

QUALITY ASSURANCE MANAGEMENT PLAN

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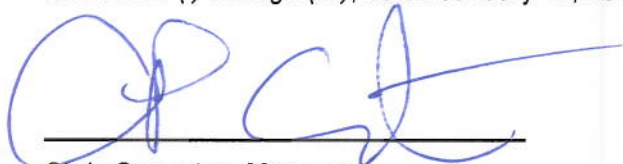
The Orange County Stormwater Program

County of Orange
Public Works Department
OC Watersheds Division
Environmental Resources Section
2301 North Glassell Street, Suite A
Orange, CA 92865

SECTION A PROJECT MANAGEMENT

A1 STATEMENT OF CERTIFICATION

It is hereby certified that this Quality Assurance Program Plan (QAMP) meets the minimal requirements set forth by the State Water Resources Control Board (SWRCB) as set forth in "*Notice of Public Solicitation of Water Quality Data and Information for 2012 California Integrated Report-Surface Water Quality Assessment and List of Impaired Waters [Clean Water Act Sections 305(b) and 303(d)]*", Enclosure 1, Data Submittal Requirements, Section 3e (i) through (vii), dated January 14, 2010.



Chris Crompton, Manager

County of Orange, OC Watersheds Division
Environmental Resources Section

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ACRONYMS

ACW	Aliso Creek Watershed Program
ACRWP	Ambient Coastal Receiving Waters Program
BIA	Benthic Infaunal Analysis Program
BMP	Best Management Practice
CA-DPHS	California Department of Public Health Services
CFU	colony forming Unit
CSDO	Coastal Storm Drain Outfall Program
DWR	Dry Weather Reconnaissance Program
EBMM	Estuary, Bay, and Marshland Monitoring Program
ELAP	Environmental Laboratory Accreditation Program, CA-DPHS
ENT	Enterococcus
ERS	Environmental Resources Section
FC	Fecal Coliforms
MDL	Method Detection Limit
MLM	Mass Load Monitoring Program
MPU	Monitoring Programs Unit
MS4	Municipal Separate Storm Sewer System
NBSCW	Newport Bay/San Diego Creek Watershed Program
NPDES	National Pollutant Discharge Elimination System
PHWQL	Public Health Water Quality Laboratory
OC HCA	Orange County Health Care Agency
OCPW	Orange County Public Works Department
OCSL	Orange County Stormwater Laboratory
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RDL	Reporting Detection Limit
SOP	Standard Operating Procedure
RWQCB	Regional Water Quality Control Board
TC	Total Coliforms
TMDL	Total Maximum Daily Load Program
USB	Urban Stream Bioassessment Program
USEPA	United States Environmental Protection Agency

A3 DISTRIBUTION LIST

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(714) 955-0630

QA Manager: Bruce Moore, Chief Environmental Data Management
(714) 955-0660

Theodore von Bitner, Ph.D, Chief Monitoring Programs Unit
(714) 955-0680

Amanda Carr, Chief Water Quality Planning Unit
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Regional Board QA Manager: Pavlova Vitale, SWAMP Coordinator of Santa Ana Regional Water Quality Control Board
(951) 782-4920

Regional Board QA Manager: Lilian Buuse, SWAMP Coordinator of San Diego Regional Water Quality Control Board
(858) 467-2971

A4 PROJECT ORGANIZATION AND RESPONSIBILITIES

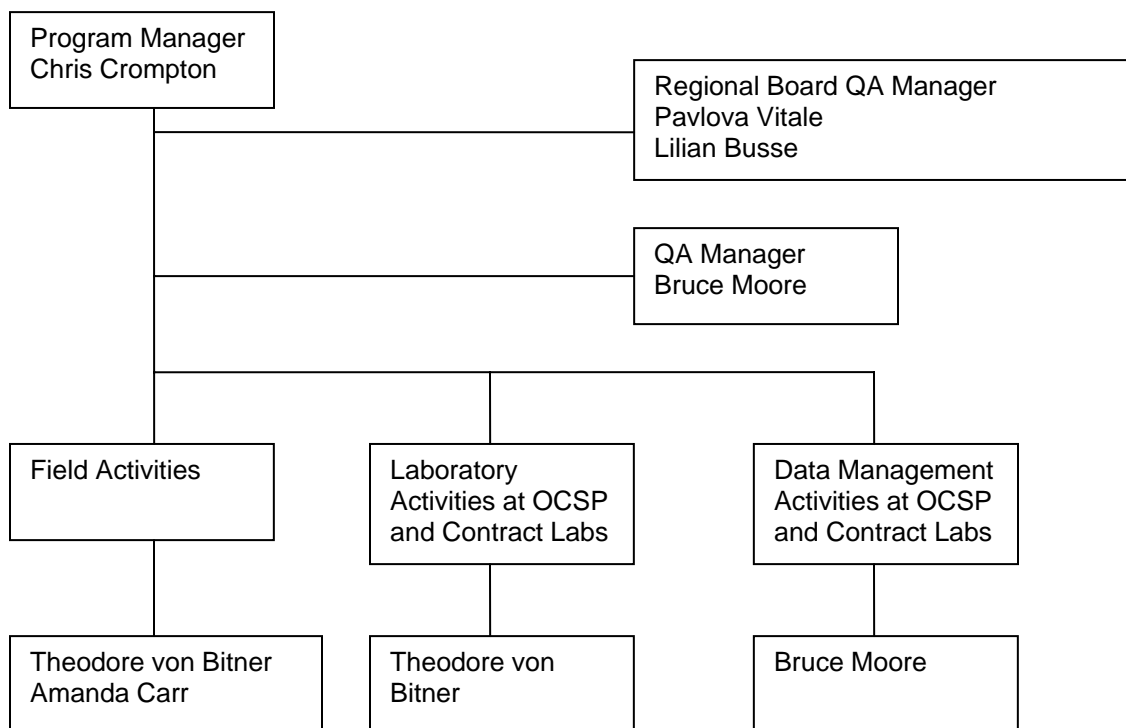
Program direction will be overseen by the Program Manager Chris Crompton, manager of the Environmental Resources Section of the OC Watersheds Program. Laboratory and field operations will be supervised by the Monitoring Programs Unit Supervisor, Theodore von Bitner, and Water Quality Planning Unit Supervisor, Amanda Carr. Review and analysis of the laboratory reports and internal QA/QC results will be supervised by Bruce Moore.

Field and laboratory equipment maintenance, and management of the internal QA/QC program will be supervised by the Laboratory Manager, Theodore von Bitner. Monitoring Programs Unit staff directs the internal QA/QC program. All laboratory analyses are provided by ELAP certified analytical service providers.

Bruce Moore, supervisor of the Data Management Unit, will be the QA Officer for QAMP. His role is to establish and implement and quality assurance and quality control procedures in this QAMP as part of the sampling, field analysis, and analysis procedures. He will review and assess all procedures in this document. He will report all

findings and request corrective actions if there are significant deviations from required practices or if there is evidence of a systematic failure.

The organization chart for OCSP is shown below:



A5 PROBLEM DEFINITION AND BACKGROUND

A5.1 NPDES Water Quality Program

In response to requirements in National Pollutant Discharge Elimination System (NPDES) county-wide municipal stormwater permits, the Orange County Stormwater Program, on behalf of the Flood Control District and its 34 cities, conducts water and sediment quality monitoring in the drainage network and its respective receiving waters. Orange County falls under the jurisdictions of the Santa Ana and San Diego Regional Water Quality Control Boards (RWQCB) and consequently has two separate NPDES permits.

In 1991 the Regional Boards each issued the first NPDES permits with concurrent terms of five years. A monitoring program was designed, approved by the Boards, and implemented shortly thereafter. In 2009, the San Diego and Santa Ana Regional Boards issued fourth-term permits CAS0108740 and CAS618030, respectively.

The objectives of the monitoring program are:

- To develop and support an effective municipal urban runoff and non-point source control program.
- To define water quality status, trends, and pollutants of concern associated with urban storm water and non-storm water discharges and their impact on the beneficial uses of the receiving waters.
- To characterize pollutants associated with urban storm water and non-storm water discharges and to assess the influence of urban land uses on water quality and the beneficial uses of receiving waters.
- To identify significant water quality problems related to urban storm water and nonstorm water discharges.
- To identify other sources of pollutants in storm water and non-storm water runoff to the maximum extent possible (e.g., atmospheric deposition, contaminated sediments, other non-point sources, etc.)
- To identify and prohibit illicit discharges.
- To identify those waters, which without additional action to control pollution from urban storm water discharges, cannot reasonably be expected to attain or maintain applicable water quality standards required to sustain the beneficial uses in the Basin Plan (TMDL monitoring).
- To evaluate the effectiveness of existing municipal storm water quality management programs, including an estimate of pollutant reductions achieved by the structural and nonstructural BMPs implemented by the permittees.
- To evaluate costs and benefits of proposed municipal storm water quality control programs to the stakeholders, including the public.

In order to meet the new requirements of each permit, a revised monitoring program proposal was prepared for each region and submitted to the respective Regional Board for approval. In August 2002 and August 2005, the San Diego Region and Santa Ana Region programs were implemented, respectively. The goal of this QAMP is to ensure the consistent collection of accurate water quality information that will used to satisfy the objectives of the Orange County Stormwater Program.

As principal permittee for the Santa Ana Region and San Diego Region NPDES permits, Orange County staff conducts the monitoring and manages the water quality data for the Orange County Stormwater Program. Logistical support for the NPDES stormwater permits, including adopted Total Maximum Daily Load programs, and other management directives is provided by the Orange County Stormwater Laboratory. The laboratory

serves as a both a central location for sampling processing and receiving in addition to providing routine equipment maintenance, calibration, and storage services. A clean-room facility is also located within the laboratory for the internal quality assurance/quality control program.

Section References

California Regional Water Quality Control Board, Santa Ana Region, Waste Discharge Requirements for Storm Water and Urban Runoff from the County of Orange, the Orange County Flood Control District (OCFCD), and the Incorporated Cities of Orange County Within the Santa Ana Region, Areawide Urban Stormwater Runoff Management Program, Orange County, Order No. R8-2009-0030 (NPDES No. CAS618030), May 2009.

California Regional Water Quality Control Board, San Diego Region, Waste Discharge Requirements for Storm Water and Urban Runoff from the County of Orange, the Orange County Flood Control District, and the Incorporated Cities Within the San Diego Region, Order No. R9-2009-0002, NPDES No. CAS0108740, December 2009.

Code of Federal Regulations, Title 40 - Protection of Environment, July 1, 1990, Chapter 1, Part 136, CFR-Appendix B.

Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Environment Federation, 20th Edition, 1999 (SM20).

Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Proposed Rule, US Environmental Protection Agency, August 3, 1997.

A6 PROJECT DESCRIPTION

The purpose of this project plan is to define a quality assurance and quality control program for maintaining uniform, accurate, precise, and representative methods of sampling, equipment calibration, sample processing, sample analyses, and data management. This project plan supports environmental sampling conducted for the NPDES stormwater permits and adopted TMDL directives.

The emphasis of the quality assurance management plan covers the data quality requirements for the following water quality monitoring programs:

- Ambient Coastal Receiving Waters Program

- Coastal Storm Drain Outfall Receiving Waters Monitoring
- Estuaries, Bay, and Marsh Monitoring
- Illicit Connection and Illegal Discharge Reconnaissance
- Mass Load Monitoring
- Urban Stream Bioassessment and
- Nutrient Total Maximum Daily Load Directive
- Indicator Bacteria Total Maximum Daily Load Directives

The QAMP for the Orange County Stormwater Program, herein referred to as the Program, combines three approaches to ensure environmental data of known and documented quality as produced for the stakeholders and end users of the information. The Program combines a traditional quality assurance protocols to monitor analytical results produced by contract laboratories in concert with an internal quality assurance program, and a collaborative partnership with contracted services in periodic intercalibration exercises.

The environmental laboratories contracted to perform many of the analyses for the Orange County Stormwater Program are required to use only approved USEPA or Standard Methods. External laboratories must be certified through the State of California Department of Public Health Environmental Laboratory Accreditation Program (ELAP) in order to provide analytical services to the stormwater program. Each of these laboratories has approved QAPP manuals on file at the respective address listed in section A7.

The internal quality assurance program heavily relies on blind laboratory check samples for data validation. The samples prepared by Program staff include laboratory fortified blanks, fortified sample matrix solutions (reagent spike), field splits/duplicates, equipment blanks, trip blanks, and certified reference materials as categorically institutionalized procedures to validate results generated by contract laboratory analyses. Examples of the constituents covered by the internal QA/QC program include but are not limited to ammonia, nitrate, phosphate, chloride, sulfate, cadmium, nickel, copper, silver, lead, zinc, arsenic, selenium, chlorpyrifos, diazinon, malathion, DDTs, chlordane, PCBs, bifenthrin, fecal indicator bacteria [Enterococcus, Fecal Coliform, and Total Coliform], and Whole Effluent Toxicity (WET) reference toxicants.

An additional priority of the QAMP is preventive contaminant control by the use of method blanks. Regular and periodic exposure of the laboratory and field instrumentation to ASTM Type 1 water (18 megaohm) provides the necessary feedback to assess systematic contamination. Type 1 water blanks are submitted on a regular basis to the contract laboratory along with the normal sample submission to insure the generation of valid results. Laboratory reagent blank (Type 1 water only) analysis is required of all ELAP-approved laboratories.

A7 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The focus of the QAMP is to ensure the consistent collection of accurate water quality information will be used to satisfy the objectives of the NPDES monitoring programs. In general, the data quality objectives for this QAMP are to ensure that the data is representative, comparable, complete, accurate, and precise. The purpose of this project plan is to define a quality assurance and quality control program for maintaining uniform and accurate methods of sampling, equipment calibration, sample processing, sample analyses, and data handling.

A7.1 Analytical Services

A7.1.1 Chemistry

The analyses of chemical environmental and QA/QC samples are performed using USEPA and Standard Methods. Services for chemical analysis of environmental samples are provided by CRG Marine Laboratories, Associated Laboratories, and Weck Laboratories Inc. Orange County and its contract laboratories maintain standard operating procedures (SOPs) for safe handling and processing water samples. In addition, each of the contract laboratories maintain SOPs for analysis and quality assurance and control as part of this overall program manual.

A7.1.2 Indicator Bacterial

The analyses of bacterial environmental and QA/QC samples are performed using USEPA and Standard Methods. Services for bacteriological analysis of environmental samples are provided by the Orange County Public Health Water Quality Laboratory. Orange County and its contract laboratory maintain standard operating procedures (SOPs) for safe handling and processing of potential pathogenic samples. In addition, the contract laboratory maintains SOPs for analysis and quality assurance and control as part of this overall program manual.

A7.1.3 Toxicity

The performance of toxicity bioassays and evaluation of reference toxicants are performed using USEPA and Standard Methods. Services for aquatic and sediment toxicity bioassays are provided by Aquatic Bioassay and Consulting Laboratories. Orange County and its contract laboratory maintain standard operating procedures (SOPs) for safe handling and processing of toxicity assay samples. In addition, the contract laboratory maintains SOPs for analysis and quality assurance and control as part of this overall program manual.

A7.1.4 Benthos and Stream Macroinvertebrate Biology

The taxonomic analysis of sediment benthic and stream macroinvertebrate assemblages are performed using the most currently accepted guidelines published by the Southern California Freshwater and Marine Invertebrate Taxonomy Associations, SAFIT and SCAMIT, respectively. All stream bioassessment sample collection and taxonomic analysis follow the Southern California Regional Watershed Monitoring Program Bioassessment Quality Assurance Project Plan. Services for taxonomic analysis are provided by Aquatic Bioassay and Consulting Laboratories. Orange County and its contract laboratory maintain standard operating procedures

(SOPs) for safe handling and processing of macroinvertebrate samples. In addition, the contract laboratory maintains SOPs for analysis and quality assurance and control as part of this overall program manual.

Table A7-1. Analytical Service Providers to the Orange County Stormwater Program

Aquatic Bioassay and Consulting Laboratories
806 North Batavia
Orange, California 92868
Tel: 714-771-6900
FAX: 714 538-1209

Associated Laboratories
806 North Batavia
Orange, California 92868
Tel: 714-771-6900
FAX: 714 538-1209

CRG Marine Labs
806 North Batavia
Orange, California 92868
Tel: 714-771-6900
FAX: 714 538-1209

Orange County Public Health Water Quality Laboratory
700 Shellmaker Road
Newport Beach, CA 92660
Tel: 949 219-0423
FAX: 949 219-0426

Weck Laboratories Inc.
14859 East Clark Avenue
City of Industry, CA 91745-1396
Tel: 626-336-2139
FAX: 626-336-2634

A7-2 Monitored Parameters

The Orange County Stormwater Program collects a wide variation of constituents in water and sediment matrices of conventional, biological, and toxic parameters as part of the core monitoring program. A complete list of the monitored parameters is provided in **Table A7-2**

Table A7-2. Summary of monitored constituents in water and sediment matrices collected during dry weather and storm events.

Parameter	Dry Season Aqueous	Wet Season Storms	Dry Season Sediment
Nutrients			
Nitrate plus Nitrite	X	X	
Total Ammonia	X	X	
Total Kjeldahl Nitrogen (TKN)	X	X	
Total Nitrogen		X	X
Total Phosphate	X	X	X
Orthophosphate	X	X	
Dissolved Organic Carbon	X	X	X
Total Organic Carbon	X	X	X
Total Suspended Solids	X	X	
Volatile Suspended Solids	X	X	
Chloride	X	X	
Sulfate	X	X	
Total Dissolved Solids	X	X	

Turbidity	X	X	
pH	X	X	X
Temperature	X	X	
Electrical Conductivity	X	X	
Hardness	X	X	
Particle Size			X
Total and Dissolved heavy metals	X	X	X
Arsenic	X	X	X
Cadmium	X	X	X
Chromium	X	X	X
Copper	X	X	X
Lead	X	X	X
Mercury	X	X	X
Nickel	X	X	X
Silver	X	X	X
Selenium	X	X	X
Zinc	X	X	X
Antimony	X	X	X
Beryllium	X	X	X
Thallium	X	X	X
Organochlorine pesticides & PCBs		X	X
Acid/Base/Neutral extractables		X	X
Volatile Organic Carbon cpds		X	
Organophosphate pesticides			
Diazinon	X	X	
Chlorpyrifos	X	X	
Malathion	X	X	
Dimethoate	X	X	
Pyrethroid pesticides			
Bifenthrin		X	X
Permethrin		X	X
Carbamate pesticides		X	X
Glyphosate	X	X	
Oil and Grease	X	X	
Total Petroleum Hydrocarbons	X	X	
Bacteria Indicators			
Enterococcus	X	X	
Fecal Coliforms	X	X	
Total Coliforms	X	X	
Toxicity			
Ceriodaphnia dubia	X	X	
Selenastrum capricornutum	X		
Hyallolela azteca	X	X	X
Pimephales promelas	X		
Strongylocentrotus purpuratus	X	X	
Americamysis bahia	X	X	
Eohaustorius estuarius			X
Mytilus galloprovincialis			X
Benthic Infauna	X		X

Episodic and special directives designed to address specific water quality issues may require constituent monitoring outside of the core parameters provided in this plan. Although special studies may require parameters outside of the scope of this plan some initial guidelines in the appendices to ensure quality data can be generated for the Program..

A7.3 Data Quality Objectives from the Internal Quality Assurance Program

To produce acceptable testing results, the general data quality objectives for this plan are to ensure that the data is representative, comparable, complete, accurate, and precise. Acceptable results are those values that fall within the acceptable range specified as detailed in sections A and B. Corrective actions for unacceptable results for specific testing methods are available from the contract laboratories are detailed in subsection A7.6.7 and in sections B and C.

A7.3.1 Representativeness

Representativeness is the degree to which the data represent the actual condition of a sampling site. The following factors determine the representativeness of the data: sampling location, sampling frequency, sample type, sample collection methods, sample preservation, sample holding times and analytical methods used. These factors are critical components of a sampling plan designed to maximize representativeness of the data to the extent practicable.

A7.3.2 Comparability

Comparability of data is the degree to which the data produced by one laboratory or study can be compared to another. The contract laboratory uses EPA approved analytical methods where possible or methods that have been determined to produce measurement data of known and quality sufficient to meet the objectives of this project. The data will be reported in commonly used Units.

A7.3.3 Completeness

The completeness of data is the percentage of planned data that will be used to meet statistical criteria needed to reach study conclusions. Acquiring 100% of the data planned is difficult due to unexpected circumstances, adverse weather conditions, equipment problems, laboratory error, and loss of samples or samples that are invalid because they do not meet all of the laboratory sample acceptance criteria. The goal of this project is to obtain 80% of data completeness. Percent completeness is the number of data values generated divided by the number of samples collected multiplied by 100.

A7.3.4 Accuracy

Accuracy is the degree to which the measurement is to its true value. Accuracy of the laboratory methods is determined by means of testing the following: (1) performance evaluation (PE) samples consisting of known

quantities of analytes, (2) performance evaluation of duplicates, (3) laboratory and field blanks and (4) split samples. In addition, equipment calibration checks are routinely done to ensure accuracy of measurements.

The accuracy measured for any submitted samples must be within the control limits as defined in **Table 7-1**. The accuracy for any submitted samples is measured by the matrix spike and LCS recoveries. Percent recovery calculations are also outlined in Section B7. The control and warning limits are set at $x + 3s$ and $x + 2s$, respectively. The mean and standard deviation are calculated as follows:

$$\bar{x} = \frac{\sum x_i}{n}$$

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

A7.3.5 Precision

The precision of a given sample is determined by the numerical agreement between replicate analysis results. The precision measured on each replicate group is defined by the relative percent difference (RPD) between duplicate matrix spikes or duplicate samples. From a group of statistically sufficient duplicate sample observations, the standard deviation of the RPD measurements (s_r) can be calculated.

$$RPD = (\sum RPD_i)/n$$

$$s_r = \sqrt{\frac{\sum RPD_i^2 - nRPD^2}{n - 1}}$$

where, RPD = mean relative percent difference
 s_r = standard deviation of measurements
 n = number of measurements

The control limit is $RPD + 3s_r$ and the warning limit is $RPD + 2s_r$. Applicable formulae for calculating these control limits are outlined in Section B7.

A7.3.6 Contract Laboratory Quality Control

The contract laboratory must maintain a formal internal quality assurance program utilizing analyses of certified reference materials (CRM), duplicates, spikes, and method blanks. The information must be maintained for periodic inspection by Unit supervisors and staff. The contract laboratory must also provide OCPW with a report

on the extent and results of the internal quality control program upon request. All of the contract laboratories currently retained by OCPW have approved Quality Assurance Project Plans on file at the addresses listed in Section A4 and are available upon request.

A7.3.7 Limits of Error

The limits of error for the common dissolved constituents in samples not containing large quantities of organic or inorganic detritus and not containing a large concentration of inorganic salts are required to maintain specific control limits. Determination of satisfactory accuracy or precision in the analysis is displayed in **Table A7-3**.

TABLE A7-3: LIMITS OF ERRORS*

Constituent	Allowable Error
Calcium	5% or 1.5 mg/L, whichever is greater
Magnesium	6% or 1.5 mg/L, whichever is greater
Sodium	5% or 2.0 mg/L, whichever is greater
Potassium	5% or 1.0 mg/L, whichever is greater
Chloride	5% or 1.0 mg/L, whichever is greater
Sulfate	5% or 2.0 mg/L, whichever is greater
Fluoride	10% or 0.1 mg/L, whichever is greater
Boron	5% or 0.2 mg/L, whichever is greater
Silica	10% or 2.0 mg/L, whichever is greater
Nitrate + Nitrite as NO ₃	10% or 1.0 mg/L, whichever is greater
Total Phosphorus as PO ₄	20% or 0.2 mg/L, whichever is greater
Ammonia Nitrogen	20% or 0.2 mg/L, whichever is greater
Total Kjeldahl Nitrogen	20% or 0.2 mg/L, whichever is greater
Pb, Cu, Cd, Ag, Cr, Zn, Ni, As, Se	±25% for concentrations greater than or equal to 5 times the reporting limit
Ion Balance (General Mineral)	0.5 milli-equivalents per liter or 5%, whichever is greater

Limits of Error for a constituent outside of this table are defined by the certified reference material control limits established by the vendor. Contracted laboratory services are required to abide by these limits as a condition of continued service to the Program.

A7.4 Measurement Quality Objectives

Measurement Quality Objectives for the contract laboratory generated data follow the programmatic quality objectives specified by the State of California Surface Water Ambient Monitoring Program. The MQOs for constituents monitored for the Santa Ana Region and San Diego Region NPDES stormwater permits are specified in **Table A7-4**.

A7.5 Intercalibration Quality Control

Intercalibration of laboratory results provides an additional quality control measure to assess the performance of contract laboratories. The Orange County Stormwater Program is a stakeholder member of the Southern California Stormwater Monitoring Coalition and conducts periodic evaluations of analytical services provided through the laboratory intercalibration exercises. Comparative assessments based on blind sample submissions to each participating laboratory are graded based on a group mean target concentration, individual accuracy, and within laboratory precision. Sample constituents for the laboratory evaluations include nutrients, total suspended solids, trace metals, indicator bacteria, and pesticides currently limited to the organophosphorus, organochlorine, and pyrethroid classes. The results of the laboratory intercalibration exercise are provided in terms of a letter grade A-F indicating the overall performance of a laboratory with respect to analytes tested. The standardization of reporting limits and methodologies across participating laboratories ensures that potential vendors to the Program have met the minimum acceptance performance standards. The intercalibration exercise provides an additional level of data integrity for the Program to ensure that environmental data of known and documented quality can be generated for the NPDES stormwater permits and the end data users.

Section References

Quality Assurance Program Plan, Surface Water Ambient Monitoring Program. Final Technical Report 2008.
Website: www.waterboards.ca.gov/swamp

Stormwater Monitoring Coalition Laboratory Guidance Document, 2009. Schiff, K. and R. Gossett.
Website: www.socalsmc.org

A8 SPECIAL TRAINING REQUIREMENTS

All personnel involved with sample collection and analysis receive thorough training. New employees are given intensive instruction in the form of training manuals, extensive hands-on mentoring for field sampling and laboratory techniques, including participation in ongoing training opportunities as new methodologies are instituted. New training opportunities included internal courses and external courses such as opportunities provided by the Southern California Coastal Waters Research Program (SCCWRP). All training is documented. OCPW has also established standard operating procedures for the safe and proper operation of field and laboratory equipment. The laboratory staff also attends seminar training sessions, and reads literature pertaining to sampling, laboratory, and safety techniques. The Monitoring Programs Unit supervisor in addition performs periodic evaluation of all field and laboratory personnel.

A9 DOCUMENTATION AND RECORDS

A9.1 Chain-of-Custody Procedures

Samples that are transferred from one agency to another agency for analysis require the use of Chain-of-Custody Form (CoC) procedures that include the following requirements for the laboratory to accept custody of samples.

A9.1.1 Sample Label

Samples must be properly labeled using waterproof ink to record the sample number/description, date and time collected.

A9.1.2 Chain-of-Custody Forms

Chain of Custody forms are provided for each sampling event to field sampling personnel for detailed record keeping. The CoC form consists of three documents which are the sample logsheet, field data sheet, and transferal chain of custody (CoC). The sample logsheet contains the project name, sample number (work request number), sample location, test required, and number of bottles per location. The field sheet contains the field sampler initials, sample location, date and time of collection, weather, sample lognumber, collection type (grab or composite), missed samples due to unexpected problems, and field observations relevant to sample integrity. The transferal chain of custody contains the project name, sample number, date and time of collection, number of samples, matrix type (marine, freshwater or other), field sampler name, and tests requested. A duplicate copy system, both copies having original signatures, is maintained in the data management files.

A9.1.2 Transfer of Custody

Immediately following receipt of water samples to the laboratory, a staff member will conduct inventory and document information regarding sample transport and laboratory processing according to the specified laboratory SOP. Samples destined for analysis by one of the contract laboratories are placed in a 4°C isothermal refrigerator and logged into the electronic database records. Both copies of transferal chain of custody are kept with the samples until transferal of the samples to the contract laboratory courier service. One sheet of the transferal chain of custody shown in **Figure 1** is placed with the sample in the refrigerator sample login notebook; the second copy is placed in the data management CoC notebook.

A9.2 Sample Log-In

The sample log-in inventory consists of checking the samples for proper labeling, cross-referencing sample labels with the sample logsheet, field sheet, and transferal chain of custody. Samples received leaking, broken, containing insufficient volumes, exceeding holding times or unpreserved will not be submitted. The sample anomalies will be pointed out by the sample deliverer and noted in the electronic database records.

Following transfer of custody, the samples are logged into the electronic database using the previously assigned laboratory number, which is used to track the sample throughout the analytical process. A unique system of sample numbering is generated by the central database (LabTrack) sample tracking program currently used by the stormwater program. Laboratory numbers are assigned in sequential numeric order of sample generation.

A9.3 Sample Storage

Sample collection procedures for water and sediment quality samples follow concise guidelines for each of the monitored constituents or parameter groups. All samples brought back to the Orange County Stormwater laboratory are stored at 4°C in a commercially available isothermal laboratory refrigerator. The refrigerator temperature is monitored weekly from a calibrated thermometer and recorded in a maintenance logbook. Sample container types, suggested volumes, and holding times are strictly observed according to the guidelines listed in the appendix

A9.4 Documentation of Laboratory Results

The time of sample analysis, analytical results, and QC evaluations from the contract laboratories are entered into the LabTrack electronic database system upon receipt of the reports. All internal QA/QC results for the method blanks, duplicates, and split samples are recorded in the electronic database and will be part of the annual QA/QC status report.

All laboratory activities related to the QA/QC Sample Preparation project are maintain in organized notebooks. The solution preparation logsheet shown in **Figure 2** is kept in a 3-ring notebook in the QA/QC room while instrument maintenance and calibration results are maintained in separate logbooks.

A9.5 Field Staff Responsibilities

The Environmental Resources Specialist is responsible for filling and labeling sample containers, and initiating proper chain-of-custody (CoC) documentation. The stormwater program has a customized chain-of-custody form that is used for all samples collected by staff as shown in **Figure 1**. The sample identification section of the CoC includes the sample identification number (work request number), date and time of sampling, number of containers, matrix description, analyses required, and remarks. The signature section of the CoC identifies the name and company affiliation of each individual in the custody chain, and the date and time of sample custody transfer. Samples collected in the field are brought directly to the appropriate laboratory at the conclusion of sampling activities. Samples must either be received by the contract laboratory or logged into the ERS sample database following the guidelines in section A9.2.

SECTION B DATA GENERATION AND ACQUISITION

B1 Sampling Process Design

B1.1 INTRODUCTION

Sampling and monitoring locations for the NPDES, adopted TMDL, and other special directive monitoring program were selected in a collaborative process with the County, the respective stakeholders, and the Regional Water Quality Control Boards. The sampling process design takes into established scientific principles to address the appropriate locations for collection of the various monitored parameters.

The methods for the preparation of laboratory check samples and quality assurance standards were developed by Orange County Public Works staff. An example of the sample preparation guidelines are displayed in **Appendix B** and **Figure 2**.

The scope of this document is limited to the chemical, bacteriological, and toxicity environmental sampling efforts conducted by OC Watershed staff for the Orange County Stormwater Program. Complete descriptions of the biological sampling and data analysis procedures for stream Bioassessment and sediment benthic invertebrates has been included in the appendices to this manual. This project plan document addresses the generation of QA/QC data within the ERS laboratory which includes all aspects of the field collection of chemical and bacterial QC samples, equipment, procedural, and safety considerations. Some of the procedures described in the Sampling Manual are from Standard Methods for the Examination of Water and Wastewater, 20th Edition.

B1.2 SAMPLE PREPARATION AND FIELD COLLECTION

B1.2.1 Field Collection of Chemistry and Aquatic Toxicity Samples

Samples for chemical analyses are collected by trained Environmental Resources Specialists. These samples are collected in I-Chem™ glass or certified Low Density Polyethylene (LDPE) containers. Disposable powder-free vinyl gloves are worn for personal protection and to prevent sample contamination. Samples from streams or flood channels are collected at about 60% of the stream depth (from the surface) in an area of maximum turbulence. Stagnant pools near the edge of the stream are avoided as collection sites. The channel is entered downstream of the sampling location and caution is exercised to disturb as little of the bottom sediment as possible. During periods of dangerously high stormwater runoff, samples are collected by lowering a clean HDPE bucket into the channel.

Particulate matter for filtered samples is removed using 0.45 micron high capacity disposable groundwater filters. The filtering capsule is connected, noting the direction of flow, to the suction end (not the discharge end) of a peristaltic pump. A piece of acid-washed (10% HCl) Teflon-lined Tygon tubing is connected to the opposite end of the filtering cartridge. The pump is run for several seconds to remove residual Type 1 rinse water from the

decontamination process after the previous sampling. After filtration, the peristaltic pump tubing is rinsed with Type 1 water, the filter is discarded, and the Tygon tubing is changed. Each filtered sample is preserved with either analytical or ultrapure - grade nitric acid in sufficient volume to adjust the pH of the sample to <2. Acid preservative is dispensed only from Teflon dropper bottles. Filtered and preserved samples are clearly labeled and stored in an ice chest until delivery to the Orange County Stormwater Laboratory.

Automated field water quality sampling equipment is required to maintain strict QA/QC protocols during the collection of samples and storage in the field following monitoring periods. All strainers and pump tubing are thoroughly cleaned in the Orange County Stormwater Laboratory (OCSL) between monitoring periods and storage in clean HDPE bags. All stormwater and TMDL automated field samplers use stainless steel or HDPE/stainless steel strainers. The automated samplers are equipped with HDPE Tygon tubing or Teflon-lined Tygon tubing. Automated field water quality sampling equipment and portable peristaltic pumps are rinsed with Type 1 water prior to and immediately after sample collection periods. Automated samplers, in addition, are required to perform a rinse cycle at the sampling location to remove the Type 1 water prior to sample collection and avoid unwarranted dilution of the stormwater. Automated samplers which are expected to remain inactive, but required to remain at the sampling station are rinsed and sealed within a clean HDPE bag. Equipment blanks of automated field sampling equipment are generated using a clean HDPE carboy filled with Type 1 water. Teflon-lined Tygon tubing connected to the carboy valve is attached to the suction end of the automated sampler pump tubing and a representative sample volume aliquot is drawn into a clean glass or acid washed HDPE field sampler bottle. The reagent blank is processed identically to the method used for nutrient or trace metal samples.

B1.2.1.1 Field QC

Field quality control samples are periodically collected and analyzed. The field QC samples collected are duplicates, splits, in addition to reagent blanks (Type 1 water only) of field collection equipment. Duplicate samples are collected simultaneously in the field in two separate sample bottles. Split samples are collected in the field in ultraclean and trace metal-free 4.0 liter HDPE container and poured into two separate sample bottles.

B1.2.1.2 Field Safety

All field monitoring staff responsible for maintaining the sample collection routes for the chemical monitoring programs are required to observe the following safety guidelines:

- A safety line is utilized when descending steep or slippery channels.
- Channels are not entered during periods of high flow.
- When collecting and handling samples, staff wear neoprene gloves, rubber boots, and other protective clothing depending on weather conditions.

B1.2.1.3 Laboratory Samples

Laboratory control standards samples for nutrients, general mineral, trace metals, and reference toxicant analyses by the contract laboratories are prepared by trained OCSL laboratory staff using volumetric glassware. These prepared samples are transferred into I-Chem or LDPE containers and submitted to the contract laboratories in the same manner as environmental samples. Disposable powder-free vinyl gloves are worn for personal protection and to prevent sample contamination. Synthetic chemistry QA/QC solutions will only be prepared using commercially available American Chemical Society certified high purity reagents and Type 1 water. An example of the sample preparation logsheet is shown in **Figure 2**.

B1.2.1.4 Laboratory Safety

All analytical equipment and glassware is maintained in safe working condition. Laboratory staff wear nitrile gloves while handling chemicals and preparing the synthetic solutions. Laboratory staff is required to wear gloves, an apron or lab coat, and safety glasses when working with acids or other dangerous solvents. In addition, all work with acids or dangerous solvents is required to be performed beneath the fume hood. All washing of glassware or dispensing of dangerous chemicals is required to be performed beneath the fume hood.

A complete and well-organized file of Material Safety Data Sheets (MSDS) maintained by the Laboratory Manager and division Safety Officer is maintained in the laboratory. Standard laboratory safety equipment including emergency shower and eye wash station, fire extinguisher, and first aid kit are easily accessible and periodically serviced or restocked.

B1.2.2.1 Field Collection of Bacterial Samples

Samples for indicator bacteria include Total Coliforms, Fecal Coliforms, and Enterococci (TC, FC, ENT,) analyses by OC HCA PHWQL laboratories are collected by trained Environmental Resources Specialists. The bacterial samples are collected in sterilized HDPE containers. Disposable powder-free nitrile gloves are worn for personal protection and to prevent sample contamination. Samples from streams or flood channels are collected at about 60% of the stream depth (from the surface) in an area of maximum turbulence. Stagnant pools near the edge of the stream are avoided as collection sites. The channel is entered downstream of the sampling location and caution is exercised to disturb as little of the bottom sediment as possible. During periods of dangerously high stormwater runoff, samples are collected from a safe position on the bank using a telescoping sampling pole to obtain water samples from a turbulent section of the flow.

B1.2.2.2 Field QC

All of the program elements that require the collection of coliform and Enterococci (TC, FC, ENT, E. Coli.) bacteria follow identical procedures for field QC samples. The field element consists of collecting sample duplicates and solution splits for submission with each sample batch. In addition, a reagent blank of certified sterile water is included with each sample batch submission to a contract laboratory. NIST-certified calibrated thermometers are included with the field collected bacterial containers to insure sample integrity.

B1.2.2.3 Field Safety

All field staff responsible for maintaining the sample collection routes for the bacterial monitoring programs are required to observe the following safety guidelines.

- A safety line is utilized when descending steep or slippery channels.
- Channels are not entered during periods of high flow.
- When collecting and handling samples staff wear neoprene gloves, rubber boots, and other protective clothing depending on weather conditions.

B1.2.3 Sediment Chemistry, Toxicity, and Benthic Infauna

B1.2.3.1 Field Methods

The collection of sediment quality samples follows established procedures from the Southern California Bight Regional Monitoring Program and the Surface Water Ambient Monitoring Program. Sediment samples for chemistry, toxicity, and benthic macrofauna analysis are collected with a 0.1 m² petite ponar grab. Sediment samples are collected from the top 2 cm of the grab and transferred into I-Chem sample jars. Estuary and marine samples for benthic infauna samples are sieved through a 1 mm mesh screen. The chemistry, toxicity, and benthic infauna are subsampled from a composite grab to ensure consistency between sample compositions. Only samples with penetration depth of at least 5 cm and no evidence of disturbance (e.g., washout) or slumping were processed.

Benthos material retained on the screen was placed in a relaxant solution of 1 kg MgSO₄ or 30 ml propylene phenoxylol per 20 L of seawater for at least 30 minutes and preserved in 10% sodium borate buffered formalin. Sediment samples were also collected for sediment chemistry and sediment toxicity analysis; the results of these analyses are provided and discussed elsewhere (Noblet et al. 2002, Bay et al. 2000).

B1.2.3.2. Laboratory Methods

Samples collected for macrofaunal analysis are transferred on the day of collection to the contract laboratories for sorting, biomass determination, identification and enumeration. Samples were rinsed and transferred from formalin to 70% ethanol 3-14 days after sample collection.

B1.2.3.3 Field QC

The field QC element for sediment samples consists primarily of duplicates samples to measure precision in laboratory analyses. Sediment toxicity samples are in addition kept refrigerator in the field to minimize the evolution of unionized ammonia will may confounded the toxicity organism response (SQOs, 2009).

B1.2.3.4 Field Safety

All field staff responsible for conducting the sampling are required to observe the following safety guidelines.

- A safety line is utilized when descending steep or slippery channels.
- Channels are not entered during periods of high flow.
- When collecting and handling samples staff wear neoprene gloves, rubber boots, and other protective clothing depending on weather conditions.

B1.2.4 External Laboratories

The internal QA/QC program for this QAMP utilizes reference materials and certified laboratory control standards to evaluate the contract laboratories. Materials are purchased from each of the vendors provided below.

Environmental Resource Associates

Arvada, Colorado 80002
1-800-372-0122

National Institute of Standards and Technology

Gaithersburg, MD 20899-2300
1-301-975-2200

VWR International Inc.

1310 Goshen Parkway
West Chester, PA 19380
1-800-932-5000

Section References

Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Environment Federation, 20th Edition, 1999 (SM20).

Southern California Bight 2003 Regional Monitoring Program.

Marine Pollution Studies Laboratory – Department of Fish and Game (MPSL-DFG) Standard Operating Procedures (SOPs) for Conducting Field Measurements and Field Collections of Water and Bed Sediment Samples in the Surface Water Ambient Monitoring Program (SWAMP), SOP Procedure Number 1.0, October 2007.

California Environmental Protection Agency, Sediment Quality Objectives, adopted August 2009.

B2 SAMPLING METHODS

The specific sampling methods for the various water quality monitoring programs within the stormwater program vary significantly from program to program. The Mass Emissions and San Diego Creek Nutrient TMDL monitoring programs require automatic samplers outfitted with stainless steel strainers, Teflon-lined suction tubing, silicone

peristaltic pump tubing, and glass or HDPE bottles. Samples are drawn from the channels or creeks by the autosampler's peristaltic pump and transferred into a single composite bottle or a series of discrete bottles.

The programs requiring collection of grab samples utilize sterilized HDPE bottles for the bacterial collections, ultraclean trace metal-free HDPE bottles for nutrients and trace metals, amber glass for light sensitive analytes, and VOA bottles for volatile organics. All samples are collected from a downstream position. Samples are preserved either at the location under safe non-storm conditions or at OCSL using high purity commercially available preservatives.

B3 SAMPLE HANDLING AND CUSTODY

The collection of water samples with an automatic sampler will be accompanied with a chain-of-custody form as shown in **Figure 1**. Filled autosampler bottles are capped in the field prior to transporting them to the ERS laboratory for further processing. Grab samples are collected in containers specific to the required analysis, labeled with a unique lognumber, the station code for the site, the sample date and time, the required analyses, and the sample preservative. A single composite sample or series of composite samples are prepared from the set of samples collected with an automatic sampler. Each composite sample is labeled in the same manner as with the grab samples.

Immediately following collection, processing, and addition of any required preservative, samples are kept in an ice-chest or refrigerator at around 4°C until they are delivered to the contract or OCSL. Maximum allowable holding times for all samples are rigidly impressed upon field staff. Chain-of-custody (CoC) documentation is used to reduce the likelihood of sample contamination or mishandling. The CoC form contains the list of the sample lognumbers, the numbers of bottles per lognumber, the required analyses, and the identities (names, affiliations, and signatures) of all persons handling those samples. A completed and signed chain-of-custody form is transferred to the contract laboratories or sample courier service prior to submission of samples. ERS maintains a duplicate chain of custody policy which provides the contract laboratories with an originally signed chain-of-custody form while a second signed chain of custody with the laboratory or courier service signature is returned and filed.

Field observations, sample dates, and collection times are logged directly into a word-processing program on a desktop computer. The program information is maintained by a database administrative staff member. Entries into the electronic logbook include flow data, storm events, equipment failure, vandalism, and equipment maintenance.

B4 ANALYTICAL METHODS

Measurements completed by the contract laboratories follow standard EPA approved and Standard Methods as described in Standard Methods for the Examination of Water and Wastewater, 20th Edition.

B4.1 Sources

The analytical procedures employed for the Orange County Stormwater Program are in accordance with the accepted standards of the appropriate state and federal regulatory agencies and the environmental industry. The methods listed in **Table B6-1** through **Table B6-6** describe the analytical procedure applied for the determination of each parameter of importance to the water quality programs. Sample detection limits can be found in **Appendix A**.

B4.2 Standard Methods for Analysis of Water and Sediment Samples

Water and sediment samples collected for chemical analysis in the Orange County Stormwater Program follow approved methods provided by USEPA, Standard Methods, or the Code of Federal Regulations as listed;

1. Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WPCF), latest edition, EPA - 600/4-79-020 Methods for Chemical Analysis of Water and Wastes, March 1983, including subsequent amendments.
2. Federal Register, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Part III, Vol. 44, No. 233, Monday, December 3, 1979, including subsequent amendments.
3. Federal Register, Guidelines for Establishing Test Procedures for the Analysis of Pollutants Under the Clean water Act; Final Rule and Interim Final Rule and Proposed Rule. Part VIII, Vol. 49, No. 209, Friday, October 26, 1986, including subsequent amendments.
4. EPA-600/4-82-057 Methods for Chemical Analysis of Municipal and Industrial Wastewater, July, 1982 and subsequent revisions.
5. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, latest edition, Revised method protocols as published under EPA Method Update Rules (MUR).
6. Other procedures established as EPA protocol, and published in the Federal Register.

California Code of Regulations, Title 40 - Protection of Environment, July 1, 1990, Chapter 1, Part 136.3, Table 1B.

Water and sediment samples collected for toxicological analysis in the Orange County Stormwater Program follow approved methods provided by USEPA, Standard Methods, or the Code of Federal Regulations as listed;

1. U.S. EPA. 1991a. *Methods for Aquatic Toxicity Identification Evaluations: Phase I Toxicity Characterization Procedures*, 2nd ed., EPA/600/6-91/003. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Duluth, Minnesota.
2. U.S. EPA, 2002. *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 5th Edition*. EPA-821-R-02-012. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
3. U.S. EPA. 1992. *Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I*, EPA/600/6-91/005F. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Duluth, Minnesota.
4. U.S. EPA. 1994. *Methods for Assessing the Toxicity of Sediment-associated Contaminants with Estuarine and Marine Amphipods*. EPA/600/R-94/025, U.S. Environmental Protection Agency, Office of Research and Development, Narragansett, Rhode Island.
5. U.S. EPA. 1994. *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms*. EPA/600/4-91/002. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio
6. U.S. EPA. 1995. *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, U. S. Environmental Protection Agency, National Exposure Research Laboratory, Cincinnati, Ohio.
7. U.S. EPA 2002. *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, 3rd Edition*.. EPA-821-R-02-014. U.S. Environmental Protection Agency, Office of Water, Washington, DC.
8. U.S. EPA. 1996b. *Marine Toxicity Identification Evaluation (TIE): Phase I Guidance Document*. EPA/600/R-95/054. U.S. Environmental Protection Agency, Environmental Effects Research Laboratory, Narragansett, Rhode Island.
9. U.S. EPA. 2000. *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates, 2nd Edition*. EPA/600/R-99/064. U. S. Environmental Protection Agency, Office of Research and Development, Mid-Continent Ecology Division, Duluth, Minnesota.
10. Other procedures established as EPA protocol and published in the Federal Register.

TABLE B4-1: LABORATORY METHODS OF ANALYSIS; TRACE METALS

Trace metal samples are prepared by digestion in HNO₃.

<u>ANALYTE</u>	<u>STANDARD METHOD</u>	<u>EPA METHOD</u>	<u>METHOD DESCRIPTION</u>
Arsenic	3125 B	EPA 200.8	ICP-Mass Spectrometry
Cadmium	3125 B	EPA 200.8	ICP-Mass Spectrometry
Chromium	3125 B	EPA 200.8	ICP-Mass Spectrometry
Copper	3125 B	EPA 200.8	ICP-Mass Spectrometry
Lead	3125 B	EPA 200.8	ICP-Mass Spectrometry
Nickel	3125 B	EPA 200.8	ICP-Mass Spectrometry
Selenium	3125 B	EPA 200.8	ICP-Mass Spectrometry

Silver	3125 B	EPA 200.8	ICP-Mass Spectrometry
Zinc	3125 B	EPA 200.8	ICP-Mass Spectrometry

TABLE B4-2: LABORATORY METHODS OF ANALYSIS; NUTRIENTS

Nutrient synthetic, duplicate, and split samples are analyzed using the following methods. Synthetic nutrient samples are analyzed only for ammonia, nitrate, total Kjeldahl nitrogen and total phosphate concentration. Seawater and freshwater samples are treated similarly, with the exception of the ammonia and Kjeldahl nitrogen analyses. During the nesslerization of seawater, one milliliter of Rochelle Salts is added to minimize the interferences caused by the cations and anions in the seawater samples.

<u>ANALYTE</u>	<u>STANDARD METHOD</u>	<u>EPA METHOD</u>	<u>DESCRIPTION</u>
Conductivity	2510 B	EPA 120.1	Conductivity
Turbidity	2130 B	EPA 180.1	Nephelometric Method
pH	4500-H B	EPA 150.1	pH Value
Nitrate Nitrogen	4500-NO3 F	EPA 353.2	Automated Cadmium Reduction
Ammonia Nitrogen	-----	EPA 350.1	Colorimetric
Total Kjeldahl Nitrogen	4500-Norg B	EPA 351.3	Macro Kjeldahl Method
Total Phosphate	4500-P E	EPA 365.1	Ascorbic Acid Method
Total Non-Filterable Residue	2540-D	EPA 160.2	Total Non-Filterable Residue Dried @ 103-105 °C
Volatile Solids	2540 E	EPA 160.4	Total Volatile and Fixed Results @ 550 °C

TABLE B4-5: LABORATORY METHODS OF ANALYSIS – BACTERIA

<u>ANALYTE</u>	<u>STANDARD METHOD</u>	<u>DESCRIPTION</u>
Total and Fecal Coliform	9222B	Membrane Filtration
Enterococcus	9230	Membrane Filtration
E. Coli	9221	Membrane Filtration

TABLE B4-4: LABORATORY METHODS OF ANALYSIS; GENERAL MINERAL

The General Mineral analysis is performed on the unaltered sample

<u>ANALYTE</u>	<u>STANDARD METHOD</u>	<u>EPA METHOD</u>	<u>DESCRIPTION</u>
Conductivity	2510 B	EPA 120.1	Conductivity
Turbidity	2130 B	EPA 180.1	Nephelometric Method
pH	4500-H B	EPA 150.1	pH Value
Calcium	3500-Ca D	EPA 215.2	EDTA Titrimetric Method

Magnesium	3500-Mg B	EPA 243.1	Atomic Absorption
Sodium	3500-Na D	-----	Flame Emission Photometry
Potassium	3500-K D	-----	Flame Emission Photometry
Chloride	4500-Cl C	EPA 325.3	Mercuric Nitrate Method
Sulfate	4500-SO4 B	EPA 300.0	Ion Chromatography
Nitrate Nitrogen	4500-NO3 F	EPA 353.2	Automated Cadmium Reduction
Carbonate, as CO3	2320 B	EPA 310.1	Alkalinity
Bicarbonate, as HCO3	2320 B	EPA 310.1	Alkalinity
Fluoride	4500-F	340.2	Electrode Method
Carbon Dioxide, calc.	4500-CO2 D	-----	CO2 by calculation
Hardness	2340 C	EPA 130.2	EDTA Titrimetric Method
Silica	4500-Si D	EPA 370.1	Molybdosilicate Method
Boron	4500-B B	EPA 212.3	Circumin Method
Total Filterable Residue -----	-----	-----	By Addition

TABLE B4-5: LABORATORY METHODS OF ANALYSIS; NON-VOLATILE ORGANICS

<u>ANALYTE</u>	<u>STANDARD METHOD</u>	<u>DESCRIPTION</u>
Organophosphorus pesticides	625/8141	Water/Sediment
Organochlorine pesticides & PCBs (Arochlors and Congeners)	625/8270	Water/Sediment
Pyrethroid pesticides	625/8270	Water/Sediment
Carbamate pesticides	531.1/8270	Water/Sediment

TABLE B4-6: LABORATORY METHODS OF WHOLE EFFLUENT TOXICITY TESTING

<u>BIOASSAY</u>	<u>REFERENCE TOXICANT</u>	<u>DESCRIPTION</u>
Americamysis bahia	Potassium chloride, salinity adjusted	Water
Ceriodaphnia dubia	Potassium chloride, salinity adjusted	Water
Pimephales promelas	Potassium chloride, salinity adjusted	Water

B5 QUALITY CONTROL

B5.1 External Laboratory QA/QC

One of the foremost important standards for data validation for the monitoring programs depends on the quality of the data from each of contract laboratories. The water quality data depends on each of the contract laboratories adhering to a thorough QA/QC program. MWH, Weck, Associated, and OC HCA PHWQL laboratories keep CA-DHS approved QAPP manuals on file at each of the individual locations listed in section A4. Concomitant with

the QAPP manuals, each of the contract laboratories currently retained by OCPW maintains a stringent QA/QC reporting process for all water quality data generated for the monitoring programs. An example of a QC report from a laboratory is shown in **Figure 3**.

B5.2 Standard Materials

The Orange County Stormwater Laboratory uses only analytical or higher-grade chemicals purchased from reputable laboratory supply companies. Trace metals standards are prepared by the QA/QC coordinator by diluting high purity 1000 part per million atomic absorption standards traceable to National Institute of Standards and Technology (NIST) standard reference materials with Type 1 water. The analyst employs high quality micro-pipettes with clean disposable tips and Pyrex Class A volumetric flasks to mix standards. All prepared standards are preserved with ultrapure or analytical grade nitric or sulfuric acid, where appropriate, to attain a final trace metal concentration within 0.2%. The expiration dates of these high purity starting materials are carefully observed.

Synthetic nutrient samples are prepared by the QA/QC coordinator by adding aliquots of prepared stock solutions. Each of these stock solutions are prepared by dissolving 1.000 gram of analytical grade sodium nitrate, ammonium chloride, potassium dihydrogen phosphate, or glycine in 1.000 liter Type 1 water. All stock nutrient stock reagent bottles are stored in a sealed desiccated container at room temperature except for the glycine solution which is refrigerated.

Synthetic rainwater samples are prepared from the nutrient stock solutions and similarly prepared stock solutions of sodium chloride and magnesium sulfate as described in Table **4-3**.

Synthetic general mineral samples are prepared in Type 1 water from high purity reagents as described in Table **4-4**. General Mineral stock solutions are prepared by the QA/QC coordinator by dissolving high purity calcium chloride dihydrate, magnesium sulfate septahydrate, sodium bicarbonate, sodium silicate nonahydrate, potassium fluoride dihydrate, sodium nitrate, potassium chloride, calcium sulfate dihydrate, and boric acid in Type 1 water. The analyst employs high quality Pyrex Class A volumetric pipettes and flasks to perform volumetric transfers in the preparing of the synthetic general mineral samples.

Documentation is kept on all purchased standard materials to enable internal traceability on all prepared standards. All prepared standards are carefully labeled and dated, and documented in the electronic logbook.

B5.3 Method Blank

A method blank is a sample containing no analyte that has been prepared and analyzed using identical methods as the remainder of a given batch. The method blank assesses the presence or absence of contamination associated with field and laboratory methodologies. For example, the method blank for assessing the contamination during the filtering process for dissolved trace metals consists of filtering Type 1 water (>17

megaohm) through a 0.45 micron filter into a 500-ml, I-Chem HDPE bottle, and preserving with ultrapure or reagent grade nitric acid. If the results show contamination each component of the filtering process is tested (Type 1 water, filter, or I-Chem bottle) to isolate the source.

B5.4 Laboratory Control Standard

A Laboratory Control Standard (LCS) is a blank that is spiked with a known amount of analyte and is used to measure the accuracy in the absence of matrix interference. The LCS is prepared at a concentration greater than 5 times the reporting detection limit.

The % LCS recovery is calculated as follows:

$$R = (LC/LT) \times 100$$

where,

R = % LCS recovery

LC = measured LCS concentration ($\mu\text{g/L}$)

LT = theoretical LCS concentration ($\mu\text{g/L}$)

$$= C \times (S/B)$$

C = concentration of standard used to spike LCS ($\mu\text{g/L}$)

S = amount of spike added to LCS

B = total amount of LCS used

B5.5 Matrix Spike

A matrix spike is a sample spiked with a known amount of analyte and is another method of measuring the accuracy of the determination. Unlike the LCS, the matrix spike measures the effects of matrix interferences. The amount of the spike should be 0.5 - 10 times the analyte concentration in the sample. Spike recovery is calculated as follows:

$$R = 100 \times (S-U)/(T-U)$$

where,

R = spike recovery

S = measured concentration of spike ($\mu\text{g/L}$)

U = measured concentration of unspiked sample ($\mu\text{g/L}$)

T = theoretical concentration of spiked sample = X + R ($\mu\text{g/L}$)

X = theoretical concentration of spike = C(A/B)

C = concentration of standard used to spike sample ($\mu\text{g/L}$)

A = amount of spike added to sample

B = total amount of sample used

B5.6 Duplicates and Duplicate Spikes

The relative percent difference (RPD) between duplicates or duplicate spikes is used to measure the precision (reproducibility) of the determination in the actual sample matrix.

The RPD is calculated as follows:

$$RPD = \frac{[R_1 - R_2] \times 100}{R_{av}}$$

where

R_1 and R_2 = measured concentration in duplicates or duplicate spikes ($\mu\text{g/L}$)

R_{av} = average concentration in duplicates or duplicate spikes ($\mu\text{g/L}$)

The sampling programs for the collection of water samples with auto-samplers are developed and adjusted in order to ensure that the data collected are representative of the urban runoff conditions actually present in the field. Standard operating procedures have been developed for all maintenance and cleaning routines performed by field staff. Strict adherence to these procedures will ensure that all water samples will be collected, handled, and processed with the highest level of quality control.

The utilization of split samples and equipment blanks will allow for checks of laboratory precision and possible field contamination. Approximately every twentieth sample will be split into two samples as long as sample volume is adequate. Split samples will be treated as independent samples measurements conducted on both samples as previously described. The split samples will be routinely submitted for analysis to each of the four contract laboratories with each field sample batch submission. In addition, equipment blanks will be submitted on a routine basis to verify sample contamination is not occurring through inadequately cleaned equipment or outside agent. On a preset schedule, a subset of the autosampler inventory (field and laboratory) will be tested in this manner. A sample from the ultrapure water system will also be submitted monthly for nutrient and trace metals analyses. Staff will be responsible for conducting these internal checks and if necessary advise the project manager of quality control problems. All field collection and laboratory analyses will be halted until the source of the problem can be detected and rectified. Data collected by field staff and generated by the contract water quality analysis laboratories will be reviewed by the staff, Unit supervisors, and database administrators. They will also conduct regular staff meetings to review data discrepancies and adherence to quality control directives.

B5.7 Additional Laboratory QC Checks

B5.7.1 Laboratory Supplies and Equipment

All laboratory methods used for the preparation of synthetic samples adhere to a strict protocol. All samples are produced from American Chemical Society certified high purity grade reagents using only Type 1 water. All laboratory and portable field equipment is cleaned using a triple rinse protocol (1. tap, 2. de-ionized, 3. Type 1, three times each). Air quality standards in the QA/QC room are maintained by a HEPA air filtration Unit. All analytical balances are NIST certified and periodically checked for accuracy.

Composite basins and ladles used for processing water quality samples in the monitoring programs are QC checked periodically in the laboratory. Stainless steel composite basins and ladles used for collecting chemistry samples are rinsed with Type 1 water and the collection volume processed identical as a trace metal sample to check for leaching of the metallic material. HDPE and stainless steel compositing equipment are checked for residue contamination due to improper cleaning techniques. Portable peristaltic pumps for sample collection and field processing, including filtration, are rinsed with Type 1 and the collection volume processed identical to chemistry samples.

B5.7.2 Water Purification System

The entire system is monitored daily to insure that only American Society for Testing and Materials (ASTM) Type I water is produced. Type I water is defined in Standard Methods as having no detectable concentration of the element to be analyzed at the detection limit of the analytical method. Dissolved trace metal levels in blanks made with water from the system have confirmed that Type I water, with respect to trace metals, is being produced.

The laboratory water purification system consists of a high purity water filtration Unit supplied by a deionizing system. A warning light on the laboratory deionization tanks indicates when the specific conductance of the deionized water exceeds 1 $\mu\text{mhos/cm}$. The water is also visually inspected for evidence of ion exchange resin particles from the deionizing tanks. If either problem occurs the water purification vendor is contacted to replace the deionization tank. The Type 1 system is similarly checked. The Type 1 system is never supplied by deionized water with conductivity $>1 \mu\text{mhos/cm}$. The internal sensor should be registering ≥ 17 megaohm. If it is below 17 megaohm, the system is producing water of inadequate purity and appropriate maintenance is performed. This maintenance may include changing the system's four cartridges and final filter.

B5.7.3 Air Purification System

The air purification system in the quality assurance room of the laboratory includes an exhaust fan and a separate portable high efficiency particulate air (HEPA) purification Unit. Each Unit is checked periodically for proper operation. The filters of the portable Unit are visually inspected and changed when necessary.

B5.7.4 Pipettes

Mechanical pipettors are periodically checked by weighing volumes of laboratory purified water dispensed by the pipettors on a calibrated Mettler Toledo AG 135 microanalytical balance. Pipettor accuracy can be calculated by comparing the actual and theoretical masses of water given the temperature-compensated density of water.

B5.7.4 Analytical Balances

The analytical and top loading balances are periodically checked for accuracy using NIST certified weights. Each balance is calibrated and serviced twice annually by a certified maintenance technician.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

B6.1 Laboratory and Portable Field Equipment

Field staff have established standard operating procedures for each piece of equipment in use. Autosamplers and laboratory equipment receive regular maintenance based on a combination of manufacturer requirements and the actual amount of equipment use in the field. The internal pump tubing of each autosampler is visually inspected regularly and is replaced as needed. At a minimum, the internal pump tubing is replaced after 50,000 revolutions of the pump (manufacturer's recommendation) or annually, whichever comes first. Autosampler collection bottles are cleaned using phosphate-free soap and a triple rinse protocol (1. tap, 2. de-ionized, 3. Type 1, three times each). The compositing basins (stainless steel and polycarbonate) and ladles (stainless steel and HDPE) are rinsed with tap water and cleaned with non-ionic, non-phosphate, neutral pH laboratory detergent, rinsed with de-ionized and Type 1 water, air dried, and sealed in HDPE plastic bags. Polycarbonate compositing basins and HDPE ladles are rinsed with a 10% aqueous hydrochloric acid solution following tap water rinse and prior to detergent cleansing.

B6.2 Maintenance of Facilities

The County of Orange, Facilities Operations Division, maintains major systems such as air conditioning, heating, telephones, and building security. Laboratory fume hoods are checked periodically for proper operation by the County of Orange Industrial Hygienist.

B6.3 Preventive Maintenance

Each instrument is constantly monitored for signs of decreased performance, and preventative maintenance is conducted regularly by the analyst to reduce the incidence of instrument failure. A summary of common preventative maintenance and frequency of maintenance is given in **Table 6-1**. A logbook to document the preventative maintenance is maintained in the laboratory. Detailed notes are kept on routine and preventative maintenance operations such as instrument calibration, cleaning of pump mechanisms, pump tubing changes, deionized water tank changes, and replacement of filter cartridges for the Type 1 system.

B6.4 Documentation

Two maintenance logbooks are kept in the laboratory. One logbook documents serial numbers, County identification numbers, and all maintenance, routine and otherwise, done on all lab equipment. Each entry in this logbook includes the date, technician, repairs or maintenance performed, and remarks.

A second logbook documents the performance and maintenance of the water and air purification equipment. Any problems, error messages or interruptions in the programs are noted.

When outside service is performed on the water or air filtration equipment, detailed notes are taken on all repairs made by staff. These notes are extremely useful when problems recur or when a technician is unfamiliar with a particular instrument's maintenance history.

Table 6-1: Preventative Maintenance

<u>EQUIPMENT</u>	<u>PARTS VENDOR</u>	<u>TYPICAL REPAIRS</u>	<u>FREQUENCY</u>
Deionization Tanks	Cal Water	1. exchange resin tank	as needed
	516 S. Santa Fe Santa Ana, CA	2. replace filter	as needed
Ultrapure Water System (ASTM type 1 water)	Pall Life Sciences 600 South Wagner Rd Ann Arbor, MI 48103	1. change cartridges 2. check resistivity	As needed daily
Portable (HEPA) Air Filter (Model PA500) Niles, IL 60714	Cole-Parmer 7425 N. Oak Park Dr	1. replace filters	as needed

B6.5 Equipment Malfunction

Each of the major instruments used in the laboratory for the QA/QC is maintained under a commercial service contract as shown in **Table 6-1**. In the event of malfunction, the Quality Assurance Coordinator or Laboratory Manager notifies the vendor and an appointment is made for the prompt repair of the instrument.

B7 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

OCSL equipment including automatic pipettors and analytical balance calibration is maintained by the QA/QC coordinator and the Laboratory Manager. The autopipettors and analytical balances are calibrated based on manufacturer recommendations and accepted laboratory protocol. Calibrated thermometers for bacterial collection programs are supplied by OC HCA PHWQL. Incubation ovens for production of the bacterial QA/QC synthetic samples are monitored weekly with a calibrated thermometer and the results recorded in a maintenance logbook.

Deionized water is produced using a commercially available water purification system from Cal Water and its purity is monitored with an inline light emitting diode, testing samples with the laboratory EC meter on a daily basis and by submitting blanks for analysis on a monthly basis.

The Ultrapure Water System (Type 1 II) is monitored for changes in resistivity each time it is operated. The resistivity readings from the digital readout are noted in a maintenance logbook. Routine and frequent submissions of blanks are used to verify the absence of nutrients and trace metals from the Type 1 water.

B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Glassware, sample bottles, and collection equipment will all be inspected prior to their use. Autosampler bottles will be washed with Aquet (nonionic, neutral pH, phosphate-free soap) laboratory detergent immediately following their use and kept in clean plastic HDPE bags between uses. All laboratory glassware will be washed with Aquet laboratory detergent. The stainless steel and HDPE compositing basins and ladles will also be washed with Aquet and stored in clean HDPE bags. The Polycarbonate compositing basins are acid washed in 10% aqueous hydrochloric acid and triply rinsed with water (1. tap, 2. de-ionized, 3. Type 1, three times each).

All chemical reagents are stored in appropriate chemical storage cabinets in the OCSL QC clean room or in an air tight desiccated container.

B9 NON-DIRECT MEASUREMENTS

Quality assurance data generated by the contract laboratories for this program are restricted to the criteria set forth in the Data Quality Objectives section as defined in section A7.6. Only the data meeting all of the criteria will be used for reporting.

B10 DATA MANAGEMENT

The management of water quality data will be initiated with the use of a chain-of-custody documents and field logs. The chain-of-custody document contains data entries for identification of the sample as well as relevant field observations such as contamination or vandalism. The monitoring specialist is responsible for completing any follow up data entry relevant to the QA/QC samples on an individual basis. A copy of each chain-of-custody document will be kept with the data management Unit. All analytical results are electronically sent to the QA/QC Coordinator, the Unit Supervisors, and the Database Manager following the completion of the analyses and quality control checks. The electronic data files are imported into the electronic database by the database administrator. Data management is also the responsibility of the database administrator. Oversight of the database is performed by the Unit Supervisor.

Currently, all data from OCSPP are submitted to the regulatory agency in Stormwater Monitoring Coalition (SMC) format. To make the data submission SWAMP-compatible, OCSPP has joined the working group administered by

SCCWRP on California Environmental Data Exchange Network (CEDEN), which is a system designed to facilitate integration and sharing of data collected by many different participants.

SECTION C: ASSESSMENT AND OVERSIGHT

C1 ASSESSMENT AND RESPONSE ACTIONS

C1.1 Corrective Action

Out-of-control QC results are documented in the sample database and on laboratory control charts. Documentation consists of the date, analyst, element, type of QC sample, condition requiring corrective action, and action taken. The analyst also informs the Unit Supervisor of the QC problem in writing.

The two types of problematic situations that may occur are quality control and systematic failures. Quality control failures are isolated or random events. Systematic failures are caused by procedural problems and may require intensive investigation to solve.

All corrective actions taken are documented. Unit Supervisors and staff will notify the Program Director of any repetitive discrepancies in sample analyses or issues that are impacted by unacceptable results.

C1.2 Quality Control Failures

When quality control samples exhibit out-of-control characteristics corrective measures are vigorously pursued. Such failures and corrective actions are documented in the logbook by date, analyst initials, description of problematic condition, and action taken.

C1.3 Method Blank

A method blank is considered problematic when a parameter is detected above the RDL. When this occurs the analyst inspects the field equipment maintenance records and laboratory equipment logbooks to identify possible sources of contamination. In the event of failure to identify the contaminate origin, the Unit Supervisor will be notified and conference with the Laboratory Manager.

C1.4 Laboratory Control Standards and Matrix Spikes

If the LCS sample is out-of-control the accuracy of the entire batch is placed into question. The proper corrective action is to reanalyze the complete batch. Similarly, if the relative percent difference of a pair of matrix spike duplicates is outside control limits the precision is suspect and the entire batch must be reanalyzed.

C1.5 Systematic Process Defects

Systematic failures are indicated in various ways including consistently out-of-control QC data, consecutive failures on performance evaluation samples, and the discovery of an improper laboratory practice. In such instances the analyst, the Unit Supervisor, the Data Management Specialist, and other Monitoring Programs staff members will meet to discuss proper corrective actions. These may include changing sampling techniques, cleaning procedures, or equipment. All program personnel are encouraged to participate in improving data quality. Once a corrective measure is implemented it is continuously evaluated for effectiveness.

C1.6 Assessment and Response towards Quality Control Objectives

The relative degree of success in the quality control objectives is determined by the adherence of the contract laboratories to proper quality assurance and quality control protocols. In parallel to these requirements the contract laboratories cannot exceed analytical limits of errors and are subject to penalties for failure to meet QA/QC standards. The limits of allowable errors in Data Quality Objectives are listed in **Table 7-1**. The Quality Assurance and Quality Control data integrity standards that ERS places on the external service vendors comes with a penalty for exceedance of the QA/QC standards.

In case of deviation from true values for known composition samples submitted by the laboratory for accuracy quality control, the QA/QC coordinators or the Program Director notifies the contract laboratory that an error in the analysis may have occurred during the analysis. If the ratio of error to allowable error exceeds 2.0, the contract laboratories are required to reanalyze all the samples in the same sample submission batch. The rerun analyses will be conducted at the sole expense of the contract laboratory. On the second occurrence, within a 60 day period, or excessive error in analysis for the same constituent, the contract laboratory invoices for all individual analyses for that constituent and group analyses containing those individual analyses are subject to the following penalties.

Average of Ratios of Errors to Allowable Errors		% Discount on Cost of Analysis
1.0 - 1.1		10
1.1 - 1.2		20
1.2 – 1.3		30
1.3 – 1.4		40
1.4 – 1.5		50

After the second occurrence, within 60 days, a formal meeting between ERS and the contract laboratory is required to identify the source(s) of the problems or further action to be taken. Within 30 days subsequent to the meeting, a certified Water Quality Control Check Sample from a quality assurance vendor will be submitted to the contract laboratory. Failure to produce a result of less than a ratio of 1.4 shall be cause for cancellation of the contract.

C2 REPORTS TO MANAGEMENT

C2.1 Internal Audits

Internal audits will be performed periodically by the Quality Assurance Coordinators under the direction of the Unit Supervisor. Internal audits will address the following:

- Results of internal quality control samples including blanks, matrix spikes, LCS, duplicates, spike duplicates.
- An evaluation of QC data in relation to data quality objectives (Section 4.2) identifying deficiencies and changes in MDLs and RDLs.
- An outline of corrective actions taken to mitigate deficiencies.
- A summary of equipment maintenance, including routine maintenance by RDMD staff and more detailed procedures and repairs by the service contractor.
- An itemized account and description of financial expenditures for equipment, chemicals, and repairs.
- Safety performance and general appearance of the Orange County Stormwater Laboratory (reviewed by division and unit safety officers).

The Orange County Stormwater Program reports environmental results to Region 9 of the EPA, the Santa Ana and San Diego RWQCBs, and the NPDES co-permittee cities. In addition, environmental consultants, environmental activist groups, and concerned private citizens occasionally request portions of the environmental database. A series of Adobe Acrobat files representing the Annual Program Effectiveness Assessment Report are produced each year and made available on the County's website (www.ocwatersheds.com). **Figure 4** is given as an example of a data spreadsheet from the annual report.

SECTION D: DATA VALIDATION AND USABILITY

The QA/QC coordinator and database administrators review each quality control parameter to determine whether it is within control limits. The nutrient, trace metal, general mineral, rain, and bacterial analyses have defined control limits for LCS, matrix spike (MS), and matrix spike duplicate (MSD), and blank sample QC parameters. For a batch to be considered in control, the QA/QC results provided by the contract vendor must pass quality assurance standards, and the internal QA/QC samples must demonstrate adequate quality control. If the batch is out-of-control, corrective action is taken. In addition, an parameter detected in a method blank above the MDL requires the performance of corrective action. Specific corrective actions are outlined in Section C1.

D1 DATA REVIEW, VALIDATION, AND VERIFICATION

The specifics of data review, validation, and verification are detailed in the Quality Control section B and C of this document. Project personnel will review the quality control data from the duplicates, split samples, and equipment blanks as described in that section to maintain quality assurance and control of the data collected.

D2 VERIFICATION AND VALIDATION METHODS

Data collected in the field will be validated and verified by the field staff, QA/QC coordinators, database administrators, and unit supervisors utilizing Chain of Custody Sheets, sample logsheets, field sheets, and analytical result summaries from sample batch submissions. The contract laboratories QA/QC reports along with Chain of Custody procedures and internal Quality Control Programs accompanies the review process. Validation and verification of the contract laboratory quality control data is the responsibility of the Laboratory Contract Manager.

Field audits are made by the unit Supervisor or referred to the Chief of Monitoring Programs. Field staff are periodically evaluated to ensure that proper sampling and collection methods are being adhered including the appropriate cleaning methods for equipment. Staff are evaluated on a person-to-person to determine whether protocols are being followed as intended. Supervisors question and inspect staff during the process and if the results are satisfactory the staff member gets a happy face sticker on their field sheets for the day. Individual staff in need of additional training or not following established procedures get a frowny face sticker on their field sheets.

The unit supervisor is responsible for oversight of data collection and the initial analysis of the raw data obtained from the individual monitoring programs. His responsibilities also include the generation of rough drafts of annual reports to the appropriate Regional Water Quality Control Boards with the aid of the Database Administrator, the

Laboratory Contract Administrator, the Laboratory QA/QC Coordinator, the Laboratory Manager, and external consultants.

D3 RECONCILIATION WITH DATA QUALITY OBJECTIVES

Quality assurance and quality control data collected during this project will provide a means of measuring the integrity of the water quality data generated for the numerous diverse monitoring programs. The interpretation of these data may have far reaching consequences such as imposition of TMDLs or the establishment of new monitoring and reporting requirements in addition to or aside from other administrative actions by the regulatory agencies.

D3.1 Annual QA/QC Report

The Orange County Stormwater Program produces an annual Quality Assurance Report for inclusion as an appendix in reports to the Santa Ana and San Diego Regional Water Quality Control Boards. These reports will contain the following information:

- Summary of all QC samples analyzed including blanks, LCS, matrix spikes, and duplicates. This summary will detail percent recoveries, relative percent differences, method detection limits, and other pertinent information.
- Updated control limits and performance of QC samples with respect to control limits.
- Quality control failures and subsequent corrective actions.
- Changes and updates in procedures, methodologies, equipment, and personnel.

Figure 1: Example of Chain of Custody Form

CHAIN OF CUSTODY

Entry Set # 30 Page 1 of 1

CONTRACT LAB: MWH
Lab PA # N 3 000 003 880
CONTACT: Bruce Moore (714) 567 6373
PNIR # _____

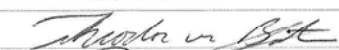
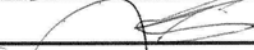

Resources Development and Management Division
1750 S. Douglass Road
Anaheim, CA 92806
Phone (714) 567-6363 FAX (714) 567-6220

DATE 2/10/2004
County Seals Intact Yes ___ No ___
Sample Ambient ___ Cooled ___ Frozen ___
Handling _____

SAMPLE#	Date&Time	#Containers	Matrix	Description	Analyses Required	Remarks	Project #
WR68297	09.18 2/10/2004	5	FW	GS	NUT OPP PO40		EF03530

/21958

TEMP 2°C
REG LOCK

	SIGNATURE	PRINT NAME	ORGANIZATION	DATE (m/d/yyyy)	TIME (hh:mm)
Relinquished by		Theodore von Bitner	OC/RDMD	2/10/04	11:37
Received by		S. MARITAN	Area	2/10/04	14:00
Relinquished by		M. JENSEN	M.W.H.	2-10-4	1630
Received by					
Relinquished by					
Received by					

SCANNED

Figure 2: Internal QA/QC Program Check Sample Preparation Logsheet

Date Prepared	Category	Analyte Volume										Final Volume
/ /	NUT	Prep. No.	NaNO ₃ ml	NH ₄ Cl ml	Glycine ml	KH ₂ PO ₄ ml	TOC	DOC	Batch ID	NaCl	g	ml
LogNumber		Prep. No.	Ag	Cd	Cr	Cu	Ni	Pb	Zn	Batch ID	NaCl	g
WR			µL	µL	µL	µL	µL	µL	µL	WR		ml
ES	TRACE	Matrix	As	Se	Hg	Be	Sb	Tl	Comment:			
Preparer	GM	Prep. No.	CaCl ₂ ml	MgSO ₄ ml	Na ₂ SiO ₃ ml	KF ml	NaNO ₃ ml	KCl ml	H ₃ BO ₃ ml			
	RAIN	Prep. No.	NaNO ₃ ml	NH ₄ Cl ml	Glycine ml	KH ₂ PO ₄ ml	MgSO ₄ ml	Zn ml	Pb ml			
	OPP	Manufacturer:				Lot No.	Aliquot Volume		Batch ID			
	MISC	AnalysisCode	Ready - to - Use (Y / N)		Manufacturer:		Lot No.	Aliquot Volume				
H ₂ O ID:	SED	AnalysisCode	Ready - to - Use (Y / N)		Manufacturer:		Lot No.	LogNumber				
									WR			
Date Prepared	Category	Analyte Volume										Final Volume
/ /	NUT	Prep. No.	NaNO ₃ ml	NH ₄ Cl ml	Glycine ml	KH ₂ PO ₄ ml	TOC	DOC	Batch ID	NaCl	g	ml
LogNumber		Prep. No.	Ag	Cd	Cr	Cu	Ni	Pb	Zn	Batch ID	NaCl	g
WR			µL	µL	µL	µL	µL	µL	µL	WR		ml
ES	TRACE	Matrix	As	Se	Hg	Be	Sb	Tl	Comment:			
Preparer	GM	Prep. No.	CaCl ₂ ml	MgSO ₄ ml	Na ₂ SiO ₃ ml	KF ml	NaNO ₃ ml	KCl ml	H ₃ BO ₃ ml			
	RAIN	Prep. No.	NaNO ₃ ml	NH ₄ Cl ml	Glycine ml	KH ₂ PO ₄ ml	MgSO ₄ ml	Zn ml	Pb ml			
	OPP	Manufacturer:				Lot No.	Aliquot Volume		Batch ID			
	MISC	AnalysisCode	Ready - to - Use (Y / N)		Manufacturer:		Lot No.	Aliquot Volume				
H ₂ O ID:	SED	AnalysisCode	Ready - to - Use (Y / N)		Manufacturer:		Lot No.	LogNumber				
									WR			
Date Prepared	Category	Analyte Volume										Final Volume
/ /	NUT	Prep. No.	NaNO ₃ ml	NH ₄ Cl ml	Glycine ml	KH ₂ PO ₄ ml	TOC	DOC	Batch ID	NaCl	g	ml
LogNumber		Prep. No.	Ag	Cd	Cr	Cu	Ni	Pb	Zn	Batch ID	NaCl	g
WR			µL	µL	µL	µL	µL	µL	µL	WR		ml
ES	TRACE	Matrix	As	Se	Hg	Be	Sb	Tl	Comment:			
Preparer	GM	Prep. No.	CaCl ₂ ml	MgSO ₄ ml	Na ₂ SiO ₃ ml	KF ml	NaNO ₃ ml	KCl ml	H ₃ BO ₃ ml			
	RAIN	Prep. No.	NaNO ₃ ml	NH ₄ Cl ml	Glycine ml	KH ₂ PO ₄ ml	MgSO ₄ ml	Zn ml	Pb ml			
	OPP	Manufacturer:				Lot No.	Aliquot Volume		Batch ID			
	MISC	AnalysisCode	Ready - to - Use (Y / N)		Manufacturer:		Lot No.	Aliquot Volume				
H ₂ O ID:	SED	AnalysisCode	Ready - to - Use (Y / N)		Manufacturer:		Lot No.	LogNumber				
									WR			

APPENDIX A: Reporting Detection Limits.

Aqueous Samples	
Na, Mg, K,Ca	1.0 mg/L
SO ₄ , Cl, HCO ₃ , CO ₃	1.0 mg/L
SO ₄ in Rainwater	0.5 mg/L
F	0.1 mg/L
B	0.1 mg/L
Nitrite + Nitrate as NO ₃	0.4 mg/L
NH ₃ as N	0.1 mg/L
TKN	0.2 mg/L
Total Phosphorus as PO ₄	0.2 mg/L
SiO ₂	0.5 mg/L
Total Non-filterable Residue	5.0 mg/L
Volatile Non-filterable Residue	5.0 mg/L
Total Filterable Residue	5.0 mg/L
Ag, Cd, Cr, Cu, Ni, Pb, Sb in freshwater	0.5 ug/L
As, Se, in freshwater	0.4 ug/L
Tl, in freshwater	0.2 ug/L
Hg in freshwater	0.1 ug/L
Zn in freshwater	2 ug/L
Fe, Mn in freshwater	5 ug/L
Ag, As, Be, Cd, Cr, Cu, Fe, Ni, Pb, Se, Sb, Tl, Zn, in seawater	0.05 ug/L
Hg in seawater	0.01 ug/L
Oil & Grease	5 mg/L
MBAS	0.1 mg/L
Organochlorine Pesticides (except Toxaphene)	2 ng/L
Toxaphene	20 ng/L
PCB Congeners	2 ng/L
PCB Arochlors	20 ng/L
Organophosphate Pesticides	5 ng/L
Carbaryl in freshwater	2 ug/L
Pyrethroid Pesticides	5 ng/L
Sediment Samples (dry/ wt)	
Organochlorine Pesticides (except Toxaphene)	2 ug/kg
Toxaphene	20 ug/kg
PCB Congeners	2 ug/kg
PCBs (arochlors)	20 ug/kg
Pyrethroid Pesticides	5 ug/kg
PAHs	2 ug/kg
Cadmium	0.05 mg/kg
Copper	0.05 mg/kg
Chromium (total)	0.05 mg/kg
Lead	0.05 mg/kg
Mercury	0.05 mg/kg
Nickel	0.05 mg/kg
Selenium	0.05 mg/kg
Silver	0.05 mg/kg
Zinc	0.05 mg/kg

APPENDIX B: Target Analyte Preparation Methodologies.

The criteria for the preparation of synthetic solutions are defined in this section. The target analyte preparation methodologies are for nutrients (freshwater and saltwater), trace metals (freshwater and saltwater), general minerals, and rainwater. The quality control SOP bacteria (total and fecal Coliforms) QA/QC sample preparation is available from Environmental Resource Associates, Arvada CO, 80002 (1-800-372-0122).

<u>Chemical Name</u>	<u>Chemical Formula</u>	<u>Molecular Weight (g/mol)</u>
Sodium Nitrate	NaNO ₃	85.0
Ammonium Chloride	NH ₄ Cl	53.5
Glycine	C ₂ H ₅ NO ₂	75.0
Potassium Dihydrogenphosphate	KH ₂ PO ₄	136.1
Sodium Chloride	NaCl	58.5
Magnesium Sulfate Septa-hydrate	MgSO ₄ .7H ₂ O	246.5
Calcium Chloride Dihydrate	CaCl ₂ .2H ₂ O	147.0
Sodium Bicarbonate	NaHCO ₃	84.0
Sodium Silicate Nona-hydrate	Na ₂ SiO ₃ .9H ₂ O	284.2
Potassium Fluoride Dihydrate	KF.2H ₂ O	68.0
Potassium Chloride	KCl	34.6
Calcium Sulfate Dihydrate	CaSO ₄ .2H ₂ O	172.2
Boric Acid	H ₃ BO ₃	61.8
Arsenic	As	74.9
Cadmium	Cd	112.4
Chromium	Cr	51.9
Copper	Cu	63.5
Lead	Pb	207.2
Nickel	Ni	58.7
Selenium	Se	78.9
Silver	Ag	107.8
Zinc	Zn	65.38

NUTRIENTS

Freshwater

1. To 1.0 L Type 1 water add aliquots of NaNO₃, NH₄Cl, C₂H₅NO₂, KH₂PO₄ stock solutions and 2.0 g NaCl, mix thoroughly and dilute to 2.0 L final volume.
2. Transfer portion of synthetic solution into a 1.0 L HDPE plastic bottle and store at 4 °C.
3. Transfer portion of synthetic solution into a 500 mL HDPE plastic sample bottle, preserved with 3-4 drops concentrated sulfuric acid and store at 4 °C.

Saltwater

1. To 1.0 L Type 1 water add aliquots of NaNO₃, NH₄Cl, C₂H₅NO₂, KH₂PO₄ stock solutions and 60.0 g NaCl, mix thoroughly and dilute to 2.0 L final volume.
2. Transfer portion of synthetic solution into a 1.0 L HDPE plastic bottle and store at 4 °C.
3. Transfer portion of synthetic solution into a 500 mL HDPE plastic sample bottle, preserved with 3-4 drops concentrated sulfuric acid and store at 4 °C.

Microsoft Excel is used to calculate the volumes of the stock solution aliquots needed to create synthetic nutrient samples. Presently nine (9) different freshwater and six (6) different saltwater combinations have been created on separate Excel worksheets for the nutrient QA/QC program.

RAIN

1. To 1.0 L Type 1 water add aliquots of NaNO_3 , NH_4Cl , $\text{C}_2\text{H}_5\text{NO}_2$, KH_2PO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and NaCl , mix thoroughly and dilute to 2.0 L final volume.
2. To 500 mL of Type 1 water add aliquots of Pb and Zn NIST certified atomic absorption standards and dilute to 1.0 L final volume.
3. Transfer portion of synthetic solution containing NaNO_3 , NH_4Cl , $\text{C}_2\text{H}_5\text{NO}_2$, KH_2PO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and NaCl into a 1.0 L HDPE plastic bottle and store at 4 °C.
4. Transfer portion of synthetic solution containing NaNO_3 , NH_4Cl , $\text{C}_2\text{H}_5\text{NO}_2$, KH_2PO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and NaCl into a 500 mL HDPE plastic sample bottle, preserved with 3-4 drops concentrated sulfuric acid and store at 4 °C.
5. Transfer portion of synthetic solution containing Pb and Zn into a 500 mL HDPE plastic sample bottle, preserved with 1.0 mL concentrated nitric acid and store at 4 °C.

As with the synthetic nutrient samples Excel is used to create synthetic rainwater samples of varying constituent concentrations.

GENERAL MINERAL

1. To 1.0 L Type 1 water add aliquots of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, NaHCO_3 , $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, $\text{KF} \cdot 2\text{H}_2\text{O}$, NaNO_3 , KCl , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and H_3BO_3 stock solutions Mix thoroughly and dilute to 2.0 L final volume.

Four (4) different combinations have been created in Excel to avoid repetitive analysis of identical sample concentrations by the contract laboratories.

TRACE METALS

All trace metal synthetic QA/QC samples are made from 1.0 g/L (1000 ppm) NIST certified atomic absorption standards.

Freshwater

1. To 500 mL Type 1 water add a given aliquot of Cd, Cr, Cu, Pb, Ni, Ag, Zn, As, Se and 1.0 g analytical grade NaCl , stir well. Dilute final volume to 1.0 L with Type 1 water.
2. Transfer portion of synthetic solution into a 500 mL HDPE plastic sample bottle, preserved with 1.0 mL concentrated nitric acid and store at 4 °C.
3. Filter a 500 mL aliquot of the synthetic solution using a ground water filter. Pour filtered synthetic solution into a 500 mL HDPE plastic sample bottle, preserved with 1.0 mL concentrated nitric acid and store at 4 °C.

Saltwater

1. To 500 mL of Type 1 water add microliter aliquots of Cd, Cr, Cu, Pb, Ni, Ag, Zn, As, Se and 30.0 g of analytical grade NaCl, stir well. Dilute final volume to 1.0 L with Type 1 water.
2. Pour synthetic solution into a 500 mL HDPE plastic sample bottle, preserved with 1.0 mL concentrated nitric acid and store at 4 °C.
3. Filter a 500 mL aliquot of the synthetic solution using a ground water filter. Pour filtered synthetic solution into 500 mL HDPE plastic sample bottle, preserved with 1.0 mL concentrated nitric acid and store at 4 °C.

Six (6) different freshwater and six (6) different saltwater combinations are used to avoid repetitive analysis of identical sample concentrations by the contract laboratories.

Table A7-4: Measurement Quality Objectives* - Field Measurements**

Water Quality Parameter	Recommended Device	Units	Resolution	Reporting Limit	“Electronic Specs” Accuracy**
Depth	Stadia Rod/Staff Gauge	m	0.01	0.02	n/a
Dissolved Oxygen	Polarographic or Luminescence Quenching	mg/L	0.1	0.2	± 0.2
pH	Electrode	None	0.1	n/a	± 0.2
Salinity	Refractometer or Conductivity Cell	‰	2	2	± 2
Specific Conductivity	Conductivity Cell	µS/cm	1	2	± 2
Temperature	Thermistor or Bulb	°C	0.1 or 0.5	n/a	± 0.1
Total Chlorophyll	Optical Fluorescence Chlorophyll Probe	µg/L	0.1	n/a	n/a
Turbidity	Portable Turbidimeter or Optical Probe	NTU	1	5	± 1
Velocity	Flow Meter	ft/s	0.05	0.1	Follow manufacturer's instructions

* Unless method specifies more stringent requirements

** This table may not include all field analyses. Please refer to method or manufacturer instructions for guidance

Table A7-4: Measurement Quality Objectives* - Conventional Analytes in Water

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 10 analytical runs	80-120% recovery
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<RL for target analyte
Reference Material	Per 20 samples or per analytical batch, whichever is more frequent	80-120% recovery
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	80-120% recovery
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent (chlorophyll: n/a)	80-120% recovery RPD<25% for duplicates
Laboratory Duplicate	Per 20 samples or per analytical batch, whichever is more frequent (chlorophyll: per method)	RPD<25% (n/a if native concentration of either sample<RL)
Internal Standard	Accompanying every analytical run as method appropriate	Per method
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	RPD<25% (n/a if native concentration of either sample<RL)
Field Blank, Travel Blank, Equipment Blank	Per method	<RL for target analyte

*Unless method specifies more stringent requirements

Table A7-4: Measurement Quality Objectives* – Conventional Analytes in Water – Solids

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<RL for target analyte
Laboratory Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	RPD<25% (n/a if native concentration of either sample<RL)
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	RPD<25% (n/a if native concentration of either sample<RL)
Field Blank, Equipment Blank	Per method	<RL for target analyte

*Unless method specifies more stringent requirements

Table A7-4: Measurement Quality Objectives* – Conventional Analytes in Water - Pathogens

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration	Check temperatures in incubators twice daily with a minimum of 4 hours between each reading	Per analytical method or manufacturer's specifications
Filter Sterility Check	Perform one filter sterility check each day samples are analyzed	No growth on filter
Laboratory Blank	Per batch of bottles or reagents	No growth on filter
Filtration Blank	Per 20 samples or per analytical batch, whichever is more frequent	No growth on filter
Reference Material	Per 20 samples or per analytical batch, whichever is more frequent	80-120% recovery
Positive Control	Per 20 samples or per analytical batch, whichever is more frequent	80-120% recovery
Negative Control	Per 20 samples or per analytical batch, whichever is more frequent	No growth on filter
Laboratory Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	RPD<25% (n/a if native concentration of either sample<RL)
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count (coliforms: one per 25 tube dilution tests)	RPD<25% (n/a if native concentration of either sample<RL; coliforms: within 95% confidence interval as defined by IDEXX Laboratories)
Field Blank, Travel Blank, Equipment Blank	Per method	Blanks<RL for target analyte

*Unless method specifies more stringent requirements

Table A7-4: Measurement Quality Objectives* - Conventional Analytes in Sediments

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 10 analytical runs (as applicable)	80-120% recovery
Laboratory Blank	TOC only: one per analytical batch (n/a for others)	<RL or <30% of lowest sample
Reference Material	TOC only: one per 20 samples or per analytical batch, whichever is more frequent (n/a for others)	80-120% recovery
Matrix Spike	n/a	n/a
Matrix Spike Duplicate	n/a	n/a
Laboratory Duplicate	One per analytical batch	RPD<25% (n/a if native concentration of either sample<RL)
Surrogate or Internal Standard	n/a	n/a
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	RPD<25% (n/a if native concentration of either sample<RL)
Field Blank, Travel Blank, Equipment Blank	Per method	<RL or <30% of lowest sample

*Unless method specifies more stringent requirements

Table A7-4: Measurement Quality Objectives* – Inorganic Analytes in Water, Sediment, and Tissue

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 10 analytical runs	80-120% recovery
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<RL for target analyte
Reference Material	Per 20 samples or per analytical batch, whichever is more frequent	75-125% recovery (70-130% for MMHg)
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	75-125% recovery (70-130% for MMHg)
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	75-125% recovery (70-130% for MMHg); RPD<25%
Laboratory Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	RPD<25% (n/a if native concentration of either sample<RL)
Internal Standard	Accompanying every analytical run when method appropriate	60-125% recovery
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	RPD<25% (n/a if native concentration of either sample<RL), unless otherwise specified by method
Field Blank, Equipment Blank	Per method	Blanks<RL for target analyte

*Unless method specifies more stringent requirements

Table A7-4: Measurement Quality Objectives* – Volatile Organic Compounds in Water and Sediment

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 12 hours	RF for SPCCs same as initial calibration; RF of CCVs must be within 20% of initial calibration
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<RL for target analyte
Reference Material	Method Validation: as many as required to assess accuracy and precision of method before routine analysis of samples; Routine Accuracy Assessment: per 20 samples or per analytical batch (preferably blind)	70-130% recovery if certified; otherwise 50-150% recovery
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	50-150% recovery, or based on 3x the standard deviation of laboratory's actual method recoveries
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	RPD<25%
Laboratory Duplicate	Per method	Per method
Surrogate or Internal Standard	Per method	Per method
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	Per method
Field Blank, Travel Blank, Equipment Blank	Per method	<RL for target analyte

*Unless method specifies more stringent requirements

Table A7-4: Measurement Quality Objectives* – Semi-Volatile Organic Compounds in Water and Sediment

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 12 h	RF for SPCCs same as initial calibration; RF of CCVs must be within 20% of initial calibration
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<RL for target analyte
Reference Material	Method Validation: as many as required to assess accuracy and precision of method before routine analysis of samples; Routine Accuracy Assessment: per 20 samples or per analytical batch (preferably blind)	70-130% recovery if certified; otherwise, 50-150% recovery
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	50-150% recovery, or based on 3x the standard deviation of laboratory's actual method recoveries
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	RPD<25%
Laboratory Duplicate	Per method	Per method
Surrogate or Internal Standard	Per method	Per method
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	Per method
Field Blank, Travel Blank, Equipment Blank	Per method	<RL for target analyte

*Unless method specifies more stringent requirements

Table A7-4: Measurement Quality Objectives* – Synthetic Organic Compounds in Water, Sediment and Tissue

Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications
Continuing Calibration Verification	Per 10 analytical runs	Water: 85-115% recovery Sediment: 85-115% recovery Tissue: 75-125%
Laboratory Blank	Per 20 samples or per analytical batch, whichever is more frequent	<RL for target analytes
Reference Material	Method Validation: as many as required to assess accuracy and precision of method before routine analysis of samples; Routine Accuracy Assessment: per 20 samples or per analytical batch (preferably blind)	70-130% recovery if certified; otherwise, 50-150% recovery
Matrix Spike	Per 20 samples or per analytical batch, whichever is more frequent	50-150% recovery, or based on 3x the standard deviation of laboratory's actual method recoveries
Matrix Spike Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	RPD<25%
Laboratory Duplicate	Per method	Water: RPD<25% (n/a if native concentration of either sample<RL) Sediment: Per method Tissue: Per method
Surrogate or Internal Standard	Per method	Per method
Field Quality Control	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	Per method
Field Blank, Travel Blank, Equipment Blank	Per method	<RL for target analytes

* Unless method specifies more stringent requirements. ELISA results must be assessed against kit requirements

Table A7-4: Measurement Quality Objectives* - Toxicity Testing (General)

Negative Controls	Frequency of Analysis	Control Limits
Laboratory Control Water	Laboratory Control Water consistent with Section 7 of the appropriate EPA method must be tested with each analytical batch.	Laboratory Control Water must meet all test acceptability criteria (Please refer to Section 7 of the EPA manuals) for the species of interest.
Conductivity Control Water	A conductivity control must be tested with each analytical batch when the conductivity of any freshwater ambient sample approaches the species' tolerance for conductivity per method.	Follow EPA guidance on interpreting data.
Additional Control Water	Additional method blanks are required whenever manipulations are performed on one or more of the ambient samples within each analytical batch (e.g. pH adjustments, continuous aeration, etc.).	No statistical difference between the laboratory control water and each additional control water within an analytical batch.
Sediment Control	Sediment Control consistent with those described in Section 7 of the EPA manual must be tested with each analytical batch of sediment toxicity tests.	Sediment Control must meet all data acceptability criteria (Please refer to Section 7 of the EPA manuals) for the species of interest.
Positive Controls	Frequency of Analysis	Control Limits
Reference Toxicant Tests	Reference Toxicant Tests must be conducted monthly for species that are raised within a laboratory. Reference Toxicant Test must be conducted per analytical batch for species from commercial supplier settings. Reference Toxicant Tests must be conducted concurrently for test species or broodstocks that are field collected.	Last plotted data point must be within 2 SD of the cumulative mean (n=20). (Reference toxicant tests that fall outside of recommended control chart limits are evaluated to determine the validity of associated effluent and receiving water tests. An out of control reference toxicant test result does not necessarily invalidate associated test results. More frequent and/or concurrent reference toxicant testing may be advantageous if recent problems have been identified in testing.)
Field Quality Control	Frequency of Analysis	Control Limits
Field Duplicate	5% of total project sample count	According to method
Field Blanks	Per method or project requirements	No statistical difference between the laboratory control water (or sediment control) and the field blank within an analytical batch
Equipment Blanks	Per method or project requirements	No statistical difference between the Laboratory Control Water and the Equipment Blank within an analytical batch

*Unless method specifies more stringent requirements.

The measurement quality objectives for water quality parameters (pH, dissolved oxygen, conductivity, temperature, unionized ammonia, salinity, alkalinity and hardness) are detailed in the Field Measurement and Conventional Analytes tables of this Appendix.

In special cases where the criteria listed in the following tables cannot be met, EPA minimum criteria may be followed. The affected data should be qualified accordingly.

Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

Deviations from the summary of recommended test conditions must be evaluated on a project specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result depending on the degree of the departure and the objective of the test. The reviewer should consider the degree of the deviation and the potential or observed impact of the deviation on the test result before rejecting or accepting a test result is valid. For example, if dissolved oxygen is measured below 4.0 mg/L in one test chamber, the reviewer should consider whether any observed mortality in that test chamber corresponded with the drop in dissolved oxygen.

Table A7-4: Measurement Quality Objectives - 7-Day *Pimephales promelas* Survival and Growth Toxicity Tests

Method Recommendation	
EPA/821/R-02/013 (Test Method 1000.0) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	80% or greater survival in controls and an average dry weight per surviving organism in control chambers equals or exceeds 0.25 mg
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static renewal (required)
Age at Test Initiation	Newly-hatched larvae <24hoursold. If shipped, <48hours old with a 24-hour age range
Replication at Test Initiation	4 (minimum)
Organisms/Replicate	10 (minimum)
Food Source	Newly-hatched <i>Artemia</i> nauplii (<24hoursold)
Renewal Frequency	Daily
Test Duration	7 days
Endpoints	Survival and biomass
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	25 ± 1.0 °C (+/- 3 °C required)
Light Intensity	10 – 20 µE/m ² /s or 50 – 100 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	>500 mL or per method specific requirements
Replicate Volume	>250 mL or per method specific requirements
Feeding Regime	< 2 times per day
Laboratory Control Water	Moderately hard water prepared in accordance with EPA protocols
Minimum Sample Volume	7 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<30% MSD If the percent minimum significant difference (PMSD) measured for the test exceeds the upper criterion and toxicity is found at the permitted receiving water concentration (RWC) based upon the value of the effect concentration estimate (NOEC or LOEC), then the test shall be accepted, unless other test review steps raise serious doubts about its validity. If toxicity is not found at the permitted RWC based upon the value of the effect concentration estimate (NOEC or LOEC) and the PMSD measured for the test exceeds the upper PMSD bound, then the test shall not be accepted, and a new test must be conducted promptly on a newly collected sample.
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, SC, pH, and temperature measurement per sample and per dilution
Initial Unionized Ammonia	One measurement per sample (recommended)
Initial Hardness and Alkalinity	One measurement per sample
Daily Water Chemistry	One DO and one pH measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement and per sample and per dilution (one DO per renewal)
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.6 mg/L
Initial pH Range	6.0 - 9.0
Conductivity Controls	Per method - recommend including appropriate controls when sample conductivities are below 100 or above 2500 µS/cm
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Conductivity Tolerance	<3000 µS/cm
Relevant Media	Water column
Sample Container Type	Amber glass or plastic (per method)
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	<48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - Chronic *Ceriodaphnia dubia* Toxicity Tests

Method Recommendation	
EPA/821/R-02/013 (Test Method 1002.0) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	80% or greater survival of all control organisms and an average of 15 or more young per surviving female. 60% of the surviving control females must produce three broods.
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static renewal (required)
Age at Test Initiation	<24 hours old and all released within an 8-h period
Replication at Test Initiation	>10
Organisms/Replicate	One (assigned using blocking by known parentage)
Food Source	YCT and <i>Selenastrum</i> or comparable food
Renewal Frequency	Daily
Test Duration	<8 days
Endpoints	Survival and reproduction
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	25 ± 1.5 °C (+/- 3 °C required)
Light Intensity	10 – 20 µE/m ² /s OR 50 – 100 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	20 - 40 mL
Replicate Volume	>15 mL
Feeding Regime	Daily
Laboratory Control Water	Moderately hard water prepared in accordance with EPA protocols
Minimum Sample Volume	2 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<47% MSD If the percent minimum significant difference (PMSD) measured for the test exceeds the upper criterion and toxicity is found at the permitted receiving water concentration (RWC) based upon the value of the effect concentration estimate (NOEC or LOEC), then the test shall be accepted, unless other test review steps raise serious doubts about its validity. If toxicity is not found at the permitted RWC based upon the value of the effect concentration estimate (NOEC or LOEC) and the PMSD measured for the test exceeds the upper PMSD bound, then the test shall not be accepted, and a new test must be conducted promptly on a newly collected sample.
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, SC, pH, and temperature measurement per sample and per dilution
Initial Unionized Ammonia	One measurement per sample
Initial Hardness and Alkalinity	One measurement per sample
Daily Water Chemistry	Two DO , one pH and one temperature per 24-h period in one sample per concentration and in the control
Final Water Chemistry	One DO, pH, and temperature measurement per sample and per dilution (One DO per renewal)
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.6 mg/L
Initial pH Range	6.0 - 9.0
Conductivity Controls	Include appropriate controls when sample conductivities are <100 or >2000 µS/cm
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Conductivity Tolerance	2500 µS/cm
Relevant Media	Water column
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	<48 hours@ 0 - 6 °C; dark

Table A7-4: Measurement Quality Objectives - 96-Hour (48- and 24-Hour) *Ceriodaphnia dubia* Toxicity Tests

Method Recommendation	
EPA/821/R-02/012 (Test Method 2002.0) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	>90% survival in controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static non-renewal or static renewal
Age at Test Initiation	<24hours
Replication at Test Initiation	>4
Organisms/Replicate	>5
Food Source	YCT and <i>Selenastrum</i> or comparable food
Renewal Frequency	Daily (unless otherwise specified by method)
Test Duration	96hours(48hoursor 24hoursoptional)
Endpoints	Survival
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	25 ± 1 °C (+/- 3 °C required)
Light Intensity	10 – 20 µE/m ² /s OR 50 – 100 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	20 - 40 mL
Replicate Volume	>15 mL
Feeding Regime	Feed while holding prior to test and 2hoursprior to test solution renewal
Laboratory Control Water	Moderately hard water prepared in accordance with EPA protocols
Minimum Sample Volume	1 L
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	No MSD available
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, SC, pH, and temperature measurement per sample and per dilution
Initial Unionized Ammonia	One measurement per sample
Initial Hardness and Alkalinity	One measurement per sample
Daily Water Chemistry	One DO and one temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample and per dilution (One DO per renewal)
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.6 mg/L
Initial pH Range	6.0 - 9.0
Conductivity Controls	Include appropriate controls when sample conductivities are <100 or >2500 µS/cm
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Conductivity Tolerance	<2500 µS/cm
Relevant Media	Water column
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 10-Day *Hyalella azteca* Water Toxicity Tests

Method Recommendation	
EPA/821/R-02/013 (Test Method 1002.0) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	90% or greater survival in controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static renewal
Age at Test Initiation	7 – 14 days old
Replication at Test Initiation	5
Organisms/Replicate	10
Food Source	YCT
Renewal Frequency	80% renewal on Day 5
Test Duration	10 days
Endpoints	Survival
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	23 ± 1.0 °C
Light Intensity	500 - 1000 lux
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	300 mL
Replicate Volume	100 mL water
Feeding Regime	1.5 mL YCT every other day
Laboratory Control Water	Moderately hard water prepared in accordance with EPA protocols
Minimum Sample Volume	1L
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	No MSD available
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, SC, pH, and temperature measurement per sample and per dilution
Initial Unionized Ammonia	One measurement per sample
Initial Hardness and Alkalinity	One measurement per sample
Daily Water Chemistry	Temperature
Final Water Chemistry	One DO, EC, pH, and temperature measurement and per sample and per dilution (DO, EC, pH per renewal)
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.7 - 8.92 mg/L
Initial pH Range	6.0 - 9.0
Conductivity Controls	Include appropriate controls when sample conductivities are below or above levels in method
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Conductivity Tolerance	<15 ppt
Relevant Media	Water
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field; 0 - 6 °C refrigeration in laboratory; dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	<48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 10-Day *Hyalella azteca* Sediment Toxicity Tests

Method Recommendation	
EPA/600/R-99/064 (Test Method 100.1) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	Mean control survival of >80% and measurable growth in the controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Whole sediment toxicity test with renewal of overlying water
Age at Test Initiation	7 – 14 days old
Replication at Test Initiation	8
Organisms/Replicate	10
Food Source	YCT
Renewal Frequency	Twice daily
Test Duration	10 days
Endpoints	Survival and growth
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	23 ± 1.0 °C
Light Intensity	500 - 1000 lux
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	300 mL
Replicate Volume	Sediment volume 100 mL; Overlying water volume 175 mL
Feeding Regime	Daily
Laboratory Control Water	Moderately hard water prepared in accordance with EPA protocols
Sediment Control	Control sediment as listed in method (Control sediment should follow EPA requirements for formulated sediments)
Minimum Sample Volume	6 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	No MSD available
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, SC, pH, and temperature measurement per sample
Initial Unionized Ammonia	One measurement per sample
Initial Hardness and Alkalinity	One measurement per sample
Daily Water Chemistry	One DO and one temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.7 - 8.92 mg/L
Initial pH Range	6.0 - 9.0
Conductivity Controls	Include appropriate controls when sample conductivities are below or above levels listed in method
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Conductivity Tolerance	<15 ppt
Relevant Media	Sediment
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 14 days (recommended) or <8 weeks (required) @ 0 - 6 °C; dark; Do not freeze

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 96-Hour *Selenastrum capricornutum* Growth Toxicity Tests

Method Recommendation	
EPA/821/R-02/013 (Test Method 1003.0) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	Mean cell density of at least 1 X 10 ⁶ cells/mL in the controls and variability (CV%) among control replicates less than or equal to 20% (non-EDTA: Mean cell density of at least 1 X 10 ⁶ cells/mL in the controls; and variability (CV%) among control replicates less than or equal to 20% (required))
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static non-renewal
Age at Test Initiation	4 - 7 days
Replication at Test Initiation	10,000 cells/mL (recommended)
Organisms/Replicate	>4
Food Source	n/a
Renewal Frequency	None
Test Duration	96 h
Endpoints	Growth
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	25 ± 1 °C (+/- 3 °C required)
Light Intensity	86 ± 8.6 µE/m ² /s OR 400 ± 40 ft-c
Photoperiod	Continuous Illumination ("cool white" fluorescent lighting)
Test Chamber Size	125 mL or 250 mL
Replicate Volume	50 mL or 100 mL
Feeding Regime	None
Nutrient Media	Media prepared in accordance with EPA protocols
EDTA Addition	EDTA required per method
Laboratory Control Water	Moderately hard water prepared in accordance with EPA protocols
Minimum Sample Volume	1 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<29% MSD If the percent minimum significant difference (PMSD) measured for the test exceeds the upper criterion and toxicity is found at the permitted receiving water concentration (RWC) based upon the value of the effect concentration estimate (NOEC or LOEC), then the test shall be accepted, unless other test review steps raise serious doubts about its validity. If toxicity is not found at the permitted RWC based upon the value of the effect concentration estimate (NOEC or LOEC) and the PMSD measured for the test exceeds the upper PMSD bound, then the test shall not be accepted, and a new test must be conducted promptly on a newly collected sample.
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, SC, pH, and temperature measurement per sample and per dilution
Initial Unionized Ammonia	One measurement per sample
Initial Hardness and Alkalinity	One measurement per sample
Daily Water Chemistry	One pH and one temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement and per sample and per dilution (One DO per renewal)
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.6 mg/L
Initial pH Range	6.0 - 9.0
Conductivity Controls	Include appropriate controls when sample conductivities are <100 or >2000 µS/cm
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Conductivity Tolerance	<3000 µS/cm
Relevant Media	Water column
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 48 hours @ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 10-Day *Eohaustorius estuarius* Sediment Toxicity Tests

Method Recommendation	
EPA/600/R-94/025 or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	Minimum mean survival of 90% in controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Whole sediment toxicity test, static
Size at Test Initiation	3 – 5 mm (no mature males of females)
Replication at Test Initiation	4 (minimum)
Organisms/Replicate	20
Food Source	Do not feed
Renewal Frequency	None
Test Duration	10 days
Endpoints	Survival
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	15 ± 1.0 °C
Light Intensity	500 – 1000 lux
Photoperiod	Continuous luminance
Test Chamber Size	1 L
Replicate Volume	Sediment volume 175 mL; Overlying water volume 800 mL
Feeding Regime	Do not feed
Laboratory Control Water	Clean, 1-µ filtered natural seawater diluted to the appropriate salinity with distilled (or similar) water
Sediment Control	Control sediment listed in method (Control sediment should follow EPA requirements for formulated sediments)
Minimum Sample Volume	2 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	No MSD available
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, salinity, pH, and temperature measurement per sample
Initial Unionized Ammonia	One measurement per sample
Daily Water Chemistry	One temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	6.45 - 7.8 mg/L
Initial pH Range	6.0 - 9.0
Conductivity Controls	n/a
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Salinity Tolerance	Overlying water salinity should be 0 - 34‰
Relevant Media	Sediment
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 14 days (recommended) or <8 weeks (required) @ 0 - 6 °C; dark; Do not freeze

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 48-Hour *Haliotis rufescens* Larval Development Tests

Method Recommendation	
EPA/600/R-95/136 (Test Method 995) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	≥80% normal shell development in the controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static non-renewal
Age at Test Initiation	n/a
Replication at Test Initiation	5 – 10 per mL
Organisms/Replicate	5
Food Source	Do not feed
Renewal Frequency	None
Test Duration	48 h
Endpoints	Normal shell development
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	15 ± 1.0 °C
Light Intensity	10 μE/m ² /s or 50 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	600 mL
Replicate Volume	200 mL or per method
Feeding Regime	Do not feed
Laboratory Control Water	Dilution water should be 1-μ filtered natural seawater of hyper-saline brine prepared from uncontaminated natural seawater plus reagent water
Minimum Sample Volume	2 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<20% MSD
Reference Toxicant Results	Larval development NOEC (statistical significant effect) must be <56 μg/L zinc
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, salinity, pH, and temperature measurement per sample
Initial Unionized Ammonia	One measurement per sample
Daily Water Chemistry	One temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.5 mg/L
Initial pH Range	6.0 - 9.0
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Salinity Tolerance	31 - 36‰
Relevant Media	Water column, pore water
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 7-Day *Holmesimysis costata* Growth and Survival Tests

Method Recommendation	
EPA/600/R-95/136 (Test Method 1007.0) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	≥75% survival, average dry weight ≥0.40 µg in the controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static renewal
Age at Test Initiation	3 - 4 days post-hatch juveniles
Replication at Test Initiation	5
Organisms/Replicate	5
Food Source	Newly hatched <i>Artemia</i> nauplii (< 24hoursold)
Renewal Frequency	75% renewal at 48hoursand 96 h
Test Duration	7 days
Endpoints	Survival and biomass
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	15 ± 1.5 °C
Light Intensity	10 – 20 µE/m ² /s OR 50 – 100 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	1000 mL
Replicate Volume	200 mL
Feeding Regime	Twice per day
Laboratory Control Water	Dilution water should be 1-µ filtered natural seawater of hyper-saline brine prepared from uncontaminated natural seawater plus reagent water
Minimum Sample Volume	3 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<40% MSD for survival and <50 µg MSD for growth
Reference Toxicant Results	Survival and growth NOECs must be <100 µg/L with zinc
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, SC, pH, salinity and temperature measurement per sample and per dilution
Initial Unionized Ammonia	One measurement per sample
Daily Water Chemistry	One temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample and per dilution (One DO per renewal)
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.5 mg/L
Initial pH Range	6.0 - 9.0
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Salinity Tolerance	32 - 36‰
Relevant Media	Water column
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 48-hour *Mytilus galloprovincialis* Embryo-Larval Development Tests

Method Recommendation	
EPA/600/R-95/136 or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	≥50% survival, ≥90% of those must have normal shell development
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static non-renewal
Age at Test Initiation	Within 4hours of fertilization
Replication at Test Initiation	4
Organisms/Replicate	150 – 300 (15-30/mL)
Food Source	Do not feed
Renewal Frequency	None
Test Duration	48 h
Endpoints	Survival of normal live prossidoconch larvae
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	15 ± 1.5 °C
Light Intensity	10 – 20 μE/m ² /s OR 50 – 100 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	20 mL
Replicate Volume	10 mL
Feeding Regime	Do not feed
Laboratory Control Water	Dilution water should be 1-μ filtered natural seawater of hyper-saline brine prepared from uncontaminated natural seawater plus reagent water
Minimum Sample Volume	1000 mL for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<25% MSD
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, salinity, pH, and temperature measurement per sample
Initial Unionized Ammonia	One measurement per sample
Daily Water Chemistry	One temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	>4.0
Initial pH Range	6.0 - 9.0
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Salinity Tolerance	28 - 36‰
Relevant Media	Water column, pore water
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 96-Hour Strongylocentrotus purpuratus Embryo Development Tests

Method Recommendation	
EPA/600/R-95/136 or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	≥80% normal shell development in the controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static non-renewal
Age at Test Initiation	Not available
Replication at Test Initiation	250 embryos
Organisms/Replicate	4
Food Source	Do not feed
Renewal Frequency	None
Test Duration	96 h
Endpoints	Normal development; survival can be included
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	15 ± 1.0 °C
Light Intensity	10 – 20 μE/m ² /s OR 50 – 100 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	30 mL
Replicate Volume	10 mL
Feeding Regime	Do not feed
Laboratory Control Water	Dilution water should be 1-μ filtered natural seawater of hyper-saline brine prepared from uncontaminated natural seawater plus reagent water
Minimum Sample Volume	1 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<25% MSD
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, salinity, pH, and temperature measurement per sample
Initial Unionized Ammonia	One measurement per sample
Daily Water Chemistry	One temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.5 mg/L
Initial pH Range	6.0 - 9.0
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Salinity Tolerance	32 - 36‰
Relevant Media	Water column, pore water
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	<48 hours @ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 20-Minute Strongylocentrotus purpuratus Fertilization Tests

Method Recommendation	
EPA/600/R-95/136 or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	≥70% egg fertilization and appropriate sperm counts in controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static non-renewal
Age at Test Initiation	n/a
Replication at Test Initiation	4
Organisms/Replicate	~1,120 eggs from not more than four females and <3,360,000 sperm from not more than four males per test tube
Food Source	Do not feed
Renewal Frequency	None
Test Duration	40 min (20 min plus 20 min)
Endpoints	Fertilization of egg
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	12 ± 1.0 °C
Light Intensity	10 – 20 μE/m ² /s OR 50 – 100 ft-c
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	16 x 100 or 16 x 125 mm
Replicate Volume	5 mL
Feeding Regime	Do not feed
Laboratory Control Water	Dilution water should be 1-μ filtered natural seawater of hyper-saline brine prepared from uncontaminated natural seawater plus reagent water
Minimum Sample Volume	1 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<25% MSD
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, salinity, pH, and temperature measurement per sample
Initial Unionized Ammonia	One measurement per sample
Daily Water Chemistry	One temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 9.1 mg/L
Initial pH Range	6.0 - 9.0
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Salinity Tolerance	31 - 36‰
Relevant Media	Water column, pore water
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.

Table A7-4: Measurement Quality Objectives - 48-Hour *Macrocystis pyrifera* Germination and Germ-Tube Length Tests

Method Recommendation	
EPA/600/R-95/136 (Test Method 1009.0) or validated and SWAMP-approved alternative method	
Data Acceptability Requirements	
<i>Parameter</i>	<i>Criteria</i>
Test Acceptability Criteria*	≥70% germination in the controls, ≥10 μm germ-tube length in the controls
Data Qualification	
<i>Test Conditions</i>	<i>Required</i>
Test Type	Static non-renewal
Age at Test Initiation	n/a
Replication at Test Initiation	5
Organisms/Replicate	7500 spores/mL of test solution
Food Source	Do not feed
Renewal Frequency	None
Test Duration	48 h
Endpoints	Germination and germ-tube length
<i>Test Conditions</i>	<i>Recommended**</i>
Temperature Range	15 ± 1.0 °C
Light Intensity	50 ± 10 μE/m ² /s
Photoperiod	16 hours of ambient laboratory light, 8 hours dark
Test Chamber Size	600 mL
Replicate Volume	200 mL
Feeding Regime	Do not feed
Laboratory Control Water	Dilution water should be 1-μ filtered natural seawater of hyper-saline brine prepared from uncontaminated natural seawater plus reagent water
Minimum Sample Volume	2 L for one-time grab sample
<i>Sensitivity</i>	<i>Performance Criteria</i>
Minimum Significant Difference	<20% MSD
Reference Toxicant Results	NOEC must be <35 μg/L in the reference toxicant test
Water Chemistry	
<i>Test Parameter</i>	<i>Required Frequency</i>
Initial Water Chemistry	One DO, salinity, pH, and temperature measurement per sample
Initial Unionized Ammonia	One measurement per sample
Daily Water Chemistry	One temperature measurement per sample
Final Water Chemistry	One DO, pH, and temperature measurement per sample
<i>Test Parameter</i>	<i>Recommended Criteria</i>
Initial DO Range	4.0 - 8.5 mg/L
Initial pH Range	6.0 - 9.0
Sample Handling/Collection	
<i>Test Parameter</i>	<i>Recommended Conditions</i>
Species' Salinity Tolerance	32 - 36‰
Relevant Media	Water column
Sample Container Type	Amber glass
Sample Preservation	Wet or blue ice in field, 0 - 6 °C refrigeration in laboratory, dark at all times
Sample Receipt Temperature	0 - 6 °C
Holding Time	< 48 hours@ 0 - 6 °C; dark

*Test data are reviewed to verify that the test acceptability criteria (TAC) requirements for a valid test have been met. Any test not meeting the minimum test acceptability criteria is considered invalid. All invalid tests must be repeated with the newly collected sample.

**Deviations from the summary of recommended test conditions must be evaluated on a project-specific basis to determine the validity of test results. Deviations from recommended conditions may or may not invalidate a test result, depending on the degree of the departure and the objective of the test.