Evaluation of Toxicity in the San Gabriel River Watershed

Quality Assurance Project Plan

Prepared by

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and

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June 30, 2005

GROUP A. PROJECT MANAGEMENT

1. APPROVAL SHEET

Quality Assurance Project Plan

Evaluation of toxicity in the San Gabriel River Watershed

APPROVED BY:

_____ _____
Terry Fleming Date
United States Environmental Protection Agency

_____ _____
Kenneth Schiff, Project Manager Date
Southern California Coastal Water Research Project

_____ _____
Jeff Brown, Quality Assurance Officer Date
Southern California Coastal Water Research Project

_____ _____
Dario Diehl, Field Sample Coordinator Date
Southern California Coastal Water Research Project

_____ _____
Chris Stransky, Lab Manager Date
Nautilus Environmental

_____ _____
Angi Hotz, Quality Assurance Officer Date
Nautilus Environmental

2. TABLE OF CONTENTS

2.1 List of Tables

2.2 List of Figures

3. DISTRIBUTION LIST

The final Quality Assurance Project Plan (QAPP) will be kept on file at the Southern California Coastal Water Resources Project (SCCWRP) office. The following individuals will receive copies of the approved QAPP and any subsequent revisions:

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rcollins@waterboards.ca.gov

4. PROJECT/TASK ORGANIZATION

4.1 Involved Parties

SCCWRP is a joint powers agency that was formed by several government agencies with a common mission to gather the necessary scientific information to effectively, and cost-efficiently, protect the Southern California aquatic environment. As the lead agency in this project, SCCWRP will coordinate the sampling and analysis programs, data analysis, and report preparation and submission with all parties involved. The planned program is a joint effort by US EPA, Los Angeles Regional Water Quality Control Board (LARWQCB), the Los Angeles County Sanitation District (LACSD) and the Los Angeles County Department of Public Works (LADPW) where SCCWRP has been contracted to carry out the project goals. SCCWRP has, in turn, sub-contracted Nautilus Environmental to conduct freshwater toxicity tests required by the program.

4.2 Roles and Responsibilities

Ken Schiff (SCCWRP), Project Manager, has established a project team (Figure 1), and defined the responsibilities of the personnel involved (Table 1).

Rod Collins (LARWQCB) is the Project Contract Manager. He is responsible for administrative overview of the project. Terry Fleming is the Project Advisor. He is responsible for regulatory overview and advice on the study. Jeff Brown (SCCWRP) is the Project Quality Assurance (QA) Officer. Jeff's role is to establish and coordinate compliance with QA and Quality Control (QC) procedures outlined in this QAPP. Jeff will ensure compliance by communicating all QA/QC issues to the QA Officer at Nautilus Environmental. Jeff will also review and assess all procedures during the life of the contract against QAPP requirements. Jeff will report all findings to Ken Schiff, including all requests for corrective action. Jeff may stop all actions, including those conducted by Nautilus Environmental if there are significant deviations from required practices or if there is evidence of a systematic failure.

The primary goal of this QAPP is to ensure that the data generated by field and laboratory personnel meet standards for published data in the peer-reviewed literature. Field and lab personnel will follow standard operating procedures (SOPs) for sampling and laboratory analysis.

The SCCWRP Project Manager and QA Officer may make changes and updates to this QAPP after a review of the evidence for change. Ken Schiff will be responsible for making the changes, submitting drafts for review, preparing a final copy, and submitting the final copy for signature.

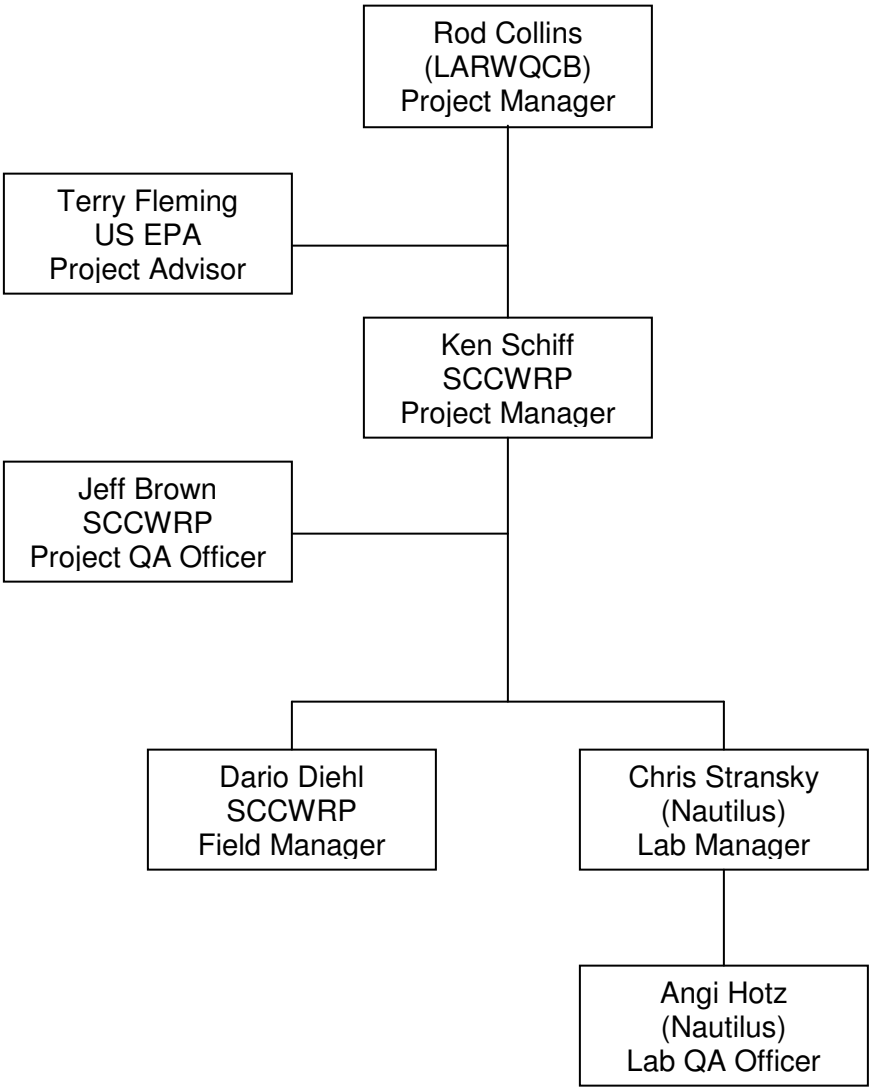

Figure 1. Organizational chart for exchanging project information.

Table 1. Personnel responsibilities.

Name	Organizational Affiliation	Project Responsibilities	Contact Information
Kenneth Schiff Project Manager	SCCWRP	Study coordination and oversight	Tel: (714) 372-9202 kens@sccwrp.org
Jeff Brown QA Officer	SCCWRP	QA/QC oversight	Tel: (714) 372-9224 jeffb@sccwrp.org
Dario Diehl Field Sample Coordinator	SCCWRP	Coordination and oversight of sample collection. Sampling QA and training.	Tel: (714) 372-9212 dariod@sccwrp.org
Terry Fleming	US EPA	Regulatory review and advice	Tel: (415) 972-3462 fleming.terrence@epa.gov
Rod Collins	LA RWQCB	Administrative overview	Tel: (213) 567-6691 rcollins@waterboards.ca.gov
Chris Stransky Laboratory Manager	Nautilus Environmental	Oversight of toxicity screens and TIEs, review and approval of all data packages submitted for this program.	Tel: (858) 587-7002 Fax: (858) 587-3961 chris@nautilusenvironmental.com
Angi Hotz QA Officer	Nautilus Environmental	Ensure testing conducted is compliant with QAPP.	Tel: (858) 587-7009 Fax: (858) 587-3961 angi@nautilusenvironmental.com

5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem Statement

In 1996, the Regional Board included Walnut Creek, San Gabriel River Reach 1, San Gabriel River Reach 3, and Coyote Creek on the 303(d) list of impaired waters for toxicity. These listings were based on data collected in 1992 and 1993. This list was carried over in the 1998 and 2002 303(d) listings. Conditions in the San Gabriel Watershed have changed significantly since the original 303(d) listing decisions were made. Most notably, the five Water Reclamation Plants (WRPs) that discharge into the watershed were all converted to include nitrification and de-nitrification facilities over a year ago. Based on data collected by LACSD and US EPA, this change appears to have greatly improved the water quality of the downstream water bodies with respect to toxicity. At the same time, data collected by LACSD indicate occasional toxicity upstream of one of the treatment plants on Coyote Creek.

Clearly, the population in the watershed has increased and land uses near the water bodies have changed since the early 1990s when the original data used to generate the toxicity listings were collected. Pesticides usage has also changed, and these changes may affect water quality either positively or negatively. Therefore, it is expected that the toxicity results from this collaborative sampling effort will be different from those found in the original 1992 and1993 studies.

6. PROJECT/TASK DESCRIPTION

6.1 Project Purpose and Goals

The proposed sampling and testing program is designed to:

1) Verify the presence or absence of toxicity in the 303(d) listed reaches;
2) Investigate the persistence and variability of toxicity in the 303(d) listed reaches of the San Gabriel River watershed; and
3) Identify the chemical constituent(s) causing any observed toxicity.

The presence or absence of toxicity in the receiving water will be defined with standard chronic toxicity tests using *Ceriodaphnia dubia* without dilution. Multiple samples will be collected over time to address the issue of variability and persistence. Samples will also be collected during multiple storm events to evaluate differences in toxicity between wet and dry-weather conditions. Finally, Toxicity Identification Evaluation (TIE) procedures will be performed on samples exhibiting substantial toxicity in order to identify constituents of concern.

6.1.1 Study Design

Dry Weather

Dry-weather samples will be collected in five river reaches within the San Gabriel River Watershed (San Gabriel River Reaches 1 and 3, Walnut Creek, San Jose Creek and Coyote Creek). The proposed sampling program is monthly sample collection at ten stations. Design considerations in the selection of the station locations involved a general upstream-downstream component to assess the effect, if any, of the WRPs, and to differentiate effects of WRPs from the effects of urban runoff. Stations were also located downstream of larger tributaries feeding into the listed reaches to determine if there are any geographic patterns in the toxicity. An emphasis has been placed on Coyote Creek where previous data have suggested problems upstream of the WRP. A monthly sampling regime was selected to assess any seasonal variability in toxic responses. We propose a one-year sampling program to generate a sufficient number of samples for evaluation relative to the State Water Resources Control Boards 303(d) listing and de-listing policy.

Wet Weather

Wet weather toxicity sampling is proposed for three storms at four sites. The four sites are located near the bottom of the watersheds for Walnut Creek, San Jose Creek, Coyote Creek and the San Gabriel River. The Coyote Creek site is co-located with the existing LADPW sample station. At the present time we only have resources for one year of wet weather sampling.

TIEs

The goal of a TIE is to identify the toxicant(s) causing toxicity in a sample. EPA methods use the responses of organisms to detect the presence of toxicity in the first stages of a TIE. The EPA manuals describe three phases of a TIE: characterization (Phase I), toxicant identification (Phase II), and toxicant confirmation (Phase III). Each test in Phase I is designed to alter or render biologically unavailable a group of toxicants such as oxidants, cationic metals, volatiles, non-polar organics or chelatable metals. At this point, only Phase I TIEs are being considered. Only samples identified as "toxic" in the baseline tests will be analyzed for Phase I TIE testing. Phase I TIE manipulations are recommended for samples exhibiting toxicity (>25% effect level).

6.1.2 Project Timetable

Table 2. Schedule for completion of work and deliverables.

Activity	Anticipated Date of Completion	Deliverable	Deliverable Due Date
Sampling	July 30, 2007	Laboratory Receipt	August 31, 2007
Toxicity Testing	July 30, 2007	Toxicity Summary	August 31, 2007
TIEs	July 30, 2007	TIE Summary Report	August 31, 2007
Final Report	December 31, 2007	Final Report	December 31, 2007

6.2 Description of Work – Definitions of tests and applicable standards.

6.2.1 Toxicity Tests

Screening Tests

Acute (96-hour) and chronic (7-day) toxicity tests consisting of full-strength sample and a laboratory control using *Ceriodaphnia dubia* will be initiated within 36 hours of sample collection. Chronic screening tests will be conducted using 10 replicates of one animal each with daily renewals, and acute screening tests will be conducted using four replicates of 5 animals each with one renewal at 48 hours. All receiving water samples should be strained through a 60-µm-mesh screen to remove potential predatory organisms prior to testing. Daily observations will include survival, reproduction, and initial and final pH, dissolved oxygen, and temperature. Chronic tests will be terminated after at least 60 percent of the surviving control females have released their third brood, or 8 days, whichever occurs first. Basic testing procedures and criteria contained in US EPA *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms*, Fourth Edition (EPA-821-R-02-013) (US EPA 2002a), *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*, Fifth Edition (EPA-821-R-02-012) (US EPA 2002b), will be followed. Laboratory controls will consist of 1) "very hard

reconstituted deionized water" to match the hardness of the dry weather samples (hardness of 280-320 mg/L $CaCO_3$) adjusted to a starting pH of 7.5 to 7.7; and 2) "diluted mineral water" (hardness of 80-100 mg/L $CaCO_3$) adjusted to pH 7.9 to 8.3, which is used for culture of the test organisms. Toxicity will be defined as a greater than 25 percent reduction in response (survival or reproduction) relative to the concurrent control in a valid test. Tests exhibiting a 25 percent effect or less will be identified as "non-toxic."

Phase I – Tier 1 TIE Tests

For the purpose of this study, a sample will be considered toxic when there is greater than a 25 percent effect relative to the control. Phase I TIE testing should be initiated as soon as possible after the conclusion of the screening toxicity test (no longer than 7 days after screening test termination). Specific Phase I – Tier 1 procedures contained in US EPA *Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I (EPA/600/6-91/005F)* (US EPA 1991) will be used for TIE testing. The testing involved in a Phase I TIE is listed in Table 3.

If toxicity in the screening test is confined to only the reproduction endpoint (no survival effects), only full-strength sample will be used for the Phase I TIE manipulations and basic chronic toxicity testing procedures will be followed. These include the use of 10 replicates with daily renewals with single neonate placement in each replicate. Daily observations during the testing for each manipulation must include survival, reproduction, and measurements of initial and final pH, dissolved oxygen, and temperature. Tests will be terminated after seven days.

If survival effects are observed in the screening tests, the testing of additional sample concentrations (e.g. 50 and 25 percent) should be considered for the Phase I TIE testing depending on the magnitude of effect. Under these conditions, an acute exposure containing fewer replicates (five) and multiple concentrations with renewals at 48-hour intervals may be more appropriate for the Phase I TIE. Depending on the "time to lethality", TIE exposures of 48 or 96 hours may be acceptable. Daily observations under these conditions for each manipulation must include survival, and initial and final pH, dissolved oxygen, and temperature.

Dilution water to be used for all Phase I TIE testing should be "very hard reconstituted deionized water." Similarly, manipulated control samples must be conducted concurrently with all sample TIE treatments. A diluted mineral water control will also be tested for comparison purposes.

Table 3. Summary of TIE manipulations.

Phase I – Tier 1	**Additional Details**
Baseline (no manipulation)	None
Filtration	Filtration through 0.45-µm nylon filter
Aeration	Samples aerated for one hour
pH Adjustment	Samples tested at pH 7.0 and pH 8.5 (pH maintained through out the test)
EDTA Additions	3.0 ppm and 8.0 ppm EDTA Addition* * EDTA added to samples a minimum of 3 hours prior to use. (EDTA is ethylendiaminetetraacetic acid)
STS Additions	10.0 ppm and 25.0 ppm STS addition * STS added to samples a minimum of 1 hour prior to use. (STS is sodium thiosulfate)
C18 Solid-Phase Extraction	None
PBO Additions	50 ppb PBO, 100 ppb PBO (PBO is piperonyl butoxide)

7. QUALITY OBJECTIVES AND CRITERIA

Data Quality Objectives (DQOs) are quantitative and qualitative statements that clarify study objectives, and specify the tolerable levels of potential errors in the data (US EPA 2000). As defined in this plan, DQOs specify the quantity and quality of data required to support the study objectives. DQOs are generally used to determine the level of error considered to be acceptable in the data produced by the sampling or monitoring program. They are used to specify acceptable ranges of field sampling and laboratory performance. Each data quality category is described below and summarized in Table 4. In the event that analytical measurements that cannot be performed at Nautilus are required, this QAPP will be amended with DQOs for the necessary measurements.

Table 4. Summary of Data Quality Objectives

Measurement	Precision	Accuracy	Completeness
Sampling	NA	NA	90%
Toxicity Reference Toxicant Tests	± 2 SD	± 2 SD	90%
Laboratory Ammonia	RPD ≤ 20%	± 20%	90%

SD = Standard Deviation

7.1 Precision

Precision describes how well repeated measurements agree. In this case, the evaluation of precision described here relates to repeated measurements/samples taken in the laboratory. This will apply to two categories; the first is toxicology, and the second is water quality measurements.

Laboratory precision for toxicity testing is assured through adherence to methods for testing environmental samples, as well as the conduct and evaluation of reference toxicant tests. For all tests, only healthy organisms of similar age are selected for testing, and environmental parameters (e.g. pH, dissolved oxygen, temperature, light and photoperiod, etc.) are constrained to a narrow range to minimize organism stress during testing (Table 5). In addition, individual tests must meet benchmark values for acceptable variation established by US EPA with a minimum significant difference (MSD) of 13-47 percent for the *Ceriodaphnia* reproduction endpoint. Finally, organism responses to reference toxicants are used to ensure organisms are not overly sensitive or insensitive compared to previous test batches. The mean organism response to reference toxicants should not differ from the mean of previous reference toxicant tests by more than two standard deviations.

Performing duplicate measurements will assess precision for analysis of ammonia. For each batch of samples (n ≤ 20) the relative percent difference (RPD) among duplicate samples must be less than 20 percent. Repeated measures will not be conducted for pH, dissolved oxygen, temperature, conductivity, alkalinity, or hardness, but specified ranges are called for in the laboratory method (Table 5).

Table 5. Environmental parameter ranges to ensure precision during toxicity testing.

Parameter	Min	Max
pH (control water only)	8.00	8.40
Alkalinity (control water only)	225 mg/L $CaCO_3$ [a] 57 mg/L $CaCO_3$ [b]	245 mg/L $CaCO_3$ [a] 64 mg/L $CaCO_3$ [b]
Hardness (control water only)	280 mg/L $CaCO_3$ [a] 80 mg/L $CaCO_3$ [b]	320 mg/L $CaCO_3$ [a] 100 mg/L $CaCO_3$ [b]
Dissolved oxygen	4.0 mg/L	~8.3 mg/L (freshwater at 25°C)
Temperature	24°C	26°C
Photoperiod	8 hours dark	16 hours light
Light Intensity	50 ft-c	100 ft-c

[a] Very hard reconstituted deionized water
[b] Diluted mineral water

7.2 Accuracy

Accuracy describes how close the measurement is to its true value. Once again, accuracy will be determined for both toxicity tests and water quality measurement procedures. It is important to note that there is no true standard against which to assess accuracy for toxicity tests. However, a measure of accuracy within a single laboratory may be the use of reference toxicant tests. As with test precision, an organism response to a reference toxicant exposure that is within two standard deviations of the mean response obtained in the laboratory may demonstrate an "accurate" response.

The accuracy of ammonia measurements will be checked by comparing ammonia concentrations in 1) an ammonia standard solution (known concentration); 2) sample material; and 3) sample material spiked with ammonia. Accuracy is measured as percent recovery and must fall within the range of 80-120 percent. Accuracy of pH and dissolved oxygen measurements is ensured by daily calibration of the meters. Post-calibration measurements of standard solutions must fall within tem percent of certified standard values prior to use (manufacturer-stated meter accuracy). Accuracy of temperature measurements is assured through routine calibration against a certified thermometer. Details of meter calibration and use are provided in the Nautilus QA Manual (Appendix D).

7.3 Completeness

A general completeness requirement of 90 percent has been set for this project (i.e. 90 percent of planned samples will be collected, and 90 percent of the toxicity tests will meet acceptability criteria, as defined in the methods). This accounts for adverse weather conditions, safety concerns, and equipment problems. We will determine completeness by comparing the number of measurements we planned to collect compared to the number of valid measurements we actually collected (an invalid measurement would be one that does not meet the sampling method requirements and the DQOs).

7.4 Representativeness

Representativeness is the bias associated with sampling and testing. Representativeness is addressed in both field and laboratory activities for this study. Field sampling representativeness is assured through site selection. Samples will be collected midstream in a narrow, but very well mixed portion of the channel. The sites are located at downstream reaches that are cumulative of upstream discharges. Laboratory representativeness is assured through test type and species selection. *Ceriodaphnia* is a species found in the watershed, and test exposures are conducted at a representative temperature of 25°C.

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Purpose

No specialized training for field or laboratory activities beyond what is required for routine performance and adherence to safety policies is required for this project. However, a brief description of training and certifications follows.

8.2 Training

SCCWRP maintains a rigorous field sampling training program based on written, oral and performance-based guidelines. Nautilus holds California Environmental Laboratory Accreditation Program (ELAP) certification for the toxicity testing procedures required for this project, and employs a rigorous training program for all personnel involved with the performance of toxicity testing.

Standard Operating Procedures (SOPs) for field, and laboratory have been developed and are updated on a regular basis in order to maintain procedural consistency. The maintenance of an SOP Manual provides project personnel with a reference guide for training new personnel as well as a standardized information source that personnel can access. SCCWRP's SOPs for sampling and Nautilus's SOPs for toxicity tests are provided in Appendices A and B, respectively.

8.3 Certification Documentation

Nautilus maintains certification and training records with regard to testing procedures and laboratory safety. Those records can be obtained from Nautilus through their QA Officer, if needed. SCCWRP maintains training records, which can also be accessed through their QA Officer.

9. DOCUMENTS AND RECORDS

9.1 Information Included in Reporting Packages

Final report packages shall include an introduction with problem statement, methods detailing protocols and equipment, results and discussion summarizing test outcomes and important caveats or interpretations of the data. Also included will be a QA/QC statement declaring the quality of the data including adherence to the DQOs outlined in this QAPP.

Additional information will be maintained, but not presented in the final report including:

1) Sample information including chain-of-custody (COC) forms and water quality measurements taken upon sample receipt at the laboratory.
2) Raw test data, including water quality measurements, survival and reproduction counts, test initiation and termination dates and times, analyst information, and test organism information.
3) Statistical analysis outputs.
4) QA/QC reports:
    a. Signatures certifying review of COC forms and receipt parameters, raw test data, and data analyses.
    b. Explanations of any protocol deviations or validation/invalidation of data falling outside of protocol test acceptability criteria.

9.2 Data Reporting Package Formats

Data packages shall be submitted in electronic format and in hard copy to SCCWRP.

9.3 Data Archival and Retrieval

Copies of all records generated in support of this project will be stored at SCCWRP. Original records from Nautilus that are pertinent to this study will be maintained at their office.

Persons responsible for maintaining records for this project are as follows: Ken Schiff will maintain the records at SCCWRP. Chris Stransky will maintain Nautilus's records. Ken Schiff will oversee the actions of these persons and will arbitrate any issues relative to records retention and any decisions to discard records.

Datasheets and COCs will be stored by SCCWRP and Nautilus in hard copy form for three years from the time the study is completed. Electronic copies of all data reporting packages will be maintained for three years as well. The directory where the files are stored is backed up weekly on a second hard drive, and backed up monthly off-site.

Copies of this QAPP will be distributed to all parties involved with the project, including field collectors and laboratory analysts. Copies will be sent to Nautilus for internal distribution. Any

future amended QAPPs will be distributed in the same fashion. All originals of this and subsequent amended QAPPs will be held at SCCWRP.

GROUP B. MEASUREMENT/DATA ACQUISITION

10. SAMPLING PROCESS DESIGN

10.1 Scheduled Project Activities

Table 6. Anticipated schedule for sampling, testing, and data review.

Task	Frequency	Turn Around Time
Dry Weather Sampling, Testing, and Data Review	Monthly	Three weeks from screening test completion
Wet Weather Sampling, Testing, and Data Review	Three storms during program	Three weeks from screening test completion
TIEs	As needed	To be determined

10.2 Study Design Rationale and Assumptions, and Contingency Planning

The study is designed to examine repetitive measurements of toxicity at selected sites in the San Gabriel River watershed. The site selection and frequency was based upon the needs of 303(d) listing policy as described by the State of California. One assumption in this policy is that systems are in semi-steady state in terms of toxicant concentrations at a site, although seasonal variations may occur. This assumption appears reasonable based on historical chemical data. While we do not expect any problems to occur, we have several contingency measures that can occur if needed:

1) Repeat sampling during a month if tests fail to meet acceptability criteria.
2) Station re-alignment for channel construction or impasse.
3) Additional monthly sampling past the end of the study to ensure adequate sample size.
4) Utilization of additional laboratories if testing capacity is exceeded.

10.3 Procedures for Selecting Environmental Samples

Sampling sites were selected using the following criteria:

1) Representative of watershed discharges.
2) Similarity to sites used in previous monitoring efforts in the watershed.
3) Safe access for field personnel.

10.4 Hierarchy of Measurement Importance

For this project, the hierarchy of measurement importance focuses first on toxicity testing, then on TIEs. TIEs will only be initiated when toxicity tests exceed a 25 percent response relative to the controls. This will ensure an adequate signal to conduct an effective TIE.

10.5 Validation of Non-Standard Methods

All methods are standard for this study.

11. SAMPLING METHODS

11.1 Preparation for Sampling

Appropriate pre-cleaned sample containers will be used. Sample bottles will be protected from contact with solvents, dust, or other contaminants. Sample bottles for this project will not be reused.

To clean tubing for sample collection, connect tubing to an ISCO pump as if preparing for field sampling. Place the intake and exhaust ends of the tubing into a container and start the pump. First flush or rinse the tubing with tap water for three minutes. Now repeat the process, but use deionized (DI) water. Next pump 10% nitric acid through the tubing for three minutes. Follow with three rinses of DI water. Remove the two cleaned Teflon hoses from the silicon tubing, place in a large plastic bag and seal. Place sheets of Teflon (cleaned with acid and DI water) over exposed ends of the silicon tubing and bind with rubber bands. Place a large plastic bag over entire pump assembly to protect from contamination.

11.2 Sample Collection

For sample collection, attach clean tubing to an ISCO peristaltic pump. Use an extension pole to continually move the intake end of the tubing to differing areas of the stream and water column. Allow 30-45 seconds of sample water to flush the tubing before filling any containers. Close each container (with no headspace) and label with site name, date, and time. Because additional volumes are necessary for potential TIEs, sample containers will have at least twice the volume necessary to perform the requested screening analyses. Place each container in an ice chest and surround them with ice (cool and dark). Fill out any field logs or station occupation datasheets. Depart site and repeat the process for any additional sampling locations.

For wet-weather monitoring, the sampling team has responsibility for assessing the safety of sampling the sites during storm events and determining whether it is safe to proceed. A two-person team will conduct all sampling during storm events, and the sampling team will have access to a cellular phone in order to alert rescue agencies should an accident occur. Sampling will be postponed if the sampling team determines that the conditions are unsafe.

Failure to collect a sample due to safety concerns or technical issues will be promptly reported to Ken Schiff, who will determine if any corrective action is needed and make arrangements to collect a replacement sample (if possible). The QA Officer will document sampling failures and the effectiveness of corrective actions.

12. SAMPLE HANDLING AND CUSTODY

As described in the sampling protocol, once sample containers are filled and sealed, they will be labeled with the site name, date, and collection time, and placed in a cooler with ice. Samples will be kept properly chilled and will be transferred to the laboratory as soon as possible to ensure test initiation within the 36-hour holding time. To provide for proper tracking and handling of the samples, COC forms will accompany water samples through all phases of collection, transport, and receipt. An example of the COC form is shown in Appendix C. Once received in the laboratory, each sample will be assigned a unique number for use and disposal tracking.

Dario Diehl of SCCWRP will coordinate all field sampling efforts and oversee shipment of sample containers. Samples will be delivered to Nautilus either by SCCWRP personnel or via overnight delivery service (e.g. FedEx). In the event samples are shipped overnight to the laboratory, sample containers will be packed in ice chests with wet ice. Ice chests will be taped securely shut using packaging tape.

13. ANALYTICAL METHODS

13.1 Analysis Methods

Toxicity test procedures will be conducted in accordance with methods published in US EPA *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms (EPA-821-R-02-013)*, Fourth Edition (EPA 2002a).

Analysis of total ammonia will be conducted using the Hach colorimetric "Test 'N Tube" Salicylate Method 10031 and a Hach DR2000 spectrophotometer. The Hach method cited is an EPA-accepted procedure equivalent to EPA Method 350.2 (Appendix B).

13.2 Sample Disposal

After analysis, including QA/QC procedures, any excess sample material will be disposed of in accordance with state and federal regulations by the laboratory.

13.3 Corrective Action

Corrective action is taken when an analysis is deemed suspect for some reason. These reasons include toxicity test control performance issues, exceeding reference toxicant control chart limits or RPD ranges, and/or problems with spike recoveries or blanks. The corrective action varies somewhat from analysis to analysis, but typically involves the following:

1) A check of procedures.
2) A review of documents and calculations to identify possible errors.
3) Correction of errors.
4) A complete re-processing and re-analysis of additional sample material, if sufficient volume is available and if the holding time has not been exceeded.

SCCWRP and Nautilus have specific QA/QC systems in place to document problems and make corrective actions.

14. QUALITY CONTROL

No additional QC elements beyond those previously described in this QAPP are required for this project. Please refer to SOPs for specific QC requirements (Appendix B).

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

15.1 Sampling Equipment

Sampling teams have established SOPs for each piece of field equipment in use. The sampling equipment receives regular maintenance based on a combination of manufacturer requirements and the actual amount of equipment use in the field.

15.2 Laboratory Equipment

Nautilus maintains its equipment in accordance with its QA Program, which includes requirements specified by the manufacturer and those specified by the method. A copy of Nautilus' QA Manual is provided in Appendix D.

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

All laboratory equipment is calibrated based on manufacturer recommendations and accepted laboratory protocols. Nautilus maintains calibration practices as part of the method SOPs and details are described in the attached Nautilus QA Manual (Appendix D).

17. INSPECTION/ACCEPTANCE FOR SUPPLIES AND CONSUMABLES

Glassware, sample bottles, and collection equipment will all be inspected prior to their use. Supplies will be purchased from VWR (vwr.com, 800-932-2500). The Field Sample Coordinator will be in charge of ordering sampling containers. Supplies will be examined for damage as they are received.

Nautilus maintains logbooks for all consumables that are checked against all materials received.

18. NON-DIRECT MEASUREMENTS

This study will not incorporate existing data or other non-direct measurements.

19. DATA MANAGEMENT

The following Nautilus SOPs describe methods for verifying, analyzing, and reporting toxicity test data (Appendix E):

1) Laboratory Bench QC Practices
2) Data Review and Report Preparation Guidelines

Nautilus will perform the following actions:

1) A 100 percent check between electronic data and the hard copy bench sheets and reports.
2) Conformity check between the COC forms and laboratory reports.
3) A check for laboratory data report completeness.
4) A check for typographical errors in the laboratory reports.
5) A check for suspect values.

Following the initial screening, a more complete QA/QC review process will be performed, which will include an evaluation of holding times, applicable test acceptability criteria, method and equipment blank contamination, and analytical accuracy and precision (where applicable). Accuracy will be evaluated by reviewing spiked sample recoveries, and reference toxicant control charts; precision will be evaluated by reviewing reference toxicant control charts, MSDs, and laboratory controls.

GROUP C. ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS AND RESPONSE ACTIONS

20.1 Laboratory Audits

As outlined in the Nautilus QA Manual (Appendix D), a series of systems are in place at the laboratory to ensure adherence to test performance and data management guidelines. For complete descriptions of these systems, please refer to the QA Manual; a brief list of these systems follows:

1) Generation of QA-related documentation regarding individual test performance, laboratory performance, and method changes. These documents include Corrective Action Records (CARs), and Management of Change (MOC) forms.
2) Daily review of test data, QA-related documentation, and equipment calibration/ performance log books by technical staff.
3) Weekly review of test data, QA-related documentation, and equipment calibration/performance log books by the laboratory supervisor.
4) Monthly review of all QA-related documentation (MOCs, CARs, equipment maintenance log books, etc.)
5) Quarterly audits of the technical staff's performance of test methods.
6) Semi-annual audits of the technical training program
7) Annual audits of the QA Program
8) Participation in annual blind sample testing for all accredited methods (i.e. Performance Evaluation testing).

20.2 Assessment of Project Activities

SCCWRP will assess project activities at three levels. First, SCCWRP will review the report packages submitted by Nautilus to ensure adherence to the activities described in this QAPP and SOPs. Second, SCCWRP will conduct audits of the raw data to ensure accurate data reporting. Third, SCCWRP will assess project management activities on a quarterly basis to ensure tasks and milestones are being completed on schedule.

21. REPORTS TO MANAGEMENT

Reports to management will occur monthly, following each toxicity test. Nautilus will report the status of data collection verbally or electronically to SCCWRP at the completion of each screening test series and/or the initiation of any TIEs. All QA deviations or problems will be noted at this time to allow for corrective actions before the next sampling event/round of testing.

Quarterly written reports will be provided by SCCWRP to the contract manager to inform status of project completion. Anticipated problems, including any QA deviations, will communicated at this time. SCCWRP will communicate such problems to other participating parties.

GROUP D. DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION

Laboratory validation and verification of the data generated is the responsibility of the laboratory. The laboratory manager maintains analytical reports in a database format as well as all QA/QC documentation for the laboratory.

SCCWRP will review all data packages received for adherence to guidelines set forth in this QAPP. COC forms will be reviewed to ensure adherence to collection, transport, and receipt requirements, including test initiation within the 36-hour holding time. Toxicity data will be evaluated for completeness, adherence to test methodology, passing acceptability criteria, choice of appropriate statistical methods, and proper reporting.

Nautilus will conduct a 100 percent raw data versus electronic data audit before delivering results to SCCWRP.

23. RECONCILIATION WITH DATA QUALITY OBJECTIVES

For data that do not meet DQOs, management has two options:

1) Retain the data for analytical purposes, but flag these data for QA deviations.
2) Do not retain the data and exclude them from all calculations and interpretations.

The choice of option is the decision of the Project Manager. If qualified data are to be used, then it must be made clear in the final report that these deviations do not alter the conclusions of the study.

APPENDIX A: SAMPLING SOPS

SAMPLE COLLECTION (SCCWRP)

SUB-SAMPLE COLLECTION (NAUTILUS)

APPENDIX B: TESTING SOPS

CERIODAPHNIA CHRONIC TEST

CERIODAPHNIA ACUTE TEST

AMMONIA ANALYSIS

APPENDIX C: SAMPLE HANDLING

CHAIN-OF-CUSTODY FORM

SAMPLE LOG-IN SHEET

APPENDIX D: NAUTILUS QUALITY ASSURANCE MANUAL

APPENDIX E: NAUTILUS DATA MANAGEMENT SOPS

LABORATORY BENCH QC PRACTICES

DATA REVIEW AND REPORT PREPARATION GUIDELINES