). Field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection. Personnel performing species identifications will have sufficient education and project experience in marine biology and ichthyology.

1.4 Procedures

When possible, fish will be collected using a semi-balloon, 7.6-meter headrope otter trawl following the methods in the Bight Field Operations Manual (BCEC 2008). If other methods need to be employed in the case an otter trawl is not feasible (e.g., lampara net, beach seine, fish trap, or hook and line), surface water ambient monitoring program (SWAMP) methods will be used (MPSL-DFG 2001).

Pre-trawl Survey

Prior to trawling at a new station, it is important to conduct a pre-trawl survey of the trawl course. Trawl gear is likely to be lost if it becomes snagged on bottom obstructions, and replacement of nets can be costly. The trawl course at a previously unsampled station should be evaluated by use of a fathometer. This pre-trawl survey can enable the navigator to avoid uncharted reefs and other obstacles. If obstacles are encountered, resurvey a new trawl course. The Field Team Leader has the sole authority to decide whether to trawl or abandon an unknown station. This survey should always be conducted at a new sampling site to determine whether the station is acceptable or if it should be abandoned. The pre-trawl survey should follow the expected trawl course along the isobath, and the fathometer will be examined for evidence of rocks and other obstacles.

If the first run indicates that a particular site is unacceptable, another survey will be conducted within 100 meters (m) or the original location and within +/-10% of the original depth. If this attempt is unsuccessful, a third attempt will be conducted at a different

location using the same protocols (within 100 m of the original location, and within +/-10% of original depth). The site will be abandoned after three unsuccessful attempts.

Net Preparation

The trawl components should be properly prepared prior to trawling so that the trawl can be deployed in an orderly and safe manner upon arrival at a station. Nets should be inspected for holes prior to deployment, and repaired as needed. The net should be laid out and stacked on the stern of the vessel in the same configuration that it will be deployed: cod-end to the stern, floats up, and foot rope down. The trawl net should be checked to make sure that the cod-end is tied correctly, the doors should be connected properly to the leg lines, and the bridles should be securely fastened to the doors and to the tow wire.

Trawling

Trawls will be towed along, rather than across, isobaths. While the vessel is underway, the net and doors will be placed in the water. It is important that the floats skim the surface and that the net is not entangled (e.g., crossed leg lines, bunched or hooked portions of the net) prior to paying out the bridles. The bridles should be paid out by personnel on either side of the net, so as to avoid becoming entangled in the rigging during deployment.

Use of the proper scope (i.e., length of hydrowire paid out versus the water depth) is important for successful trawls. After the net touches the bottom, a sufficient length of hydrowire (towing wire) should be paid out to ensure that the net is pulled from a horizontal rather than a vertical position. Insufficient scope will prevent the net from consistently fishing the bottom and will result in a no-catch or a short-catch situation. In general, the required scope declines with increasing depth because the additional weight of the hydrowire enhances the horizontal component of the towing forces (Table 1).

Table 1.

Recommended Scope and Length of Wire for Trawling at Different Depths in the Southern California Bight

Water Depth (m)	Tow Wire Out (m) ¹	Approximate Scope (m)
<5	50	10.0:1
10	80	8.0:1
30	180	6.0:1
60	300	5.0:1
100	400	4.0:1
150	550	3.6:1
175	625	3.5:1
200	700	3.5:1
500	1,100	2.2:1

Note:

 $\,{\bf 1}\,$ Note that 25 m of bridle is included in this scope

m = meter

These scopes are for 1.0-centimeter (cm) (0.38-inch [in]) hydrowire. These scopes will have to be adjusted accordingly when using hydrowire of a different diameter.

Trawling is conducted at a speed-over-ground of 1.0 meter per second (m/sec) (or 1.5 to 2.0 knots). At stations of less than 200 m water depth, the net is towed for 10 minutes, measured on deck from the start to the end of the trawl (i.e., lock down of winch to start of retrieval). Under normal circumstances, this distance over ground is equivalent to 450 to 600 m. Trawl speed and distance can be determined by differential global positioning system (DGPS). In confined areas (e.g., bays and harbors) the trawl duration may be reduced to 5 minutes, or a distance over ground of 225 to 300 m.

Trawls are conducted in a similar manner at stations exceeding depths of 200 m. Archival tags will be employed at these stations to verify on-bottom duration. While 10 minutes on the bottom is the nominal target time for each trawl, a working range of 8 to 15 minutes is acceptable. Upon completion of each trawl, the archival tag information will be immediately downloaded to determine the on-bottom duration. If bottom time is less than 8 minutes, the trawl will be repeated, adjusting the deployment duration as necessary to fall as close to 10 minutes as possible.

All archival tag information should be retained electronically and submitted with the other data types at the end of the project.

At the end of the prescribed trawl time, the net will be retrieved and brought on board the vessel, the cod-end will be opened, and the catch will be deposited into a tub or holding tank. The catch will subsequently be released to the scientific crew for processing.

Criteria for Accepting a Trawl

If a trawl is retrieved with little or no catch in the cod-end, its acceptability will be evaluated according to whether the trawl was conducted properly. The criteria used to evaluate the success of any trawl will include ensuring that proper depth, scope, speed, and distance (or duration) were maintained; whether the net was fouled (net tangled); and whether the catch shows evidence that it was on the bottom (e.g., rocks, benthic invertebrates, or fish). If any of the trawl procedures were not followed, if the net was fouled or torn (the tear must be sufficient to allow escapement), or if there was no evidence of contact with the bottom (downloading the archival tag information can be useful), the trawl will be considered unacceptable and the site will be re-trawled. When evaluating whether to abandon or retrawl a station, the Field Team Leader should keep in mind that the goal is to collect the targeted species.

If a retrieved net has been sufficiently torn to allow escapement during the course of a trawl, the station will be abandoned. If the trawl hangs up on the bottom, the site will be resampled or abandoned at the discretion of the Field Team Leader. If re-trawling the station proves unsuccessful after two further attempts, the site will be abandoned.

Trawl Data Log

If for any reason the field computer stops functioning, the field crew will be responsible for keeping a trawl data log. The information recorded in the log will include water depth, length of tow wire used, and times and coordinates (latitude and longitude) for the net on the bottom and the end of the trawl (beginning of trawl retrieval). Similar information may also be recorded for when the net was deployed (net over) and when the net was retrieved (net on deck). Any anomalous conditions, such as rocky substrate, rocks in the catch, or a torn net, should also be recorded in the log.

1.5 Quality Assurance/Quality Control

It is the responsibility of the Field Team Leader to periodically check to ensure that fish collection procedures are in conformance with those stated in this SOP.

STANDARD OPERATING PROCEDURE: FISH COLLECTION (ALL OTHER METHODS)

Project Num	ber:	Project Name:		
My signature below certifies that I have read and understand the procedures specified in this				
Standard Operating Procedure. Date Name (print) Signature Company			Company	
	Traine (printy	0.8.10.00	- Company	

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the collection of targeted fish species via methods other than otter trawling (i.e., lampara net, beach seine, fish trap, or hook and line). Fish tissue samples will be collected and analyzed for chemical contaminants of concern. Sampling, processing, and testing methods will be carried out in accordance with surface water ambient monitoring program (SWAMP) methods (MPSL-DFG 2001). Necessary permits (e.g., scientific collection, incidental take) will be secured prior to fish collection.

Targeted species:

- White croaker (*Genyonemus lineatus*)
- California halibut (*Paralichthys californicus*)
- Shiner surfperch (*Cymatogaster aggregata*)

1.2 Health and Safety Warnings

Use caution when sorting through the catch. Field personnel are likely to encounter a variety of organisms that are potentially harmful. California scorpionfish (Scorpaena guttata) have venomous fin spines that can cause severe pain. This species should be handled with leather gloves and/or pliers. Hot water, meat tenderizer, or ammonia should be applied to any puncture wound inflicted by this fish; heat is useful in breaking down the protein in the venom. Several species of rockfishes and the spotted ratfish (*Hydrolagus colliei*) also have mildly venomous spines that can cause a burning sensation. The round sting ray (Urobatis halleri), the California butterfly ray (Gymnura marmorata), and the bat ray (Myliobatis californica) all have venomous spines on their tails. The wound should be immersed in hot water to break down the protein in the venom. The Pacific electric ray (*Torpedo californica*) can emit a very strong electric shock. If you must handle this species, wear rubber gloves and hold it by the tail. Do not grasp the disk with both hands. Pacific angel sharks (Squatina californica), spiny dogfish (Squalus acanthias), spotted ratfish, Pacific electric rays, and California halibut (*Paralichthys californicus*) all have sharp teeth that can result in painful bites if they are not handled properly. Care must also be taken in handling the blueleg mantis shrimp (Hemisquilla ensigera). This species is capable of severely cutting a person

with its raptorial appendages. Care should also be taken in handling any of the large crabs and octopi.

1.3 Personnel Qualifications

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this SOP and corresponding documents (i.e., Coordinated Compliance Monitoring and Reporting Plan [CCMRP] and Programmatic Quality Assurance Project Plan [PQAPP]). Field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection. Personnel performing species identifications will have sufficient education and project experience in marine biology and ichthyology.

1.4 Procedures

Fish will be collected using the appropriate gear for the desired species and existing water conditions.

Fyke or Hoop Net

Six 36-inch-diameter hoops connected with 1-inch square mesh net will be used to collect fish, primarily catfish. The net will be placed parallel to the shore with the open hoop end facing downstream. The net will be placed in areas of slow moving water. A partially opened can of cat food will be placed in the upstream end of the net. Between two and six nets will be placed at a site overnight. Upon retrieval a grappling hook will be used to pull up the downstream anchor. The hoops and net will be pulled together and placed on a 30-gallon plastic bag in the boat. With polyethylene gloves, the desired fish will be placed in a 30-gallon plastic bag and kept in an ice chest with ice until the appropriate number and size of fish are collected.

Gill Nets

A 100 yard monofilament gill net of the appropriate mesh size for the desired fish will be set out over the bow of the boat parallel to shore. The net will be retrieved after being set for 1 to 4 hours. The boat engine will be turned off and the net pulled over the side or bow of the boat. The net will be retrieved starting from the down-current end. If the current is too

strong to pull in by hand, then the boat will be slowly motored forward and the net pulled over the bow. Before the net is brought into the boat, the fish will be picked out of the net, placed in another 30 gallon plastic bag, and kept in an ice chest with ice.

Beach Seines

In areas of shallow water, beach seines of the appropriate length, height, and mesh size will be used. One sampler in a wetsuit or waders will pull the beach seine out from shore. The weighted side of the seine must drag on the bottom while the float side is on the surface. The offshore sampler will pull the seine out as far as necessary, and then will pull the seine parallel to shore and then back to shore, forming a half circle. Another sampler will hold the other end on shore while this is occurring. When the offshore sampler reaches shore, the two samplers will come together with the seine. The seine will be pulled onto shore, making sure that the weighted side drags the bottom. When the seine is completely pulled onshore, the target fish will be collected with polyethylene gloves and placed in a 30-gallon plastic bag and kept in an ice chest with ice. The beach seine will be rinsed off in the ambient water and placed in the rinsed 30-gallon plastic bucket.

Cast Net

A 10- or 12-foot cast net will be used to collect fish off a pier, boat, or shallow water. The cast net will be rinsed in ambient water prior to use and stored in a covered plastic bucket. The target fish will be sampled with polyethylene gloves, placed in a 30-gallon plastic bag, and kept in an ice chest with ice.

Hook and Line

Fish will be caught off a pier, boat, or shore by hook and line. Hooked fish will be taken off with polyethylene gloves, placed in a Ziploc[™] bag or a 30-gallon plastic bag, and kept in an ice chest with ice.

Spearfishing

Certain species of fish are captured more easily by SCUBA divers spearing the fish. Only appropriately trained divers following the dive safety program guidelines will be used for this method of collection. Generally, fish in the kelp beds are more easily captured by spearing. The fish will be shot in the head area to prevent the fillets from being damaged or

contaminated. Spear tips will be washed with a detergent and rinsed with ambient water prior to use.

1.5 Quality Assurance/Quality Control

It is the responsibility of the Field Team Leader to periodically check to ensure that fish collection procedures are in conformance with those stated in this SOP.

STANDARD OPERATING PROCEDURE: FISH PROCESSING

1 STAN	STANDARD OPERATING PROCEDURE ACKNOWLEDGEMENT FORM								
Project N	umber:	Project Name:	Project Name:						
	My signature below certifies that I have read and understand the procedures specified in this tandard Operating Procedure.								
Date	Name (print)	Signature	Company						
Date	rame (print)	Signature	Company						

1.1 **Scope and Application**

Fish tissue samples will be collected and analyzed for chemical contaminants of concern. Sampling, processing, and testing methods will be carried out in accordance with Bight protocols (BCEC 2008, 2009a). Necessary permits (e.g., scientific collection, incidental take) will be secured prior to fish collection.

Targeted species

- White croaker (*Genyonemus lineatus*)
- California halibut (*Paralichthys californicus*)
- Shiner surfperch (*Cymatogaster aggregata*)

1.2 **Personnel Qualifications**

Field personnel executing these procedures will read, be familiar with, and comply with the requirements of this Standard Operating Procedure (SOP) and corresponding documents (i.e., Coordinated Compliance Monitoring and Reporting Plan [CCMRP] and Programmatic Quality Assurance Project Plan [PQAPP]). Field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection. Personnel performing species identifications will have sufficient education and project experience in marine biology and ichthyology.

1.3 **Procedures**

Once the catch is onboard the vessel, the targeted species will be identified and separated for subsequent processing. At each station, 12 individuals of each fish species will be collected for further processing. There is currently no legal size limit for white croaker. An ocean fish contaminant survey was performed from 2002 to 2004 (NOAA 2007). In part, this survey sought to generate information on contaminants of concern for fish caught for sustenance in Southern California. Collection of white croaker for the Harbor Toxics TMDL study should be consistent with this survey, which recommended a minimum length of 160 millimeters (mm) (total length). Collection of California halibut that are of legal size limit is preferred. The current regulations specify at least 22 inches, or 559 mm, (total length) for California halibut (FGC 2012). Collection of adult shiner surfperch (i.e., second year age-class with a target length of 88 mm [Odenweller 1975]) is preferred. Additional individuals of the three

June 2013 Fish Processing Standard Operating Procedure Page 2 target species and non-target species will be returned to the ocean as soon as possible to minimize loss. It should be noted that field personnel may encounter bycatch that are potentially harmful while sorting for targeted species. The Bight Field Operations Manual (BCEC 2008) and Fish Collection SOPs in Appendix A provide information on the safe handling of these organisms.

Each targeted fish kept will be tagged with a unique identification number; measured for total length, fork length, and weight; and examined for gross pathology in accordance with guidance established in the Bight Field Operations Manual (BCEC 2008). Three composite samples per species per station will be created. A composite sample will be composed of four individuals; therefore, a total of 12 individuals per station are required. If more than 12 specimens are caught, the 12 individuals best and most closely distributed about the 75th percentile of the length distribution of all individuals will be used for the composites. The selected 12 individual fish will then be arranged by size, and the smallest four fish, the middle four fish, and the largest four fish within a species will be grouped for each composite to satisfy the 75 percent rule (the smallest individual in a composite is no less than 75 percent of the total length of the largest individual in a composite; USEPA 2000). This may permit data evaluation based on size class, if necessary. Skin-off fillets will be used. Dissection and compositing methods will be performed in the analytical laboratory in accordance with U.S. Environmental Protection Agency (USEPA) guidance (USEPA 2000).

Fish tissue will be analyzed for chemical parameters, processing, and preservation according to the methods described in the Bight Field Operations Manual and Bioaccumulation Workplan (BCEC 2008, 2009). Fish will be processed according to these steps:

- 1. Sacrifice fish and leave the whole body intact.
- 2. Blot fish dry and pack each fish in aluminum foil (shiny side out).
- 3. Place each packed fish in a labeled, food-grade, resalable plastic bag and store on ice.
- 4. Ship overnight to the analytical laboratory on wet or blue ice. If samples are held more than 24 hours, they will be packed on dry ice.

Chain-of-custody forms will be maintained. Tissue compositing will be conducted by the analytical laboratory. Recommended conditions for sampling containers, sample handling, and storage are listed in Table 11 of the CCMRP.

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1.4 Quality Assurance/Quality Control

Guidance for data quality objectives (DQOs) for field measurements is derived from the surface water ambient monitoring program (SWAMP) guidance from the Bight Field Operations Manual for fish tissue parameters (BCEC 2008). Quality objectives for parameters that will be measured in the field are presented in Table 1.

All field measurements will be made in triplicate. Each result will be recorded along with the average of the three results, the difference between the largest and smallest result, and the percent difference between the largest and smallest result. The percent difference will be calculated as follows:

Percent difference = 100*(largest-smallest)/average

Triplicate measurements, the average of the results, and percent difference will be recorded on the field data sheet. The percent difference will be compared against the precision criteria established for field measurements in Table 1, as appropriate. If precision does not meet the established criteria, the equipment should be inspected to ensure that it is working properly. Equipment will be recalibrated, if necessary, and then the triplicate measurements process will be repeated until DQOs are achieved.

Fish Processing

June 2013

Standard Operating Procedure

Page 4

Table 1 **DQOs for Field Measurements**

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
Fish Tissue	Fish species identification	95 percent	NA	NA	NA	NA
Fish Tissue	Fish enumeration	90 percent	NA	NA	NA	NA
Fish Tissue	Fish lengths	90 percent	90 percent	NA	NA	NA
Fish Tissue	Fish weights	90 percent	Within 0.2 kg	NA	NA	NA

Notes:

kg = kilogram NA = not applicable

APPENDIX B FIELD EDD FILE SPECIFICATIONS

Table B-1 Sample Location EDD Field Requirements

	Required /	
Field	Conditional / Optional	Description
#station_id	Required	#Unique location/station identifier used to track spatial point through database system. This is a key field
		in the database and must be unique for each collection. If the same location is sampled more than once-
		append the date to the location. Set to 'Field QC' if sample_type is 'RB', 'EB', or 'TB'.
coord_datum_code	Required	Code used to identify correct coordinate system and datum for point projection. This field's vocabulary is
		controlled. See 'valid coord type codes' tab.
x_coord	Required	Easting/Longitude
y_coord	Required	Northing/Latitude
sample_id	Required	Unique sample identifier, these values must match the IDs provided on the Chain of Custody document.
		Refer to the 'Sample Nomenclature' tab for ID construction decision making flowchart.
sample_type	Required	Code used to identify sample type. This field's vocabulary is controlled and must match a provided valid
		value. See 'valid sample type codes' tab.
sample_parent	Conditional	Parent sample identifier for field duplicate/replicate; must match an entry in column E. This field is
		required if sample_type_code is 'FD' or composite_yn is 'Y'.
matrix_code	Required	Code used to identify type of sample material. This field's vocabulary is controlled and must match a
		provided valid value. See 'valid sample matrix codes' tab.
sample_date	Required	Date and time of field sample collection, time must be in 24-hour military time.
start_depth	Conditional	Shallowest point of the interval. Required for soil/sediment samples. Not required for composite samples.
end_depth	Conditional	Deepest point of the interval. Required for soil/sediment samples. Not required for composite samples.

Field	Required / Conditional / Optional	Description
depth_unit	Conditional	Code used to identify depth units. This field's vocabulary is controlled and must match a provided valid value. See 'valid units' tab.
composite_yn	Required	'Y' for Yes if sample is a composite or 'N' for No if not.
composite_desc	Conditional	General description of composite. Required if composite_yn is 'Y'. Should include the list of samples combined in the composite.
archive_yn	Required	'N' if the sample is active, 'Y' if the sample is archive.
sampler	Required	Initials or name of the custodian responsible for sampling.
sampling_company	Required	Company responsible for field sampling.
comment	Optional	Optional comment about sample.

Table B-2 Tissue Sample EDD Field Requirements

Field	Required / Conditional / Optional	Description
#sample_id	Required	#Unique sample identifier, these values must match the IDs entered in the Loc_Smp tab. Refer to the
		'Sample Nomenclature' tab for ID construction decision making flowchart.
parent_composite	Required	Points to the composite that the individual is a part of.
measurement_date	Required	Date and time of sample measurement, time must be in 24-hour military time.
species	Required	Common name (Genus species).
specimen_length	Required	Measured fish length (nose to caudal fork).
length_unit	Required	This field's vocabulary is controlled and must match a provided valid value. See 'valid units' tab.
specimen_weight	Required	Measured fish weight.
weight_unit	Required	This field's vocabulary is controlled and must match a provided valid value. See 'valid units' tab.

#station_id #Text(20) #Required	coord_datum_code Text(20) Required	x_coord Text(20) Required	y_coord Text(20) Required	sample_id Text(40) Required	sample_type Text(20) Required	sample_parent Text(40) Conditional	matrix_code Text(10) Required	sample_date Date/Time Required	start_depth Numeric Conditional	end_depth Numeric Conditional	depth_unit Text(15) Conditional	composite_yn Text(1) Required	composite_desc Text(255) Conditional	archive_yn Text(50) Required	sampler Text(50) Required	sampling_company Text(20) Required	comment Test(2000) Optional
#Unique location/station identifier used to track spatial point through database system. This is a key field it the database and must be unique fo each collection. If the same location is sampled more than once-append the date to the location. Set to 'Field QC' if sample_type is 'RB', 'EB', or 'TB'. #Example Data Set:	or Code used to identify correct coordinate system and datum for		Northing/Latitud	Unique sample identifier, these values must match the IDs provided on the Chain of Custody document. Refer to the 'Sample Nomenclature' tab for ID construction decision making flowchart.	type. This field's vocabulary is e controlled and f must match a	identifier for field duplicate/replicate; must match an entry in column E. This fiel is required if	ld controlled and must match a provided valid value. See 'valid	Date and time of field sample collection, time must be in 24-	Shallowest point of the interval. If Required for soil/sediment samples. Not required for ne. composite sample	Deepest point of t interval. Required for soil/sediment samples. Not required for	he Code used to identify depth units. This field's vocabulary is controlled and must match a provided valid value. s. See 'valid units' tab.		General description of composite. Required if composite _yn is 'Y'. Should include the list of samples combined in the composite.	'N' if the sample is active, 'Y' if the sample archive.	is Initials or name of the custodiar responsible for sampling.	Company responsible for field sampling.	Optional comment about sample.
#OA-4-SG-20130211	NAD83CAVII	5121	18	284512 OA-4-SC-0-15-20130211	N		SE	2/11/2013 13:	30	0	15 cm	N		N	CHS	Anchor QEA	This is an example Normal Sediment Core record.
#OA-4-SG-20130211	NAD83CAVII	5121	18	284512 OA-204-SC-0-15-20130211	FD	OA-4-SC-0-15-201302	21:SE	2/11/2013 13:	45	0	15 cm	N		N	CHS	Anchor QEA	This is an example Field Duplicate for a Sediment Core.
#OA-4-TA-20130211	NAD83CAVII	5121	18	284512 OA-4-WO-CM-20130211-1	N	OA-4-TA-COMP-2013	302 TA	2/11/2013 14:	30			N		N	CHS	Anchor QEA	This is an example individual fish specimen record. This is an example individual fish
#OA-4-TA-20130211	NAD83CAVII	5121	18	284512 OA-4-WO-CM-20130211-2	N	OA-4-TA-COMP-2013	302TA	2/11/2013 14:	30			N		N	CHS	Anchor QEA	specimen record. This is an example individual fish
#OA-4-TA-20130211	NAD83CAVII	5121	18	284512 OA-4-WO-CM-20130211-3	N	OA-4-TA-COMP-2013	302TA	2/11/2013 14:	30			N		N	CHS	Anchor QEA	specimen record. This is an example individual fish
#OA-4-TA-20130211	NAD83CAVII	5121	18	284512 OA-4-WO-CM-20130211-4	N	OA-4-TA-COMP-2013	302TA	2/11/2013 14:	30			N		N	CHS	Anchor QEA	specimen record. This is an example composite fish
#OA-4-TA-20130211	NAD83CAVII	5121	18	284512 OA-4-WO-COMP-20130211	N		TA	2/11/2013 14:	30			Υ	Fish tissue composite.	N	CHS	Anchor QEA	sample record.

#sample_id #Text(40)	parent_composite Text(40)	measurement_date Date/Time	species Text(255)	specimen_length Text(255)	length_unit Text(15)	specimen_weight Text(255)	weight_unit Text(15)
#Required	Required	Required	Required	Required	Required	Required	Required
#Unique sample identifier, these value must match the IDs entered in the	S				This field's vession dame is		This field's vesselvelens is
Loc_Smp tab. Refer to the 'Sample		Date and time of sample			This field's vocabulary is controlled and must match a		This field's vocabulary is controlled and must match a
Nomenclature' tab for ID construction	Points to the composite that the	measurement, time must be in 24-		Measured fish length (nose to	provided valid value. See		provided valid value. See 'valid
decision making flowchart.	individual is a part of.	hour military time.	Common name (Genus species).	caudal fork).	'valid units' tab.	Measured fish weight.	units' tab.
#Example Data Set:							
#OA-4-WO-CM-20130211-1	OA-4-WO-COMP-20130211	2/11/2013 14:3	30 Chub mackerel (Scomber japonicus)	-	l8 cm		1315.42 g
#OA-4-WO-CM-20130211-2	OA-4-WO-COMP-20130211	2/11/2013 14:3	30 Chub mackerel (Scomber japonicus)	17	.9 cm		1224.7 g
#OA-4-WO-CM-20130211-3	OA-4-WO-COMP-20130211	2/11/2013 14:3	30 Chub mackerel (Scomber japonicus)	-	19 cm		1406.14 g
#OA-4-WO-CM-20130211-4	OA-4-WO-COMP-20130211	2/11/2013 14:3	30 Chub mackerel (Scomber japonicus)	19	.2 cm		1451.5 g
#Start Here:							

Sample IDs are structured like the following: [Waterbody]-[Station]-[Media]-[Depth]-[Date]

Waterbody or Other Area Codes		Station Number		Media Codes		Organism (Common Name)		Depth (if applicable)		Date of Collection	
Area	Code	Station	Code	Media	Code	Organism	Code	Depth	Format	Date	Format
OuterHarbor-LA	OA	1	1	Surface Sediment	SS	White Croaker	wc	0-15 cm	0-15	1-Jul-13	20130701
OuterHarbor-LB	ОВ			Sediment Core	SC	Top smelt	TS	15-60 cm	15-60		
InnerHarbor -LA	IA			Overlying Water	ow	Queenfish	QF	1-2 ft	1-2		
InnerHarbor -LB	IB			Mid Water	MW	California Halibut	СН				
Consolidated Slip	CS			Surface Water	SW	Chub Mackerel	СМ				
Fish Harbor	FH			Porewater	PW	Barred Sand Bass	BS				
Cabrillo Marina	CM			Stormwater	SW	Kelp Bass	КВ				
Cabrillo Beach	СВ			Whole Organism	wo						
San Pedro Bay	SP			Fish Fillet skin off (muscle)	FF						
Dominguez Channel	DC			Other Tissue	ОТ						
Cabrillo Pier	СР			Field Blank	FB						
				Equipment rinsate blank	EB						_

Code	Description
GCSNAD83	GCS North American Datum 1983 latitude/longitude
GCSWGS84	GCS World Geodetic System 1984 latitude/longitude
NAD27WAN	NAD 1927 StatePlane Washington North FIPS 4601 (US Feet)
NAD27WAS	NAD 1927 StatePlane Washington South FIPS 4602 (US Feet)
NAD27WISTM	NAD 1927 Wisconsin TM (Meters)
NAD83CAIII	NAD 1983 StatePlane California III FIPS 0403 (US Survey Feet)
NAD83CAIV	NAD 1983 StatePlane California IV FIPS 0404 (US Survey Feet)
NAD83CAV	NAD 1983 StatePlane California V FIPS 0405 (US Survey Feet)
NAD83LAS	NAD 1983 StatePlane Louisiana South FIPS 1702 (US Survey Feet)
NAD83MAML	NAD 1983 StatePlane Massachusetts Mainland FIPS 2001 (US Feet)
NAD83MISPIFT	NAD 1983 State Plane Michigan South FIPS 2113 (International Feet)
NAD83MISSE	NAD 1983 StatePlane Mississippi East FIPS 2301 (US Survey Feet)
NAD83NH	NAD 1983 StatePlane New Hampshire FIPS 2800 (US Survey Feet)
NAD83NJ	NAD 1983 StatePlane New Jersey FIPS 2900 (US Survey Feet)
NAD83NYC	NAD 1983 StatePlane New York Central FIPS 3102 (US Survey Feet)
NAD83NYLI	NAD 1983 StatePlane New York Long Island FIPS 3104 (US Survey Feet)
NAD83ORN	NAD 1983 StatePlane Oregon North FIPS 3601 (International Feet)
NAD83ORNF	NAD 1983 StatePlane Oregon North FIPS 3601 (US Survey Feet)
NAD83ORNH	NAD 1983 HARN StatePlane Oregon North FIPS 3601 (International Feet)
NAD83TN	NAD 1983 StatePlane Tennessee
NAD83TXSC	NAD 1983 StatePlane Texas South Central FIPS 4204 (US Survey Feet)
NAD83UTM10N	NAD 1983 UTM Zone 10N (Meters)
NAD83UTM11N	NAD 1983 UTM Zone 11N (Meters)
NAD83UTM15N	NAD 1983 UTM Zone 15N (Meters)
NAD83UTM19N	NAD 1983 UTM Zone 19N (Meters)
NAD83WAN	NAD 1983 StatePlane Washington North FIPS 4601 (US Survey Feet)
NAD83WANH	NAD 1983 HARN StatePlane Washington North FIPS 4601 (US Survey Feet)
NAD83WAS	NAD 1983 StatePlane Washington South FIPS 4602 (US Survey Feet)
NAD83WASH	NAD 1983 HARN StatePlane Washington South FIPS 4602 (US Survey Feet)
NAD83WISC	NAD 1983 StatePlane Wisconsin Central FIPS 4802 (US Survey Feet)

Code	Description
AB	Ambient Conditions Blank
EB	Equipment Blank
FB	Field Blank
FD	Field Duplicate Sample
FI	Field Individual
FM	Field Measurement
FS	Field Spike
KD	Known (External Reference Material) Duplicate
MN	Normal Non-project Environmental Sample used for QC purposes
MS	Lab Matrix Spike
MSD	Lab Matrix Spike Duplicate
MTB	Material Blank
N	Normal Environmental Sample
RB	Material Rinse Blank
RD	Regulatory Duplicate
RM	Known (External Reference Material) Rinsate
SRM	Standard Reference Material
TB	Trip Blank

Code	Description
AIR	Air
BM	Bank Debris (or Bank Material)
LF	Floating/Free Product on Groundwater Table
OIL	Oil
PC	Paint Chip
PR	Product
SA	Sand
SE	Sediment
SH	Solid Waste Containing greater than or equal to 0.5% Dry Solids
SL	Sludge
SM	Water Filter (Solid Material used to filter Water)
SN	Miscellaneous Solid Materials - Building Materials
SO	Soil
SPMD	Semipermeable membrane device
ST	Solid Waste
STRAP	Sediment Trap
STS	Stormwater Solids
TA	Animal Tissue
TP	Plant Tissue
TQ	Tissue Quality Control Matrix
TS	Treated Sediment
WCD	Dewatering Water (construction)
WD	Well Development Water
WE	Estuary Water
WG	Ground Water
WH	Equipment Wash Water, i.e., Water used for Washing
WIPE	Swab or Wipe
WL	Leachate (synonymous with Elutriate)
WO	Ocean Water
WOFL	Outfall
WP	Drinking Water
WQ	Water Quality Control Matrix
WR	River Water
WS	Surface Water
WSP	Seep Water
WST	Storm Water
WW	Waste Water
WX	Porewater

cfu/100mL colony forming units per 100 milliliters cm centimeters counts/sample deg C degrees celsius deg F degrees celsius deg F degrees Kelvin dpm/g disintegrations per minute per gram (radiochem) each each ft feet ft bgs ft below ground surface ft/sec feet per second g grams g/cm3 grams per cubic centimetre g/g grams per gram g/kg grams per gram g/L grams per milliliter gal/day gallons per hour gal/ons per second in inches in ags total inches above ground surface L liter L/fday liters per hour L/frin liters per minute L/sec liters per second liters per nour g/second lib/ft3 pounds per ft3 lbs pounds m meter meq/100g milligrams per gram mg/kg-OC milligrams per kilogram mg/mL milligrams per gram mg/ml milligrams per gram mg/ms per filligrams per gram mg/ms per minute mg/ms per minute liters per mour l/min liters per minute liters per hour l/sec liters per second lib/ft3 pounds per ft3 lbs pounds m meter mg/g milligrams per gram mg/kg-OC milligrams per kilogram organic carbon mg/ms milligrams per kilogram organic carbon mg/ms/ms milligrams per kilogram organic carbon mg/ms milligrams per kilogram organic carbon mg/ms/ms milligrams per kilogram organic carbon mg/ms/ms milligrams per kilogram organic carbon mg/ms milligrams per kilogram organic carbon mg/ms/ms milligrams per cubic meter mg/ms/ms/ms/milligrams per cubic meter mg/ms/ms/ms/ms/ms/ms/ms/ms/ms/ms/ms/ms/ms/	Code	Description
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mL milliliter		
	min	minutes
mL/L milliliter per liter	mL	milliliter
	mL/L	milliliter per liter

Code	Description
mm	millimeter
mmhos/cm	millimhos per centimeter (millisiemens per centimeter)
mmol/kg	micromoles per kilogram
mpn/100mL	most probable number per 100 ml
mrem/yr	millirems/year
ms/cm	milliseimens per centimeter
mV	millivolt
NA	Not applicable. Used for calcs, ie. pMax.
ng/cart	nanograms per cartridge
ng/g	nanograms per gram
ng/kg	nanogram per kilogram
ng/L	nanogram per liter
ng/m3	nanogram per cubic meter
ng/mL	nanograms per milliliter
no/100mL	number per 100 ml (coliform)
none	no unit of measure
NTU	Nephelometric turbidity units
ORPUnit	Place holder for ORP units
pcf	pounds per cubic foot
pci/g	picocuries per gram
pci/L	picocuries per liter
pci/mg	picocuries per milligram
pci/mL	picocuries per milliliters
pct	percent
pctv/v	percent by volume
pg/g	picogram per gram
pg/kg	picograms per kilogram
pg/L	picogram per liter
pg/wipe	picogram per wipe
ppb	parts per billion
ppbv	parts per billion by volume
ppm	parts per million
ppmv	parts per million by volume
ppt	NULL
ppth	part per thousand
pptr	parts per trillion
psf	pounds per square foot
psi	pounds per square inch
ratio	ratio
sec	second
su	standard unit
TU	Toxicity unit
ug	micrograms
ug/100cm2	micrograms per 100 square centimeters
ug/cm2	micrograms per square centimeters

Code	Description
ug/filter	micrograms per filter
ug/g	micrograms per gram
ug/kg	micrograms per killogram
ug/kg-OC	ug/kg organic carbon normalized
ug/L	micrograms/liter
ug/L-OC	ug/l organic carbon normalized
ug/m3	micrograms per cubic meter
ug/samp	micrograms per sample
ug/wipe	micrograms per wipe
uL	microliter
um	micrometer
um/sec	micrometer per second
umhos/cm	umhos per centimeter (microsiemens per centimeter)
umol/g	micromoles per gram
umol/g foc	umol/g foc (For SEM-AVS ratio)
unitless	unitless
unk	unknown unit
US Survey feet	US Survey feet
uS/cm	microsiemens per centimeter
wipe	per wipe
yd	yard
yr	year

APPENDIX C LABORATORY DATA EDD FILE SPECIFICATIONS

ADR Electronic Data Deliverable (EDD) File Specifications

The ADR EDD consists of three separate, comma-delimited ASCII text files or Excel CSV files (two, if instrument calibration information is not required by the project). Each file corresponds to a table in the ADR application. These tables are identified as the Analytical Results Table (A1), Laboratory Instrument Table (A2), and Sample Analysis Table (A3). Each file follows the naming convention of using the Laboratory Reporting Batch ID (SDG Number or some other identifier for the EDD) followed by the table identifier (A1, A2, or A3), and then a ".txt" or ".csv" extension. For example, the EDD file names for a laboratory reporting batch identified as SDG001 that includes instrument calibration data would be as follows.

SDG001A1.txt or SDG001A1.csv SDG001A2.txt or SDG001A2.csv (A2 file is optional) SDG001A3.txt or SDG001A3.csv

Analytical Results Table (A1 File)

The Analytical Results table contains analytical results and related information on an analyte level for field samples and associated laboratory quality control samples (excluding calibrations and tunes). Field QC blanks and laboratory method blanks must report a result record for each analyte reported within a method. The method target analyte list is matrix dependent and specified in the project library. Laboratory control samples (LCS and LCSD) and matrix spike samples (MS and MSD) must report a result record for every analyte specified as a spiked analyte in the project library. The project library is a reference table ADR uses for both EDD error checking and automated data review. The project library is populated with information from the project QAPP. Refer to the User Manual for detailed information on project libraries. Table 1 in this document lists all field names and their descriptions for the Analytical Results Table (A1).

Laboratory Instrument Table (A2 File)

The Laboratory Instrument table contains results and related information on an analyte level for instrument initial calibration standards, initial calibration verification standards, continuing calibration standards, and GC/MS tunes. A record must exist for each target analyte reported in a method (specified in the project library), for every calibration type (the field named QCType) associated to samples reported in the EDD. Initial calibrations, initial calibration verifications, and associated samples are linked to each other using a unique Run Batch ID for every distinct initial calibration within a method. Continuing calibrations and associated samples are linked to each other using a unique Analysis Batch ID for every distinct continuing calibration within a method. GC/MS tunes are linked to initial and continuing calibrations (and hence samples) using the Run Batch and Analysis Batch IDs respectively. The Laboratory Instrument Table (A2) is optional. Depending on the level of validation required by the data user, the Laboratory Instrument table may not be requested in the deliverable. Table 2 in this document lists field names and descriptions for the Laboratory Instrument Table (A2).

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Sample Analysis Table (A3 File)

The Sample Analysis table contains information on a sample level for field samples and laboratory quality control analyses (excluding calibrations and tunes). A sample record exists for each sample/method/matrix/analysis type combination. Table 3 in this document lists field names and descriptions for the Sample Analysis Table (A3).

EDD Field Properties

Tables 1, 2, and 3 in this document specify the EDD field properties for each file. These include the field name and sequence, field name description, data type and length for each field, and whether or not a particular field requires a standard field. Field elements in the EDD must be sequenced according to the order they appear in Tables 1, 2, and 3. For example, in the Analytical Result table (the A1 file), the field "ClientSampleID" will always be the first piece of information to start a new line of data (or database record), followed by the fields "LabAnalysisRefMethodID", "AnalysisType", and so on.

Table 4 in this document lists standard values for those fields that hold standard values. Required field constraints depend on the combination of sample, matrix, method, analyte type, and calibration or QC type information reported in a record. Tables 5 through 9 in this document indicate required fields for each EDD file (table) according to the method category, matrix, analyte type, sample, and QC or calibration type reported in a record.

When creating an EDD as a text file, use the ASCII character set in a file of lines terminated by a carriage return and line feed. No characters are allowed after the carriage return and line feed. Enclose each data set in double quotes (") and separate each field by a comma (comma delimited). Data fields with no information (null) may be represented by two consecutive commas. For example, in the Sample Analysis table, since the "Collected", "ShippingBatchID", and "Temperature" fields do not apply to laboratory generated QA/QC samples, the record for a Laboratory Control Sample by Method 8270C would be entered as follows. Note that the first two fields ("ProjectNumber" and "ProjectName") are omitted in this example.

```
..."LCSW100598",,"AQ","LCSW100598","LCS",,"8270C",... (and so on)
```

Do not pad fields with leading or trailing spaces if a field is populated with less than the maximum allowed number of characters. In the above example, although the "MatrixID" field can accommodate up to 10 characters, only 2 characters were entered in this field.

The EDD can be constructed within Excel and saved as .csv file for import into the application. Be sure to format all cells as text beforehand, otherwise Excel will reformat entered values in some cases.

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Table 1 Field Descriptions for the Analytical Results Table (A1 file) Contains laboratory test results and related information for field and QC samples (excluding instrument calibrations) on an analyte level for environmental chemistry including radiochemistry

calibrations) on an analy	te level for environmental chemistry including radiochemist		Et al d	Ctandand
Field Name	Field Name Description	Field Type	Field Length	Standard Value List
ClientSampleID	Client or contractor's identifier for a field sample as reported on the chain-of-custody		25	NO NO
	If a sample is analyzed as a laboratory duplicate, matrix spike, or matrix spike duplicate, append suffixes DUP, MS and MSD respectively to the Client Sample ID with no intervening spaces or hyphens (i.e. MW01DUP, MW01MS, and MW01MSD). For Method Blanks, LCS, and LCSD enter the unique LaboratorySampleID into this field			
	Do not append suffixes to the ClientSampleID for dilutions, reanalyses, or re-extracts (the AnalysisType field is used for this distinction). For example, MW01 <u>DL</u> and MW01 <u>RE</u> are not allowed			
	Parent sample records must exist for each MS and MSD. If an MS/MSD is shared between two EDDs, records for the MS/MSD and its parent sample must exist in the Analytical Results table for both EDDs.			
LabAnalysisRefMethodID	Laboratory reference method ID. The method ID may be an EPA Method number or a Lab Identifier for a method such as a SOP Number, however; method ID is specified by the project. The method ID must be entered into the standard list.	Text	25	YES (specified in project plan)
AnalysisType	Defines the analysis type (i.e., Dilution, Reanalysis, etc.). This field provides distinction for sample result records when multiple analyses are submitted for the same sample, method, and matrix; for example dilutions, re-analyses, and re-extracts.	Text	10	YES (See Table 4)
LabSampleID	Laboratory tracking number for field samples and lab generated QC samples such as method blank, LCS, and LCSD. There are no restrictions for the LabSampleID except for field length and that the LabSampleID must be distinct for a given field sample or lab QC sample and method.	Text	25	NO
	Suffixes may be applied to the LabSampleID to designate dilutions, reanalysis, etc.			
LabID	Identification of the laboratory performing the analyses.	Text	7	NO
ClientAnalyteID	CAS Number or unique client identifier for an analyte or isotope. If a CAS Number is not available, use a unique identifier provided by the client or contractor. The ClientAnalyteID for a particular target analyte or isotope should be specified by the project and must exist in the standard value tables for Analytes.	Text	12	YES (specified by project)
	For the LCS, LCSD, MS, and MSD, it is only necessary to report the compounds designated as spikes in the library (and surrogates for organic methods.)			
	For TICs from GC/MS analyses, enter the retention time in decimal minutes as the Client Analyte ID.			

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Field Descriptions for the Analytical Results Table (A1 file)

Contains laboratory test results and related information for field and QC samples (excluding instrument calibrations) on an analyte level for environmental chemistry including radiochemistry

	yte level for environmental chemistry including radiochemis	Field	Field	Standard
Field Name	Field Name Description	Type	Length	Value List
AnalyteName	Chemical name for the analyte or isotope. The project specifies how an analyte or isotope is named. The analyte name must be associated to a ClientAnalyteID in the standard values table for Analytes (excluding compounds designated as TIC's).	Numeric	60	YES (specified by project)
Result	Result value for the analyte or isotope.	Text	10	NO
	Entries must be numeric. For non-detects of target analytes or isotopes and spikes, do not enter "ND" or leave this field blank. If an analyte or spike was not detected, enter the reporting limit value corrected for dilution and percent moisture as applicable. Do not enter "0"			
ResultUnits	The units defining how the values in the Result, DetectionLimit, and ReportingLimit fields are expressed. For radiochemistry this also includes how the value in the Error field is expressed.	Text	10	YES (specified by project in the library)
LabQualifiers	A string of single letter result qualifiers assigned by the lab based on client-defined rules and values.	Text	7	YES (See Table 4)
	The "U" Lab Qualifier must be entered for all non-detects. Other pertinent lab qualifiers may be entered with the "U" qualifier. Order is insignificant. Lab qualifiers other than those listed in the standard values table may be used. If so, these must be added to the standard value table in the application.			
DetectionLimit	For radiochemistry methods, the minimum detectable activity for the isotope being measured.	Numeric	10	NO
	For all other methods: The minimum detection limit value for the analyte being measured.			
	For DoD QSM enter the Limit of Detection (LOD)			
DetectionLimitType	Specifies the type of detection limit (i.e., MDA, MDL, IDL, etc.).	Text	10	YES (See Table 4)
RetentionTime or Error	For radiochemistry methods only, enter the 2 Sigma Counting Error. The units for error are entered in the ResultUnits field.	Text	5	NO
	For GC/MS methods only, enter the time expressed in decimal minutes between injection and detection for GC/MS TICs only			
	For target analytes in all other methods, leave this field blank. Note: GC retention times are not evaluated at this time.			
AnalyteType	Defines the type of result, such as tracer, surrogate, spike, or target compound.	Text	7	YES (See Table 4)

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Field Descriptions for the Analytical Results Table (A1 file)

Contains laboratory test results and related information for field and QC samples (excluding instrument calibrations) on an analyte level for environmental chemistry including radiochemistry

calibrations) on an analyte level for environmental chemistry including radiochemistry				
Field Name	Field Name Description	Field Type	Field Length	Standard Value List
PercentRecovery	For radiochemistry methods: The tracer yield, if applicable. For all other analytical methods: The percent recovery value of a spiked compound or surrogate. If the spike or surrogate was not recovered because of dilution,	Numeric	5	NO
	enter "DIL". If a spike or surrogate was not recovered because of matrix interference, enter "INT". If a spike or surrogate was not recovered because it was not added to the sample, enter "NS".			
RelativePercentDifference	The relative percent difference (RPD) of two QC results, such as MS/MSD, LCS/LCSD, and Laboratory Duplicates. Report RPD in Laboratory Duplicate, LCSD, and MSD records only.	Numeric	5	NO
ReportingLimit	Reporting limit value for the measured analyte or isotope Factor in the dilution factor and percent moisture correction, if applicable. The Reporting Limit for each analyte and matrix in a given method is specified in the project library or QAPP. For DoD QSM enter the Limit of Quantitation (LOQ)	Numeric	10	NO
ReportingLimitType	Specifies the type of reporting limit (i.e., CRQL, PQL, SQL, RDL, etc). The Reporting Limit Type for each method and matrix is specified in the project library or QAPP.	Text	10	YES (specified by the project)

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Field Descriptions for the Analytical Results Table (A1 file)

Contains laboratory test results and related information for field and QC samples (excluding instrument calibrations) on an analyte level for environmental chemistry including radiochemistry

T. 1137		Field	Field	Standard
Field Name	Field Name Description	Type	Length	
ReportableResult	This field indicates whether or not the laboratory chooses an	Text	3	YES (See Table
	individual analyte or isotope result as reportable. Enter "YES" if			4)
	the result is reportable. Enter "NO" if the result is not reportable.			
	This field applies to target analytes only.			
	If only one analysis is submitted for a particular sample and			
	method, enter "YES" for all target compounds (where Analyte			
	Type = TRG). For GC/MS methods enter yes for tentatively			
	identified compounds (where Analyte Type = TIC).			
	If two or more analyses are submitted for a particular sample and			
	method (i.e. initial analysis, reanalysis and/or dilutions), enter			
	"YES" from only one of the analyses for each target compound.			
	For example: a sample was run a second time at dilution because			
	benzene exceeded the calibration range in the initial, undiluted			
	analysis. All target analytes are reported in each analysis. For the			
	initial analysis, (Analysis Type = RES), enter "NO" for benzene			
	and enter "YES" for all other compounds. For the diluted analysis			
	(Analysis Type = DL), enter "YES" for benzene and enter "NO"			
	for all other compounds.			
	For TICs (Analyte Type = TIC), if more than one analysis is			
	submitted for a particular sample and method, choose only one of			
	the analyses where Reportable Result = YES for <u>all</u> TICs. For			
	example, a sample was run a second time because one or more			
	target compounds exceeded the calibration range in the undiluted			
	analysis. Choose a particular analysis and enter "YES" for all			
	TICS. In the other analysis enter "NO" for all TICs.			
	Note that it is not necessary to report the full target analyte list for			
	the initial result, dilution, re-analysis, or re-extraction. However,			
	each target analyte must be reported YES once and once only in the			
	case of multiple analyses for a given sample, method, and matrix.			
	In the case of organics, all surrogates must be reported for all			
	analyses submitted for a given sample, method, and, matrix.			
MDL_DoD	This field is not part of the standard ADR EDD format.	Numeric	10	NO
	For DoD QSM enter the MDL, otherwise leave blank. (ADR does not perform error checks on this field)			

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Field Descriptions for the Laboratory Instrument Table (A2 file) Contains related to laboratory instrument calibration on an analyte level and GC/MS Tune information. This table

is optional depending on project requirements. Do not report Table A2 for radiochemistry methods.

	project requirements. Do not report Table A2 for radioche	Field	Field	Standard	
Field Name	Field Name Description	Type	Length	Value List	
InstrumentID	Laboratory instrument identification.	Text	15	NO	
QCType	Type of instrument QC (i.e., Instrument_Performance_Check or type of calibration standard).	Text	10	YES (See Table 4)	
Analyzed	Analysis date/time for BFB, DFTPP, initial calibration verification standards, calibration verification standards, and continuing calibration standards. For the <u>initial calibration</u> , enter date and time of the <u>last</u> standard analyzed. Also, see comments about initial calibrations in the Alternate_Lab_Analysis_ID field name description.	Date/ Time	*	NO	
AlternateLab_AnalysisID	Common laboratory identification used for standards (i.e., VOA STD50, CCAL100, BFB50, etc). For initial calibration, enter ICAL. Information from the initial calibration is entered as one record for each analyte that summarizes the results of the initial calibration (i.e. %RSD, correlation coefficient, and avg RF). Records are <u>not</u> entered for each individual standard within the initial calibration.	Text	12	NO	
LabAnalysisID	Unique identification of the raw data electronic file associated with the calibration standard or tune (i.e., 9812101MS.DV). Leave this field blank for the initial calibration. See comments about initial calibrations in the Alternate_Lab_Analysis_ID field description. This field is only applicable where an electronic instrument file is created as part of the analysis.	Text	15	NO	
LabAnalysisRefMethodID	Laboratory reference method ID (i.e., 8260B, 8270C, 6010B, etc.). The method ID is specified by the project. The LabAnalysisRefMethodID must be in the standard value list for Method IDs.	Text	25	YES (specified by the project)	
ClientAnalyteID	CAS number or unique client identifier for an analyte. If a CAS number is not available, use a unique identifier provided by the client. The unique identifier for a particular analyte should be specified by the project and must exist in the standard value list for ClientAnalyteID. Records for each calibration must report the full target analyte list including surrogates as applicable. The target analyte list is specified for each method and matrix in the project	Text	12	YES (specified by the project)	
AnalyteName	The chemical name for the analyte. The project specifies how an analyte is named. The AnalyteName must be associated to a ClientAnalyteID in the standard values.	Text	60	YES (specified by the project)	

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$\begin{tabular}{ll} Field Descriptions for the Laboratory Instrument Table (A2 file) \\ Contains related to laboratory instrument calibration on an analyte level and GC/MS Tune information. This table \\ \end{tabular}$

is optional depending on project requirements. Do not report Table A2 for radiochemistry methods.

	n project requirements. <u>Do not report Table A2 for radioche</u>	Field	Field	Standard	
Field Name	Field Name Description	Type	Length		
RunBatch	Unique identifier for a batch of analyses performed on one instrument under the control of one initial calibration and initial calibration verification. The Run Batch ID links both the initial calibration and initial calibration verification to subsequently analyzed and associated continuing calibrations, field samples, and QC analyses. For GC/MS methods, the Run_Batch ID also links a BFB or DFTPP tune and the initial calibration and initial calibration verification standards to associated samples and method QC analyses. A new and unique Run Batch ID must be used with every new initial calibration.	Text	12	NO	
AnalysisBatch	Unique laboratory identifier for a batch of analyses performed on one instrument and under the control of a continuing calibration or continuing calibration verification. The Analysis Batch ID links the continuing calibration or calibration verification to subsequently analyzed and associated field sample and QC analyses. For GC/MS methods, the Analysis Batch ID also links the BFB or DFTPP tune. A new and unique Analysis Batch ID must be used with every new continuing calibration or continuing calibration verification. For GC methods, only report opening standards, do not include closing standards (unless the closing standard functions as the opening standard for a subsequent set of analyses, in which case a new and unique Analysis Batch ID is assigned). When dual or confirmation columns/detectors are used, enter results from the primary column/detector only (this is similar to CLP Pesticide reporting).	Text	12	NO	
LabReportingBatch	Unique laboratory identifier for a batch of samples including associated calibrations and method QC, reported as a group by the lab (i.e., lab work order #, log-in #, or SDG). Links all instrument calibrations, samples, and method QC reported as a group or SDG.	Text	12	NO	
PercentRelativeStandard Deviation	The standard deviation relative to the mean used to evaluate initial calibration linearity. Organic methods may use either %RSD or Correlation Coefficient. If applicable, enter the %RSD. Leave this field blank if the Correlation Coefficient is used.	Numeric	5	NO	
CorrelationCoefficient	The correlation coefficient resulting from linear regression of the initial calibration. For metals by ICAP, enter '1.0' if a two-point initial calibration was analyzed. Organic methods may use either %RSD or Correlation Coefficient. If applicable, enter the Correlation Coefficient. Leave this field blank if the %RSD is used	Numeric	5	NO	
RelativeResponseFactor	This field applies to GC/MS only. For continuing calibration enter the relative response factor. For initial calibration enter the <u>average</u> relative response factor. Refer to comments about initial calibration records in the field description for Alternate_Lab_Analysis_ID.	Numeric	5	NO	

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Field Descriptions for the Laboratory Instrument Table (A2 file) Contains related to laboratory instrument calibration on an analyte level and GC/MS Tune information. This table is optional depending on project requirements. Do not report Table A2 for radiochemistry methods.

is optional depending o	on project requirements. <u>Do not report Table A2 for radioche</u>			Ctondond	
Field Name	Field Name Description	Field Type	Field Length	Standard Value List	
Percent_Difference (or	For organic methods, this field is the difference between 2	Numeric	5	NO	
Percent Recovery)	measured values expressed as a percentage. If %RSD is reported, enter the % difference between the average response factor of the initial calibration (IC) and the response factor of the initial calibration verification (ICV) or continuing calibration (CCV).				
	If correlation coefficient is used, enter the % difference between the true value and the measured value.				
	The Percent_Difference is expressed as a negative or positive value. Do not express Percent_Difference as an absolute value. Use a negative value if the CCV or ICV response factor is less than the IC average response factor or, in the case of correlation coefficient, the CCV or ICV measured value is less than the true value. Use a positive value if the CCV or ICV response factor is greater than the IC average response factor, or in the case of correlation coefficient, the CCV or ICV measured value is greater than the true value.				
	For <u>inorganic methods</u> , this field is the recovery of an analyte expressed relative to the true amount (i.e., %R for a metal in the continuing calibration or initial calibration verification by Method 6010B).				
PeakID01	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 50, for DFTPP enter 51.	Numeric	10	NO	
PercentRatio01	For BFB enter the relative percent abundance of m/z 50 measured relative to the raw abundance of m/z 95. For DFTPP enter the relative percent abundance of m/z 51 measured relative to the raw abundance of m/z 198.	Numeric	10	NO	
	ineasured relative to the raw abundance of 111/2 176.				
PeakID02	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 75, for DFTPP enter 68.	Numeric	10	NO	
PercentRatio02	For BFB enter the relative percent abundance of m/z 75 measured relative to the raw abundance of m/z 95.	Numeric	10	NO	
	For DFTPP enter the relative percent abundance of m/z 68 measured relative to the raw abundance of m/z 69.				
PeakID03	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 95, for DFTPP enter 69.	Numeric	10	NO	
PercentRatio03	For BFB enter the ion abundance of m/z 95 as 100 percent.	Numeric	10	NO	
	For DFTPP enter the relative percent abundance of m/z 69 measured relative to the raw abundance of m/z 198.				
PeakID04	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 96, for DFTPP enter 70.	Numeric	10	NO	

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Field Descriptions for the Laboratory Instrument Table (A2 file) Contains related to laboratory instrument calibration on an analyte level and GC/MS Tune information. This table is optional depending on project requirements. Do not report Table A2 for radiochemistry methods.

		Field	Field	Standard
Field Name	Field Name Description	Type	Length	Value List
PercentRatio04	For BFB enter the relative percent abundance of m/z 96 measured relative to the raw abundance of m/z 95.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 70 measured relative to the raw abundance of m/z 69			
PeakID05	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 173, for DFTPP enter 127.	Numeric	10	NO
PercentRatio05	For BFB enter the relative percent abundance of m/z 173 measured relative to the raw abundance of m/z 174.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 127 measured relative to the raw abundance of m/z 198			
PeakID06	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 174, for DFTPP enter 197.	Numeric	10	NO
PercentRatio06	For BFB enter the relative percent abundance of m/z 174 measured relative to the raw abundance of m/z 95.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 197 measured relative to the raw abundance of m/z 198.			
PeakID07	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 175, for DFTPP enter 198.	Numeric	10	NO
PercentRatio07	For BFB enter the relative percent abundance of m/z 175 measured relative to the raw abundance of m/z 174. For DFTPP enter the ion abundance of m/z 198 as 100 percent.	Numeric	10	NO
PeakID08	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 176, for DFTPP enter 199.	Numeric	10	NO
PercentRatio08	For BFB enter the relative percent abundance of m/z 176 measured relative to the raw abundance of m/z 174.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 199 measured relative to the raw abundance of m/z 198.			
PeakID09	Identifies individual m/z ions for GC/MS tuning compounds. For BFB enter 177, for DFTPP enter 275.	Numeric	10	NO
PercentRatio09	For BFB enter the relative percent abundance of m/z 177 measured relative to the raw abundance of m/z 176.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 275 measured relative to the raw abundance of m/z 198.			
PeakID10	Identifies individual m/z ions for GC/MS tuning compounds. For BFB leave blank, for DFTPP enter 365.	Numeric	10	NO

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Field Descriptions for the Laboratory Instrument Table (A2 file) Contains related to laboratory instrument calibration on an analyte level and GC/MS Tune information. This table

is optional depending on project requirements. Do not report Table A2 for radiochemistry methods.

		Field	Field	Standard
Field Name	Field Name Description	Type	Length	Value List
PercentRatio10	For BFB leave blank.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 365 measured relative to the raw abundance of m/z 198.			
PeakID11	Identifies individual m/z ions for GC/MS tuning compounds. For BFB leave blank, for DFTPP enter 441.	Numeric	10	NO
PercentRatio11	For BFB leave blank.	Numeric	10	NO
	For DFTPP the percent abundance of m/z 441 measured relative to the raw abundance of m/z 443			
PeakID12	Identifies individual m/z ions for GC/MS tuning compounds. For BFB leave blank, for DFTPP enter 442.	Numeric	10	NO
PercentRatio12	For BFB leave blank.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 442 measured relative to the raw abundance of m/z 198.			
PeakID13	Identifies individual m/z ions for GC/MS tuning compounds. For BFB leave blank, for DFTPP enter 443.	Numeric	10	NO
PercentRatio13	For BFB leave blank.	Numeric	10	NO
	For DFTPP enter the relative percent abundance of m/z 443 measured relative to the raw abundance of m/z 442.			

^{*} Date/time format is: MM/DD/YYYY hh:mm where MM = month, DD = day, YYYY = four digits of the year, hh = hour in 24 hour format, and mm = minutes.

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Table 3 Field Description for the Sample Analysis (A3 file) This table contains information related to analyses of field samples and laboratory QC samples (excluding

This table contains information related to analyses of field samples and laboratory QC samples (excluding calibrations and tunes) on a sample level for environmental chemical analyses including radiochemistry

Eald Name	Field Name Description	Field	Field	Standard Value List
Field Name ProjectNumber	Field Name Description Project number assigned by the client.	Type Text	Length 30	
ProjectiNumber	,			YES (specified by project)
ProjectName	Project name assigned by the client.	Text	90	YES (specified by project)
ClientSampleID	Client or contractor's identifier for a field sample	Text	25	NO
	If a sample is analyzed as a laboratory duplicate, matrix spike, or matrix spike duplicate, append suffixes DUP, MS and MSD respectively to the Client Sample ID with no intervening spaces or hyphens (i.e. MW01DUP, MW01MS, and MW01MSD). For Method Blanks, LCS, and LCSD enter the unique LaboratorySampleID into this field Do not append suffixes to the ClientSampleID for dilutions, reanalyses, or re-extracts (the Analysis_Type field is used for this distinction). For example, MW01DL and MW01RE are not allowed Parent sample records must exist for each MS and MSD. If an MS/MSD is shared between two EDDs, records for the MS/MSD and its parent sample must exist in the Sample Analysis table for			
Collected	both EDDs. For radiochemistry methods the Date of sample collection. Refer to the date format for radiochemistry methods at the end of this table. For all other methods the Date and Time of sample collection. Refer to the date/time format at the end of this table. Leave this field blank for Method Blank, LCS, and LCSD	Date/ Time	16*	NO
MatrixID	Sample matrix (i.e., AQ, SO, etc.)	Text	10	YES (See Table
LabSampleID	Laboratory tracking number for field samples and lab generated QC samples such as method blank, LCS, and LCSD. There are no restrictions for the LabSampleID except field length and that the LabSampleID must be unique for a given field sample or lab QC sample and method.	Text	25	4) NO
QCType	This record identifies the type of quality control sample QC (i.e., Duplicate, LCS, Method Blank, MS, or MSD). For regular samples, leave this field blank.	Text	10	YES (See Table 4)
ShippingBatchID	Unique identifier assigned to a cooler or shipping container used to transport client or field samples. Links all samples to a cooler or shipping container. No entry for method blanks, LCS, and LCSD. This field is optional.	Text	25	NO
Temperature	Temperature (in centigrade degrees) of the sample as received. This field is not required for radiochemistry methods.	Numeric	10	NO

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Field Description for the Sample Analysis (A3 file)

This table contains information related to analyses of field samples and laboratory QC samples (excluding calibrations and tunes) on a sample level for environmental chemical analyses including radiochemistry

calibrations and tunes) or	n a sample level for environmental chemical analyses includ	ing radio	chemisti	y
Field Name	Field Name Description	Field Type	Field Length	Standard Value List
LabAnalysisRefMethodID	Laboratory reference method ID. The method ID may be an EPA Method number or laboratory identifier for a method such as a SOP number, however; values used for Laboratory Method IDs are specified by the project and must in the in standard value list for method IDs.	Text	25	YES (Specified by the project)
PreparationType	Preparation Method Number (i.e., 3010A, 3510C, 3550C, 5030B, etc.) For analytical procedures that do not have a specific preparation method number, use "Gen Prep".	Text	25	YES (See Table 4)
AnalysisType	Defines the type of analysis such as initial analysis, dilution, reanalysis, etc. This field provides distinction for sample records when multiple analyses are submitted for the same sample, method, and matrix, for example: dilutions, re-analyses, and re-extracts.	Text	10	YES (See Table 4)
Prepared	For radiochemistry leave this field blank. For all other methods enter the date and time of sample preparation or extraction. Refer to the date/time format at the end of this table.		16*	NO
Analyzed	For radiochemistry methods the date of sample analysis. Refer to the date format for radiochemistry methods at the end of this table. For all other methods the date and time of sample analysis. Refer to the date and time format at the end of this table.		*	NO
LabID	Identification of the laboratory performing the analysis.	Text	7	NO
QCLevel	The level of laboratory QC associated with the analysis reported in the EDD. If only the Analytical Results Table (A1) and the Sample Analysis Table (A3) information are submitted for the sample, enter "COA". If the Laboratory Instrument Table (A2) information is also submitted for the sample, enter "COCAL"		6	YES (See Table 4)
ResultBasis	Indicates whether results associated with this sample records are reported as wet or percent moisture corrected. This field is only required for soils and sediments. Enter "WET" if results are not corrected for percent moisture. Enter "DRY" if percent moisture correction is applied to results.		3	YES (See Table 4)
TotalOrDissolved	This field indicates if the results related to this sample record are reported as a total or dissolved fraction. This field is only required for metal methods. For all other methods leave this field blank.	Text	3	YES (See Table 4)
Dilution	Dilution of the sample aliquot. Enter "1" for method blanks, LCS, and LCSD, or if the field samples was analyzed without dilution.		10	NO
HandlingType	Indicates the type of leaching procedure, if applicable (i.e., SPLP, TCLP, WET). Leave this field blank if the sample analysis was <u>not</u> performed on a leachate.	Text	10	YES (See Table 4)

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Table 3 Field Description for the Sample Analysis (A3 file)

This table contains information related to analyses of field samples and laboratory QC samples (excluding calibrations and tunes) on a sample level for environmental chemical analyses including radiochemistry

	on a sample level for environmental chemical analyses include	Field	Field	Standard
Field Name	Field Name Description	Type	Length	
HandlingBatch	Unique laboratory identifier for a batch of samples prepared together in a leaching procedure (i.e., SPLP, TCLP, or WET preparation). The HandlingBatch links samples with leaching blanks. Leave this field blank if the sample analysis was not performed on	Text	12	NO
LeachateDate	Date and time of leaching procedure (i.e., date for SPLP, TCLP, or WET preparation). Refer to the date and time format at the end of this table.	Date /Time	16*	NO
	Leave this field blank if the sample analysis was <u>not</u> performed on a leachate			
Percent_Moisture	Percent of sample composed of water. Enter for soil and sediment samples only.	Numeric	10	NO
MethodBatch	Unique laboratory identifier for a batch of samples of similar matrices analyzed by one method and treated as a group for matrix spike, matrix spike duplicate, or laboratory duplicate association The method batch links the matrix spike and/or matrix spike duplicate or laboratory duplicates to associated samples. Note, the	Text	12	NO
D. C. D. L.	MethodBatch association may coincide with the PreparationBatch association. The MethodBatch is specifically used to link the MS/MSD and/or DUP to associated samples.		12	NO
PreparationBatch	Unique laboratory identifier for a batch of samples prepared together for analysis by one method and treated as a group for method blank, LCS and LCSD association. The PreparationBatch links method blanks and laboratory control samples (blank spikes) to associated samples. Note, the PreparationBatch association may coincide with the MethodBatch association but the PreparationBatch specifically links the Method Blank and LCS to associated samples.	Text	12	NO
RunBatch	For all other methods the RunBatch is the unique identifier for a batch of analyses performed on one instrument under the control of one initial calibration and initial calibration verification. The RunBatch links both the initial calibration and initial calibration verification to subsequently analyzed and associated continuing calibrations, field samples, and QC analyses. For GC/MS methods, the RunBatch also links a BFB or DFTPP tune. A distinct RunBatch must used with every new initial calibration within a method The value entered in this field links a particular sample/method/analysis type record to a set of associated initial calibration and initial calibration verification records from Table A2. This field is only required if the A2 table is included with the EDD.		12	NO

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Table 3 Field Description for the Sample Analysis (A3 file)

This table contains information related to analyses of field samples and laboratory QC samples (excluding calibrations and tunes) on a sample level for environmental chemical analyses including radiochemistry

	a sample level for environmental chemical analyses includ	Field	Field	Standard
Field Name	Field Name Description	Type	Length	Value List
AnalysisBatch	For radiochemistry methods leave this field blank. For all other methods the AnalysisBatch is the unique identifier for a batch of analyses performed on one instrument and under the control of a continuing calibration or continuing calibration verification. The AnalysisBatch links the continuing calibration or calibration verification to subsequently analyzed and associated field sample and QC analyses. For GC/MS methods, the AnalysisBatch also links the BFB or DFTPP tune. A distinct AnalysisBatch must be used with every new continuing calibration or continuing calibration verification within a method The value entered in this field links a particular sample/method/analysis type record to a set of associated continuing calibration records in the Laboratory Instrument table. This field is only required if the A2 table is included with the EDD.	Text	12	NO
LabReportingBatch	Unique laboratory identifier for the EDD. This is equivalent to the sample delivery group, lab work number, login ID, etc. The LabReportingBatch links all records in the EDD reported as one group. The value entered in this field must be the same in all records.	Text	12	NO
LabReceipt	Date and time the sample was received in the lab. A time value of 00:00 may be entered. Refer to the date/time format at the end of this table.	Date/ Time	16*	
LabReported	Date and time hard copy reported delivered by the lab. A time value of 00:00 may be entered. Refer to the date/time format at the end of this table.	Date/ Time	16*	

^{*} For radiochemistry methods format Date as MM/DD/YYYY (where MM = two digit month, DD = two digit day, and YYYY = four digit year)

For all other methods format Date and Time as MM/DD/YYYY hh:mm YYYY (where MM = two digit month, DD = two digit day, and YYYY = four digit year, hh = hour in 24 hour format, and mm = minutes)

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Table 4 Standard Value List

Analysis Type Oil Dilution of the original sample Disconnection of the original sample Disconnection of the original sample RE RE RE RE RE RE RE RE RE R		Stai	luaru varue List
DL2 Second dilution of the original sample DL3 Third dilution of the original sample RE RE Reanalysis/re-extraction of sample RE2 Second reanalysis/re-extraction of sample RE3 Third reanalysis/re-extraction of sample RE4 Fourh reanalysis/re-extraction of sample RE5 Third reanalysis/re-extraction of sample RE6 Third reanalysis/re-extraction of sample RE7 Third reanalysis/re-extraction of sample RE8 Third reanalysis/re-extraction of sample RE8 Fourh reanalysis/re-extraction of sample RE8 The Initial or original sample RE7 The Initial or original sample RE8 Survail or original sample RE8 The Initial original sample RE8 Survail original sample RE8 Survail original sample RE9 The Initial Sample	Field Name	Standard Value	
DL2 Second dilution of the original sample DL3 Third dilution of the original sample RE RE Reanalysis/re-extraction of sample RE2 Second reanalysis/re-extraction of sample RE3 Third reanalysis/re-extraction of sample RE4 Fourh reanalysis/re-extraction of sample RE5 Third reanalysis/re-extraction of sample RE6 Third reanalysis/re-extraction of sample RE7 Third reanalysis/re-extraction of sample RE8 Third reanalysis/re-extraction of sample RE8 Fourh reanalysis/re-extraction of sample RE8 The Initial or original sample RE7 The Initial or original sample RE8 Survail or original sample RE8 The Initial original sample RE8 Survail original sample RE8 Survail original sample RE9 The Initial Sample	Analysis_Type	DL	Dilution of the original sample
DL3 Third dilution of the original sample DL4 Fourth dilution of the original sample RE Reanalysis/re-extraction of sample RE2 Second reanalysis/re-extraction of sample RE3 Third reanalysis/re-extraction of sample RE4 Fourth reanalysis/re-extraction of the original sample RE5 The initial or original sample RE5 The initial or original sample RE6 The reanalysis/re-extraction of the original sample RE7 Fourth reanalysis/re-extraction of the original sample RE8 The initial or original sample Refer to CAPP Analyte names are specified by the project and entered into the library for each method and matrix. Analyte Names used in project libraries must list exist in the standard value table. The same holds rue for the ClientAnalyteD Analyte_Type SPK Silked analyte SURR Surrogate as defined as per CLP usage TiC Tentatively identified compound for GC/MS analysis TRG Target compound Detection_Limit_Type 1 CRDL Contract required detection limit MDA Method detection limit MDA Minimum detectable activity MDL Method detection limit MDA Minimum detectable activity MDL Method detection limit Handling_Type 2 WET Wet leaching procedure SPLP Synthetic Precipitation Leaching Procedure TCLP Toxicity Characteristic Leaching Procedure TCLP Toxicity Characteristic Leaching Procedure Wet leaching procedure SPLP Synthetic Precipitation Leaching Procedure TCLP Toxicity Characteristic Leaching Procedure Wet land project Library Method 10 Is are specified by the project and entered into the library. Methods used in project libraries must first exist in the standard value table Method 10 Is are specified by the project and entered into the library. Methods used in project libraries must first exist in the standard value table Method 10 Is are specified by the project and entered into the library. Methods used in project libraries must first exist in the standard value table Method 10 Is are specified by the project and entered into the library. Methods used in project libraries must first exist in the standard value table Method 10 Is		DL2	
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RE2 Second reanalysis/re-extraction of sample RE3 Third reanalysis/re-extraction of the original sample RE4 Fourth reanalysis/re-extraction of the original sample RE5 The initial or original sample. Re6r to QAPP and Project Library Refer to QAPP and Project Library Re7 Second and matrix. Analyte Names used in project libraries must first exist in the standard value table. The same holds true for the Client/AnalyteID Analyte_Type IS Internal standard as defined per CLP usage Syrk Survagate as defined as per CLP usage Syrk Survagate as defined as per CLP usage TirC Intentively identified compound for GC/MS analysis TRS Survagate as defined as per CLP usage TirC Intentively identified compound for GC/MS analysis TrRS Target compound Detection_Limit_Type 1 GRDL Contract required detection limit IDL Instrument detection limit MDA Minimum detectable softwity MDL Minimum detectable softwity MDL Minimum detectable softwity MDL Minimum detectable softwity MDL Syrthetic Precipitation Leaching Procedure SPLP Synthetic Precipitation Leaching Procedure TotLP TotLP TotLP TotLP Synthetic Precipitation Leaching Procedure Lab_Analysis_Ref_Method_ID Refer to QAPP and Project Library Lab_Qualifiers 3 No Ref. Second Sec			
RE3 Third reanalysis/re-extraction of sample RE4 Fourth reanalysis/re-extraction of the original sample RE5 The initial or original sample. Refer to QAPP and Project District Project and entered into the library for each method and matrix. Analyte Names used in project libraries must first exist in the standard value table. The same holds true for the ClientAnalyteID internal standard as defined per CLP usage SPK Spiked analyte SURR Surrogate as defined as per CLP usage SPK Spiked analyte SURR Surrogate as defined as per CLP usage TTC Tentalityvil identified compound for GCMS analysis TRG Target compound CRDL Contract required detection limit MDA Minimum detectable activity MDL Method detection limit MDA Method detection limit MDA Minimum detectable activity MDL Method IDs are specified by the project und entered into the library. Methods used in project libraries must first exist in the standard value table used in project libraries must first exist in the standard value table Lab_Analysis_Ref_Method_ID Refer to QAPP and Project Library Lab_Qualifiers 3 * INORG: Duplicate analysis was not within control limits NORG: Correlation coefficient for the method of standard additions (MSA) was less than 0.993 NORG: Correlation coefficient for the method of standard additions (MSA) was less than 0.993 NORG: Correlation coefficient for the method of standard additions (MSA) in the method of standard additions (MSA) (NORG: Spiked samp			Second reanalysis/re-extraction of sample
RE4 RE5 Re5 Re6 Re7 Re6 Re7 Re7 Re7 Re6 Re6 Re7 Re6			Third reanalysis/re-extraction of cample
RES The initial or original sample. Analyte_Name Refer to QAPP and Project Library the standard value table. The same holds true for the ClientAnalyteID test standard value table. The same holds true for the ClientAnalyteID test standard value table. The same holds true for the ClientAnalyteID syrk SpK Spiked analyte SyrK Spiked analyte SyrK Spiked analyte Surrogate as defined as per CLP usage Surrogate as defined as per CLP usage Surrogate as defined per CLP usage TTG Tentatively identified compound for GC/MS analysis TRG Target compound CRDL Contract required detection limit MDA Minimum detection limit Handling_Type 2 WET Wet leaching procedure SPLP Synthetic Precipitation Leaching Procedure TCLP Toxicity Characteristic Leaching Procedure TCLP Toxicity Characteristic Leaching Procedure TCLP Toxicity Characteristic Leaching Procedure Analysis_Ref_Method_ID Refer to QAPP and Project Library Method IDs are specified by the project and entered into the library. Methods used in project libraries must first exist in the standard value table Library Lab_Qualifiers 3 NORG: Surrogate values outside of contract required QC limits + NORG: Surrogate values outside of contract required QC limits + NORG: Correlation coefficient for the method of standard additions (MSA) was less than 0.995 A ORG: Tentatively identified compound (TIC) was a suspected aldo-condensation product B NORG: Value less than contract required detection limit, but greater than or equal to instrument detection limit B NORG: Compound is found in the associated blank as well as in the sample C ORG: Analyte presence confirmed by QC/MS D Result from an analysis at a secondary dullion factor E NORG: Reported value was estemined by the method of standard additions (MSA) ORG: Compound outside method or client-specified holding time requirement N NORG: Specified and use was not within control limits N NORG: Post dige			Fourth reanalysis/re-extraction of the original cample
Analyte_Name Refer to QAPP and Project Library Analyte_Type IS Internal standard and matrix. Analyte Names used in project libraries must first exist in the standard value table. The same holds true for the ClientAnalyteID Analyte_Type IS Internal standard as defined per CLP usage SPK Spiked analyte SURR Surgoate as defined per CLP usage TIC Tentatively identified compound for GC/MS analysis TRG Target compound TIC Tentatively identified compound for GC/MS analysis TRG Target compound Detection_Limit_Type CRDL Contract required detection limit MDA Minimum detectable activity MDL Method detection limit MDA Method detection limit MDA Minimum detectable activity MDL Method detection limit TCLP Toxicity Characteristic Leaching Procedure TOXICITY Toxicity Characteristic Leaching Procedure TCLP Toxicity Characteristic Leaching Proced			
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and Project Library Analyte_Type IS Internal standard value table. The same holds true for the ClientAnalyteID SPK SPK SPK SPK SPK SPK SPK SPK SPK SP	Analyte Name	Refer to OAPP	Analyte names are specified by the project and entered into the library for each
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Analyte_Type IS Internal standard as defined per CLP usage SPK Spiked analyte SPK Spiked analyte SURR Surgate as defined as per CLP usage TIC Tentatively identified compound for GC/MS analysis TRG Target compound CRDL Contract required detection limit IDL Instrument detectable activity MDL Method detection limit Handling_Type ² WET Wet leaching procedure SPLP Synthetic Precipitation Leaching Procedure SPLP Synthetic Precipitation Leaching Procedure TCLP Toxicity Characteristic Leaching Procedure Lab_Analysis_Ref_Method_ID Refer to QAPP and Project Library Wethod IDs are specified by the project and entered into the library. Methods used in project libraries must first exist in the standard value table Library Lab_Qualifiers ³ INORG: Duplicate analysis was not within control limits ORG: Surrogate values outside of contract required QC limits NORG: Fenatively identified compound (TIC) was a suspected aldol-condensation product B NORG: Tentatively identified compound (TIC) was a suspected aldol-condensation product B NORG: Value less than contract required detection limit, but greater than or equal to instrument detection limit B ORG: Compound is found in the associated blank as well as in the sample C ORG: Analyte presence confirmed by CC/MS D Result from an analysis at a secondary dilution factor E NORG: Reported value was estimated because of the presence of interference E ORG: Concentrations exceed the calibration range of the instrument N INORG: Diplicate injection precision was not met N INORG: Presumptive evidence of a compound ORG: Presumptive evidence of a compound or Compound and Surface analysis performed by Cc/MS Reported value was determined by the method of standard additions (MSA) U Compound was analyzed for, but not detected. Analyte result was below the Reporting Limit. W INORG: Post digestion spike was out of control limits X Reserved for a lab-defined data qualifier Y Reserved for a lab-defined data qualifier			
SPK Spiked analyte SURR Surgate as defined as per CLP usage TIC Tentatively identified compound for GC/MS analysis TRG Target compound TRG Target compound TRG Target compound TRG Target compound for GC/MS analysis TRG Target compound TRG Target compound Target compound TRG Target compound Target compound Target compound TRG Target compound Target compound TRG TARGET TARGE		Library	the standard value table. The same holds true for the olientanalyterb
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SURR Surrogate as defined as per CLP usage TIC Tentatively identified compound for GC/MS analysis TRG Target compound TRG TRG TARGET TAR	Analyte_1ype		
TC Tentatively identified compound for GC/MS analysis TRG Target compound TRG TRG Target compound TRG TRG Target compound TRG TRG TARGET TRG TRG TRG TRG TRG TRG TRG TRG TRG TR			
Detection_Limit_Type 1 CRDL Contract required detection limit DETECTION_LIMIT_Type 1 CRDL Contract required detection limit			
Detection_Limit_Type 1			
IDL		IRG	rarget compound
IDL	D 1	CDDI	Contract required detection limit
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Table 4 Standard Value List

	Stai	idard value List
Field Name	Standard Value	Standard Value Description
Matrix_ID (continued)	BIOTA FILTER	Biological matter
		Filter
	LIQUID	Non-aqueous liquid
	OIL	Oil
	SED	Sediment
	SLUDGE	Sludge
	SO	Soil
	SOLID	Non-soil/sediment solid
	TISSUE	Tissue
	WASTE	Waste
	WIPE	Wipe
D " T 4	3005A	Acid Digestion of Waters for Total Recoverable or Dissolved Metals by FLAA or
Preparation_Type 4	3005A	ICP
	3010A	Acid of Aqueous Samples and Extracts for Total Metals by FLAA or ICP
	3015	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts
	3020A	Acid Digestion of Aqueous Samples and Extracts for Total Metals by GFAA
	3031	Acid Digestion of Oils for Metals Analysis by AA or ICP
	3050B	Acid Digestion of Sediments, Sludges, and Soils
	3051	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils
	3052	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices
	3060A	Alkaline Digestion for Hexavalent Chromium
	3510C	Separatory Funnel Liquid-Liquid Extraction
	3520C	Continuous Liquid-Liquid Extraction
	3535	Solid Phase Extraction
	3540C	Soxhlet Extraction
	3541	Automated Soxhlet Extraction
	3545	Pressurized Fluid Extraction
	3550B	Ultrasonic Extraction
	3560	Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons
	5030B	Purge and Trap for Aqueous Samples
	5035	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and
		Waste Samples
	7470A	Acid digestion of waters for Mercury analysis
	7471A	Acid digestion of soils and solids for Mercury analysis
	Gen Prep	Generic preparation type when a preparation method ID does not exist (used
		mostly for general chemistry methods)
QC Level	COA	Certificate of Analysis (accuracy and precision, no calibration)
QC_Level	COACAL	
	COACAL	Certificate of Analysis (accuracy and precision including calibration)
QC_Type	MB	Analytical control consisting of all reagents and standards that is carried through
	_	the entire procedure (Method Blank)
	CV	(Calibration Verification) Analytical standard run at a specified frequency to
	- '	verify the calibration of the analytical system
	CCV	(Continuing Calibration Verification) Analytical standard run every 12 hours to
		verify the calibration of the GC/MS system
	DUP	A second aliquot of a sample that is treated the same as the original aliquot to
	201	determine the precision of the method
	IC	(Initial Calibration) Analysis of analytical standards for a series of different
		specified concentrations
	ICV	(Initial Calibration Verification) Analytical standard run at a specified frequency
		to verify the accuracy of the initial calibration of the analytical system
	IPC	(Instrument Performance Check) Analysis of DFTPP or BFB to evaluate the
		performance of the GC/MS system
	LCS	(Laboratory Control Sample) A control sample of known composition
	LCSD	(Laboratory Control Sample Duplicate) A duplicate control sample of known
		composition
	MS	(Matrix Spike) Aliquot of a matrix spiked with known quantities and subjected to
		the entire analytical procedure to measure recovery
	MSD	(Matrix Spike Duplicate) A second aliquot of the same matrix as the matrix spike
		that is spiked in order to determine the precision of the method
į.		
Reporting_Limit_Type ¹	CRDL	Contractrequired detection limit
Reporting_Limit_Type ¹	CRDL CRQL	Contractrequired detection limit Contractrequired quantitation limit

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Table 4 Standard Value List

Field Name	Standard Value	Standard Value Description
Reporting_Limit_Type (continued)	PQL	Practical quantitation limit
	SQL	Sample quantitation limit
	RDL	Reportable detection limit
Result_Basis	DRY	Result was calculated on a dry weight basis
	WET	Result was calculated on a wet weight basis
Result_Units 5	ug/L	Micrograms per liter
	mg/L	Milligrams per liter
	ug/Kg	Micrograms per kilogram
	mg/Kg	Milligrams per kilogram
	pg/L	Picograms per liter
	ng/Kg	Nanograms per kilogram
Total_Or_Dissolved	DIS	Dissolved
	TOT	Total

- 1 Additional Detection Limit Types and Reporting Limit Types may be used. These must be added to the application standard values.
- 2 Additional Handling Types (leachate procedures) may be used. These must be added to the application standard values
- 3 Additional Lab Qualifiers may be used, or listed Lab Qualifiers may be used in a different manner than described in this table. New lab qualifiers must be added to the application standard value tables. NOTE: The "U" Lab Qualifier must be used for all non-detects.
- 4 Additional Preparation Types may be used. These must be added to the application standard value tables.
- 5 Additional Result Units may be used. The project library specifies the reporting limit used for each method and matrix

Note: If new standard values are used then these standard values must be entered in the software standard values for both the lab and contractor. The application will automatically update the standard values tables if an importing library contains standard values (method, client analyte ID, and analyte name) that do not exist in the software importing the new library.

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Table 5
Required Fields in the Analytical Results Table for GC/MS, GC, and HPLC Methods

	GC/MS Methods			GC and HPLC Methods			
Field	Regular Sample*	MS/MSD	Method Blank, LCS/LCSD	Regular Sample*	MS/MSD	Method Blank, LCS/LCSD	
Client_Sample_ID	Х	Х	Х	X	Х	Х	
Lab_Analysis_Ref_Method_ID	Х	Х	Х	Х	Х	Х	
Analysis_Type	Х	Х	Х	Х	Х	Х	
Lab_Sample_ID	Х	Х	Х	Х	Х	Х	
Lab_ID	Х	Х	Х	Х	Χ	Х	
Client_Analyte_ID	Х	Х	Х	Х	Х	Х	
Analyte_Name	Х	Х	Х	Х	Х	Х	
Result	Х	Х	Х	Х	Х	Х	
Result_Units	Х	Х	Х	Х	Χ	Х	
Lab_Qualifiers	Q	Q	Q	Q	Q	Q	
Detection Limit	Х	Х	X	Х	Х	Х	
Detection_Limit_Type	Х	X	X	Х	Χ	Х	
Retention_Time	Т		Т				
Analyte_Type	Х	Х	X	Х	Χ	Х	
Percent_Recovery	S	R	R	S	R	R	
Relative_Percent_Difference		D	D		D	D	
Reporting_Limit	Х	Х	Х	Х	Χ	Х	
Reporting_Limit_Type	Х	Χ	Х	Х	Χ	Х	
Reportable_Result	Х	X	Х	Χ	X	Х	

Key

- X Required Field
- D Required field for spiked compounds in the LCSD and MSD only
- Q Required field if laboratory has qualified result. The "U" qualifier MUST be entered if the result is non-detect.
- R Required field if Analyte_Type = "SPK" or "SURR"
- S Required field for surrogate compounds only
- T Required field for tentatively identified compounds by GC/MS only
- * Also includes Equipment Blanks, Field Blanks, and Trip Blanks

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Table 6
Required Fields in the Analytical Results Table for ICAP, AA, and IC Methods

	ICAP and AA Methods			IC and Wet Chemistry Methods			
		Sample	Method		Sample	Method	
	Regular	Duplicate,	Blank,	Regular	Duplicate	Blank,	
Field	Sample*	MS/MSD	LCS/LCSD	Sample*	MS/MSD	LCS/LCSD	
Client_Sample_ID	Х	Х	Х	Х	Х	Х	
Lab_Analysis_Ref_Method_ID	Х	Х	Х	Х	Х	Х	
Analysis_Type	Х	Х	Х	Х	Х	Х	
Lab_Sample_ID	Х	Х	Х	Х	Х	Х	
Lab_ID	X	Х	X	Х	X	X	
Client_Analyte_ID	Х	Х	Х	Х	Х	Х	
Analyte_Name	Х	X	X	Х	X	Х	
Result	Х	Х	Х	Х	Х	Х	
Result_Units	Х	Х	Х	Х	Х	Х	
Lab_Qualifiers	Q	Q	Q	Q	Q	Q	
Detection Limit	Х	Х	Х	Х	Х	Х	
Detection_Limit_Type	Х	Х	Х	Х	Х	Х	
Retention_Time							
Analyte_Type	Х	Х	Х	Х	Х	Х	
Percent_Recovery		S	S		S	S	
·							
Relative_Percent_Difference		R	R		R	R	
Reporting_Limit	Х	Х	Х	Х	Х	Х	
Reporting_Limit_Type	Х	Х	Х	Х	Х	Х	
Reportable_Result	X	X	Х	Х	X	Х	

Key

- X Required field
- Q Required field if laboratory has qualified result. The "U" qualifier MUST be entered if the result is non-detect
- R Required field for spiked compounds in LCSD or MSD, or target compounds in the Sample Duplicate only
- S Required field if Analyte_Type = "SPK"
- * Also includes Trip Blanks, Equipment Blanks, and Field Blanks

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Table 7 Required Fields in the Laboratory Instrument Table

		/MS nes	Init	ial Calibra	ation		Initial (Calibrati	on Verific	ation	Calibration Verification, Continuing Calibration
Field	VOA	SVOA	GC/MS	GC HPLC	ICP/AA	IC*	GC/MS	GC HPLC	ICP/AA	IC*	ALL METHODS
Instrument_ID	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
QC_Type	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Analyzed	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Alternate_Lab_Analysis_ID	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Lab_Analysis_ID	Х	Х					Х	Х	Х	Х	Х
Lab_Analysis_Ref_Method_ID	Х	Х	Х	Х	х	Х	Х	Х	х	Х	X
Client_Analyte_ID	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Analyte_Name	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Run_Batch	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Analysis_Batch	С	С									Х
Lab_Reporting_Batch	х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
Percent_Relative_Standard_Deviation			Х	Х							
Correlation_Coefficient			В	В	Х	Х					
Relative_Response_Factor			Х				Х				M
Percent_Difference							Х	Х	Х	Х	Х
Peak_ID_01	Х	Х									
Percent_Ratio_01	Х	Х									
Peak_ID_02	Х	Х									
Percent_Ratio_02	Х	Х									
Peak_ID_03	Х	Х									
Percent_Ratio_03	Х	Х									
Peak_ID_04	Х	Х									
Percent_Ratio_04	Х	Х									
Peak_ID_05	Х	Х									
Percent_Ratio_05	Х	Х									
Peak_ID_06	Х	Х									
Percent_Ratio_06	Х	Х									
Peak_ID_07	Х	Х									
Percent_Ratio_07	Х	Х									
Peak_ID_08	Х	Х									
Percent_Ratio_08	Х	Х									
Peak_ID_09	Х	Х									
Percent_Ratio_09	Х	Х									
Peak_ID_10		Х									
Percent_Ratio_10		Х									
Peak_ID_11		Х									
Percent_Ratio_11		Х									
Peak_ID_12		Х									
Percent_Ratio_12		Х									
Peak_ID_13		Х									
Percent_Ratio_13		Х									

<u>Key</u>

- X Required field (some fields are not applicable to some General (Wet) Chemistry tests)
- B Required field if reporting best fit
- C Required field if BFB or DFTPP associated with a continuing calibration only
- M Required field for GC/MS continuing calibration only

*IC Includes Ion Chromatography and Classical or Wet Chemistry methods. Methods such as pH, Conductivity, and others do not use traditional calibration procedures—therefore some fields marked as a required field under the "IC" column do not apply for these methods.

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Table 8
Required Fields in the Sample Analysis Table

	GC, GC/MS, HPLC Methods		ICAP and	d AA Methods	IC and Wet Chemistry Methods		
Field	Method Blanks, LCS/LCSD	Regular Samples*, Sample Duplicate, MS/MSD	Method Blanks, LCS/LCSD	Regular Samples*, Sample Duplicate, MS/MSD	Method Blanks, LCS/LCSD	Regular Samples*, Sample Duplicate, MS/MSD	
Client_Sample_ID	Х	Х	Χ	X	Χ	X	
Collected		Х		Х		Х	
Matrix_ID	Х	Х	Х	X	Х	X	
Lab_Sample_ID	Х	Х	Х	Х	Х	X	
QC_Type	Х	Q	Χ	Q	Χ	Х	
Shipping_Batch_ID		Х		Х		Х	
Temperature		Х				X	
Lab_Analysis_Ref_Method_ID	Х	Х	Х	X	Х	X	
Preparation_Type	Х	Х	Х	X	Χ	X	
Analysis_Type	Х	Х	Х	Х	Χ	Х	
Prepared	Α	Α	Х	Х	N	N	
Analyzed	Х	Х	Χ	X	Χ	X	
Lab_ID	Х	Х	Χ	X	Χ	X	
QC_Level	Х	Х	Χ	X	Χ	X	
Results_Basis		S		S		S	
Total_Or_Dissolved			W	W			
Dilution	Х	Х	Х	X	Х	X	
Handling_Type	L	L	L	L	L	L	
Handling_Batch	L	L	L	L	L	L	
Leachate_Date	L	L	L	L	L	L	
Percent Moisture		S		S		S	
Method_Batch	Х	Х	Χ	X	Χ	X	
Preparation_Batch	Х	Х	Χ	X	Χ	X	
Run_Batch	С	С	С	С	С	С	
Analysis_Batch	С	С	С	С	С	С	
Lab_Reporting_Batch	Х	Х	Χ	X	Х	Х	
Lab_Receipt		Х		X		X	
Lab_Reported	Х	Х	Х	Х	Х	Х	

Key

- X Required field
- A Required field for samples prepared by methanol extraction
- C Required field if Instrument Calibration Table (A2) is included in EDD
- L Required field if analysis performed on SPLP, TCLP, or WET extracts
- N Required field only for samples that require preparation before analysis
- Q Required field for Sample Duplicate, MS, and MSD only
- S Required field if "Matrix_ID" = "SO" or "SED"
- W Required field for aqueous samples only
- * Includes Trip Blanks, Equipment Blanks, and Field Blanks

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Peninsula CIMP Appendix H Updated Monitoring and Reporting Plan and Quality Assurance Project Plan for Combined Machado Lake Nutrient and Toxics TMDL

Palos Verdes Peninsula Coordinated Monitoring Plan

In Compliance with the Machado Lake Nutrient Total Maximum Daily Load

February 1, 2011

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1. Introduction

The Palos Verdes Peninsula Coordinated Monitoring Plan (Plan) was developed in compliance with the Machado Lake Eutrophic, Algae, Ammonia, and Odors (Nutrient) Total Maximum Daily Load (TMDL)¹. The Nutrient TMDL lists eleven responsible parties tributary to Machado Lake. Among the responsible parties listed are the cities of Rancho Palos Verdes, Palos Verdes Estates, Rolling Hills, and Rolling Hills Estates, which together constitute the Palos Verdes Peninsula (Peninsula Cities). The unique characteristics and isolated geographic setting of the Palos Verdes Peninsula (Peninsula) encouraged a collaborative approach from these Peninsula Cities. This document is the result of that collaboration. Not participating in this plan are the cities of Carson, Lomita, Los Angeles, Redondo Beach, and Torrance, Caltrans, and the unincorporated areas of the County of Los Angeles (County). These agencies have indicated that they will be submitting separate Monitoring and Reporting Plans.

The purpose of this document is to establish a plan to monitor and assess the water quality of discharges exiting the Peninsula. The Plan describes several representative monitoring sites for the Palos Verdes Peninsula drainage system which are situated at the furthest accessible downstream locations of this system before it exits the Peninsula. These sites will be monitored for TMDL compliance as described herein. Results from this monitoring will be beneficial in determining the scope of work needed for the implementation of Best Management Practices (BMPs) to be used in order to achieve compliance with the water quality objectives set forth in the Machado Lake Nutrient TMDL.

1.1. Background

Machado Lake is located in the City of Los Angeles' Ken Malloy Harbor Regional Park. The park is situated to the west of the Harbor (110) Freeway and east of Vermont Avenue. The park is bounded by the Tosco refinery to the south and Pacific Coast Highway to the north. Machado Lake is approximately 40 acres in size and averages approximately 3 feet in depth. It supports a diverse range of wildlife including several threatened and endangered species. The Machado Lake Subwatershed is located within the harbor portion of the larger Dominguez Channel Watershed. Machado Lake receives urban and stormwater runoff from a subwatershed area of approximately 20 square miles consisting of nine incorporated cities, Caltrans highways and roads, and areas of unincorporated County land. Water from Machado Lake overflows a dam located at its southern end before entering the ocean through the Harbor Outflow.

Machado Lake is listed on the 1998, 2002, and 2006 Clean Water Act 303(d) lists of impaired water bodies due to eutrophic conditions, algae and odors. The listed impairments are caused by the overloading of nutrients, such as nitrogen and phosphorus, resulting in excessive algal growth which leads to increased turbidity, decreased levels of oxygen, and odor problems. These occurrences affect the recreational, aesthetic, and ecological functioning of Machado Lake. The Water Quality Control Plan for the Los Angeles Region (Basin Plan) identifies seven existing (E) or potential (P) beneficial uses for Machado Lake.

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¹ State Water Resources Control Board, Los Angeles Region Resolution No. R08-006, Amendment to the Water Quality Control Plan – Los Angeles Region to incorporate the Total Maximum Daily Load for Eutrophic, Algae, Ammonia, and Odors (Nutrient) in Machado Lake

Table 1.1. Potential and Existing Beneficial Uses of Machado Lake as Outlined in the Basin Plan							
Waterbody	MUN (Municipal Water Supply)	REC1 (Water Contact Recreation)	REC2 (Non- Contact Water Recreation)	WARM (Warm Freshwater Habitat)	WILD (Rare, Threatened, or Endangered Species)	RARE (Endangered Species)	WET (Wetland Habitat)
Machado Lake	Р	Е	E	Е	E	E	E

The Clean Water Act section 303(d) requires the prioritization and development of TMDLs to address impairments and outline plans to restore the beneficial uses of listed water bodies. TMDLs require the reduction of pollutant loading by assigning waste load allocations, load allocations, and numeric targets to responsible parties which must be met at set interim and final compliance dates. The TMDL addressing the nutrient impairment of Machado Lake was adopted by the State Water Resources Control Board, Los Angeles Region (Regional Board) on May 1, 2008. It was subsequently approved by the United States Environmental Protection Agency and became effective on March 11, 2009. This TMDL sets forth stringent numerical limits for nitrogen and phosphorus, as well as numerical targets for ammonia, dissolved oxygen and chlorophyll a which will help assess the overall water quality in the lake.

1.2. Geographic Description of Palos Verdes Peninsula

The Peninsula is situated in the southwestern portion of the Machado Lake Subwatershed atop the Palos Verdes Hills which are bounded to the north by Torrance, to the east by City of Los Angeles, and to the south and west by the Pacific Ocean. The Peninsula consists of the four incorporated cities of Rancho Palos Verdes, Palos Verdes Estates, Rolling Hills, and Rolling Hills Estates along with areas of unincorporated County land. The Peninsula Cities are all very similar in topography and land usage. The major land use designation on the Peninsula is residential. There are also significant portions of open space and soft bottom canyons. There is one commercial district and several areas of institutional land. There are also notable areas where horse uses exist. Figure 1.1 depicts the major land uses that characterize the Peninsula. There is a large drainage divide which dissects the Peninsula from the northeast to the southwest with the westerly portion draining into the Santa Monica Bay. The portion of the Peninsula which drains to Machado Lake consists of approximately 5.63 square miles, which is about 25% of the Machado Lake Subwatershed drainage area. This drainage flows in an easterly or northeasterly direction, contributing flow to three of the four major drainage systems entering Machado Lake (i.e. Wilmington Drain, Project 77 and Project 510). Drainage from the Peninsula Cities is conveyed via the natural soft bottom canyon systems in conjunction with structured storm drain systems. These systems are intertwined and cross-connected warranting a Peninsula-wide coordinated approach to end-of-pipe monitoring.

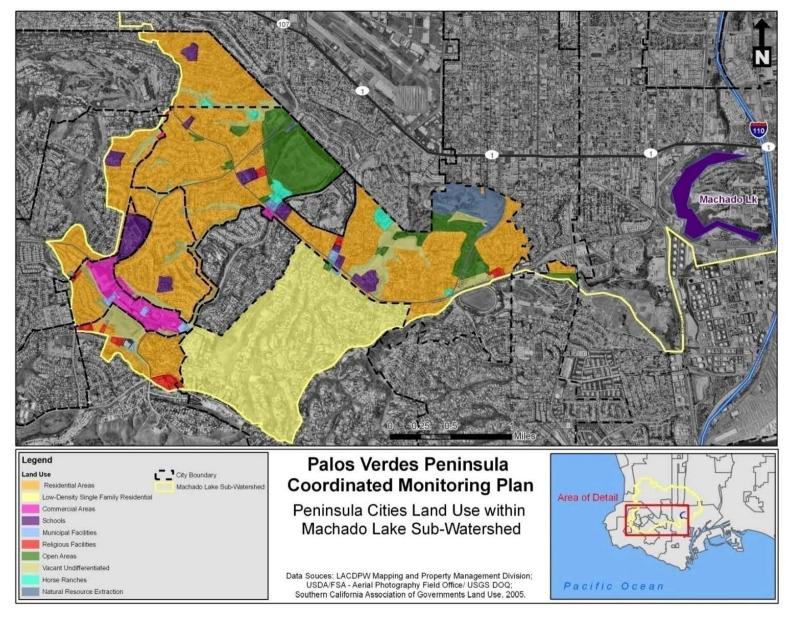


Figure 1.1 Major Land Uses Characterizing the Palos Verdes Peninsula

1.3. Waste Load Allocation Compliance

The Nutrient TMDL for Machado Lake outlines three options for compliance. It assigns waste load allocations, or limitations on pollutant discharges contained in storm drain discharges, to responsible parties which drain to Machado Lake. Interim and final waste load allocations [Table 1.2] can be demonstrated through one of the following methodologies:

- Concentration-based waste load allocations with in-lake monitoring
- Concentration-based waste load allocations with monitoring at the end of the responsible party's drainage system (end-of-pipe)
- Mass-based waste load allocations with end-of-pipe monitoring

Table 1.2. Interim and Final Waste Load Allocations as Specified in the Machado Lake Nutrient TMDL				
Compliance Date	Total Phosphorus	Total Nitrogen		
March 11, 2009	1.25 mg/L	3.5 mg/L		
March 11, 2014	1.25 mg/L	2.45 mg/L		
September 11, 2018	0.1 mg/L	1 mg/L		

The Peninsula Cities met and determined that the best option for compliance was Option 2, concentration based waste load allocations with end-of-pipe monitoring. However, the systems which convey drainage from the Peninsula Cities are intertwined and cross-connected. Drainage from one city generally flows through at least one of the other three cities before exiting the Peninsula. It would be difficult and redundant for each city to monitor its own drainage independent of the other Peninsula Cities. For this reason, it was appropriate for the Peninsula Cities to coordinate efforts in order to comply with the Nutrient TMDL. The Peninsula Cities decided to determine compliance with concentration-based waste load allocations by choosing monitoring sites at the termini of the shared Peninsula drainage system. This Plan satisfies the first deliverable requirement outlined in the compliance schedule for the selected approach [Table 1.3]. Monitoring in accordance with this Plan will continue until the Peninsula Cities have established compliance with final waste load allocations. Once compliance with final waste load allocations is established, the results of this monitoring plan and other available information may be used to revise the amount of monitoring required to demonstrate continued TMDL compliance under a revised monitoring plan or other Regional Board order.

Table 1.3. Compliance Schedule for Option 2: End-of-Pipe Concentration-Based Waste Load Allocations				
Compliance Date	TMDL Requirement			
March 11, 2009	Meet 1 st interim waste load allocations (shown in Table 2)			
March 11, 2010	Submit Monitoring and Reporting Plan (MRP) to the Regional			
	Board for approval			
60 days from date of MRP approval	Begin monitoring as outlined in MRP			
Annually from date of MRP approval	Submit annual monitoring reports			
March 11, 2011	Submit Implementation Plan (IP) to Regional Board for approval			
60 days from date of IP approval	Begin implementation as outlined in IP			
March 11, 2014	Meet 2 nd interim waste load allocations (shown in Table2)			
September 11, 2016	TMDL re-opener period			
September 11, 2018	Meet final waste load allocations and numeric targets (shown in			
	Table 2)			

2. Monitoring Program Design

Drainage on the Peninsula is conveyed via a network of natural soft-bottom canyons augmented by improved storm drain structures in the more developed areas. A drainage divide running northwest to southeast along the crest of the Peninsula separates the Machado Lake watershed from the Santa Monica Bay watershed. Within the Machado Lake watershed the canyons convey stormwater flow in an easterly or northeasterly direction. Stormwater runoff from the four incorporated cities on the Peninsula is closely intertwined and is therefore conducive to the implementation of a coordinated monitoring plan.

2.1. Criteria and Methodology for Monitoring Site Selection

The Peninsula Cities have selected monitoring sites that are representative of the drainage from each of the Cities' land uses on the Peninsula tributary to Machado Lake. These monitoring sites have been selected to ensure that:

- Each city has drainage tributary to at least one sampling location
- Each city has each of its major land use/zoning types represented in the tributary area to at least one location
- Taken together the sampling locations are representative of major Peninsula land uses and development intensity, e.g., commercial, residential with curb-and-gutter, residential with soft bottom canyons, equestrian use, schools/ball fields, open space, parks, etc.
- Monitoring could be conducted in a safe manner considering traffic and stormwater access conditions

In order to establish appropriate and representative monitoring locations, subdrainage areas were delineated based on desktop examination of County GIS-based drainage maps, topographic drainage maps and aerial photographs. Several potential monitoring locations near the foot of each of the major subdrainage areas on the Peninsula were identified based on this desktop analysis. Final monitoring sites were selected based on field reconnaissance to identify representative locations that could be safely accessed for monitoring.

The Machado Lake subdrainage areas and monitoring locations are discussed in the following subsections in order progressing from northwest to southeast across the Peninsula. Taken together, the subdrainage areas and monitoring locations proposed in this plan directly monitor 2,108 acres within the total 3,608 acres of the Peninsula Cities' tributary area to Machado Lake. These subdrainage areas and monitoring locations together will provide direct monitoring of all the significant land uses tributary to Machado Lake in the four incorporated cities on the Peninsula. Currently, of the 1,500 acres not directly monitored, 707 acres is tributary to a local infiltration basin, the Chandler Quarry pit, which does not discharge to Machado Lake unless an unusually large storm such as a 50-year storm occurs, effectively isolating that subdrainage area from Machado Lake. The remaining 800 acres of Machado Lake tributary area which are not directly monitored by one of the proposed monitoring sites will be indirectly monitored by a surrogate monitoring location with similar land use and development intensity. Figure 2.1 Water Quality Monitoring Sites and Associated Sub-Drainage Areas depicts the

subdrainage areas and monitoring sites. These same subdrainage areas are shown overlaid onto the land use map in Figure 2.2 for ease of reference in the subsequent discussions of each monitoring site. This figure shows which land uses are captured within each subdrainage area.

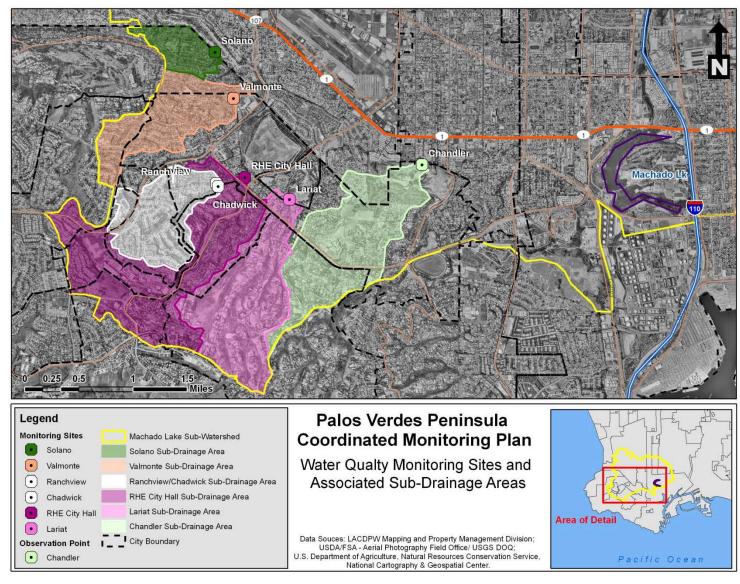


Figure 2.1 Water Quality Monitoring Sites and Associated Sub-Drainage Areas

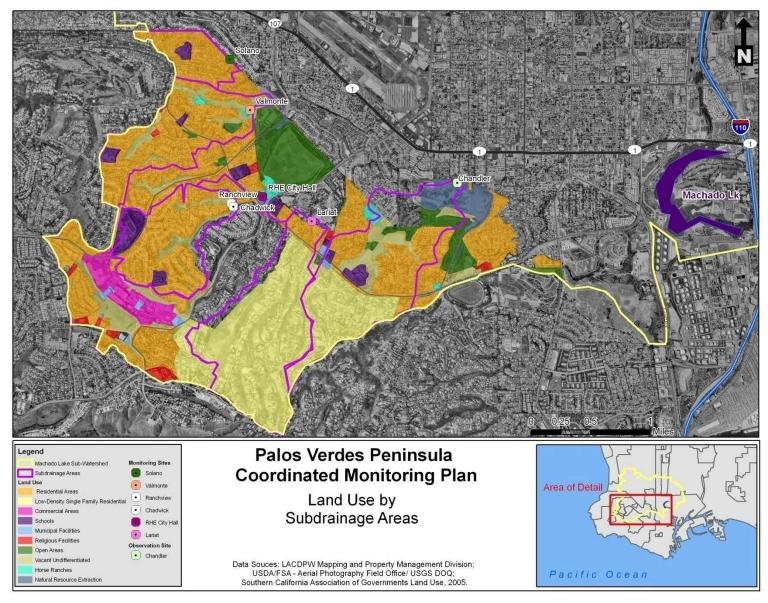


Figure 2.2 Palos Verdes Peninsula Land Use by Subdrainage Areas

2.1.1. Solano Subdrainage Area

A portion of the Peninsula drains to the Walteria Lake storm water detention basin located in Torrance via the City of Torrance Project No. 8102 storm drain. This subdrainage area is approximately 144 acres located entirely within Palos Verdes Estates and situated east of Palos Verdes Drive North, south and west of the City of Palos Verdes Estates' border with the City of Torrance, and north of Via Valmonte [Figure 2.3]. The primary land use in this subdrainage area is residential with curb-and-gutter. There is one elementary school located in the subdrainage area. The curb-and-gutter system (storm drain system) in the subdrainage area collects storm water runoff as well as dry-weather runoff and discharges flow through the subsurface Miscellaneous Transfer Drain (MTD) 1495-2 near Via Verderol into the City of Torrance. Monitoring will occur in this storm drain as the flow here is representative of runoff from the entire subdrainage area. Figure 2.3 shows the manhole atop of the MTD 1495-2 at the Solano monitoring site to where the flow discharges from the Peninsula into the City of Torrance.



Figure 2.3 Solano Monitoring Site

2.1.2. Valmonte/Ferncreek Subdrainage Area

Valmonte Canyon and Ferncreek have a combined drainage area of 415 acres and are both soft-bottom natural drainage courses which converge at the base of Ernie Howlett Park. At the convergence of these canyons [Figure 2.4] the stormwater flow is directed into a subsurface storm drain which runs under Ernie Howlett Park and connects to a Los Angeles County Flood Control District (LACFCD) storm drain MTD 227 below Hawthorne Boulevard at which point the drainage exits the City of Rolling Hills Estates and the Peninsula and enters the City of Torrance.

The Valmonte Canyon Subdrainage Area is the larger of the two and collects stormwater runoff from residential areas of Palos Verdes Estates, Rancho Palos Verdes and Rolling Hills Estates. Ferncreek collects runoff only from Rolling Hills Estates.

The Valmonte/Ferncreek subdrainage area is predominantly residential and includes some residential properties in the lower reaches of the drainage area in the equestrian overlay where horses are kept. A municipal stable also lies within this drainage area. This monitoring site receives runoff from three of the four Peninsula Cities (Rolling Hills Estates, Rancho Palos Verdes and Palos Verdes Estates).



Figure 2.4 Looking West From Ernie Howlett Park at Ferncreek Converging from Left and Valmonte Canyon from Right

The safest, most accessible downstream location for monitoring of this subdrainage area is at the convergence of the two drainage courses (Valmonte Canyon and Ferncreek [Figure 2.5]) where the flow enters a subsurface storm drain under Ernie Howlett Park. A baseline dry weather flow enters the subsurface storm drain under Ernie Howlett Park, either from groundwater seeping from below Ernie Howlett park (see weep holes visible in Figure 2.5) or from Ferncreek or both. A routine dry weather and wet weather monitoring site named "Valmonte" will be established at this location.

Valmonte Canyon does not appear to have discharge during dry weather so in the event that a source tracking monitoring investigation is needed for this subdrainage area, a dry weather monitoring site will be established at the storm drain pipe conveying runoff from Valmonte Canyon to the subsurface storm drain below Ernie Howlett Park to document the presence/absence of dry weather discharge from Valmonte Canyon. [Figure 2.6] This location will thus serve as a Tier 2 source tracking monitoring site in the event that samples collected from flow entering the subsurface storm drain under Ernie Howlett Park at the Valmonte monitoring site trigger a source tracking investigation.



Figure 2.5 Valmonte Monitoring Site; Pipe Conveying Drainage from Valmonte Canyon is in the Foreground and Flow From Ferncreek Enters From the Right



Figure 2.6 Valmonte Canyon Tier 2 Monitoring Site

2.1.3. Ranchview/Chadwick Canyon Subdrainage Areas

Ranchview Canyon and Chadwick Canyon are both soft-bottom natural drainage courses [Figure 2.7] with a combined drainage area of 385 acres. These two canyons converge and enter a subsurface storm drain which then crosses under Palos Verdes Drive North and connects with LACFCD subsurface storm drain RDD 275 behind Rolling Hills Estates City Hall.

The upper reach of Ranchview Canyon collects runoff from residential areas of Rancho Palos Verdes, from the playing fields and classroom buildings of Palos Verdes Peninsula High School, as well as a section of a major arterial roadway, Hawthorne Blvd. The lower reach of Ranchview Canyon collects runoff from residential areas in Rolling Hills Estates within the equestrian overlay, however only a few of those property owners currently keep horses [based on Community Emergency Response Team (CERT) map].

Chadwick Canyon collects runoff from residential areas of Rancho Palos Verdes, including an elementary school, as well as residential areas within County unincorporated areas. No equestrian areas lie within the Chadwick Canyon drainage area [confirmed by CERT map].

Neither Ranchview Canyon nor Chadwick Canyon subdrainage areas appear to have discharge to RDD 275 during dry weather [Figure 2.7]. These locations will serve as Tier 2 source tracking monitoring sites in the event that samples collected from the RHE City Hall monitoring site trigger a source tracking monitoring investigation. Flow observations made at the storm drain entry structures for each of these canyons will document the presence/absence of dry weather discharge from these two subdrainage areas.

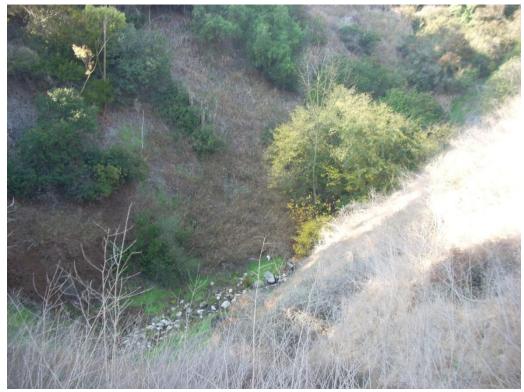


Figure 2.7 Upper Ranchview Canyon



Figure 2.8 Ranchview Canyon Tier 2 Site



Figure 2.9 Chadwick Canyon Tier 2 Site Entering Subsurface Storm Drain

2.1.4. RDD 275 Subdrainage Area—RHE City Hall Monitoring Site

Unlike most of the drainage courses on the Peninsula, the RDD 275 subdrainage area, comprised of 860 acres excluding Ranchview and Chadwick Canyons, consists primarily of hardened conveyances; a combination of curb-and-gutter, subsurface storm drains, and a section of large open channel (trapezoidal ditch). This is the most diverse subdrainage area from a land use perspective as it includes the downtown commercial area of the Peninsula located mainly within Rolling Hills Estates, residential areas in Rancho Palos Verdes and Rolling Hills, a County unincorporated residential area with some equestrian properties and a private K-12 academy, as well as arterial roadways (Silver Spur Road and Crenshaw Blvd.) The City of Palos Verdes Estates is the only one of the Peninsula cities without land area in this subdrainage area. This subdrainage area is to be directly monitored and will also serve as a surrogate monitoring site for areas on the Peninsula not being directly monitored.

Baseline dry weather flow from this subdrainage area is evident where it daylights in a trapezoidal ditch along Crenshaw Boulevard [Figure 2.10]. The safest, most accessible downstream location for monthly monitoring of this subdrainage area is at the manhole behind Rolling Hills Estates City Hall [Figure 2.11] where RDD 275 joins drainage from Ranchview and Chadwick Canyons.

The trapezoidal ditch location adjacent to Crenshaw Blvd. will be utilized as a Tier 2 source tracking monitoring site along with Ranchview and Chadwick Canyons in the event that wet weather samples collected from the "RHE City Hall" monitoring site behind Rolling Hills Estates City Hall trigger a source tracking investigation.



Figure 2.10 Looking South/Upstream RDD 275 along Crenshaw Boulevard



Figure 2.11 RHE City Hall Monitoring Site at Manhole behind Rolling Hills Estates City Hall

2.1.5. <u>Agua Magna/Sepulveda/Blackwater Canyon Subdrainage Area</u> <u>Lariat Monitoring Site</u>

Three canyon drainage ways within Rolling Hills (Agua Magna, Sepulveda, and Blackwater Canyons) cross under Palos Verdes Drive North, pass for a short distance through Rolling Hills Estates, cross under Lariat Lane and converge into a drainage structure just inside the boundary of the South Coast Botanic Garden which lies within County unincorporated land [Figure 2-12]. The predominant land use within this 650 acre, three canyon subdrainage area is low density residential development with some horse keeping.

Based on preliminary field reconnaissance, it appears that this subdrainage area may not have discharge to Machado Lake during dry weather. A monitoring site, "Lariat", will be established for this subdrainage area at the drainage structure just inside the South Coast Botanic Garden.



Figure 2.12 Lariat Monitoring Site at Drainage Structure Collecting Flow from Agua Magna/Sepulveda/Blackwater Canyons

2.1.6. Project 77 Storm Drain Subwatershed within Palos Verdes Peninsula

As currently developed, only a minor area within the Peninsula currently contributes discharge to Machado Lake via the Project 77 Storm Drain. This is because of a unique geologic/hydrologic condition associated with the former Chandler Quarry, now an inert landfill. The Chandler quarry pit collects flows from the majority of the areas west of Palos Verdes Drive East within the Project 77 Subwatershed, including the Rolling Hills Country Club golf course. The Chandler Quarry/Landfill is currently proposed for redevelopment and, according to the Chandler Ranch/Rolling Hills Country Club Project EIR hydrology study, the tributary area of the Chandler quarry pit is 707 acres and has the capacity to retain and infiltrate up to the 50-year storm without discharging to the Project 77 storm drain². So as currently developed, the tributary area to the Chandler Quarry does not result in discharge to Machado Lake except under very rare, large storms. The City of Rolling Hills Estates intends to place conditions of approval on the Chandler Ranch/Rolling Hills Country Club Project to achieve compliance with the Machado Lake Nutrient TMDL targets. At the time of redevelopment, depending on the final hydrologic analysis of the project, consideration will be given to placing an additional monitoring site at the discharge point from the Chandler Ranch/Rolling Hills Country Club project to Project 77 Storm drain.

There is currently no safely accessible, representative monitoring location for the areas east of Project 77 storm drain not tributary to the Chandler quarry pit because those flows are conveyed via a

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² The EIR can be found on the City of Rolling Hills Estates website at http://www.ci.rolling-hills-estates.ca.us/index.aspx?page=209&recordid=37

subsurface County storm drain in the right-of-way for Palos Verdes Drive East which manholes cannot be safely accessed for monitoring. Consequently, we are not proposing to monitor this subdrainage area. Those areas within Project 77 storm drain subwatershed on the Peninsula not tributary to the Chandler quarry pit will be assumed to be represented by the surrogate monitoring site, RHE City Hall.

2.2. Monitoring Schedule and Frequency

During the first twelve (12) months of the monitoring program, the four (4) monitoring sites (Solano, Valmonte, RHE City Hall, and Lariat) will be visited by a monitoring crew on a monthly basis during dry weather. Dry weather is defined as a day when there has been no rainfall of 1/10th inch or greater on that day or on the 72 hours preceding. If flow is observed, a Field Conditions Data Sheet will be completed, a sample collected and flow measurements recorded. If no flow or insufficient flow for sampling is present, a No Flow or Low Flow Conditions Data Sheet will be completed. Based on the results of the first year of monitoring, each monitoring site will be classified as either a routine *dry weather/wet weather sampling location*, or as a *wet weather-only sampling location*. Monitoring sites which had sufficient flow for sampling on three (3) or more out of the twelve (12) routine monthly site visits during the first year of the monitoring program will be classified as a *dry weather/wet weather monitoring site*.

Monitoring Sites	Subdrainage Description	
Solano	PVP subdrainage to Walteria Lake	
Valmonte	Valmonte and Ferncreek subdrainage	
RHE City Hall	RDD 275, Ranchview and Chadwick Canyons, also	
	surrogate for areas not directly monitored	
Lariat	Agua Magna, Sepulveda and Blackwater Canyons	

2.2.1. No/Low Flow Observation Sites

Following the first year of monitoring, sites which are identified as being wet weather-only sampling locations due to no or insufficient flow for sampling on eight or more out of twelve dry weather observations, will be visited on a quarterly basis and a No Flow or Low Flow Conditions Data Sheet will be completed to confirm that the status has not changed. After a year of quarterly confirmation, sites which have no or insufficient flow for sampling on at least three (3) of the four (4) quarterly confirmatory site visits will be removed from the routine dry weather monitoring program and no further monitoring visits will be made for these sites during dry weather. See No/Low Flow Site Classification Decision Process [Figure 2.13 No/Low Flow Site Classification Decision Process].

2.2.2. Dry Weather Sampling

Monitoring sites which have sufficient flow for sampling on three (3) or more out of the twelve (12) routine monthly site visits during the first year of the monitoring program will be classified as *dry weather/wet weather monitoring sites*. These sites will be monitored on a monthly basis for the duration of the monitoring program unless implementation measures result in decreased flows which would trigger reclassification of these sites as No/Low Flow Observation Sites in accordance with the No/Low Flow Site Classification Decision Process.

2.2.3. Wet Weather Sampling and Flow Measurement

In addition to routine dry weather sampling, at least two qualifying wet weather sampling and flow measurement events per year will be conducted at the four (4) monitoring sites (Solano, Valmonte, RHE

City Hall, and Lariat). Wet weather sampling events will be scheduled by monitoring weather forecasts for the 90274 and 90275 zip code areas on weather.com. Qualifying wet weather sampling events are those work days (non-holiday week days) with a forecast of an 80% chance of at least 0.25 inch of rainfall. Wet weather sampling events will begin as early in the day as possible to ensure that samples are transported to the laboratory within required holding times.



Figure 2.13 No/Low Flow Site Classification Decision Process

2.3. Interim Waste Load Allocation Source Tracking Monitoring Investigation

Based on the first year of baseline dry weather monitoring data collected from the Peninsula monitoring sites as outlined in Section 2.2 above, an evaluation will be made to assess compliance with the monthly average criteria in the Machado Lake Nutrient TMDL shown in Table 2.1. An Interim Waste Load Allocation Source Tracking Monitoring investigation will be conducted for any monitoring sites where monthly averages are exceeding the Year 0 waste load allocation. The Peninsula Cities will meet to establish a flow tracking and sampling scheme to identify branch(s) of drainage system contributing to interim waste load allocation exceedance. The source tracking will be conducted in an iterative, adaptive manner to identify potential sources contributing to the waste load allocation exceedance and will be informed by the results of low flow/no flow observation data.

After two years of combined wet weather and dry weather monitoring data are collected and reviewed, an updated evaluation will be made to assess compliance with the monthly average criteria in the Machado Lake Nutrient TMDL. An Interim Waste Load Allocation Source Tracking Monitoring investigation will be conducted for sites with monthly averages exceeding the Year 0 or Year 5 waste load allocation. The Peninsula Cities will meet to establish a source tracking sampling scheme to identify monitoring sites in the various branch(s) of the drainage system and to determine the particular land uses and defined areas of the drainage system that are contributing to interim waste load allocation exceedance. Findings of source tracking investigations will inform appropriate action under the Palos

Verdes Peninsula Implementation Plan for Machado Lake Nutrient TMDL (to be submitted by March 11, 2011).

Table 2.1. Interim and Final Waste Load Allocations for Storm Drain Discharges					
MS4 Permittees	Years After Effective Date (03/11/2009)	Date of Compliance	Total Phosphorus (mg/L)	Total Nitrogen (mg/L)	
Caltrans, General Construction and	0	03/11/2009	1.25	3.5	
Industrial Stormwater	5.0	03/11/2014	1.25	2.45	
Permits	9.5	09/11/2018	0.10	1.00	

A source tracking monitoring scheme would include the monitoring of upstream locations (Tier 2 monitoring sites) tributary to a Tier 1 monitoring site which has exceeded interim waste load allocations. A preliminary list of several Tier 2 monitoring sites already identified for a few of the Tier 1 monitoring sites are provided in Table 2.2. Tier 3 sites will be established by the Peninsula Cities at the time a source tracking investigation is initiated or as needed in an iterative process. A description of the technical design and rationale for source tracking investigations planned for the coming year will be included as an attachment or appendix to the annual monitoring report. Results of any source tracking investigations performed during the reporting year will be included as an appendix to the annual monitoring report.

Table 2.2. Preliminary List of Tier 2 Monitoring Sites				
Tier 1 Monitoring Site	Tier 2 Monitoring Sites			
Solano				
Valmonte	Valmonte Canyon storm drain pipe			
	Ferncreek stream bed			
RHE City Hall	Ranchview Canyon at inlet structure			
also surrogate monitoring site	Chadwick Canyon at inlet structure			
	RDD 275 trapezoidal open channel @ Crenshaw			
	Blvd.			
Lariat	Agua Magna Canyon @ PV Drive North			
	Sepulveda Canyon @ PV Drive North			
	Blackwater Canyon @ PV Drive North			

3. Field Monitoring Methods and Procedures

This Chapter provides the methods and procedures to be used in the field when conducting water quality monitoring.

3.1. Water Quality Sampling Parameters

Compliance with the Nutrient TMDL will be shown through concentration-based monitoring. The water quality constituents to be analyzed and the analytical methods are shown in Table 3.1. A State Certified Laboratory will provide the analytical services for this Plan.

Table 3.1. Water Quality Constituents To Be Sampled			
Analyte	Method		
Nitrate-Nitrite	EPA method 300.0; 353.2		
Total Kjeldahl Nitrogen (TKN)	EPA 351.2		
Total Phosphorus	SM 4500-P E; EPA 365.3		

3.2. Sampling and Flow Measurement Methods

All samples will be collected using manual grab sampling methods as this is the most relevant technique for the conditions found on the Peninsula. Sampling Teams comprised of two (2) to three (3) members will be responsible for obtaining the water quality samples from each of the identified monitoring sites. Each Sampling Team will carry all necessary equipment to be able to sample in various environmental and physical conditions (i.e. high or low flow, natural or manmade conveyances, etc). A list of necessary equipment is presented in the following section. The Sampling Team will fill out a Field Conditions Data Sheet at each monitoring site for each day of sampling. An example Field Conditions Data Sheet is located in Appendix A.

A protocol for making instantaneous flow measurements will be established by the field team and approved in advance by the Peninsula Cities' representatives for each permanent monitoring location. Flow measurements will entail the use of a velocity meter plus measurement of the depth and width of cross-sectional flow area or the use of an area-velocity flow meter calibrated for the particular conveyance structure at each location. A minimum of three velocity readings will be made immediately following each sample collection.

3.3. Monitoring Site Procedures

The following are the specific procedures that will be followed by the Sampling Teams at each monitoring site regardless of whether it is an open manmade channel, an open natural area, or a subterranean storm drain and regardless of the flow type (high or low). The locations and descriptions of each identified monitoring site are provided in Chapter 2.

3.3.1. Sampling Preparations

Each Sampling Team should be certain that they have all of the necessary equipment to conduct the sampling as shown in Table 3.2.³

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³ Adapted from Minnesota Pollution Control Agency, Biological Monitoring Program. 2001. Water Chemistry Assessment Protocol for Depressional Wetland Monitoring Sites.

Table 3.2. Sampling Equipment Inventory					
Equipment	Purpose	Operation Check			
Sample Bottles: Poly Ethylene/ High Density Poly Ethylene – 250 mL	Sample bottle	Sufficient quantity for sampling all sites Clean labels attached			
Amber glass bottles – 250 mL	Sample bottle	Sufficient quantity for sampling all sites Clean labels attached			
Sulfuric Acid (H ₂ SO ₄)	Preservative	Sufficient volume for sampling all sites			
Other Equipment	Purpose	Operation Check			
Cooler with ice	Short term sample preservation	Properly working cooler and adequate amount of ice			
Color wheel	Measure water color in field	Deionized water for reference Instruction manual			
Cell phone	Communication	Phone charger/batteries present			
Field Sampling Plan	Site location information	Correct maps for each site			
Portable Flow Meter	Measurement of volumetric flow rate	Calibration per manufacturer's instructions			
Camera	Document sampling	Associated charger, batteries, instruction manual, etc			
Data sheets and clipboard	Record field observations	Correct data sheets for each site			
Pencils/pens	Recording data	Sharp pencil point/working pen			
Fine point permanent marker	Label sample bottles	Working marker			
Chain of Custody Forms from Sate Certified Laboratory	Request analyses for samples	Adequate number for sampling all sites			
Rain gear	Keep Sampling Team dry	Working rain gear			
Safety vests/cones	Ensure Sampling Team safety	Enough for Sampling Team(s)			

3.3.2. Arrival at Monitoring Site

Upon arrival at the monitoring site, the Sampling Teams will inspect the location for general safety. It is important to be aware of the surroundings when working in a street or other right-of-way and is imperative to place safety cones so that traffic is aware of the situation.

3.3.3. Field Conditions Sheet

Site conditions are general observations that will be recorded when the Sampling Team first arrives at the monitoring site. The following general observations should be recorded on the Site Conditions Field Sheet:

- Date and time of arrival;
- The weather conditions;
- The air temperature;
- The general flow conditions of the water;
- The appearance and odor of the water; and
- If there is trash or debris at the monitoring site.

3.4. Sampling in Open Channels or Creeks/Streams Procedures

The following are the procedures that will be employed for sampling open manmade channels or creek/stream sites. Water Quality samples will be collected prior to making flow measurements in order to minimize disturbance of deposited sediment prior to sampling to ensure that samples collected are as representative as possible of the discharged storm water.

A designated sampling apparatus must always be used to fill a sample bottle containing preservative. It is important that the sample bottles do not overflow. If a sample bottle overflows, it must be discarded and a new sample must be taken using a new sample bottle. Listed below are the steps to be taken during open channels or creeks/streams sampling:⁴

- An ice chest with sufficient ice to properly store any samples will be utilized;
- Only the sample bottles with the correct site number will be used at each monitoring site;
- The sampling apparatus for each site will be acclimated by rinsing it out with water from the waterbody three (3) times;
- Grab samples will be taken from the section of the manmade channel or creek/stream with the deepest flow (if it is safe to do so);
- The Sample Team will always walk upstream to ensure that they do not disturb the sediments which could taint the sample;
- Samples will be taken by facing the sampling apparatus upstream to reduce the possibility of contamination;
- The Sampling Team will avoid touching the inside of the sampling apparatus to further prevent contamination;
- The water in the sampling apparatus will be transferred to the sample bottle;

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⁴ Procedures adapted from: US EPA, Office of Water. 1992. *NPDES Storm Water Sampling Guidance Document*. EPA 833-92-001.

- The sample bottles labeled with the appropriate site number will be placed in the cooler standing straight up surrounded and supported by ice;
- The number of each sample from the sample bottle, the time the samples were collected, and the time the samples were put on ice will be recorded on the Chain of Custody Form;
- All Sampling Team members that had custody of any samples will sign the Chain of Custody Form;
- The courier used to transport the samples to the lab will be listed as receiving the samples for transport. However, they will not sign the Chain of Custody Form;
- The Chain of Custody Form will be placed into a large watertight resealable bag and placed inside the cooler with its corresponding samples;
- The cooler will be secured with packing tape and transported to the State Certified Laboratory within the designated method holding times; and
- Upon the laboratory receiving custody of the samples, the State Certified Laboratory's representative will sign the Chain of Custody Form.

3.5. Sampling in Subsurface Storm Drains Procedures

Subsurface storm drain sampling involving manholes can be more involved than open channel sampling and may be inherently more dangerous. These types of areas may be considered confined entry spaces requiring compliance with OSHA regulations. Therefore, any sites that require entry into a manhole will be handled by city crews with the proper equipment and experience. However, most of the sampling sites will not require entry into a manhole.

Water Quality samples will be collected prior to making flow measurements in order to minimize disturbance of deposited sediment prior to sampling to ensure that samples collected are as representative as possible of the discharged storm water. A designated sampling apparatus must always be used to fill a sample bottle containing preservative. It is important that the sample bottles do not overflow. If a sample bottle containing preservative overflows, it must be discarded and a new sample must be taken using a new sample bottle. Listed below are the steps to be taken during subsurface storm drain sampling:⁵

- An ice chest with sufficient ice to properly store any samples will be utilized;
- The required Occupational Safety and Health Administration safety checks and preparations for the removal of a manhole cover and entry into a manhole safely will be completed;
- The designated sampling apparatus labeled with the appropriate site number will be used;
- The sampling apparatus for each site will be acclimated by rinsing it out with water from flow in the drain three (3) times;
- The grab sample will be taken from the horizontal and vertical center of the storm drain (if it is safe to do so);
- The bottom sediments (if there are any) in the drain will not be disturbed so as to avoid contaminating the sample;
- The sampling apparatus will be held so the opening faces upstream (with the Sampling Team member also facing upstream);
- The inside of the sampling apparatus will not be touched in order to prevent contamination;

⁵ id.

- The sample water from the sampling apparatus will be transferred into the proper sample bottles without overflowing them;
- The sample bottles labeled with the appropriate site number will be placed in the cooler standing straight up surrounded and supported by ice;
- All Sampling Team members that had custody of any samples will sign the Chain of Custody Form;
- The courier used to transport the samples to the lab will be listed as receiving the samples for transport. However, they will not sign the Chain of Custody Form;
- The Chain of Custody Form will be placed into a large watertight Ziploc bag and placed inside the cooler with its corresponding samples;
- The cooler will be secured with packing tape and transported to the State Certified Laboratory within the designated method holding times; and
- Upon the laboratory receiving custody of the samples, the State Certified Laboratory's representative will sign the Chain of Custody Form.

3.6. No Sample Taken Procedures

There may be circumstances that would cause a particular monitoring site to not be sampled. These circumstances may involve:

- Lack of flow or insufficient flow
- Site inaccessibility.

3.6.1. Low Flow Conditions

Sampling will be attempted even in extreme low flow conditions. If a sample cannot be taken due to insufficient or a lack of flow, a separate data sheet will be completed to explain why no sample was taken.

3.6.2. Site Inaccessibility Due to Storm Event

If a monitoring site becomes inaccessible due to a storm event in which it would be dangerous to approach the manmade channel, stream/creek, storm drain inlet or manhole; the Sampling Team will delay sampling for 24 hours to 48 hours after the storm event. However, if an alternative monitoring site is in close proximity and provides a sample which is representative of the original monitoring site, then sampling will occur on schedule at the alternative monitoring site.

3.6.3. <u>Site Inaccessibility Due to Temporary Physical Obstruction or Condition</u>

If a monitoring site is temporarily or permanently blocked by a physical obstruction, such as downed trees or evidence of a landslide or rockslide, the Sampling Team will attempt to move 25-50 feet (ft) upstream or downstream from the monitoring site and conduct sampling there. If there still is no suitable access, the Sampling Team will determine the possibility of sampling further away (up to 100 ft) from the original monitoring site.

3.6.4. Site Inaccessibility Due to Ownership Change

This condition is unexpected, but if the monitoring site comes under new ownership, such that previously granted access is now denied, permission will be requested from the new owner. If this is denied, a permanent new monitoring site will be selected in close proximity to the original monitoring site provided the proposed new monitoring site is as representative as the previous monitoring site.

3.7. Corrective Action for Field Measurements

The Sampling Team will have the primary responsibility for responding to equipment failures during sampling. Deviations from defined protocols will be documented in the comment section of the Field Conditions Data Sheet. If any equipment fails, Sampling Team personnel will report the problem in the comment section of the Field Conditions Data Sheet and will not record the data values for the water quality constituents in question. Actions will be taken to replace or repair broken equipment prior to the next field use. Data that are known to be collected with faulty equipment will be entered into the project database, but will not be used for determining compliance. It is the combined responsibility of all members of the Sampling Team to determine if the performance requirements of the specific sampling method have been met, and to collect an additional sample if required.

3.8. Sample Management

In order for the samples to be considered valid, each sample must be taken to the State Certified Laboratory for chemical analyses:

- In the proper container as provided by the State Certified Laboratory;
- With a sufficient volume of sample as prescribed by the State Certified Laboratory;
- Having a sufficient amount of preservative as pre-supplied in the appropriate sampling bottles by the State Certified Laboratory; and
- In less time that the method holding time for that type of sample (i.e. water quality constituent type).

3.8.1. <u>Container Type, Container Volume, Sample Preservation, and Holding</u> Time

Each Sampling Team will use a designated filling container that will be rinsed with deionized water (no soap) three times prior to use. The State Certified Laboratory will supply a sufficient number of sampling bottles to the Sampling Teams who will label the sampling bottles with the correct monitoring site information. After collection of the samples, the Sampling Team will write the following information on the label:

- Analyses to be performed on the sample: For this project, the State Certified Laboratory will be
 notified in advance that each label will state "PVP Nutrient TMDL". The PVP Nutrient TMDL
 label will signify to the State Certified Laboratory what parameters to analyze for;
- Date and Time sample collected;
- Sample number: identifies sample location, date, and aliquot (see sample assignment numbers shown in Table 5); and
- Full names of individuals who collected the samples.

Total Phosphorous requires a 250 milliliter (mL) amber glass bottle or a 250 mL Poly Ethylene bottle for sampling under EPA method 635.3 and a 250 mL amber glass bottle for sampling undere SM 4500-P E. Total Kjeldahl Nitrogen (TKN) requires a 250 mL Poly Ethylene bottle for sampling under EPA method

351.2. Nitrate (NO_3) and Nitrite (NO_2) require a 250 mL Poly Ethylene bottle for sampling under EPA method 353.2 and require a 125 mL High Density Poly Ethylene (HDPE) bottle for sampling under EPA method 300.0.

TKN, Total Phosphorus, and Nitrate-Nitrite (under EPA method 353.2) require sulfuric acid (H_2SO_4) as a preservative. Nitrate-Nitrite, under EPA method 300.0, do not require H_2SO_4 as a preservative during sampling. Each sample bottle will be prepared with the correct amount of H_2SO_4 . All samples must be kept under 4° Celsius (C) regardless of the constituent and the method.

The amount of time that a representative valid sample can be held from the time the sample is taken until the time the sample is analyzed is the method holding time. The allowed holding time assumes that the sample has been properly preserved and kept on ice (< 4° C) from sampling until custody of the sample is relinquished to the State Certified Laboratory. Table 3.3 lists the analytical method used, the bottle type and volume, the preservative, and the method holding time required for each water quality constituent.

Table 3.3. Water Quality Sampling Method, Bottle Types, Preservatives, and Holding Time.							
Analyte	Method	Bottle/Volume	Preservative	Holding Time			
Total Phosphorous	EPA 365.3	250 mL Poly Ethylene	<4° C, H ₂ SO ₄	28 days			
Total Phosphorous	SM 4500-P E	250 mL Amber glass	<4° C, H ₂ SO ₄	28 days			
TKN	EPA 351.2	250 mL Poly Ethylene	<4° C, H ₂ SO ₄	28 days			
NO ₂ + NO ₃ -N	EPA 353.2	250 mL Poly Ethylene	<4° C, H ₂ SO ₄	28 days			
NO ₂ + NO ₃ -N	EPA 300.0	125 mL HDPE	<4° C	48 hours			

3.8.2. Sample Naming Methodology

Because several cities are coordinating together for this Plan, the identification and use of a specific water quality sample naming protocol is very important. Each sample will have the name of the specific monitoring site written first, the date in mmddyyyy format second, and a letter denoting the sample order (for multiple samples at one location on one day) last. Table 3.4 lists the sample naming protocol for each monitoring site.

Table 3.4. Sample Nomenclature						
Monitoring Site Name	Location	Sample Numbering				
Solano	Palos Verdes Estates	Solano – mmddyyyy – A, B, C,				
		D, E,				
Valmonte	Rolling Hills Estates	Valmonte – mmddyyyy – A, B,				
		C, D, E,				
RHE City Hall	Rolling Hills Estates	RHE City Hall – mmddyyyy – A,				
		B, C, D, E,				
Ranchview	Rolling Hills Estates	Ranchview – mmddyyyy – A,				
		B, C, D, E,				
Chadwick	Rolling Hills Estates	Chadwick – mmddyyyy – A, B,				
		C, D, E,				
Lariat	Rolling Hills Estates	Lariat – mmddyyyy – A, B, C,				
		D, E,				

3.8.3. Chain of Custody Procedures

The State Certified Laboratory will supply the Chain of Custody Forms that will be utilized by each of the Sampling Teams. An example of a Chain of Custody Form can be found in Appendix B. Chain of custody procedures will be used for all samples throughout the collection, transport, and analytical process to ensure the most accurate results. Samples will be considered to be in custody if they are (1) in the custodian's possession or view, (2) retained in a secured place (under lock) with restricted access, or (3) placed in a container and secured with an official seal such that the sample could not be reached without breaking the seal. The principal documents used to identify samples and to document possession will be the Field Conditions Data Sheet and the Chain of Custody Form.

The chain of custody procedures will be initiated during sample collection. A Chain of Custody Form will be provided with each sample or group of samples. Each Sampling Team Member having custody of the samples will sign the Chain of Custody Form and ensure that the samples were not left unattended unless properly secured. Documentation of sample handling and custody will include the following:

- Sample identification;
- Type of sample;
- Sample collection date and time;
- Any special notations on sample characteristics or analysis;
- Analyses to be performed;
- The initials of the Sampling Team member that collected the sample;
- The date the sample was delivered to/sent to the State Certified Laboratory; and
- The shipping company and waybill information if shipped.

Once samples have been collected, each Sampling Team will deliver the samples for chemical analyses with the respective chain of Chain of Custody Form to the State Certified Laboratory or coordinate with a reliable courier for sample drop off to the State Certified Laboratory. The completed Chain of Custody Form will be placed into a plastic envelope and kept inside the sampling cooler. Upon delivery to the State Certified Laboratory, the Chain of Custody Form will be signed by the person receiving the samples and by the person delivering the samples. Chain of custody records will be included in the final reports prepared by the analytical laboratories and will be considered an integral part of the report.

3.9. Health and Safety Concerns

There is the potential for the Sampling Teams to be out in adverse conditions. Therefore, the safety of the Sampling Teams is of the upmost concern. The Sampling Team coordinator will prepare a health and safety plan and will train the Sampling Team on that plan. The following sections detail the methods that will be undertaken to ensure the safety of the Sampling Teams.

3.9.1. Traffic Hazards and Traffic Control

Due to the fact that water quality monitoring often occurs in severe weather, there is potential for the Sampling Teams to be driving in poor conditions. It is important that all traffic rules and regulations as well as all traffic control signs and devices be obeyed in order to ensure Sampling Team safety.

Vehicle traffic is also a major concern in water quality monitoring. Vehicle traffic can present a hazard to Sampling Teams when they are working close to roadways because there is a potential for a Sampling Team member to be hit by oncoming traffic. While working in areas with traffic, the Sampling Team will:

- Park as far off the road as feasible to avoid interfering with traffic flow;
- Utilize the vehicle's flashing yellow warning lights and hazard lights;
- Use safety cones to mark off the work area and wear a reflective safety vest;
- Place a yellow barricade around open manholes to clearly mark the area; and
- Wear bright rain gear during storms to be more visible.

3.9.2. Inclement Weather

Extreme heat, cold, humidity, and rain can adversely affect monitoring instrument response and reliability. Rain and wet conditions also increase slipping and tripping hazards, braking distances of vehicles, and the potential for slippage or handling difficulties of field equipment. Winter storms will bring in colder than normal temperatures to the area. Sampling Teams should be prepared to work long hours in wet and cold conditions and should wear extra layers of clothing under rain gear since there may be a variety of temperature changes.

4. Quality Assurance and Quality Control (QA/QC)

This section discusses the quality assurance and quality control measures that will be implemented for both field and laboratory activities to verify that data quality objectives are being met under this Plan.

4.1. Field Sampling QA/QC Procedures

The following quality assurance and quality control procedures will be implemented as part of the field sampling procedures that have been described in detail in Section 3.

4.1.1. <u>Trip Blank</u>

Sample blanks containing deionized water are provided by the State Certified Laboratory with each batch of sample bottles. The field Sampling Teams should ensure that trip blanks are kept on ice with the sample bottles as a check on proper temperature of preservation. Upon receipt of samples from the courier or field Sampling Team, the laboratory staff will check the temperature of the trip blank to confirm that samples have been properly held on ice at a temperature of 4°C or lower. Trip blanks will be included at a frequency of one per cooler.

4.1.2. Equipment Blank

Although it is preferable to collect water samples directly into the sample bottle in order to minimize cross-contamination, this may not be feasible due to field conditions and/or to avoid flushing preservative from the sample bottles. When intermediate sampling apparatuses are necessary, they must be made of appropriate materials for the project target analytes, and must be decontaminated at the start of sampling and between monitoring sites if the device is to be re-used. Any intermediate apparatuses that are used for collecting samples and dispensing them into sample bottles such as handheld sampling devices, bailers and/or tubing will be tested with equipment blanks to evaluate the potential for cross-contamination associated with decontamination procedures.

The sampling equipment should be thoroughly pre-cleaned and placed in a sealed bag or wrapped in protective covering prior to transport to the field. Pre-cleaning will utilize either manual or ultrasonic techniques aided by Liquinox® (or other acceptable non-phosphate detergent), followed by a tap water rinse, and a final rinse with deionized water. It is preferable to dedicate a pre-cleaned sampling apparatus for each monitoring site in order to avoid the need for field decontamination, however depending on the type of equipment, this may be cost-prohibitive in which case field decontamination between monitoring sites will be necessary. Field decontamination of intermediate sampling apparatuses between monitoring sites will utilize manual scrubbing and three rinses with deionized water (no detergent).

Effectiveness of pre-cleaning and/or field decontamination procedures will be evaluated by collecting an equipment blank for laboratory analysis. The equipment blank will be collected by pouring laboratory grade deionized water into the sampling device which has been decontaminated using the specified method and then transferring the water to a sample bottle. The equipment samples will be given a fictitious sample I.D., handled in the manner used for surface water/stormwater samples, and submitted to the laboratory as "blind" samples. An equipment blank will be collected at a minimum frequency of once per sampling event for the first three sampling events and then the frequency reduced to one for every 20 samples (5%) or for every change in field personnel, decontamination methodology, or change in intermediate sampling device, whichever is more frequent.

4.1.3. <u>Duplicate Samples</u>

Duplicate samples are two samples collected at the same time and place in sequential order. Analysis of duplicate samples evaluates field sampling precision and sample homogeneity. A duplicate sample is to be collected as soon as possible after the initial surface water sample has been collected and will be subjected to identical handling and analysis. Duplicate samples will be given a fictitious sample I.D. and will be submitted to the laboratory as "blind" samples. Duplicate samples will be collected a minimum of once per sampling day. The location of the duplicate sample collection will be rotated among monitoring sites from one event to the next.

Table 4.1. Field QA/QC Sample Collection Requirements							
QA/QC Samples	Initial Frequency	Ongoing Frequency					
	(1 st three months)						
Trip blanks	1 per cooler	1 per cooler					
Field equipment method blanks	1 per decontamination method	1 per decontamination method					
	per event	per every 20 samples or at					
		change in field crew,					
		decontamination methodology,					
		or sampling device whichever is					
		more frequent					
Field duplicate samples	1 per event, rotating location	1 per event, rotating location					

4.1.4. Collection of Sample for Laboratory Spike and Duplicate Analyses

The State Certified Laboratory performs laboratory duplicate and spike analyses on environmental samples to evaluate accuracy, precision and potential matrix interference. Matrix spike and sample duplicate analyses should be performed by the laboratory by using project samples whenever possible. This requires that adequate sample volume is provided, consequently bottles will be filled leaving only a small head space. If an additional sample bottle is needed by the laboratory in order to perform Matrix Spike/Matrix Spike Duplicate analyses, field personnel will specify on the chain-of-custody form the sample to be used for the Matrix Spike/Matrix Spike Duplicate analyses.

4.1.5. Training Sessions and QA/QC Review

Sampling Team personnel will receive training so that they are familiar with the field sampling plan and are aware of analysis holding times. Quality control and training sessions will be held prior to the start of sampling to verify the proper working order of field equipment, refresh monitoring staff in monitoring techniques and familiarize them with the field sampling plan. At least twice per year the Sampling Teams will consult with the QA manager to determine whether the data quality objectives are being met, and decide if any changes in field sampling methods are necessary.

4.2. Laboratory QA/QC

A laboratory certified by the State of California in the analytical methods specified in this Plan will conduct the laboratory analysis of samples. Analytical methods to be used for laboratory analyses are listed in Table Table 4.2 Analytical Methods and Limits. The certified laboratory will maintain custody logs sufficient to track each sample submitted and to analyze or preserve each sample within specified holding times.

	Table 4.2 Analytical Methods and Limits						
Parameter	Method	Units	Target Reporting Limit	Method Detection Limit			
Total Phosphorus	SM 4500 P-E or EPA 365.3	mg/L	0.05	0.01			
Nitrate/Nitrite	EPA 300.0 or EPA 353.2	mg/L	0.1	0.03			
Total Kjeldahl Nitrogen (TKN)	EPA 351.2	mg/L	0.1	0.07			

Method Detection Limit (MDL)—The MDL is the lowest concentration at which an analyte can be detected in a sample that does not cause matrix interferences (typically determined using spiked reagent water). In this context, "detected" means that a sample that contains the analyte detected at the MDL can be distinguished from a blank with 99% certainty. Detection limits are established by the laboratory during MDL studies using clean, undiluted matrix. If, during analysis, it is determined that a sample needs to be diluted prior to analysis, the detection limit will be modified based on the dilution and the detection limit adjusted by "best professional judgment".

Reporting Limit (RL) ⁶—The RL is the lowest concentration at which an analyte can be detected in a sample and its concentration can be reported with a reasonable degree of accuracy and precision. A criterion of ± 20% accuracy and 20% relative standard deviation (RSD) for replicate determinations is often used to define "reasonable". The acceptable ranges depend somewhat on the analytical methodology used. For samples that do not pose a particular matrix problem, the RL is typically about three to five times higher than the MDL. Similar to the MDL, the RL is a laboratory-specific number, which may change with time. When a sample has to be diluted before analysis, either because of matrix problems or to get the instrument response within the linear dynamic range, the RL is raised by a factor corresponding to the dilution factor. This number may change with time.

4.2.1. Laboratory Performance Measurements

The certified laboratory routinely includes performance measurements in the analysis stream as part of its internal QA/QC and certification requirements to assess whether data quality criteria are met. These results are reported along with results of project sample analysis. These types of laboratory performance QA/QC checks are briefly described below.

- 1. Method Blanks (also called extraction blanks or preparation blanks): These account for contaminants present in the preservative and analytical solutions and equipment used during the preparation and quantification of the parameter.
- 2. Injection Internal Standards and/or Surrogates: These account for error introduced by the analytical instrument or extraction process.
- 3. Matrix Spike Samples: These are field samples to which a known amount of contaminant is added and used to measure potential analytical interferences present in the field sample.

⁶ California Department of Public Health

- 4. Replicate Samples: These are replicates of extracted material that measure the instrumental precision.
 - a. Laboratory Replicate Samples: These are replicates of the raw material that are extracted and analyzed to measure laboratory precision.
 - b. Matrix Spike Replicate Samples: These are used to assess both laboratory precision and accuracy. They are particularly useful when the field samples analyzed do not contain many of the target compounds (measuring non-detects in replicate does allow the data reviewer to measure the precision or the accuracy of the data in an analytical batch).
- 5. Certified Reference Materials (CRMs): Analysis of CRMs is another way of determining accuracy of the analysis by comparing a certified value of material with similar concentrations as those expected in the samples to be analyzed.

4.2.2. Reporting of Results

Analytical results will be reported to the Quality Assurance Manager (QA Manager) within ten (10) business days (ten-day turnaround time). The certified laboratory will provide analytical data reports to the QA manager in electronic format along with summaries of QA/QC analyses and copies of the chain-of-custody forms. The certified laboratory quality assurance manager will review analytical data reports and ensure that data has been internally validated in accordance with the laboratory's published Standard Operating Procedures (SOPs) for each analytical method and that non-conformances are flagged and that the project QA Manager is promptly notified.

Flagging of data:

- Analytical results below the Method Detection Limit are to be reported as less than ("<") followed by the actual MDL value, and flagged with an "ND" or not detected.
- Results reported by a laboratory at levels between the Reporting Limit and the Method Detection Limit are flagged with a "j" to indicate that the analyte is present but not within the range that can be reliably quantified.
- Other QA qualification codes will be used if QC criteria are not met or qualification is deemed appropriate by the contract laboratory QA manager.

4.3. Quality Assurance Manager

A QA Manager, independent of the field sampling contractor and laboratory, will be designated to verify that quality assurance and quality control procedures are being carried out in accordance with the Plan. The QA Manager will review laboratory data reports and field data sheets as well as chain-of-custody forms for conformance with procedures and data quality objectives specified in this Plan. The QA Manager will also perform periodic observations of field sampling procedures to confirm that the field methodology specified in this Plan is being followed. At least twice per year the QA Manager will consult with the field Sampling Team to discuss whether data quality objectives are being met and whether any modifications to the Plan or field sampling procedures are necessary or advisable. The QA Manager will also consult with the Peninsula Cities at least twice per year following the assessment of conformance with data quality objectives to advise them of any necessary or advisable modifications to the monitoring plan or field sampling procedures. Plan revisions will be submitted to Regional Board staff for review and approval.

5. Data Analysis and Reporting

Monitoring in accordance with this Plan will continue until the Peninsula Cities have established compliance with final waste load allocations. Compliance will be based on three contiguous years of monitoring data wherein monthly average concentrations are at or below the final waste load allocations for Total Nitrogen and Total Phosphorous. Once compliance with final waste load allocations is established, the results of this monitoring plan and other available information may be used to revise the amount of monitoring required to demonstrate continued TMDL compliance under a revised monitoring plan or other Regional Board order. If final waste load allocations are established at one or more Tier 1 monitoring sites, but not at others, then reduced monitoring may be proposed at the compliant locations after three contiguous years of compliant monthly average data are achieved.

5.1. Annual Monitoring Reports

The data collected as described in this Plan shall be compiled and reported to the Regional Board annually beginning one year from the date of approval of the Plan. The report will include the results from the preceding year and will be submitted to the Regional Board within 45 days of the end of each reporting year. Compliance⁷ will be based upon the monthly samples, or in the case of multiple samples being collected during one month, the monthly average.

Data transmitted shall include:

- A discussion of the Peninsula Cities' compliance with interim and final waste load allocations and targets set for nutrients in Machado Lake.
- A tabular database in Excel or Access format including: Sample Dates, Sample Locations, Laboratory Results, and Detection Limits.
- Copies of field observation/sampling comment logs in PDF or equivalent format.
- A discussion of any requested changes or modifications to this Plan along with supporting documentation.
- Results of source tracking investigations included in an appendix

A description of the technical design and rationale for source tracking investigations planned for the coming year will be included as an attachment or appendix to the annual monitoring report.

The Annual Report shall be signed by the Executive Officer or authorized designee of the Peninsula City acting as current Chair in accordance with an MOA to be established among the Peninsula Cities, and transmitted electronically to the Regional Board. The certification shall read:

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted.

Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility, of a fine and imprisonment for knowing violations.

Executed c	on the	day of		. 20)
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-

['] Basin Plan Amendment, page 11, Implementation Plan Element

Printed Name:	Title:			
City of				

5.2. Receiving Waters Limitation Compliance Reports

In the event that any of the monitoring sites described herein are deemed out-of-compliance with interim or final waste load allocations, the annual monitoring reports prepared as part of this Plan may be used by the Peninsula Cities tributary to those monitoring sites to prepare individual Receiving Waters Limitation Compliance Reports (if required by the Regional Board).

Appendix A

Palos Verdes Peninsula Machado Lake Nutrient TMDL Coordinated Monitoring Plan

Field Data Sheet-Page 1

Date:			
Site Name:			
Station ID No.:	20	(Example: Site Name	e-MMDDYEAR-A)
Time arrived on site:		(24-hr clock)	
TIME OF SAMPLE COLLEC	TION		
Time (24-hr clock):	Date:/	/ Number of containers	s:
FLOW MEASUREMENTS			
Depth of water:	(in, ft)	Width of flow:	(in, ft)
Flow rate:	(gal/min or linear	vel.) Time (24-hr clock):	
Depth of water:	(in, ft)	Width of flow:	(in, ft)
Flow rate:	(gal/min or linear	vel.) Time (24-hr clock):	
Depth of water:	(in, ft)	Width of flow:	(in, ft)
Flow rate:	(gal/min or linear	vel.) Time (24-hr clock):	

Field Data Sheet-Page 2

OBSERVATIONS:	
Water Conditions: (Circle the Appropriate Identifier) Odor: None, Musty, Sewage, Rotten egg, Sour milk, Fishy, Other:	
Color: None, Yellow, Brown, Grey, Green, Red, Other:	
Clarity: Clear, Cloudy, Opaque, Suspended Solids, Other:	
Floatables: None, Oil sheen, Foam, Animal waste, Green Waste (Leaves), Food, Paper, Plastic, Grease, Hydrophytes, Trash, Other:	
Settleables: None, Salt, Clay, Oil, Rust, Microbes, Other:	
Weeds: None, Normal, Excessive, Note:	
Biology:None, Algae bloom, Larvae, Crawfish, Frogs, Fish, Waterfowl, Hydrophytes, Blue-green algae,	
Other	
Sky: Stormy, Overcast, Partial clouds, Haze, Fog, Clear	
Wind: Calm, Light breeze, Strong breeze, Windy, Gusty	
Flow Characterization: Storm/Flood, Rapid, Tranquil, Laminar, Standing, Dry	
Low Flow/ No Flow Conditions	
Station ID No.:(Example: Site Name-MMDDYEAR-A)	
Time (24-hr clock):	
Was there Flow? (Circle answer) YES NO	
f there was flow but no sample was taken, why was no sample taken? Explain:	
Time left site: (24-hr clock)	

Appendix B

Example Chain of Custody Form

W		adveter - 1	CA 041	Analytical Labo	aboratories,			CHA		F C	JST	ODY RI	ECC	ORD
14859 East Clark Tel 626-336-213	9 ♦ Fax 62	16-336-263	5A91 4 ♦ W	/ 45 /ww.wecklabs.com				STANI	JAKU			Page	1	Of 1
CLIENT NAME:				PROJECT:				ANALY	SES REQ	UESTED		SPECIA	Same D	NDLING ay Rush 150% Rush 100%
ADDRESS:				PHONE: FAX: EMAIL:									4 - 5 Day Rush Ex	our Rush 75% y Rush 30% tractions 50% Business Days
PROJECT MANAGE	R			SAMPLER								Charges will	QA/QC	Data Package r weekends/holidays
ID# (For lab Use Only)	DATE SAMPLED	TIME SAMPLED	SMPL TYPE	SAMPLE IDENTIFICATION	VSITE LOCATION	# OF CONT.						Method of S COMMENTS	hipment	
2.0						42.00								
				v.		- 300	<u> </u>					-		
		88				3 33 5								
				·										
		30	-	V.			<u> </u>					-		
												,		
		2				- NE:								
RELINQUISHED	BY		DAT	E/TIME	RECEIVE) BY	3	1 h		0.00		CONDITION:		SAMPLE TYPE CODE
RELINQUISHED	BY		DAT	E / TIME	RECEIVE) BY				Rece Pres Evid	al Tempera sived On Id erved ence Seals ainer Attac	e Present	Y / N Y / N Y / N Y / N	NA= Non Aqueous SL = Sludge DW = Drinking Water WW = Waste Water RW = Rain Water GW = Ground Water
RELINQUISHED	BY		DAT	E/TIME	RECEIVE	BY				Pres	erved at La	sb	Y / N	SO = Soil SW = Solid Waste OL = Oil OT = Other Matrix
PRESCHEDULED RI OVER UNSCHEDUL Client agrees to Term	ED RUSH REQ	UESTS		RITY SPECIAL RI	EQUIREMENTS/	BILLING IN	IFORM	MATION						COC version 042707

Appendix C

Monitoring Site Summary

Site ID: Solano	Land Uses: residential, elementary school,
Type: Tier 1 dry and wet weather	Tributary Area: 144 acres
Tributary Agencies:	
Palos Verdes Estates	
Site ID: Valmonte	Land Uses: residential, residential with horse keeping, schools, municipal stable, religious, parks, open space
Type: Tier 1 dry and wet weather	Tributary Area: 415 acres (Valmonte Canyon and Ferncreek)
Tributary Agencies:	
Rolling Hills Estates	
Rancho Palos Verdes	A TANK THE PROPERTY OF THE PARTY OF THE PART
Palos Verdes Estates	

Site ID: RHE City Hall	Land Uses: Commercial, residential, low-density single family
Site ID. THE City Hall	residential, K-12 schools, municipal facilities, religious facilities,
	arterial roadways
	·
Type: Tier 1 dry and wet weather	Tributary Area: 1245 acres (860 acres from RDD 275 and 385
	acres from Ranchview and Chadwick Canyons). Note: this
	includes 334 acres of County unincorporated which is not
	counted in PVP incorporated cities area.
Tributary Agencies:	
Rolling Hills Estates	
Rancho Palos Verdes	
Rolling Hills	
County unincorporated	
Site ID: Lariat	Land Uses: low density residential, residential, some residential horse keeping
Type: Tier 1 dry weather observation	Tributary Area: 602 acres (Agua Magna, Sepulveda and
and wet weather sampling	Blackwater Canyons)
Tributary Agencies: Rolling Hills Rolling Hills Estates	

Site ID: Valmont Cyn	Land Uses: residential, residential with horse keeping, schools, municipal stable, religious, parks, open space
Type: Tier 2 subdrainage of	Tributary Area: TBD
Valmonte	
Tributary Agencies:	
Palos Verdes Estates Rolling Hills Estates	
Site ID: Ferncreek	Land Uses: residential, residential with horse keeping, open
	space
Type: Tier 2 subdrainage of Valmonte	Tributary Area: TBD
Tributary Agencies: Rolling Hills Estates	

Site ID: Ranchview	Land Uses: : Residential, K-12 schools, arterial roadways
Type: Tier 2 subdrainage of RHE City Hall	Tributary Area: TBD
Tributary Agencies: Rancho Palos Verdes	
Rolling Hills Estates	
Site ID: Chadwick	Land Uses: : Residential, K-12 schools, arterial roadways
Type: Tier 2 subdrainage of RHE City Hall	Tributary Area: TBD
Tributary Agencies:	
Rancho Palos Verdes	
County unincorporated	

Site ID: RDD 275Trap Type: Tier 2 subdrainage of RHE City	Land Uses: : Commercial, residential, low-density single family residential, municipal facilities, religious facilities, arterial roadways Tributary Area: TBD
Hall	
Tributary Agencies: Rolling Hills Estates	
Rancho Palos Verdes	
Rolling Hills	
County unincorporated	
Site ID: Blackwater	Land Uses: : Low-density single family residential
Type: Tier 2 subdrainage of Lariat	Tributary Area: TBD
Tributary Agencies: Rolling Hills	

Peninsula CIMP Appendix I Peninsula Outfall Screening Report

Peninsula Outfall Screening Report May 2015





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Outfall Screening Field Datasheet Forms

1. Introduction

The Monitoring and Reporting Program (MRP) section of the Los Angeles Region Municipal Separate Storm Sewer System Permit (Order No. R4-2012-0175, "MS4 Permit") outlines a significant suite of requirements. The overarching purpose of the MRP is to assess chemical, physical, and biological impacts from the MS4 on receiving waters; assess compliance with Receiving Water Limitations (RWLs) and Water Quality Based Effluent Limits (WQBELs); characterize pollutant loads; identify sources of pollutants in MS4 discharges; and measure and improve the effectiveness of controls. In response to these requirements, the Palos Verdes Peninsula Watershed Management Group (Peninsula WMG) completed and submitted a watershed specific Coordinated Integrated Monitoring Program Plan (CIMP) to the Los Angeles Regional Water Quality Control Board on June 28, 2014.

Part of this program was to conduct the Non-stormwater (NSW) Outfall Screening Program, which is a multi-step process to identify and address significant non-stormwater discharges to the receiving water. These studies were conducted during dry weather and in the months of September through December of 2014.

2. REQUIREMENTS

The outfall screening process is intended to develop criteria or other means to ensure that all outfalls with significant nonstormwater discharges are identified and assessed during the term of the MS4 Permit. Following this screening process the Peninsula WMG will meet the following objectives (Part IX.A of the MRP):

- 1. For outfalls determined to have significant non-stormwater flow, determine whether flows are the result of Illicit Connection/Illicit Discharges (IC/IDs), authorized or conditionally exempt non-stormwater flows, natural flows, or from unknown sources.
- 2. Refer information related to identify IC/IDs to the IC/ID Elimination Program (Part VI.D.10 of the MS4 Permit) for appropriate action.
- 3. Based on existing screening or monitoring data or other institutional knowledge, assess the impact of non-stormwater discharges (other than identified IC/IDs) on the receiving water.
- 4. Prioritize monitoring of outfalls considering the potential threat to the receiving water and applicable TMDL compliance schedules.
- 5. Conduct monitoring or assess existing monitoring data to determine the impact of nonstormwater discharges on the receiving water.
- 6. Conduct monitoring or other investigations to identify the source of pollutants in nonstormwater discharges.
- 7. Use results of the screening process to evaluate the conditionally exempt nonstormwater discharges identified in Parts III.A.2 and III.A.3 of the MS4 Permit and take appropriate actions pursuant to Part III.A.4.d of the MS4 Permit for those discharges that have been found to be a source of pollutants. Any future reclassification shall occur per the conditions in Parts III.A.2 or III.A.6 of the MS4 Permit.
- 8. Maximize the use of resources by integrating the screening and monitoring process into existing or planned CIMP efforts.

3. GEOGRAPHICAL AREA

The participating agencies for this study were the cities of Rancho Palos Verdes, Rolling Hills Estates, and Palos Verdes Estates, the County of Los Angeles, and the Los Angeles County Flood Control District. The City of Rolling Hills, who is a party to the Peninsula CIMP, required a separate outfall screening within the Rolling Hills city boundary consistent with the City of Rolling Hills Non-Storm Water Screening and Monitoring Program, September 2014. Figure 1 below shows the outfall screening locations.

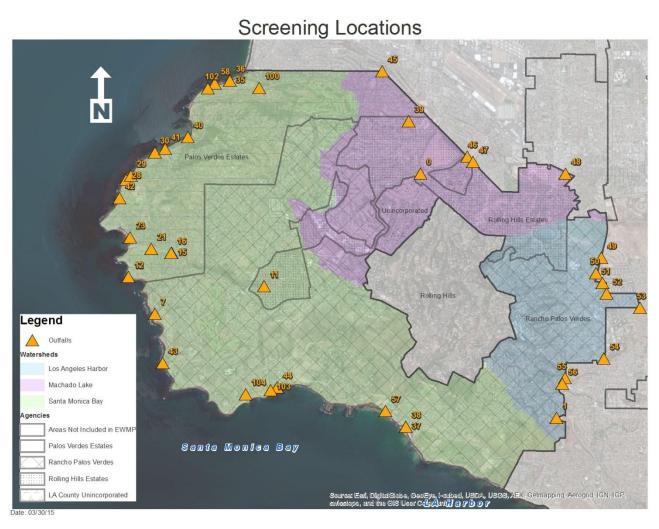


Figure 1: Palos Verdes Peninsula Outfall Screening Locations.

4. Procedure

The outfall screening was conducted consistent with the procedure described in Section 4.2 of the Peninsula CIMP. All screenings were conducted only in dry weather with a minimum of 72 hours after any rain event of 0.1 inches or greater. Three rounds of outfall screenings were conducted within the months of September through December of 2014¹ with the first initial round of 40 outfalls greater than 36 inches in diameter. All measurements and observations were based on the following (See Appendix C for the Field Datasheet Forms):

- a) Date, Time, Weather
- b) Photos of outfall and receiving water
- c) GPS coordinates of outfall
- d) Physical descriptions of outfall, site condition, and accessibility
- e) Discharge characteristics, such as odor and color
- f) Presence of flow greater than trickle or no flow
- g) Receiving water characteristics

Access to the Los Angeles County Flood Control District's right of way and storm drains were done with a Flood Control District Permit. A Company Health and Safety Plan was also prepared, signed, and carried to all outfall screening locations.

Outfall measurements were taken with a tape measure (see Figure 2). When certain access points were too deep or hazardous, a pre-measured pole with visible markings was used in lieu of a tape measure and photos were taken to determine the diameter without risking injury. For accessible outfalls, the outfall specifics were written on a dry-erase board and photographed.



Figure 2: Outfall measurement process.

Certain locations were too hazardous or difficult to access and could not be physically measured. For example, the outfalls located on the cliffs in the Santa Monica Bay Watershed (e.g. Outfall ID_7) and manhole covers located in the middle of traffic lanes.

¹ Outfall screening was performed with an expedited schedule to ensure that the source investigation could be conducted on schedule (25% by December 2015 and 100% by December 2017). Rescreening will occur during different seasons, as feasible.

5. OBSERVATIONS AND RESULTS

Outfalls with non-significant stormwater discharges (NSWD) were labeled as either "no flow" or "trickle flow," whereas the outfalls with more significant flow were indicated as either "moderate flow" or "substantial flow." See figures below for representative pictures for each condition.



Figure 3: Outfall ID 44 with no flow.



Figure 5: Outfall ID 57 with moderate flow.



Figure 4: Outfall ID 41 with trickle flow.



Figure 6: Outfall ID 100 with Substantial Flow.

Latitude and longitude coordinates from all locations were recorded and entered into a GIS database to be geographically linked to maps. All other data (i.e. addresses, time of day, photographs, etc.) were placed in an outfall database (See Appendix A).

Table 1 below shows the results of the first outfall screening round. Pictures can be found in Appendix B.

Flow Measurement	Santa Monica Bay	LA Harbor	Machado Lake	Total
Substantial flow	1	0	0	1
Moderate Flow	3	2	1	6
Trickle flow	10	1	0	11
No flow	11	5	5	21
Unknown	0	1	0	1
Total Outfalls	25	9	6	40

Peninsula Outfall Screening Report

The outfalls identified as having more than a trickle flow were screened on two additional dry weather occasions. These are considered "Significant Outfall" locations. Additionally, the outfall at Rolling Hills Estates City Hall is (RHE City Hall) is known to have substantial flow as observed during more than three years of monitoring as reported by the Peninsula Cities in the 2011-12, 2012-13, and 2013-14 Yearly Stormwater Monitoring Reports for the Machado Lake Nutrient TMDL. Therefore, this location is considered a Significant Outfall, but was excluded from the screening process. No observed flows reached the wave wash during any of the three screening events. Table 2 shows the screening results for each of the Significant Outfalls. Figure 7 identifies the locations of the Significant Outfalls.

Table 2: Significant Nonstormwater Outfall Screening Results.²

Outfall ID	Latitude	Longitude	Nearest Major Intersection/Closest Accessible Street Address	City	Receiving Water	Flow Results
100	33.8016	-118.3908	Palos Verdes Drive W and Via Corta (300 Via Corta)		Santa Monica Bay	09/12/14 – Substantial 11/25/14 – Substantial 12/10/14 – Substantial
43	33.7464	-118.4131	PV Drive W and Via Vicente (end of Pacifica del Mar)		Santa Monica Bay	09/17/14 – Moderate 11/25/14 – No Flow 12/10/14 – Moderate
57	33.7372	-118.3609	Palos Verdes Dr S and Yacht Harbor Dr (44 Seawall Rd)		Santa Monica Bay	09/17/14 – Moderate 11/25/14 – Moderate 12/10/14 – Moderate
53	33.7577	-118.3010	Between W Capitol Dr and Bloomwood Dr		LA Harbor	10/02/14 – Moderate 11/25/14 – Moderate 12/10/14 – Moderate
50	33.7645	-118.3114	Western Ave and Delasonde Dr (28020 Pontevedra Dr)		LA Harbor	10/02/14 – Moderate 11/25/14 – Moderate 12/10/14 – Moderate
48	33.7841	-118.3186	Palos Verdes Dr E and Bridlewood Circle (along Bridlewood Trail)	RHE	Machado Lake	09/17/14 – Moderate 11/25/14 – No Flow 12/10/14 – Moderate

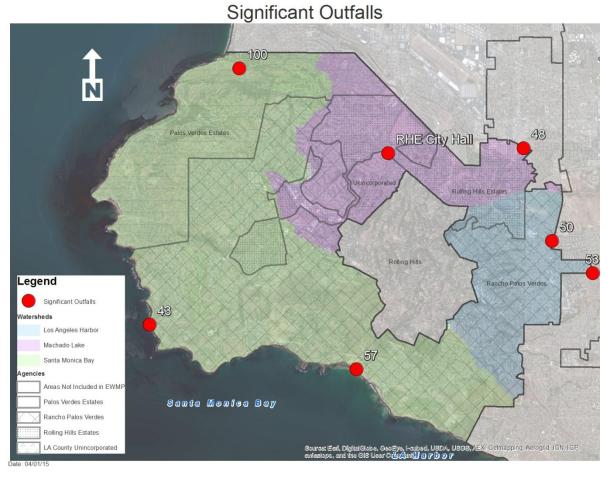


Figure 7: Significant Nonstormwater Outfall Locations.

Out of the remaining outfalls that required follow-up screenings, the NSW discharges comprised of either unknown or conditionally exempt non-essential discharges or potential illicit discharges. Potential sources considered exempt non-essential discharges include natural groundwater. According to local residents, business owners, and city officials, this area is known to have high groundwater which commonly seeps into streams, channels, and canyons. One particular outfall, ID 100, was found to have heavy flow, thick vegetation, no odor and no signs of trash. This outfall is suspected to have natural groundwater. Other unknown sources, such as an outfall, ID 57, showed significant indicators such as odor and visual stains that will trigger further investigation.



Figure 8: Outfall ID 57 with moderate flow requiring additional investigation.

6. ALTERNATE OUTFALL LOCATIONS

There were 5 outfall locations which were too hazardous to screen or take accurate measurements. Hazards and obstacles that deterred the outfall screening included conditions such as steep cliffs, tidal changes, bio-hazardous conditions, and slippery surfaces. Alternate upstream monitoring locations were selected for four of the five outfalls that were too hazardous to screen (see Figure 9 and Figure 10 below).



Figure 9: Outfall location.



Figure 10: Alternate monitoring location.

Table 3 below provides a list of each outfall location identified as being too hazardous to sample. The only location without an alternate was ID 49 which was inaccessible due to construction activities.

Outfall ID	Outfall Location	Hazard/Restriction	Alternate Location
ID 1	Residential area	Steep canyon	998 Friendship Park Dr.
ID 7	Rocky shore	Steep cliffs	Upstream SD manhole
ID 49	Construction Zone	No access	No access due to construction
ID 58	Rocky shore	High tide/Steep cliffs	Upstream SD manhole
ID 100	Malaga Creek	Heavy vegetation	Upstream SD manhole

Table 3: Alternate outfall locations.

7. NEXT STEPS

From the total of 40 outfalls that were screened, six (6) were considered to be more than a trickle flow. In addition, the outfall at RHE City Hall is known to have substantial flow. These seven (7) outfalls will require follow-up source investigations. The significant NSW outfalls are summarized in Table 2. The summary of results is based on the measurements of outfalls from the cities of Rancho Palos Verdes, Rolling Hills Estates, and Palos Verdes Estates, and the County of Los Angeles.

Since there are unknown sources of NSW in the Palos Verdes Peninsula, there will be a complete source investigation for 25%, approximately two (2), of the seven (7) outfalls by December 28, 2015, and 100% by the end of 2017. As required by the MRP Section IX.E.2 of the MS4 Permit, If it is determined that a source of significant non-stormwater discharges is comprised of unknown or conditionally exempt or illicit discharges, then monitoring will begin within 90 days of completing the source investigation or after the CIMP has been approved by the EO, whichever is later. Source control and monitoring procedures will follow those outlined in the Peninsula CIMP.

Appendix A Outfall Database

Outfall Screening Event Number 1

Outfall ID	Size	Latitude	Longitude	Nearest Major Intersection/Closest Accessible Street Address		Receiving Water	Photo ID	Flow category	Date of Screening	Further Source ID	Notes
0	18"	33.784054	-118.352886	Crenshaw Blvd/PV Drive N - Chandler Park	RHE	Machado Lake	ID_0_10-1-14	No flow	10/1/2015	N	No flow from MH. Size "18." Pipe runs vertical. Inspectors CS,HG.
1	NA	33.735958	-118.320597	Chandeleur Dr and Rue le Charlene - Averil Canyon Creek	RPV	LA Harbor	ID_1_10-2-14	No flow	10/2/2015	N	No access. Located behind homes in canyon. No flow downstream. Inspectors CS,HG.
7	N/A	33.756221	-118.415305	PV Drive W and Calle Entradero (End of Marguerite Dr.)	RPV	Santa Monica Bay	ID_7_9-17-14	Trickle Flow	9/17/2015	N	Trickle flow Hard to access. No measurements. Gate locked. Inspectors JR, HG.
11	NA	33.76169	-118.389611	Hawthorne and Crest Rd (End of Santa Cruz)	RHE	Santa Monica Bay	ID_11_11-25-14	No flow	11/25/2015	N	No flow near club house. Open channel, difficult to get measurements. Inspectors JR, MG
12	48"	33.762844	-118.418894	Paseo del Mar and Via Segovia (2809 Via Segovia)	PVE	Santa Monica Bay	ID_12_9-17-14	No flow	9/17/2014	N	No Flow. Inhabited by Cattail. Algae present after box. Pounding present. Inspectors JR, HG.
15	36"	33.768195	-118.411425	Paseo Lunado and Via Rivera (2630 Via Rivera)	PVE	Santa Monica Bay	ID_15_9-12-14	Trickle Flow	9/12/2014	N	Inside grate gate. 36 inch. Diameter. Wet ground no significant flow. Graffiti. Inspectors JR, CS.
16	66"	33.768213	-118.411505	Paseo Lunado and Via Rivera (2630 Via Rivera)	PVE	Santa Monica Bay	ID_16_9-12-14	Trickle Flow	9/12/2014		Inside grate gate. 67 inch. Diameter. Wet ground no significant flow. Graffiti. Inspectors JR, CS.
21	NA	33.769014	-118.416261	Paseo del Mar and Via Anacapa (2821 Via Anacapa)	PVE	Santa Monica Bay	ID_21_9-12-14	No flow	9/12/2014	N	Locked gate Could not get measurements. Inspectors JR, CS.
23	36"	33.771235	-118.421206	Paseo del Mar and Via Bandini (2499 Paseo del Mar)	PVE	Santa Monica Bay	ID_23_9-12-14	No flow	9/12/2014	N	Could not access from outlet because the area is filled with water. Took measurements from catch basin pipe which was 36 inches and no flow was observed. Inspectors JR,CS.
28	86" x 77"	33.782599		Paseo del Mar and Cloyden Rd (end of Cloyden Rd - Drainage Pipe Trail)	PVE	Santa Monica Bay	ID_28_9-12-14	Trickle Flow	9/12/2014	N	Trickle flow. End of Drain Pipe Trail. Some trash, graffiti, algae, and a small pond of water. Grate gate could not take measurement of pipe but the rectangle box height was 86" and length 77". Inspectors JR, CS.
29	44"	33.784943		Paseo del Mar and Cloyden Rd (end of Cloyden Path) (1733 Paseo del Mar)	PVE	Santa Monica Bay	ID_29_9-12-14	Trickle Flow	9/12/2014	N	Trickle flow Inside grate gate. 44 inch Diameter. Inspectors JR, CS.
30	42"	33.787964	-118.415445	Paseo del Mar and Chelsea Road	PVE	Santa Monica Bay	ID_30_9-17-14	No flow	9/17/2014	N	No flow, graffiti present, 42 inches. Inspectors JR, HG.
35	48	33.80225	-118.397889	Paseo del Mar and Via Arroyo (just south of the Beach and Athletic Club)	PVE	Santa Monica Bay	ID_35_36_9-12- 14	Trickle Flow	9/12/2014	N	Only one outlet notes have two listed Trickle flow, ponding water maybe from hide tide. Site has a gate. Some algae present. Inspectors JR, CS.

Outfall ID	Size	Latitude	Longitude	Nearest Major Intersection/Closest Accessible Street Address		Receiving Water	Photo ID	Flow category	Date of Screening	Further Source ID	Notes
36	48	33.80225	-118.397889	Paseo del Mar and Via Arroyo (just south of the Beach and Athletic Club)	PVE	Santa Monica Bay	ID_35_36_9-12- 15	Trickle Flow	9/12/2014	N	Only one outlet notes have two listed Trickle flow, ponding water maybe from hide tide. Site has a gate. Some algae present. Inspectors JR, CS.
37	52"	33.73446	-118.354928	Palos Verdes Dr. S and Yacht Harbor Dr (3 Yacht Harbor Dr)	RPV	Santa Monica Bay	ID_37_38_9-17- 14	No flow	9/17/2014	N	No Flow 52 inches, Fenced area near security post. Only one outlet. Inspectors JR, HG.
39	82" x 96"	33.794416		Hawthorne Blvd and PV Drive N (end of Sugarhill Dr)	RHE	Machado Lake	ID_39_10-1-14	No flow	10/1/2014	N	No flow from pipe outlet. Channel had algae present. Located in private property (Rancho Del Canyon). Inspectors CS, HG.
40	36"	33.790918	1_112/1027/1/	Palos Verdes Dr W (Bluff Cove Shoreline)	PVE	Santa Monica Bay	ID_40_9-17-14	No flow	9/17/2014	N	No Flow, 36 inches. Feces present. Long hike to access point. Inspectors JR, HG
41	60"	33.788707	-118.413004	Paseo del Mar and Chiswick Rd.	PVE	Santa Monica Bay	ID_41_9-17-14	Trickle Flow	9/17/2014		Trickle flow, 60 inches. Tide reaches outlet. Inspectors JR, HG.
42	>36"	33.778371	-118.424206	Paseo del Mar and Epping Rd	PVE	Santa Monica Bay	ID_42_9-12-14	Trickle Flow	9/12/2014	N	Site has a gate. Accurate measurements could not be obtained but definitely bigger than 36". Some trash, graffiti, and algae. Drainage pipe out of cliff. No access. Inspectors JR, CS.
43	N/A	33.746404	I_11X /I1X1X5	PV Drive W and Via Vicente (end of Pacifica del Mar)	RPV	Santa Monica Bay	ID_43_9-17-14	Moderate	9/17/2014	Y	Outlet difficult to access. Moderate flow present. Soap suds present. MH was access on Pacific Del Mar. Inspectors JR, HG.
44	53"	33.742301		PV Drive S and Seacoast Dr (21 Barkentine Rd)	RPV	Santa Monica Bay	ID_44_9-17-14	No flow	9/17/2015	N	No flow 53 inches. Inspectors JR, HG
45	18" x 11"	33.804201	-118.361916	Paseo de las Tortugas and Via el Sereno (4401 Paseo de las Tortugas) (along Boundary Trail)	PVE	Machado Lake	ID_45_10-1-14	No flow	10/1/2014		No flow, 18" x 11". Alternative outfall located near curb inlet, 17". Inspectors CS, HG
46	29"	33.787394	-118.341851	Crenshaw Blvd and Rolling Hills Rd	County UNK	Machado Lake	ID_46_10-1-14	No flow	10/1/2014	N	No flow, Catch Basin. Inspectors CS, HG.
47	NA	33.786369		Crenshaw Blvd and Rolling Hills Rd (26198 Rolling Hills Rd)	County UNK	Machado Lake	ID_47_12-10-14	No flow	12/10/2014	N	No flow, MH in the middle of traffic lane. Sampling tube tied to steps. Inspectors JR, CS.
48	25"	33.784153	-118.318644	Palos Verdes Dr E and Bridlewood Circle (along Bridlewood Trail)	RHE	Machado Lake	ID_48_10-1-14	Moderate	10/1/2014	Υ	Moderate flow inside private property. Fertilizer odor. Inspectors CS, HG.
49	N/A	33.767523	-118.310145	Western Ave and Redondela Dr	RPV	LA Harbor	ID_49_10-2-14	NA	10/2/2014	Υ	Inside fence area no access. Inspectors CS, HG.
50	60"	33.764504	-118.311436	Western Ave and Delasonde Dr (28020 Pontevedra Dr)	RPV	LA Harbor	ID_50_10-2-14	Moderate	10/2/2014	I Y	Moderate flow MH, 60 inches. Inspectors CS, HG.

				Nearest Major	Outlan Screening Event Number 1							
Outfall ID	Size	Latitude	Longitude	Intersection/Closest Accessible Street Address	Agency	Receiving Water	Photo ID	Flow category	Date of Screening	Further Source ID	Notes	
51	18"	33.762613	-118.309869	Western Ave and Westmont Dr (N side of Eastview Park)	RPV	LA Harbor	ID_51_10-1-14	No flow	10/1/2014	N	No flow, leave litter. Inspectors CS, HG.	
52	12"	33.760522	-118.308924	Western Ave and Westmont Dr (SW side of Eastview Park)	RPV	LA Harbor	ID_52_10-1-14	No flow	10/1/2014	N	No flow, 12 inches. Located between housing and apartment complex. Inspectors CS, HG.	
53	6' by 12'	33.757753	-118.301026	Between W Capitol Dr and Bloomwood Dr	RPV	LA Harbor	ID_53_10-2-14	Moderate	10/2/2014	Y	Moderate flow, Garbage odor, trash sediment, No access locked gate. MH on street has access to outfall. 6' H x 12' W. Inspectors CS, HG.	
54	18"	33.747632	-118.309669	Western Ave and Summerland (SE side of Peck Park)	RPV	LA Harbor	ID_54_10-2-14	Trickle Flow	10/2/2014	N	Trickle flow, 18 inches. Inspectors CS, HG.	
55	48"	33.743791	-118.318581	S Miraleste Dr and W 1st St (30100 Miraleste Dr)	RPV	LA Harbor	ID_55_10-2-14	No flow	10/2/2014	N	No flow, graffiti present, 48 inches. Inspectors CS, HG.	
56	24"	33.742659	-118.319299	S Miraleste Dr and W 1st St (4375 S Miraleste Dr)	RPV	LA Harbor	ID_56_10-2-14	No flow	10/2/2014	N	No flow, 24 inches, faint feces smell, some sediment. Inspectors CS,HG.	
58	36"	33.801659		Paseo del Mar and Via Aromitas (just south of Neighborhood Church)	PVE	Santa Monica Bay	ID_58_11-25-14	No flow	9/12/2014	N	High tide difficult to get to. Phone got wet near this location. 36 inches will need picture from next schedule screening. Inspectors JR, CS.	
100	N/A	33.801624	-118.390813	Palos Verdes Drive W and Via Corta (300 Via Corta)	PVE	Santa Monica Bay	ID_100_9-12-14	Substantial	9/12/2014	Y	Substantial flow to Malaga Canyon, heavy vegetation and would need to cross stream to get measurements. The outfall across was dry. Inspectors JR, CS.	
102	48"	33.800741	-118.40306	Paseo del Mar and Via Chino	PVE	Santa Monica Bay	ID_102_9-12-14	Trickle Flow	9/12/2014	N	Trickle flow, outlet was 48 inches. Big trapezoidal box with some litter and graffiti. Inspectors JR,CS.	
103	65"	33.740532	-118.387692	32079 Sea Gate Dr.	RPV	Santa Monica Bay	ID_103_9-17-14	No flow	9/17/2014	N	No flow 65", Graffiti inside outlet. Inspectors JR, HG.	
104	60"	33.740065	-118.39395	32636 Nantasket Dr	RPV	Santa Monica Bay	ID_104_9-17-14	No flow	9/17/2014	N	No flow 60". Inside golf course. Algae bloom. Pounding water. Inspectors JR, HG.	
57 A	48"	33.737229	-118.360913	Palos Verdes Dr S and Yacht Harbor Dr (44 Seawall Rd)	RPV	Santa Monica Bay	ID_57_9-17-14	Moderate	9/17/2014	Y	Moderate flow from two outlets 32" and 48". Foul odor. Water colorless but heavy brown stain present. Spoke with Kristen Lenders, (Yacht resident). Inspectors JR, HG.	
57 B	32"	33.737229	-118.360913	Palos Verdes Dr S and Yacht Harbor Dr (44 Seawall Rd)	RPV	Santa Monica Bay	ID_57_9-17-15	Moderate	9/18/2014	Y	Moderate flow from two outlets 32" and 48". Foul odor. Water colorless but heavy brown stain present. Spoke with Kristen Lenders, (Yacht resident). Inspectors JR, HG.	

Outfall ID	Size	latitude	longitude	Nearest Major Intersection/Closest Accessible Street Address	Agency	Receiving Water	Photo ID	Flow category	Date of Screening	Further Source ID	Notes
43	N/A	33.746404	- I I X 4 I 3 I 3 5	PV Drive W and Via Vicente (end of Pacifica del Mar)	RPV	Santa Monica Bay	ID_43_11-25-14	No flow	11/24/2014	Υ	Outlet difficult to access. No Flow but CB had traces of discharge. MH was access on Pacific Del Mar. Inspectors JR, MG.
48	25"	33.784153	-118.318644	Palos Verdes Dr E and Bridlewood Circle (along Bridlewood Trail)	RHE	Machado Lake	ID_48_11-25-14	No flow	11/24/2014	Υ	No flow from MH on Oak st. Inspectors JR, MG.
50	60"	33.764504	-118 311//36	Western Ave and Delasonde Dr (28020 Pontevedra Dr)	RPV	LA Harbor	ID_50_11-25-14	Moderate flow	11/24/2014	Υ	Moderate flow MH, 60 inches. Inspectors JR, MG.
53	6' by 12'	33.757753	-118 301026	Between W Capitol Dr and Bloomwood Dr	RPV	LA Harbor	ID_53_11-25-14	Moderate flow	11/24/2014	Υ	Moderate flow, from open channel. Inspectors JR, MG.
57A	48"	33.737229	-118 360913	Palos Verdes Dr S and Yacht Harbor Dr (44 Seawall Rd)	RPV	Santa Monica Bay	ID_57_11-25-14	Moderate flow	11/24/2014	Υ	Moderate flow from two outlets 32" and 48". Foul odor. Water colorless but heavy brown stain present. Inspectors JR, MG.
57B	32"	33.737229	-118 360913	Palos Verdes Dr S and Yacht Harbor Dr (44 Seawall Rd)	RPV	Santa Monica Bay	ID_57_11-25-14	Moderate flow	11/24/2014	Υ	Moderate flow from two outlets 32" and 48". Foul odor. Water colorless but heavy brown stain present. Inspectors JR, MG.
100	NA	33.801624	-118 390813	Palos Verdes Drive W and Via Corta (300 Via Corta)	PVE	Santa Monica Bay	ID_100_11-25- 14	Substantial flow	11/24/2014	Υ	Substantial flow to Malaga Canyon, heavy vegetation The outfall across was dry. Inspectors JR, MG.

Outfall ID	Size	latitude	longitude	Nearest Major Intersection/Closest Accessible Street Address	Agency	Receiving Water	Photo ID	Flow category	Date of Screening	Further Source ID	Notes
43	N/A	33.746404	I-11X 413135I	PV Drive W and Via Vicente (end of Pacifica del Mar)	RPV	Santa Monica Bay	ID_43_12-10-14	Moderate flow	12/10/2014	Υ	Outlet difficult to access. Moderate flow but CB . MH was access on Pacific Del Mar. Inspectors JR, CS.
48	25"	33.784153	-118 3186///	Palos Verdes Dr E and Bridlewood Circle (along Bridlewood Trail)	RHE	Machado Lake	ID_48_12-10-14	Moderate flow	12/10/2014	Υ	Moderate flow from MH on Oak st. Inspectors JR, CS.
50	60"	33.764504	-118.311436	Western Ave and Delasonde Dr (28020 Pontevedra Dr)	RPV	LA Harbor	ID_50_12-10-14	Moderate flow	12/10/2014	I Y	Moderate flow MH, 60 inches. Inspectors JR, CS.
53			119 201026	Ratwoon W Canital Dr and	RPV	LA Harbor	ID_53_12-10-14	Moderate flow	12/10/2014		Moderate flow from open channel. Inspectors JR, CS.
57A	48"	33.737229	1-118 3609131	Palos Verdes Dr S and Yacht Harbor Dr (44 Seawall Rd)	RPV	Santa Monica Bay	ID_57_12-10-14	Moderate flow	12/10/2014	Υ	Moderate flow from two outlets 32" and 48". Foul odor. Water colorless but heavy brown stain present. pH 7. Inspectors JR, CS.
57B	32"	33.737229	1-118 360913	Palos Verdes Dr S and Yacht Harbor Dr (44 Seawall Rd)	RPV	Santa Monica Bay	ID_57_12-10-14	Moderate flow	12/10/2014	Υ	Moderate flow from two outlets 32" and 48". Foul odor. Water colorless but heavy brown stain present. pH 7. Inspectors JR, CS.
100	NA	33.801624	1-118 3908131	Palos Verdes Drive W and Via Corta (300 Via Corta)	PVE	Santa Monica Bay	ID_100_12-10- 14	Substantial flow	12/10/2014	Y	Substantial flow to Malaga Canyon, heavy vegetation The outfall across was dry. Spoke with Antonia Graeber-Director of Town & Country Nursery school (310) 375-2829. She stated that the discharge from the outfall is from natural spring water. Inspectors JR, CS.

Appendix B Outfall Pictures



















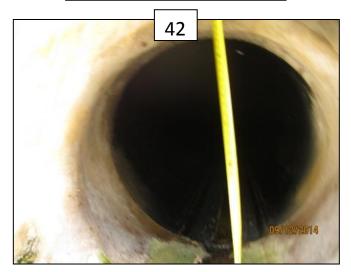












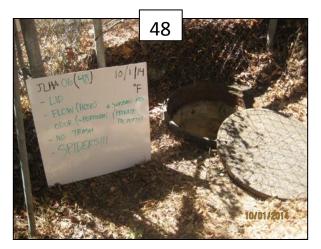


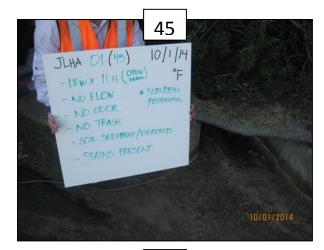


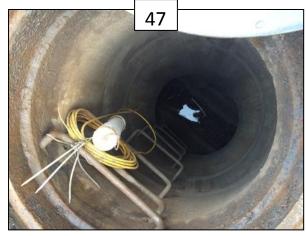




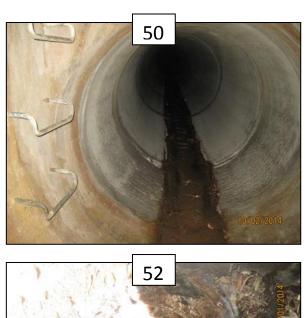












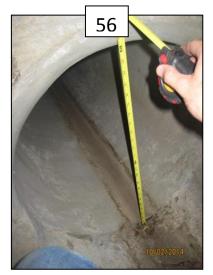






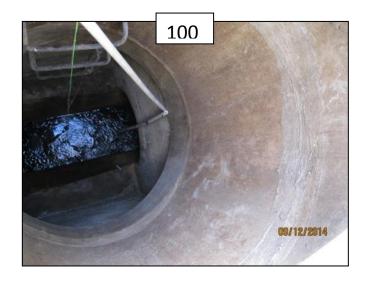


















Appendix C Outfall Screening Field Datasheet Forms

OUTFALL RECONNAISSANCE INVENTORY/ SAMPLE COLLECTION FIELD SHEET

Section 1: Back	ground Data										
Subwatershed:				Outfall ID:	Outfall ID:						
Today's date:				Time (Military):							
Investigators:				Form completed by:							
Temperature (°F):		Rainf	fall (in.): Last 24 hours:	Last 48 hours:	:						
Latitutde:		Longitude:		GPS Unit:		GPS LMK #:	:				
Camera:				Photo #s:							
Land Use in Drain	age Area (Check all tha	at apply):									
☐ Industrial				☐ Open Space							
Ultra-Urban Re	esidential			☐ Institutional							
☐ Suburban Resid	dential			Other:							
☐ Commercial				Known Industries:	-						
Notes (e.g, origin	n of outfall, if known):										
Section 2: Outfa	all Description										
LOCATION		ERIAL	SH	APE	DIMENSIO	NS (IN.)	SUBMERGED				
	□RCP	□СМР	☐ Circular	Single	Diameter/Dimens	sions:	In Water:				
	□ PVC	☐ HDPE	☐ Eliptical	☐ Double			☐ No ☐ Partially				
☐ Closed Pipe	☐ Steel		Box	☐ Triple			☐ Fully				
	Other:		☐ Other:	☐ Other:			With Sediment:				
			Guier.	U Outer.			Partially Fully				
	Concrete		+				77777777				
	☐ Earthen		Trapezoid		Depth:		<i>\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\</i>				
☐ Open drainage			☐ Parabolic		Top Width:	_	1///////				
ı			☐ Other:		Bottom Width:						
— ~.	Other:						<u> </u>				
☐ In-Stream		hen collecting									
Flow Present?	☐ Yes	☐ No	If No, Ski	ip to Section 5							
Flow Description (If present)	☐ Trickle	☐ Moderat	te Substantial								
Section 3: Quar	ntitative Characte	erization									
			FIELD DATA FOR F	LOWING OUTFALLS	5						
PA	ARAMETER		RESULT		UNIT	EC	QUIPMENT				
□Flow #1	Volume				Liter		Bottle				
	Time to fill				Sec						
	Flow depth				In	Ta	ape measure				
□Flow #2	Flow width		,		Ft, In		ape measure				
	Measured length	ı	, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		Ft, In		ape measure				
	Time of travel				S	,	Stop watch				

Temperature

pН

Ammonia

۰F

pH Units

mg/L

Thermometer

Test strip/Probe

Test strip

Outfall Reconnaissance Inventory Field Sheet

Section 4: Physical Indicators for Flowing Outfalls Only Are Any Physical Indicators Present in the flow?
Yes □ No (If No, Skip to Section 5) **CHECK if INDICATOR** DESCRIPTION **RELATIVE SEVERITY INDEX (1-3)** Present ☐ Rancid/sour ☐ Petroleum/gas Sewage ☐ 3 – Noticeable from a Odor ☐ 1 – Faint ☐ 2 – Easily detected distance Sulfide Other: ☐ Clear ☐ Brown ☐ Gray ☐ Yellow ☐ 2 – Clearly visible in \square 1 – Faint colors in ☐ 3 – Clearly visible in Color outfall flow sample bottle sample bottle Green ☐ Orange Red Other: See severity \square 1 – Slight cloudiness \square 2 – Cloudy 3 – Opaque Turbidity 3 - Some; origin clear \square 2 – Some; indications Floatables Sewage (Toilet Paper, etc.) ☐ Suds (e.g., obvious oil \square 1 – Few/slight; origin of origin (e.g., -Does Not Include not obvious possible suds or oil sheen, suds, or floating Other: Petroleum (oil sheen) Trash!! sheen) sanitary materials) Section 5: Physical Indicators for Both Flowing and Non-Flowing Outfalls Are physical indicators that are not related to flow present? \square Yes \square No (If No. Skip to Section 6) **INDICATOR CHECK if Present DESCRIPTION COMMENTS** Spalling, Cracking or Chipping Peeling Paint Outfall Damage Corrosion Deposits/Stains П Oily Flow Line Paint Other: ☐ Inhibited Abnormal Vegetation ☐ Excessive ☐ Colors Odors O ☐ Floatables ☐ Oil Sheen Poor pool quality Suds ☐ Excessive Algae Other: Orange Green Other: Pipe benthic growth ☐ Brown **Section 6: Overall Outfall Characterization** Potential (presence of two or more indicators) Suspect (one or more indicators with a severity of 3) Obvious Unlikely **Section 7: Data Collection** ☐ No Sample for the lab? Yes ☐ Pool If yes, collected from: ☐ Flow

Caulk dam

Section 8: Any Non-Illicit Discharge Concerns (e.g., trash or needed infrastructure repairs)?

☐ Yes

Intermittent flow trap set?

☐ No