

# QUALITY ASSURANCE PROJECT PLAN

for

Investigation of pyrethroid pesticides in the American River

Version 1.0

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## **Section A01. Title and Approval Sheets; Citation for QAPP; Preface**

<b>Project Title</b>	Investigation of pyrethroid pesticides in the American River
<b>Lead Organization</b>	Central Valley Regional Water Quality Control Board 11020 Sun Center Drive Sacramento, CA 95695 Stephanie Fong (CVRWQCB), SWAMP Grant Manager
<b>Primary Contact</b>	Aundrea Asbell Project Director UC Berkeley 3060 Valley Life Sciences Bldg. Integrative Biology Dept. Berkeley, CA 94720-3140 (510) 665-3421
<b>Effective Date</b>	This Quality Assurance Project Plan (QAPP) is effective from date of approval to March 2011 unless otherwise revised, approved and distributed accordingly at an earlier date.
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### **QAPP Preface**

This Quality Assurance Project Plan (QAPP) document defines procedures and criteria that will be used for this project conducted by the University of California, Berkeley (UCB) in association with Southern Illinois University (SIU). Included are criteria for data quality acceptability, procedures for sampling, testing (including deviations) and calibration, as well as preventative and corrective measures. The responsibilities of UCB and SIU are also contained within.

This work is funded through the Surface Water Ambient Water Quality Program (SWAMP).

**Approvals**

Stephanie Fong  
CVRWQCB SWAMP Grant Manager

\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

Beverly Van Buuren  
SWAMP Quality Assurance Officer

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Signature

\_\_\_\_\_  
Date

Aundrea M. Asbell  
UCB Project Director

\_\_\_\_\_  
Signature

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Date

Donald P. Weston  
UCB Project QA Officer

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Signature

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Date

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**Section A03. Distribution List**

The distribution list below includes at least one individual from each participating organization. Each of these individuals will receive a copy of this QAPP in electronic or hard copy, as well as any future revisions. These individuals may distribute the QAPP within their respective organizations as needed to complete, monitor, or evaluate the study.

<u>Title</u>	<u>Name (Affiliation)</u>	<u>Phone</u>	<u>No. of copies</u>
UCB Project Director	Aundrea Asbell (Univ. California, Berkeley)	510-665-3590	1
UCB Project QA Officer	Donald Weston (Univ. California, Berkeley)	510-665-3421	1
SWAMP Grant Manager	Stephanie Fong (Central Valley RWQCB)	916- 464-4822	Original
SWAMP QA Officer	Beverly Van Buuren (Moss Landing Marine Laboratory)	206-781-1692	1
Analytical Lab. Director (Illinois)	Michael Lydy (Southern Illinois University)	618-453-4091	1

**Section A04. Project/Task Organization**

The principal parties involved are listed below, along with their project responsibilities. Lines of authority are indicated in the project organization flowchart of Figure 1. All individuals discussed in the text below are integral members of the project team with varying degrees of responsibility for deliverables. The CVRWQCB SWAMP Grant Manager, Stephanie Fong, will have a technical advisory role in addition to her administrative duties.

4.1 Involved Parties and Roles

The Project Director, Aundrea Asbell, Staff Research Associate, University of California, Berkeley (510-665-3590; [aasbell@berkeley.edu](mailto:aasbell@berkeley.edu)) will be responsible for overall project oversight and act as primary contact. She or delegated technical staff at UCB will be responsible for sample collection, calibration of field instruments, and sample transport, custody and storage.

Pesticide analyses will be conducted at Southern Illinois University under the direction of Dr. Michael Lydy (618-453-4091; [mlydy@siu.edu](mailto:mlydy@siu.edu)). A subcontract will be issued to Southern Illinois University for analysis of water samples collected under this project, with analysis in accordance with the procedures described in this QAPP.

4.2 Quality Assurance Officer role

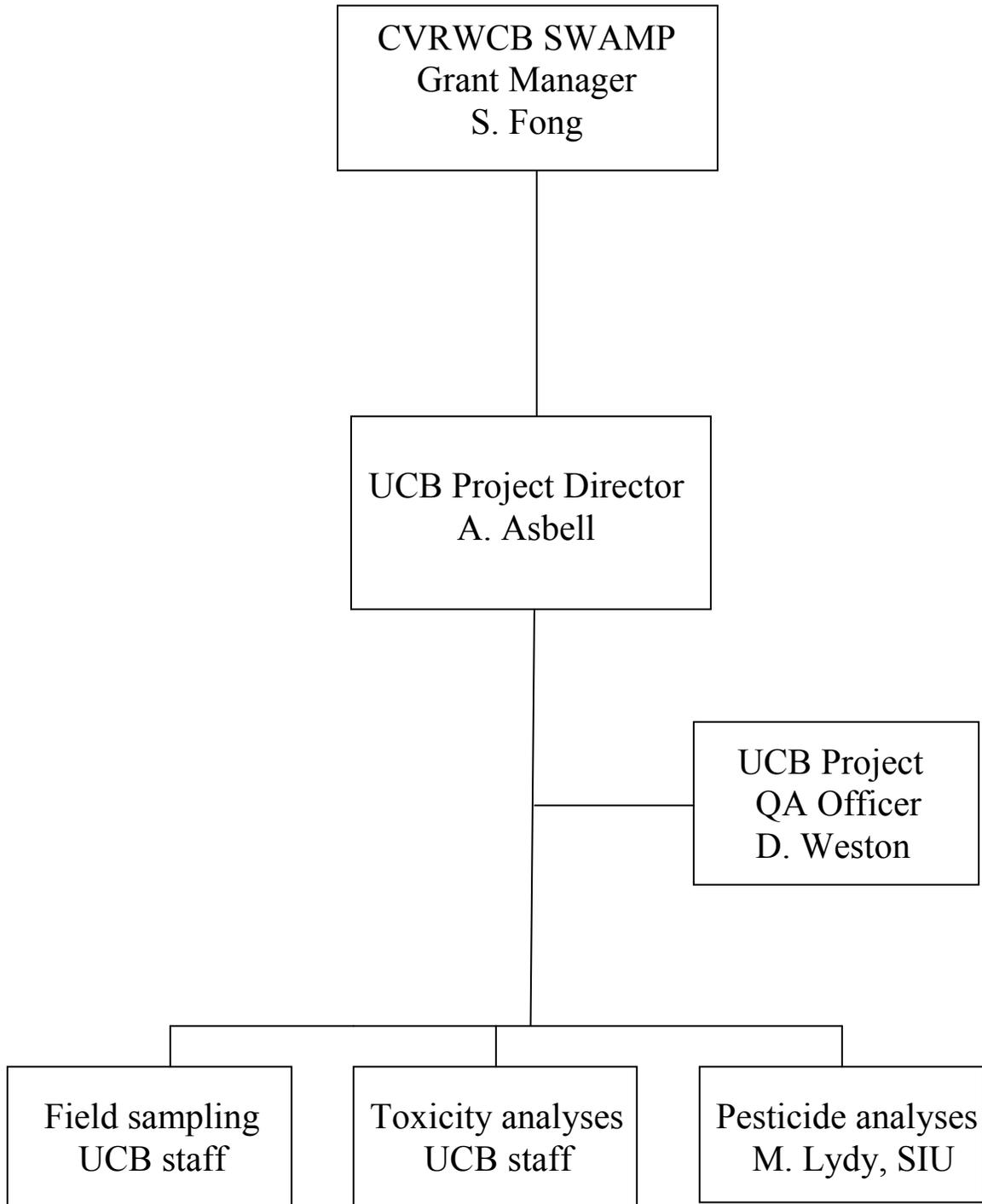
Donald Weston, Adjunct Professor, University of California, Berkeley (510-665-3421; [dweston@berkeley.edu](mailto:dweston@berkeley.edu)) will serve as the Project QA Officer. He will be responsible for retaining the most current approved QAPP. He will be responsible for implementation of the QA procedures outlined in this QAPP, and monitoring QA performance throughout the project. He will assess compliance of both the prime and subcontractors, and will report to the Project Director should any corrective action be needed. He may stop actions of any project participants if there are significant deviations from required practices or evidence of systematic failure.

#### 4.3 Persons responsible for QAPP update and maintenance

Changes to this QAPP will be made by the Project Director with concurrence of the Project QA Officer, Regional Board SWAMP Grant Manager, and SWAMP QA Officer. The Project Director will be responsible for making the changes, obtaining approval signatures, and distribution of copies to project participants.

#### 4.4 Organizational Chart and Responsibilities

Figure 1. Organizational chart



## Section A05. Problem Definition

### 5.1 Problem Statement

Two emerging and potentially converging issues have provided the impetus for the current project. First, the decline in populations of several pelagic fish species native to Sacramento-San Joaquin Delta has been of critical concern for the past several years. Though the cause(s) for the decline in these Delta populations are not known, toxic contaminants are among the possibilities often suggested. Second, pyrethroid pesticide use in California has grown dramatically in recent years, with much of the increase in use coming from urban areas (Moran, 2007; Oros and Werner, 2005). The current use of pyrethroids in California is twice what it was just ten years ago (CDPR, 2007), leading to the suggestion, as yet untested, that this increased usage could be linked to the decline in pelagic fish species either directly or indirectly through pesticide effects on critical prey species. It is known that pyrethroids are reaching surface waters within the watershed at concentrations toxic to aquatic life. Approximately one out of five sediment samples from agricultural drainage dominated water bodies (Weston et al. 2004; Weston et al., 2008), and two of three sediment samples from urban drainage dominated water bodies (Weston et al., 2005, Amweg et al., 2006), contain pyrethroids at concentrations that exceed acutely toxic levels for standard toxicity testing species.

Though not a standard water toxicity testing species, but used because of its sensitivity to pyrethroids, the amphipod *Hyalella azteca* was employed in water toxicity tests of samples collected from discharges to the Delta by UC Berkeley investigators. Notably, only one out of twenty water column samples from agricultural drainages contain pyrethroids at concentrations that exceed acutely toxic levels. More alarmingly, however, nearly all water samples from urban storm drains and about half the samples from publicly owned treatment works (POTWs) contain pyrethroids at concentrations that exceed acutely toxic levels. Urban inputs of pyrethroids into the lower American River following rain events is sufficient to cause water column toxicity to *H. azteca*. In samples taken over four successive storm events in early 2009, 7 out of 8 samples taken from the American River between Folsom Dam and the confluence with the Sacramento River exhibited acute toxicity. Correlational evidence and toxicity identification evaluation procedures both indicated that the pyrethroid bifenthrin was likely responsible for the observed toxicity.

The presence and demonstrated toxicity of pyrethroids in the American River waters was unexpected and disturbing as the river provides both recreational and natural value as it passes through the greater Sacramento urbanized area. The river provides habitat to fall run Chinook salmon and other salmonids, it is a water source for the Nimbus hatchery, and it provides municipal drinking water. Obtaining information on the storm water contributions natural creeks and constructed drains make to the American River, and establishing if these conveyances contain pyrethroids at toxicologically significant concentrations, is critical to protecting aquatic life in general, and specifically to the protection of fish species that are currently at risk.

The Lower American River encompasses the river immediately downstream of Folsom Dam, Lake Natoma to Nimbus Dam and the 23 miles of mainstem river from Nimbus Dam to the

confluence with the Sacramento River at Discovery Park. The Lower American River is valued as an area supporting important fish and wildlife habitat and riparian vegetation, and a regional recreational parkway, including fishing opportunities. It is also a major source of drinking water for several municipalities and a critical floodway. A wide variety of urban, industrial, fisheries, environmental, and recreational stakeholders all have a vital stake in the American River and all have a need to understand the health of the River and its complex interrelationships.

## 5.2 Decisions or Outcomes

The current project will provide critical information to many of the interested stakeholders and agencies. For example, management decisions related to pesticide use and water quality impacts are made by the California Department of Pesticide Regulation (DPR), the Regional Water Quality Control Boards (Water Boards), the US EPA, and other agencies. These agencies work together to establish which pesticide products are available for agriculture, urban, and other uses, and permissible application practices for these products.

The project report will consider the needs of the DPR and the Water Boards. The information gained from this project will also assist Water Board staff in reporting for 305(b) requirements as well as in determinations of those water bodies to be placed on the 303(d) impairment list, and if stressor identification and load allocation assessments for total maximum daily load (TMDL) development are necessary.

## 5.3 Water Quality or Regulatory Criteria

There currently exist no guideline values or Basin Plan Objectives specifically for pyrethroid pesticides in water, though the Water Board is pursuing their development. However, the CVRWQCB Basin Plan contains narrative objectives for aquatic toxicity. The results of this study can potentially be used to achieve toxicity objectives and protect water quality for beneficial uses, as these two goals are defined in Region 5's Basin Plan for the Sacramento watershed.

## **Section A06. Project/Task Description**

### 6.1 Work statement and produced products

Further details of the project can be found in the Monitoring Plan, but briefly, sampling sites will be identified in the American River watershed at the following locations:

- 1) At least five urban creeks or urban storm water drains/discharges
- 2) Four mainstem river sites (at Discovery Park, the Howe and Sunrise Accesses on the American River Parkway, and Rainbow Bridge at Folsom)

Sampling at these sites is intended to identify the pyrethroids contributed by each discharge and their concentration prior to discharge to river waters, as well as in ambient river waters at intervals throughout the greater Sacramento urbanized area.

The following description is based on the presumption of a two-day storm event (designated as Days 1 and 2). The design may be adjusted if the duration of heavy rains is appreciably shorter or longer. Given a storm event of two-day duration, sampling is planned to begin one day prior to onset of rains and last for four days total including a post-storm sampling. On the day before the storm (Day 0), baseline samples will be collected at two of the four river sites, specifically at Discovery Park and Sunrise Access. On Day 1 all four river sites and at least five discharge sites will be sampled during initial rains. On Day 2, the two river sites and all discharge sites will be re-sampled. On Day 3, all four river sites will be re-sampled; no discharges will be sampled. Day 3 is anticipated to be post-storm conditions, that is, rains are expected to terminate sometime during Day 2 in this hypothetical scenario.

Whole water samples from the urban creeks and drains and American River receiving waters will be analyzed for pyrethroid concentration; river water samples will be tested for toxicity to *Hyalella azteca*. If toxicity is identified, up to three samples over the life of the project will be evaluated by any of several Toxicity Identification Evaluation (TIE) procedures specifically designed to identify pyrethroid-related toxicity (i.e., temperature manipulation, piperonyl butoxide addition, addition of engineered esterases). Total suspended solids analysis will be done on all water samples.

A draft and final report will be provided at project completion. It is currently anticipated this report will take the form of one or more manuscripts submitted to a peer-reviewed journal, though publishability will depend upon findings, and a technical report alone would be sufficient to satisfy contract requirements.

## 6.2 Constituents to be monitored and measurement techniques

The following parameters will be measured:

- a) Pyrethroid pesticides will be quantified in water samples. We will first extract the sample using liquid:liquid extraction following EPA Method 3510C. There are no standard EPA procedures for pyrethroid quantification, but we have published a paper on a gas chromatography technique specifically designed for pyrethroids in water (Wang et al., 2009).
- b) Toxicity of whole water samples will be determined using *H. azteca*, a species chosen because it is far more sensitive to pyrethroids than any of the more typical species for freshwater testing (i.e. *Ceriodaphnia*, *Selenastrum*, fathead minnow). There are no EPA procedures for acute toxicity testing of water samples with *H. azteca*, but EPA procedures do provide for a reference toxicant test with a 4-d water-only exposure (EPA, 2002). In addition, we have published several peer-reviewed papers using *H. azteca* for toxicity testing of water samples (Weston and Jackson, 2009, Weston and Lydy, in press). This procedure is described in greater detail in section B04.4.
- c) Total suspended solids in water samples will be measured following EPA Method 160.2.
- d) Field measurements are limited to ancillary site characteristics determined during

sampling (temperature, dissolved oxygen, pH, and conductivity as measured by a handheld meter).

### 6.3 Project schedule and number of test samples

Chemical analysis will be initiated within approved holding times noted below. Biological testing will be initiated as soon as possible after sample receipt, but no later than as specified in the toxicity testing procedures described in section B04.4 of this document or as prescribed in EPA protocols.

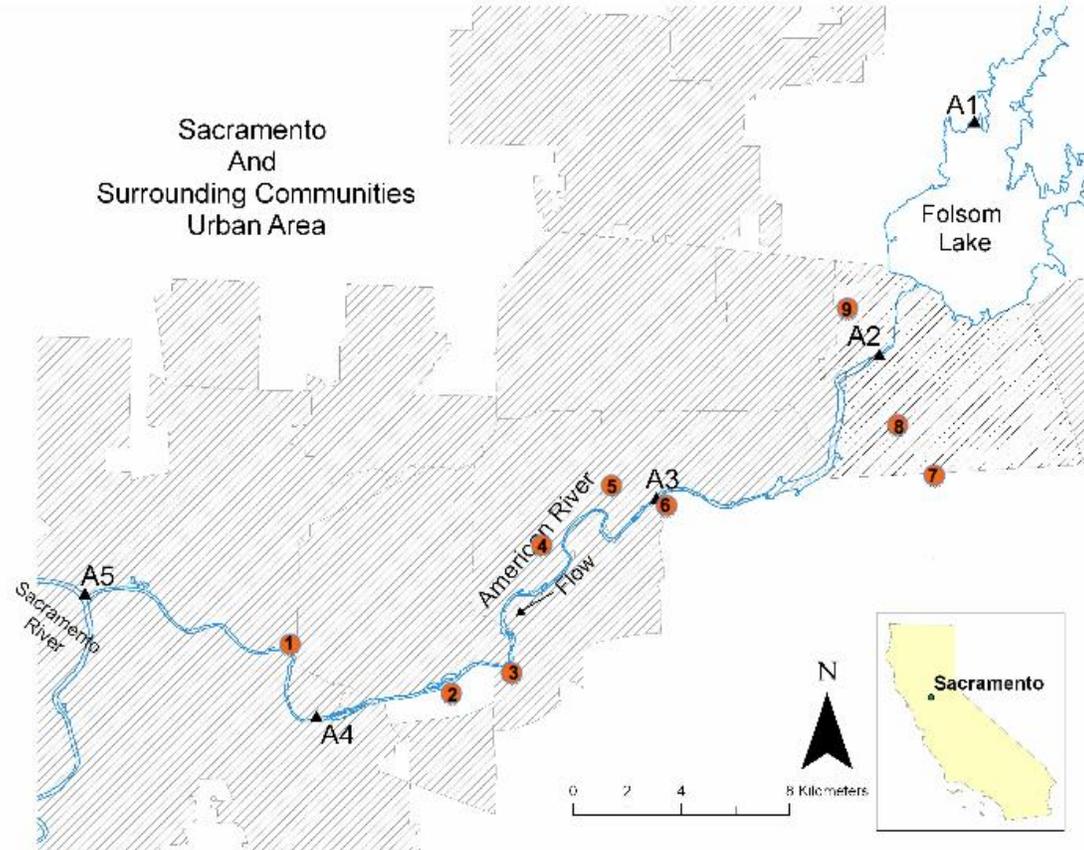
**Table 1. Project timeline**

Activity	Initiation	Completion	Deliverable	Due date
Project start	late 2009 (as soon as contractual arrangements finalized)		None	
Field sampling	late 2009 (as soon as contractual arrangements finalized)	4/30/10	Oral quarterly report  Field data sheets	10 <sup>th</sup> of the month following the quarter.  30 days after completion of all sampling
Laboratory analyses	late 2009 (as soon as contractual arrangements finalized)	6/31/10	Electronic data reports	90 days after completion of all analyses
Draft report	8/1/10	2/28/11	Draft report	2/28/11
Final report	3/1/11	4/30/11	Final report	4/30/11

### 6.4 Geographical setting and sample sites

All sampling will occur within the Lower American River watershed (Figure 2). At least five sampling site locations at natural creeks, constructed drains, or sumps discharging to the American River will be selected as representative of the major potential pyrethroid sources. Four mainstem American River sampling locations will be sampled to represent the receiving waters as it traverses the greater Sacramento urbanized area from Folsom Dam to its confluence with the Sacramento River.

Figure 2. Tentative sampling locations within Lower American River Watershed



Designation on map	Site description
A1	(Not sampled in current study)
A2	Rainbow Bridge
A3	Sunrise Access
A4	Howe Access
A5	Discovery Park
1	Chicken and Strong Ranch Sloughs
2	Mayhew Drain
3	Mather Drain
4	Carmichael Creek
5	Minnesota Creek
6	Buffalo Creek
7	Alder Creek
8	Willow Creek
9	Hinkle Creek

Pre-field investigations of potential sampling sites will be performed using information provided by the CVRWQCB, cooperating municipal water agencies, and commercially available maps including aerial photographs obtained from GoogleMaps. Sites identified through pre-field investigations will be verified on the ground and evaluated for accessibility during field reconnaissance prior to the initiation of sampling. Because this study is an investigation prompted by prior detections of pyrethroids and positive toxicity testing results recorded in spring 2009, sampling locations for the mainstem river have been previously determined and, and with one exception, are intended to be re-sampled; the exception being to add a site at Rainbow Bridge, just below Folsom Dam, to represent dam outflows. Tentative sampling locations, as shown on Figure 2, are not yet finalized pending further ongoing discussion with stormwater management agencies. As sample locations are finalized, the CVRWQCB SWAMP Grant Manager must approve the final site list.

## 6.5 Constraints

Much of the sampling is planned to occur during winter storm events. Sampling of drain outflow is inherently challenging because of the extreme variation in flow rates. The sites will be selected so as to be accessible under all flow conditions, however, should conditions arise under which reliable samples can not be obtained, or to do so would present a risk to safety, the CVRWQCB SWAMP Grant Manager will be notified. The SWAMP Grant Manager, with concurrence of the UCB Project Director and QA Officer, has the authority to designate alternative sites for sampling at any time during the project.

The SWAMP Quality Assurance Management Plan recommends water toxicity testing be initiated within 48 hours. Every effort will be made to meet this limit, but the inherent uncertainties of storm event sampling, and the probability that field crews will be away from the laboratory for two days for sample collection may occasionally result in exceedance of holding time. In the event that time limit is exceeded the SWAMP Grant Manager will be notified, and holding time exceedance will be noted in data reports.

A major difficulty with testing for pyrethroids in Delta waters is that analytical detection limits are often at or even above concentrations that are acutely toxic to sensitive aquatic species. To address this concern, this study will focus on storm water runoff conveyed by storm drains and natural creeks that may contain pyrethroids. Such samples would represent worst-case conditions (i.e., greatest potential movement of pyrethroids to waterways resulting in highest possible concentrations). If the compounds are not detected in the drains and creeks themselves, then it is unlikely toxicity would remain after release to and dilution within American River waters.

## **Section A07. Measurement Quality Objectives And Criteria For Measurement Data**

Measurement quality objectives for this project will consist of the following:

Field measurements (e.g., temperature, dissolved oxygen) – Accuracy, Precision, Completeness

Pesticide analyses – Accuracy, Precision, Recovery, Completeness

Toxicity testing – Accuracy, Precision, Completeness

Total suspended solids – Accuracy, Precision, Recovery, Completeness

Accuracy is a measure of how much of a constituent actually present is determined by the analysis. It will be determined by measuring standard solutions, laboratory reference materials, or spiked matrices, and will typically be reported as percent recovery. Analytical bias, that is a laboratory condition or process causing persistent distortion of the measurement in one direction, will also be assessed by these same measurements of materials with known concentrations, and would be reflected by a percent recovery that consistently shows error in one direction.

Precision is a measure of the reproducibility of the measurement in repeated analyses, and is quantified by Relative Percent Difference (RPD; difference between measurements as a proportion of the mean) or Relative Standard Deviation (RSD; standard deviation as a proportion of the mean). Precision will be determined by analysis of laboratory and field replicates.

Completeness is the relationship between the total potential data anticipated and that actually available for use. While 100% completeness is desirable, and may for some parameters be achievable, it is possible that completeness could be diminished by sample breakage, laboratory error, field conditions preventing sample collection, etc. Completeness will be calculated as the number of samples that provide usable data as a proportion of the total samples expected, and thresholds are established that define the proportion of usable data that must be produced before conclusions can be drawn.

Representativeness is largely dictated by field sampling procedures. It is a qualitative indication of how well the sample taken reflects the true conditions at the sample site. The term sampling bias is used to describe deviations from representativeness. With respect to this study, the primary issue of representativeness is how well the water sample collected reflects the water 1) discharging to the American River at the time of the storm event and 2) flowing in the American River before, during and after the storm event. Discharge sampling sites have been selected so as to optimize representativeness of the surrounding land use, such as locating the discharge samples downstream of urban land use and as close to be point of discharge to the river as access permits. River sampling sites have been selected so as to optimize representativeness of the waters by locating the sites at intervals throughout the greater Sacramento metropolitan area, and avoiding river locations that are immediately downstream of known runoff inputs.

Bias is the persistent distortion of a measurement that causes errors in one direction. We go to considerable lengths to avoid bias. Some of the quality control procedures previously noted, such as analysis of matrix spikes or lab control spikes serve to minimize distortion of results by bias.

Comparability relates to similarity of data from different data sets and sources. It is an indication of the confidence with which one data set can be compared to another. Project participants adhere to US EPA test protocols, laboratory SOPs, and QA measures outlined herein, and acceptable reference toxicant test results. Therefore, the laboratory results obtained in one project can be compared to results from previous projects, as well as from previous projects from other laboratories that adhere to the same US EPA protocols.

**Table 2. Measurement quality objectives**

Group	Parameter	Accuracy	Precision	Recovery	Rep. Limit	Project Action Limit	Completeness
Field data	D.O.	±0.5 mg/L	±0.5 mg/L	NA	0.2 mg/L	NA	90%
	Temp.	±0.5°C	±0.5°C	NA	NA	NA	90%
	pH	±0.5	±0.5	NA	NA	NA	90%
	Conductivity	±5%	±5%	NA	0.1 μS/cm	NA	90%
Lab data	Pyrethroids	LCS within 50-150%	MS/MSD/lab dup within ±25% RPD	MS within 50-150%.	1 ng/L	NA	90%
	Tox. Testing: D.O.	±0.5 mg/L	±0.5 mg/L	NA	0.2 mg/L	>2.5 mg/L	90%
	Tox. Testing: Temp.	±0.5°C	±0.5°C	NA	NA	22-24 °C	90%
	Tox. Testing: pH	±0.5	±0.5	NA	NA	6-9 pH units	90%
	Tox. Testing: Conductivity	±10%	±5%	NA	0.1 μS/cm	500 μS/cm	90%
	Tox. Testing: Hardness	Within ±10% of standard	Lab. Dup. 25% RPD	NA	1 mg/L	NA	90%
	Tox. Testing: Alkalinity	Within ±10% of standard	Lab. Dup. 25% RPD	NA	1 mg/L	NA	90%
	Tox. Testing: Ammonia	Within ±30% of standard	Lab. Dup. 25% RPD	NA	0.02 mg/L	<10 mg/L	90%
	Tox Testing: Mortality	Ref. Tox. 2 s.d. of running avg.	NA	NA	2%	>80%	90%
	Tox Testing: Swimming	Ref. Tox. 2 s.d. of running avg.	NA	NA	2%	>80%	90%
	Total suspended solids	NA	Lab dup. within ±25% RPD	NA	0.5 mg/L	NA	90%

## 7.1 Test acceptability criteria

When the measurement quality objectives discussed above are applied to new data collected, they are known as performance criteria, and when applied to previously collected data, they are acceptance criteria. Data collected under our prior SWAMP-funded project in the Delta may be utilized in interpretation of data from the present study, but this prior work was done following methods and measurement quality objectives essentially identical to those proposed here.

## 7.2 Quality Assurance

Quality assurance measures will be included in this project to ascertain the reliability of the data gathered, including whether the participating laboratories' test results can be duplicated, and to assess whether test species are responding typically, relative to historical test results. To determine whether test species are responding typically during this study, reference toxicant tests will be conducted monthly for the duration of the project. These tests will serve as positive controls; the reference toxicant for these tests will be cadmium chloride ( $\text{CdCl}_2$ ) and tests will include a laboratory control and a toxicant dilution series in laboratory control water. The  $\text{LC}_{50}$  for each reference toxicant test is compared to the laboratory running means to ascertain whether it falls within the acceptable range. The US EPA acceptable range is plus or minus two standard deviations around a running mean. Sensitivity of toxicity tests refers to the ability to distinguish a statistical difference between test organism responses in laboratory control water compared to an environmental sample. Test sensitivity is frequently expressed as the percent difference between the control and environmental sample that can be detected. The level of effect that can be detected will vary, depending on control performance, variability among replicates, the test species and endpoint measured. At this time, there are no acceptability criteria for test sensitivity.

Chemical analyses will be verified through the use of blanks, spikes, and field and laboratory duplicates to ensure adequate accuracy and precision as defined above. Each batch of 20 samples will be accompanied by a set of samples designated for QA/QC purposes (e.g., LCS, MS, MSD, blank, field duplicate). Chemical analysis detection limits may be affected by instrument sensitivity or by bias due to contamination or matrix interferences. Common laboratory practice is to adjust detection limits upward in cases where high instrument precision (i.e., low variability) results in calculated detection limits that are lower than the absolute sensitivity of the analytical instrument. In these cases, best professional judgment is used to adjust detection limits upward to reduce false positives and values below the detection limit are not reported. In all cases, results cannot be reported for values less than the calculated Method Detection Limit (MDL).

Quality assurance procedures include several measures to ensure precision and accuracy, and to avoid bias. As mentioned, QA/QC samples (field duplicates, laboratory duplicates, spikes, and blanks) will be done at a rate of 1 per 20 field samples. Blanks and spikes will be included in each batch of samples analyzed.

## **Section A08. Special Training Needs/Certification**

### 8.1 Specialized training and certifications

There is no ELAP certification for the primary laboratory analyses to be conducted under this project (pyrethroid chemical analyses or *Hyalella* water toxicity testing).

There are no formal training courses offered for the type of work relevant to this project, but instruction in appropriate techniques in accordance with laboratory SOPs is provided by one-on-one training as soon as new employees begin working in the laboratory. New staff are first provided oral instruction and demonstration of the various techniques, and initially work under close supervision with rechecking of their work by the QA officer. As they become proficient, work is performed more independently, though performance is continually checked against compliance with stated Data Quality Objectives stated herein.

### 8.2 Training and certification documentation

Training records for new personnel are maintained in the Weston lab at UCB and available for review. Documentation consists of a record of the training date, skill in which the new employee is being trained, the instructor, and signatures to indicate completion.

### 8.3 Training personnel

The Project QA Officer will be responsible for overseeing staff training through demonstration and oral instruction. New personnel undergoing training will be directly supervised until they have demonstrated proficiency to the satisfaction of the QA Officer and meet the Measurement Quality Objectives stated in this QAPP. For those staff involved in field sampling, training will include the new staff member accompanying experienced field personnel on a minimum two sampling trips, prior to the new staff member performing any independent sampling. During the training period, sampling procedures will be demonstrated by experienced staff, and activities of the new staff monitored by the Project QA Officer and/or field team leader until acceptable performance is reliably shown.

## **Section A09. Documents And Records**

The QAPP original will be held by the Regional Board Grant Manager, and copies will be distributed to all parties identified in Section 3. Any later amended versions will be similarly distributed, either electronically or in hard copy, with this distribution being the responsibility of the Project Director. When new copies are received, versions other than the most current will be discarded upon receipt of the amended version so as to avoid confusion, except that a single of all versions will be archived at UCB.

UCB will generate records for sample collection, receipt, and storage. Transfer of samples from collecting staff at UCB to the other participating laboratories will be accompanied by Chain of Custody documentation. These records will be retained by the UCB Project Director.

Other documentation produced by the project include: 1) field data sheets, 2) laboratory notebooks, 3) toxicity testing laboratory forms, 4) instrument calibration sheets, 5) performance results from analyses of laboratory control material, and 5) data reports from subcontracted laboratories. These records will all be maintained by the UCB Project Director. Records specific to the analytical chemistry in support of but other than the final numerical results provided to UCB, will be held by the Analytical Laboratory Director at Southern Illinois University (pesticide analyses). All records will be held for at least three years after project completion.

All raw data are recorded with ink on standardized printed data sheets. All electronic project data will be organized in Excel spreadsheets and maintained on personal desktop computers. For most data, duplicate files will be maintained by the Project Director, the Project QA Officer, and the laboratory producing the data. Files are backed up to an off-site file archiving service automatically and immediately upon every modification.

All data related to field sampling will be prepared for inclusion in the SWAMP database. The data report package will consist of SWAMP templates, primarily those relating to chemistry and toxicity testing, filled out with the project-specific information. These will be submitted to SWAMP data management staff, via the Regional Water Board's SWAMP Grant Manager.

The investigators place a strong emphasis on publication of study results in the peer-reviewed literature. Publication provides for both broader distribution of project findings, and provides an additional level of quality assurance as a consequence of the peer-review process. The report provided to the State's Grant Manager at the completion of the study is anticipated to consist of manuscripts that have either been published, or are in a format suitable for publication if there has been inadequate time for peer review and publication. These published or publishable reports will contain the data necessary to justify the conclusions reached, with a level of detail typical of scientific publications. Additional supportive data that would be too detailed for publication due to journal space limitations will be provided to the Regional Board SWAMP Grant Manager upon request.

## **Section B01. Sampling Process Design**

### **1.1 Sample process**

Sampling process design and field collection procedures are described herein, but more detailed information can be found in the Monitoring Plan prepared for this project, and available through the SWAMP Grant Manager, Project Director, or Project QA Officer.

To characterize pyrethroid inputs and the potential impacts of these pesticides on aquatic life in the Lower American River, sample sites will be selected based on the selection criteria below.

**Table 3. Lower American River Sample Site Selection Criteria**

1. Geographic distribution throughout the Sacramento urbanized area, after release from Folsom Dam and before the American River confluence with the Sacramento River
2. Urban land use represented among the discharges
3. Storm water discharges sampled to be among the more significant in terms of flow to American River
4. Flow data available if possible (govt. gauging station or monitored by discharger)
5. Presence of access points to discharges and receiving waterways
6. Evidence of previous data suggesting pyrethroid occurrence or link to toxicity

Sampling will consist of a single grab sample at each site on each sampling occasion, with an attempt to obtain creek or drain samples during high flow. Excluding the river samples, all other discharges will be sampled as close to the point of release to river waters as possible, and where access permits.

Sampling trips are expected to be day-long trips for 3-4 day in a row. Whole water samples will be maintained on ice while in the field. They will be returned to the laboratory and held at 4°C until processing (within the holding times as further discussed below). Samples will be sent to contract laboratories for chemical analysis, typically within less than 30 days of collection, but always within a timeframe adequate to insure holding times are within prescribed limits.

Field sampling locations will generally be marked ahead of time on a DeLorme Atlas. Field crews will use the detailed maps provided in the atlas (e.g., roads, railroad lines, water bodies, county boundaries) in order to locate the intended sampling site. If the site has been occupied before, the GPS coordinates taken during that earlier visit will be available to the field crew, and confirmed when the site is re-occupied.

All sites are anticipated to be sampled during three rain events of the 2009-10 wet season. River samples will be sampled for chemical and toxicity analysis. Discharges (sumps, constructed drains) will only be sampled for chemical analyses.

Excluding QA samples, field sampling is expected to yield about 36 samples for whole water toxicity samples, at least 66 samples for pyrethroids pesticide analysis, and 66 samples for total suspended solids (Table 4).

**Table 4. Anticipated number of samples (QA samples not included in totals).**

Sampling event	Site	Pre-storm sampling	Storm event sampling		Post-storm sampling	Anticipated # of samples
		Day 0	Day 1	Day 2	Day 3	
Each of three rain events	Discovery Park	yes	yes	yes	yes	12 tox. 12 chem. 12 TSS
	Howe Access	no	yes	no	yes	6 tox. 6 chem. 6 TSS
	Sunrise Access	yes	yes	yes	yes	12 tox. 12 chem. 12 TSS
	Rainbow Bridge	no	yes	no	yes	6 tox. 6 chem. 6 TSS
	At least 5 discharges	no	yes	yes	no	30 chem. 30 TSS
	<b>TOTALS</b>	6 tox., 6 chem., 6 TSS	12 tox., 27 chem., 27 TSS	6 tox., 21 chem., 21 TSS	12 tox., 12 chem., 12 TSS	36 tox. 66 chem. 66 TSS

For purposes of the SWAMP QAPP checklist distinction between data that are "critical" and those that are "informational", pesticide concentration and toxicity are considered critical data. General environmental quality data collected concurrently with the sampling such as TSS, dissolved oxygen, conductivity, and pH are considered informational.

### 1.2 Variability

Urban storm water quality is inherently highly variable, and it is precisely for this reason that multiple sampling events are planned. Discharges will typically be sampled twice during three winter storm events and the river at multiple locations will be sampled before, during, and after the same storm events.

Due to the lack of data to support a standard organism response against comparable test results, variability is expected in toxicity testing. While there are no current methods to rectify such variability, organism response can be monitored through the application of reference toxicant tests. Inferences about organism response can be made from reference toxicant results, and used to determine whether or not an organism's response is within the acceptable limits dictated by US EPA. In instances where such variability is unusually high, the Project Director will be contacted, and the associated data will be noted in interim and final reports.

### 1.3 Bias

Some forms of bias are inherent and desirable aspects of the sampling design. Our intended sampling sites are drains and natural creeks discharging to American River receiving waters, with site selection preference toward larger drains so that samples collected are better representative of the majority of runoff reaching the river. However, interpretation of the data will make clear sampling effort was not randomized.

Another form of bias is proximity to a discharge point. By sampling the effluents from the various discharges, without allowing the opportunity for any dilution with receiving waters, the sampling is biased towards worst-case conditions. This has been done because pyrethroid detection limits are very near the threshold for toxicity to aquatic life, and thus if we were to sample only in receiving waters where the organisms of concern are located, we could not be sure pyrethroid concentrations were below toxic levels even if they were undetected. However, by sampling the discharges themselves, failure to find detectable residues there would make it unlikely concentrations would be of toxicological concern once dilution is provided for.

## **Section B02. Sampling Methods**

### 2.1 Water sampling

Water sampling of the discharges and river waters will follow protocols described in the SWAMP QAPP for Field Collection of Water Samples and employ SWAMP Water Chemistry Data Sheets. Sample jars will be prepared for pesticide analysis (1000 ml I-Chem jar pre-cleaned for pesticides), toxicity testing (4000 ml I-Chem jar pre-cleaned for pesticides), and TSS (500 ml jar). The jars will be immersed in the water by hand, and filled just below the water surface in an area that best represents the water currently being discharged from the creek or drain. In cases where it is not possible to reach the water level, such as when sampling from a stormwater sump when the water might be 20 ft below the person sampling, a stainless steel bailer will be used. The bailer will be pre-cleaned with detergent and acetone. The water obtained by the bailer will be poured in to the various jars. The jars will be labeled with sample number and date, and transported on ice to the laboratory.

Any acetone generated as a by-product of cleaning equipment in the field will be returned to the laboratory and disposed of in accordance with UC Berkeley Environmental Health and Safety requirements.

There are no equipment or support facilities needed beyond that described above.

Adherence to sampling protocols will be the responsibility of the sample team leader. Only individuals with several years of experience sampling aquatic environments will be placed in this position. In the event field conditions prevent compliance with the standard protocols, it will be the responsibility of the team leader to identify optimal alternatives, and to document any deviation or corrective action in the notebook associated with the project.

**Section B03. Sample Handling And Custody**

It is the responsibility of the field sampling team leader to document the sampling event in the field notebook, including any deviations from standard protocols, as well as on the appropriate field data sheets generated for each sample collected. This same individual is responsible for the handling and transportation of samples, including preventing contamination, degradation or sample loss, until return to the laboratory. Samples will be logged in upon return to the laboratory. As samples are sent to outside laboratories for analysis Chain of Custody forms will be generated to accompany each shipment, and copies maintained both by the shipping and receiving laboratories. An example Chain of Custody Form is provided in Attachment 1.

All samples will be delivered to the laboratory and analyses initiated within the maximum holding times specified in Table 5. Data generated from samples handled differently than stated in Table 5 will be flagged as such.

**Table 5. Sample Type, Collection, and Holding Information**

Parameter for analysis	Collection Container	Typical Sample Volume	Initial Field Preservation	Maximum Holding Time
Pyrethroids	1000 ml I-Chem jar cleaned for pesticides	1000 ml	Cool to 4°C, dark, addition of 10 ml hexane as a keeper solvent.	7 d to extraction, 40 d to analysis
Toxicity	4000 ml I-Chem jar cleaned for pesticides	4000 ml	Cool to 4°C, dark	48 hr
Total suspended solids	500 ml amber glass bottle	500 ml	Cool to 4°C, dark	7 days at 4°C

Water samples will originally be collected in glass containers labeled with a unique sample identifying number and date of collection, and held on ice until return to the laboratory. Upon arrival, samples will be transferred to a 4°C refrigerator. Samples intended for whole water chemical analysis of pyrethroids will be preserved by addition of 10 ml hexane. Hexane acts as a keeper solvent preserving the pyrethroids in a hydrophobic solvent (Wang et al., 2009).

Extracted pesticide samples will be sent to subcontracted Southern Illinois University accompanied by chain of custody documentation (example in Attachment 1). The sample team leader, or if unavailable, the Project QA Officer, will sign the chain of custody form, relinquishing sample possession. These forms accompany the samples in transit, typically in ice chests sealed with tape, and shipped overnight by FedEx. Upon receipt, an employee of the subcontracted laboratory will sign the chain of custody form indicating receipt of the material,

and mail the completed form back to the Project Director. These forms will be retained with other project-related documentation.

Upon completion of analyses, it is the responsibility of each participating laboratory to dispose of remaining material in accordance with their institution's policies for waste disposal.

#### **Section B04. Analytical Methods**

Analytical methods are described briefly below. Detailed methodology can be found in the Standard Operating Procedures (SOP) provided in the appendices. SOPs may be found there for determination of alkalinity, hardness, dissolved oxygen, conductivity, pH, ammonia, total suspended solids, toxicity testing, and pesticide analyses. Method performance criteria are generally discussed elsewhere within this QAPP (e.g., Sections A07 and B05), though two of the SOPs (toxicity testing and pesticide analyses) contain additional method specific performance criteria.

##### 4.1 Water quality measurements

Responsible person: A. Asbell of the University of California will be responsible for insuring compliance with procedures. All deviations will be reported to the UCB Project QA Officer and to the RWQCB SWAMP Grant Manager within 24 hours. The QA Officer is responsible for documenting such deviations and issuing corrective actions, if appropriate. Deviations and corrective actions will be noted in interim and final reports.

##### *Relevant SOPs:*

*SOP 3.4 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF ALKALINITY (Attachment 6)*

*SOP 3.5 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF HARDNESS ((Attachment 7)*

*SOP 3.6 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF DISSOLVED OXYGEN (Attachment 8)*

*SOP 3.7 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF CONDUCTIVITY ((Attachment 9)*

*SOP 3.8 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF pH (Attachment 10)*

*SOP 3.9 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF AMMONIA (Attachment 11)*

Laboratory measurements for dissolved oxygen and temperature will be made using a YSI Model 55 meter. Field measurements for dissolved oxygen, temperature, conductivity, and pH will be made with a YSI Model 556 meter. Both dissolved oxygen meters work on the principle that consumption of oxygen at a cathode causes a current to flow, and the rate at which oxygen crosses a membrane to reach the cathode is proportional to its partial pressure in the surrounding environment. Additional laboratory water quality measurements done in conjunction with toxicity testing include hardness (EDTA titration, EPA 130.1), alkalinity (H<sub>2</sub>SO<sub>4</sub> titration, EPA

310.1), ammonia (salicylate method, Hach Method 8155), pH and conductivity (both measured using a Fisher Accumet XL50 meter).

All meters are calibrated the day of use, and calibration data entered on data sheets maintained with each meter.

#### 4.2 Pesticide analyses

Responsible person: M. Lydy of Southern Illinois University will be responsible for insuring compliance with procedures. All deviations will be reported to the UCB Project QA Officer and to the RWQCB SWAMP Grant Manager within 24 hours. The QA Officer is responsible for documenting such deviations and issuing corrective actions, if appropriate. Deviations and corrective actions will be noted in interim and final reports.

##### *Relevant SOPs:*

*SOP 1.2 – STANDARD OPERATING PROCEDURE FOR COLLECTION OF WATER SAMPLES (Attachment 12)*

*SOP 5.1 – STANDARD OPERATING PROCEDURE FOR LIQUID-LIQUID EXTRACTION OF PYRETHROID INSECTICIDES FROM WATER (Attachment 13)*

*SOP 5.3 - STANDARD OPERATING PROCEDURE FOR ANALYSIS OF SEDIMENT PESTICIDES BY GC-ECD (Attachment 14)*

The extraction method for pyrethroids in water will be consistent with EPA Method 3510C (liquid:liquid extraction). Briefly, the 1000 ml water sample will be placed into a 2L separatory funnel and then spiked with 25 ng of the surrogates dibromooctoflourobiphenyl (DBOBF) and decachlorobiphenyl (DCBP). The water sample will be extracted three times in succession with 60 ml methylene chloride, and all extracts combined. One 60 ml methylene chloride addition will be used to extract the original sampling bottle in order to recover pesticides that may have adsorbed to the glass walls. The volume of the combined extract will be reduced under nitrogen to ~10ml for shipment to the analytical lab. The extract will then be further reduced under a stream of nitrogen at 40°C and 15 psi using a TurboVap II evaporator. Ten ml of hexane will be added, and evaporation continued until 5 ml of extract remains. The extract will be removed from the Turbovap immediately, transferred to a disposable culture tube and further reduced to 1 ml under nitrogen gas using Reactivap. An Envi-Carb-II/PSA cartridge will be conditioned with 3.0 ml hexane, and 1.0 ml of the extract transferred to the cartridge. The tube will be rinsed with 0.5 ml hexane three times, with the rinsate transferred to the cartridge. Analytes will be eluted from the cartridge with 7.0 ml of 30% methylene chloride in hexane, and eluate collected with the disposable culture tubes. The solvent will be concentrated to ~0.5 ml, the analytes transferred to a 2.0 ml GC vial with hexane. The hexane will be reduced to near dryness, and 0.5 ml 0.1% acetic acid in hexane added for the GC analysis.

The following pyrethroids are routinely quantified by our analytical procedures: bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, and permethrin. The target reporting limit for all pyrethroids in water will be 1 ng/L.

Turnaround time for pesticide analyses will be dependent upon the sample load of the laboratory at any given time, but is expected to typically be 1 month.

Upon completion of pesticide analyses, it is the responsibility of the analytical laboratory (Southern Illinois University) to dispose of remaining material in accordance with that institution's policies for waste disposal.

#### 4.3 Total suspended solids

Responsible person: A. Asbell of the University of California will be responsible for insuring compliance with procedures. All deviations will be reported to the UCB Project QA Officer and to the RWQCB SWAMP Grant Manager within 24 hours. The QA Officer is responsible for documenting such deviations and issuing corrective actions, if appropriate. Deviations and corrective actions will be noted in interim and final reports.

*Relevant SOP: SOP 3.1 - STANDARD OPERATING PROCEDURE FOR TOTAL SUSPENDED SOLIDS ANALYSIS (Attachment 15)*

Total suspended solids analysis will be done by filtration of the sample on a glass fiber filter, following by drying at slightly over 100°C. Procedures will follow EPA Method 160.2.

Turnaround time for total suspended solids analysis is expected to be one week.

Upon completion of analyses, it is the responsibility of the UC Berkeley laboratory to dispose of remaining material in accordance with that institution's policies for waste disposal.

#### 4.4 Toxicity testing

Responsible person: A. Asbell of the University of California will be responsible for insuring compliance with procedures. All deviations will be reported to the UCB Project QA Officer and to the RWQCB SWAMP Grant Manager within 24 hours. The QA Officer is responsible for documenting such deviations and issuing corrective actions, if appropriate. Deviations and corrective actions will be noted in interim and final reports.

Relevant SOPs:

*SOP 4.1 – STANDARD OPERATING PROCEDURE FOR PREPARATION OF MODERATELY HARD WATER FOR HYALELLA AND CHIRONOMUS USE (Attachment 16)*

*SOP 4.3 – STANDARD OPERATING PROCEDURE FOR 96-HR WATER TOXICITY TESTING USING HYALELLA AZTECA (Attachment 17)*

Water toxicity will be assessed using 96-hr survival of *Hyaella azteca*. This species is normally used for freshwater sediment toxicity testing, and there are well-established standard protocols for this purpose (EPA, 2002). In this project water toxicity, rather than sediments, is the concern, and the compounds of particular interest are pyrethroids. The invertebrate normally used for water toxicity testing, *Ceriodaphnia dubia*, is relatively insensitive to pyrethroids compared to *Hyaella*. With a sensitivity to pyrethroids approximately 100-fold greater, *Hyaella* is a better

choice given the objectives of this study. While *Hyaella* use in sediment testing is the norm, we have used 96-hr water-only with good results. In fact, even when using the *Hyaella* for sediment testing, the EPA protocol calls for a cadmium reference toxicity test, and this test is done as a 96-hr water only exposure.

Other than the substitution of species, testing procedures generally follow EPA protocols for 96-h acute toxicity testing with *Ceriodaphnia* or fathead minnow (EPA, 2002). *H. azteca* are maintained in laboratory culture by the project participants and are maintained at standard testing temperature (23°C). Prior to initiating a test, individuals from the cultures will be sieved to recover animals of the appropriate size and age.

Exposures will be done in beakers containing the test water and a 1 cm by 1 cm piece of Nitex screen to provide substrate for the amphipods. To initiate a test, 10 *H. azteca* individuals will be added to each beaker. Aeration will be provided if dissolved oxygen falls below 4 mg/l. Conductivity, pH, ammonia, alkalinity, and hardness will be recorded in one beaker and the control at the beginning of the test; conductivity, pH and ammonia recorded at the end; temperature and dissolved oxygen will be checked and recorded regularly throughout the test. Food (1 ml yeast/cerophyll/trout food) will be provided after approximately 42 hr, and the animals allowed to feed for approximately 6 hr. After that time, as much water as possible will be removed from the test beaker without disturbing the amphipods (approx. 80% of total volume), and replaced with fresh water from the sampling site. Test water replacement after 48 hr is consistent with EPA protocols for freshwater testing of other species (e.g. *Ceriodaphnia*, fathead minnow),

On the fourth day of the test, animals will be recovered from the test water by elutriation on a 425 µm screen. Survivors will be enumerated.

The *Hyaella* water test is nonstandard, but is a modification of the standardized and broadly utilized sediment test, and we have had two peer-reviewed publications using the technique (Weston and Jackson, 2009; Weston and Lydy, in press). An SOP for the *Hyaella* water test is provided in Attachment 17. A similar test is now in use at UC Davis for work under the Pelagic Organism Decline project, and *Hyaella* is used for water testing by several NPDES permittees.

As observed in prior toxicity test responses, *Hyaella* can demonstrate paralysis in response to various pyrethroids dissolved in water. In numerous cases, *Hyaella* will be alive but unable to swim, thus a mortality endpoint is not sensitive enough to demonstrate toxicity in such cases. To account for this, we will implement a second endpoint for animals showing this kind of toxicity; the scores for this will be interpreted as “dead or unable to swim”

If during the course of toxicity testing corrective actions are deemed necessary or appropriate, they will be issued and reported to the RWQCB SWAMP Grant Manager within 24 hours. The QA Officer is responsible for documenting such deviations and issuing corrective actions. This deviation and any ensuing corrective actions will be noted in interim and final reports.

Turnaround time for toxicity testing will be two weeks.

Upon completion of analyses, it is the responsibility of the UC Berkeley laboratory to dispose of remaining material in accordance with that institution's policies for waste disposal.

## **Section B05. Quality Control**

### 5.1 Field sampling

Field duplicates of water samples will be collected at a rate of 1 per 20 samples. These duplicates will be processed identically to all other samples using the protocols described herein.

### 5.2 Data quality indicators

The following procedures will be used to calculate the data quality measures discussed below:

$$\text{Recovery} = \frac{\text{Amount of constituent measured in analysis}}{\text{Amount of constituent known to be in sample}} \times 100$$

$$\text{Relative standard deviation} = \frac{\text{Standard deviation of multiple measurements}}{\text{Mean of multiple measurements}} \times 100$$

$$\text{Relative percent difference} = \frac{\text{Absolute difference between two measurements}}{\text{Mean of the two measurements}} \times 100$$

### 5.3 Pesticide analyses

**Blanks** – Blanks are designed to identify possible contamination during sample preparation and analysis. One laboratory blank will be run every 20 samples. The data acceptability criteria will be no analytes above the reporting limit.

**Accuracy** – A matrix spike will be used to determine the accuracy of reported data, One matrix spike will be analyzed every 20 samples. Measured concentrations are expected to be between 50 and 150% of the nominal values of the analytes. A laboratory control spike will also be used for routine verification of accuracy. The laboratory control spike will be done at a rate of one per 20 samples, with results expected to be between 50 and 150% of expected values.

**Precision** – Precision will be determined by use of a matrix spike duplicate, at a rate of one per 20 samples. Precision, as quantified by RPD, is expected to be within 25%. In addition, field duplicates will be collected at a rate of one per 20 samples, with the same precision criterion. The field duplicates in part assess precision, but are also reflective of the field or sampling variability.

**Recovery** – Surrogate spikes of DBOFB and DCBP will be added to every sample, with recovery of 70-130% as the criteria for analytical acceptance.

**Method validation** – There are no standardized analytical protocols for the compounds of primary interest in this study (pyrethroids). However, the analytical laboratory has published a description and validation of the methods (Wang et al., 2009).

#### 5.4 Total suspended solids

Blank – A method blank will be run every 20 samples or less with reported TSS at less than the reporting limit.

Precision - Precision will be determined by use of a lab duplicate and a field duplicate, all at a rate of one per 20 samples. Precision, as quantified by RPD, is expected to be within 25%.

#### 5.5 Toxicity testing

Negative control – Survivorship in lab control water greater than or equal to 80% is required for test results to be considered acceptable.

Test conditions – Conditions will be monitored for compliance with standard EPA guidelines for dissolved oxygen (>2.5 mg/L) and temperature (22-24°C). Ammonia, conductivity, alkalinity and hardness will also be monitored.

Representativeness – This freshwater amphipod is generally considered an acceptable surrogate for resident species, but one for which testing protocols are available. Additionally, it is a resident species in many California surface waters.

Accuracy – Organisms from the cultures will be tested monthly with a reference toxicant (cadmium chloride) in water exposures. If the LC<sub>50</sub> falls beyond two standard deviations of the laboratory's running average, any sample data produced since the previous test that was within normal bounds will be flagged. The same culture will be immediately retested with the reference toxicant to confirm the atypically high or low sensitivity.

Precision – Precision will be measured by field duplicates at a rate of 1 per 20 samples collected. Duplicates would help to estimate variability associated with laboratory procedures, though the field duplicate would also be susceptible to heterogeneity in water quality at the collection site. There are, however, no SWAMP acceptability criteria for variability in toxicity testing duplicates.

#### 5.6 Water quality measurements associated with toxicity testing

Accuracy – Accuracy of dissolved oxygen, pH, conductivity and ammonia measurements will be determined by calibrating to a standard solutions at the beginning of each batch of samples, and then retesting the standard at the end of the batch. If the RPD exceeds 10% (30% for ammonia) all measurements since the last accuracy check will be repeated.

Precision – Precision will be determined from the beginning/end measurement described above. The RPD will be reported if it exceeds 10% (30% for ammonia),

#### 5.8 Control actions

Should control limits specified above be exceeded, the nature of the response will depend upon the discrepancy. Typically, the first step will involve inquiry to the lab responsible for producing the data, to verify the values submitted were correct and not the result of a data entry error, for example. Presuming the data were correct, samples within the affected batch would, at a minimum, be flagged, and the potential extent of the problem would be ascertained. The discrepancy may be explainable and have very limited ramifications, such as matrix spike recovery out of control limits due to high levels of the constituent already present in the matrix chosen for spiking. A systematic bias could have broader ramifications, and could require reanalysis of multiple affected samples. In some instances reanalysis would be the only acceptable response, such as exceedance of permissible control mortality in a toxicity test. Such retesting would be done, though a second analysis may cause exceedance of holding times, and the sample will be flagged to that effect. The effectiveness of the control measures will be assessed by how well the re-analysis meets established project measurement quality objectives as described elsewhere in this QAPP. Control actions will involve both the Project Director and Project QA Officer, and if sufficiently serious, the Regional Board's SWAMP Grant Manager and SWAMP QA Officer. Control actions will be documented in written form in project files.

### **Section B06. Instrument/Equipment Testing, Inspection And Maintenance**

Field equipment will be checked when preparing for field sampling, and checked again for damage upon return. It is the responsibility of the field team leader to assemble all field material when preparing for sampling, both equipment and consumables, and to insure the equipment is properly functioning.

The GPS unit is taken on all field sampling trips, and it is the team leader's responsibility to insure that spare batteries are taken in to the field with the unit.

Dissolved oxygen meter consumables (batteries, membrane) are replaced when indicated by meter readings during use. It is the responsibility of the employee using the meter at the time replacement is indicated to perform this replacement, verify proper functioning of the unit, and to document those actions on the calibration sheet that is kept next to the instrument. Spare batteries and membranes are available in the laboratory, and will accompany the meter when taken in to the field. Procedures and criteria testing of the dissolved oxygen meter prior to use can be found in the Standard Operating Procedures (Attachment 8).

The pH/conductivity meter used in the field may occasionally require replacement of the solutions within the probes (e.g., KCl) when indicated by meter readings. Spare solutions are maintained with the meter. It is the responsibility of the employee using the meter at the time replacement is indicated to perform this replacement, verify proper functioning of the unit, and to document those actions on the calibration sheet that is kept next to the instrument. Procedures and criteria for testing of the meter prior to use can be found in the Standard Operating Procedures (Attachments 9 and 10).

Spare memory cards and a spare battery for the camera are stored in the camera case, though it is the responsibility of the field team leader to confirm their availability and the fully charged status for the battery when the camera is taken in to the field.

The principal laboratory equipment to be used on this project includes an Accumet XL50 pH/conductivity meter, recirculating temperature control units, microscopes, analytical balance and a gas chromatograph.

The pH/conductivity meter used in the lab may occasionally require replacement of the solutions within the probes (e.g., KCl) when indicated by meter readings. The unit has no user-serviceable spare parts, but spare probe-filling and calibration solutions are maintained in the laboratory with the meter. It is the responsibility of the employee using the meter at the time replacement is indicated to perform this replacement, verify proper functioning of the unit, and to document those actions on the calibration sheet that is kept next to the instrument. The calibration of the unit (both pH and conductivity) are checked and documented prior to every batch of samples. Procedures and criteria for testing of the meter prior to use can be found in the Standard Operating Procedures provided as attachments.

Temperature control units maintaining water bath temperatures during toxicity testing are checked daily for proper temperature. This responsibility varies depending on which lab employee is responsible for maintaining tests on any given day, though each test requires daily documentation that such inspection was done, with a space for sign-off by the responsible employee. Testing of the temperature within the exposure beakers provides an independent measure of the accuracy of the temperature display on the main heater/chiller unit. Any deviation will be reported to the Project Director, who will determine and document any impact on samples that may be in testing at the time. The temperature control units have no user-serviceable spare parts, though the manufacturer maintains a phone number for technical support and arranging repair.

The analytical balance used has an auto-calibration feature that, several times a day, recalibrates the unit to help insure the accuracy of the reading. In addition, a set of standard weights are available in the lab, and stored next to the balance. These weights are used to test the accuracy of the balance on a monthly basis, with results expected to be within 1% of the nominal value of the standard weight. There are no user-serviceable spare parts for the balance, though service by a manufacturer's technician is done as required.

Microscopes used to count test organisms at the beginning and end of the toxicity tests generally require little maintenance. Spare bulbs for the light sources are available in the laboratory, and replacement would be the responsibility of the employee using the microscope at the time of bulb failure. There are no testing criteria for microscopes.

Inspection and maintenance of the gas chromatogram (GC) is the responsibility of the instrument operator assigned to the instrument in any given day. The GC inlet septum, liner and gold seal will be changed every two weeks. Approximately 0.5 m of the front-end of the column will be removed when chromatographic problems are encountered. Wipe tests will be conducted every six months on the ECD to check for possible leaks. The ECD will be thermally cleaned by

“baking-out” when the baseline becomes noisy. All such maintenance is documented by the instrument operator to provide verification it was performed and so that all operators are aware of when regular maintenance procedures would again be required. Available spare supplies related to GC operation include columns, regulators, gas cylinders, and gold seals. There is also a second, identical GC unit in the laboratory should problems be experienced with the first unit. Procedures and criteria for testing of the GC can be found in the Standard Operating Procedures provided as attachments.

For all equipment discussed above, the operator of the instrument is responsible for the testing, inspection, and maintenance. Each meter or instrument has its own notebook or form where the results of tests, inspections, maintenance and repairs are documented. In instances where a meter or instrument’s test results fail to meet accuracy and/or precision Method Quality Objectives, the meter or instrument will be either replaced or sent to the manufacturer or qualified service center for maintenance. The instrument operator is responsible for documentation of the failure and resulting actions, and verifying proper functioning after these actions. If the failure may have impacted any collected data, it is the responsibility of the operator to notify the QA Officer. The QA Officer will determine the extent of impact, identify corrective action if appropriate, notify the RWQCB SWAMP Grant Manager, and be responsible for documentation in interim and final reports.

### **Section B07. Instrument/Equipment Calibration And Frequency**

Pesticide analyses will be done by gas chromatography with electron capture detection. Analytical instrumentation will be calibrated based on three external calibration standards (10, 50 and 100 ng/ml). A calibration verification standard will be run at least every 10 samples to insure that the calibration curve is within 15% of the calibration range. Should instrument drift result in failure to meet this standard, the instrument will be recalibrated. Further details on calibration of the instrument can be found in the Standard Operating Procedures provided as attachments.

The dissolved oxygen meter, pH meter, conductivity probe, and ammonia colorimeter will all be calibrated against known standards at the beginning and end of each sample batch. A calibration sheet is maintained next to each of these meters on which readings are recorded before and after each sample batch. Any needed corrective action, such as replacement of the D.O. membrane or probe electrolytes, is noted by the instrument operator on these sheets. Further details on calibration of these instruments can be found in the Standard Operating Procedures provided as attachments.

Pipettes will be professionally calibrated. In addition, accuracy is verified prior to any use when accuracy is of particular importance by dispensing a given amount of water and determining its mass on an analytical balance. Any pipettes found to not be dispensing fluids accurately are labeled as such, immediately removed from service, and held until recalibration and/or repair can be arranged.

The analytical balance will be checked monthly using weights of known mass. A record of this check will be maintained on a sheet kept next to the balance. Service and recalibration by a

specialized balance repair technician will be arranged if measurements vary by more than 1% from the known weight.

In general, all field and laboratory equipment has a dedicated log which documents calibration, maintenance, or replacement of parts. If analytical instrumentation fails to meet performance requirements, the instrument will be checked and recalibrated. If the instrument again does not meet specifications, it will be repaired and retested until performance criteria are achieved. The maintenance will be entered in the instrument log. If sample analytical information is in question due to instrument performance, the Regional Board's SWAMP Grant Manager will be contacted regarding the proper course of action including reanalyzing the sample or sending the samples to an outside laboratory for analysis.

### **Section B08. Inspection/Acceptance Of Supplies And Consumables**

All supplies will be examined for damage as they are received. Ordering personnel will review all supplies as they arrive to ensure the shipment is complete and intact. All chemicals are logged in to the appropriate logbook and dated upon receipt. All supplies are stored appropriately and are discarded upon expiration date. The following items are considered for accuracy, precision, and contamination: meters, sample bottles, balances, chemicals, standards, titrants, and reagents. If these items are not found to be in compliance with the above considerations, they will be returned to the manufacturer.

Most consumables are obtained from Fisher Scientific. The University of California, Berkeley is a major Fisher customer, and thus the ordering and delivery of supplies is routine and rapid. Nearly any item can be obtained within 24 hr if needed.

Some of the most critical consumables, and procedures for insuring uninterrupted availability include:

*H. azteca* for toxicity testing – Organisms are cultured on site, not ordered from an outside supplier. Three independent cultures are maintained to insure at least one is always available. Commercial vendors can supply ample quantities of *H. azteca* for toxicity testing purposes within 24 hrs, should the laboratory cultures for some reason be unusable.

Chemicals – Reordered when supplies on hand drop to less than a two week supply.

Deionized water – Available in a nearby building should the primary supply in the lab become unavailable.

Pre-cleaned jars for pesticide samples - Reordered when supplies on hand drop to less than a two week supply. These are checked for breakage upon arrival by the individual accepting the shipment.

It is the responsibility of the UCB Project Director to insure required consumables are available when needed. All laboratory employees are instructed to notify the Project Director when available supplies of any consumable are nearing exhaustion. The Project Director will then decide, depending on the amount of consumable remaining and how critical it is to lab operation,

whether to: 1) order the item immediately and request overnight delivery; 2) order the item immediately but with standard delivery of typically 2-3 days; or 3) delay ordering until other supplies are needed, and then ordering them together as a batch.

### **Section B09. Non-Direct Measurements**

The project may involve use of two types of non-direct measurements. First, some of the discharges to be sampled, such as the urban stormwater outfalls, have information available on volume discharged. Generally these data are based on the known discharge rate for specific pumps (i.e., pump capacity in gallons/min) and electronic records of the times the pumps turned on and turned off. Taken together, these data establish how many gallons were discharged over any given time period, and when integrated with concentration data collected under this project, can provide an estimate of loading. We have been in contact with engineers from the municipal utilities, and they have agreed to provide the discharge data. Both the engineers and project investigators will inspect the records for accuracy to insure the pump on/off sensors were recording run times properly and that discharge volumes are consistent with historical norms for the specific pump stations.

Second, analysis of the data is likely to also involve use of library resources, including electronic resources, for review of previous relevant studies in the peer-reviewed literature (e.g., quality of urban runoff, pyrethroid toxicity). This published data will be used in a general way in interpretation of the data, such as to put the research in to context or for comparison with similar studies elsewhere. Previously published data from the literature will not be assessed by the same data acceptance criteria, for publications typically do not contain sufficient information to do so, but any difference in methodology that could affect previous findings and cause them to differ from results of the current study will be noted.

### **Section B10. Data Management**

Field data sheets will be completed at time of sample collection. The sheets to be used are the standard SWAMP field data sheets for water sampling, as downloaded from the SWAMP website. These sheets provide information such as GPS coordinates of the sample site, date/time of sampling, prevailing weather conditions at time of sampling, and ancillary water quality measurements of the water body (e.g., temperature, dissolved oxygen). In addition, field crews carry a field notebook to record any other relevant information for which there is no appropriate field on the SWAMP field data sheets.

Examples of the toxicity testing data sheets are provided in the appendices to this QAPP (Attachments 2 and 3). Toxicity testing data sheets will be generated for each sample tested. These sheets include data on the start/finish dates of the test, documentation of daily feeding and water changes, water quality measurements taken throughout the exposure, and survival for each individual replicate. A cover sheet is generated for each test batch and provides a place for sign-off each day by a lab technician that required test maintenance was performed. Each test will also be accompanied by a second sheet for each individual sample, providing fields for recording water quality parameters, and documenting survival at test completion.

After completion of a test, the lab technician will review the toxicity testing sheets for completeness and accuracy, and provide them to the Project Director. The data will be reviewed by the Project Director for compliance with testing procedures and method quality objectives (Attachment 5). The Project Director or designee will transfer the data to Excel spreadsheets for manipulation and analysis. The data are also prepared in accordance with the format of the SWAMP toxicity template, for later upload to that database. The original laboratory data sheets will be archived in the event there is a need to refer to them in the future.

Instrument calibration sheets will be maintained for water quality parameters (dissolved oxygen, ammonia, pH, conductivity, hardness, alkalinity). These forms document the dates on which calibration was performed, and the reading obtained prior to calibration to a known standard. An example of the dissolved oxygen calibration sheet is provided in Attachment 4, and calibration sheets for the other instruments are comparable. An entry is made to the sheet every day the instrument is in use by the technician using the device. Any corrective action such as replacing batteries would also be noted on the sheets. When a sheet becomes filled with entries, it will be given to the Project Director who will archive it for later review if necessary. These water quality instruments are routinely used in connection with the toxicity testing, and the data from measurements are recorded on the toxicity testing data sheets noted above and shown in Attachments 2 and 3.

Chemistry data will be transferred in to Excel spreadsheets for manipulation and analysis by the instrument technician responsible for performing the analyses and quantifying area under the peaks on the chromatogram. After review for accuracy and completeness by that technician, the data will be provided to the Laboratory Director for further review and verification, and then submitted to the Project Director as an Excel spreadsheet. The data are also prepared in accordance with the format of the SWAMP chemistry template, for later upload to that database. The original laboratory data, including chromatograms, will be archived in the event there is a need to refer to them in the future.

Data not associated with a routine analysis for which a laboratory data sheet is employed will be recorded in to a bound notebook. This data could include information such a record of lab work done on a specific day, any unique characteristics of a sample noted during processing, breakage and loss of a sample, etc. Each project in the laboratory has its own notebook for recording of information relevant to that project, and entries may be made by technicians running analyses or the Project Director.

All project data generated as described above are subject to a 100% check for accuracy by the UCB QA Officer. Electronic data reports submitted by subcontracted laboratories, will be organized in Excel spreadsheets and maintained on a personal desktop computer. All data are analyzed and proofread for accuracy, and files are backed up automatically to an offsite archiving service every time they are modified.

Document control will be the responsibility of the Project Director. Field data sheets will be provided to the Project Director after each field event, and hard copies stored in a metal file cabinet. Toxicity testing data sheets, once completed, verified, and all data entered on to Excel spreadsheets, will be maintained by the Project Director. Instrument calibration sheets will be

archived for future review if necessary. Chemistry data are normally provided to the Project Director electronically, and it will be the responsibility of the individual analytical labs supplying the electronic files to maintain the hard copy documents that support them. The project notebook is kept available in the laboratory so that entries can be made during the duration of the project by laboratory staff, but once complete, it will be held by the Project Director. Electronic files will be maintained by the Project Director and shared with the Project QA Officer. Any modification to those files, once the data are entered and verified, will require their joint agreement.

Data collected under this project will be uploaded to the SWAMP database. The field data sheets are those routinely used by SWAMP; the laboratory data sheets have been developed by the respective laboratories, but contain the data required by SWAMP. It is the responsibility of the Project Director, or designee, to enter, verify, and submit the data to the SWAMP data management team. Most data will initially be available in Excel spreadsheets, and such data will be reformatted for SWAMP entry by the Project Director or designee. Chemistry data are entered in to SWAMP format by the analytical laboratory, and provided to the Project Director for review prior to upload. All data are subject to review by the Project QA Officer for accuracy and compliance with QAPP and SWAMP criteria.

Two elements of the SWAMP QA checklist are not applicable to this project. First, there is no continuous monitoring and associated data management needs. Secondly, there are no specialized hardware or software requirements for this project. Data are maintained on a standard personal computer using widely available software (e.g., Microsoft Excel). Statistics associated with toxicity testing are determined using standard toxicity testing software (e.g., CETIS).

### **Section C01. Assessments And Response Actions**

Tests are conducted according to standardized procedures when possible, and described in this QAPP and associated SOPs. Deviations from these procedures will be documented by the UCB Project Director and reported to the Regional Board SWAMP Grant Manager. Best professional judgment will be used in interpretation of results obtained when deviations have occurred, and deviations will be noted in project reports.

Internal assessments will be performed by the Project QA Officer. The QA Officer will periodically observe laboratory practices and field sampling activities to insure compliance with SOPs and this QAPP. In addition, on approximately a quarterly basis the Project QA Officer will perform a review of all data generated for compliance with SOPs and this QAPP. This assessment will occur roughly concurrently with submission of the quarterly reports (early January, April, July, and October of each year). This review will include, but not be limited to, an assessment of whether data quality objectives have been met with respect to accuracy, precision, representativeness, and completeness.

Any deficiencies identified during lab surveillance or data audits will be immediately reported to the Project Director via e-mail (so as to retain written documentation), and if appropriate, any

individual staff member responsible for the deficiency. After allowing a reasonable period for corrective action (typically a few days to a few weeks, depending on the nature of the deficiency), the QA Officer will again meet with the Project Director to determine what actions have been taken to address the problem, and assess what data, if any, may be adversely affected. Subsequent data of the same type previously found to be deficient will be carefully monitored for compliance with data quality objectives as soon as it becomes available, until it is clear the deficiency has been corrected to the satisfaction of the Project QA Officer. The Project QA Officer has the authority to stop sampling and/or laboratory analysis if there is reason to believe data quality may be compromised.

Ultimate responsibility rests with the Project QA Officer for identifying data deficiencies, taking steps to correct them, verifying that the corrective action has been successful, and documenting these actions in written form in project files. Assessment reports will be provided to the Project Director, and if there are any findings indicating that the quality of the data produced is in question, the information will be communicated in writing to the Regional Board SWAMP Grant Manager.

The laboratory will also be available for external assessments by the SWRCB upon request.

**Section C02. Reports To Management**

**Table 6. QA Management Reports**

<b>Type of report</b>	<b>Frequency</b>	<b>Due date</b>	<b>Responsible for report prep.</b>	<b>Report recipient</b>
Quarterly report	Quarterly	10 <sup>th</sup> of the month following the quarter	Project Director	RWQCB SWAMP Grant Manager
Electronic data reports	Following sampling	90 days after completion of all analyses	Project Director	RWQCB SWAMP Grant Manager
Draft report	Once	2/28/11	Project Team	RWQCB SWAMP Grant Manager
Final report	Once	4/30/11	Project Team	RWQCB SWAMP Grant Manager

**Section D01. Data Review, Verification, And Validation**

Data produced will be evaluated against the quality assurance practices and measurement quality objectives. SWAMP-consistent criteria for acceptance or rejection of data were described previously in this QAPP, particularly in Section A07.

Data will be separated into three categories:

1. Data meeting all data quality objectives
2. Data meeting data quality objectives, but failing to meet precision criteria
3. Data failing to meet accuracy criteria

Should any data appear to be deficient during data verification, the first step will be to confirm the reported data with those in the project team who produced it. The objective will be to determine if the data only appears deficient due a failure in data review (e.g. failure to report results from a blank analysis that had in fact been done, or typographical error in data entry), or if quality assurance procedures had indeed not been fully instituted. If the former is the case, revisions to the data report will be accepted, and the data may be fully acceptable for inclusion in the database upon passing further data verification.

Data meeting all data quality objectives, but failing to meet QA/QC criteria will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the third category. Data falling in the first category is considered usable by the project. Data falling into the third category which are determined to be deficient in some aspect related to quality assurance will be thoroughly assessed to establish the severity of potential problems. If the data are lacking in some regard unrelated to accuracy (e.g., no documentation of precision), but there is reason to believe the data are otherwise reliable, then the data may be suitable for inclusion in the database though flagged with a qualifier. Any data suspected to be inaccurate, or without reasonable justification to presume accuracy, will be rejected.

Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved into the first category, but flagged with a qualifier in the final database.

## **Section D02. Verification And Validation Methods**

Data verification will initially be conducted by those personnel involved in generating the data. Before filing an official data report, these individuals will review the data to insure proper reporting, for example, watching for typographical errors, incomplete data fields, inconsistencies between the number of samples received and those reported, etc. All personnel will verify their own work products to insure they are producing output of the best possible quality.

A more formal data verification will be conducted by the Project Director. First, this effort will establish whether all required project documentation has been produced and determine the location of those records. This assessment would include insuring that the field data sheets had been properly completed, that sample custody had been documented as the material changed hands, and establishing the location of all relevant project records. Secondly, the data verification will assess whether the methods used for sample collection and analysis satisfy project needs and are consistent with intended protocols. This evaluation would include comparison of the methods and the output with accepted protocols such as this QAPP, SOPs, or standardized protocols.

Data validation will be performed by the Project QA Officer. Its primary purpose will be to determine if the data quality objectives have been met. The verified data will provide the primary input for the validation exercise, though the validator will also rely upon this QAPP and appropriate SOPs. The data validation process will evaluate records for consistency, review QC information, and identify and deviations from project measurement quality objectives. In the event that deviations are identified, it will be the responsibility of the data validator to add data qualifiers if not already noted, and to assess the impact of these deviations on overall project results. An example of a checklist for data validation is provided in Attachment 5. This example is specific to data generated by the 96-hr *H. azteca* toxicity test, and evaluates test performance against performance criteria and data acceptability criteria.

The Project QA Officer will be responsible for informing data users of the problematic issues that were discussed, along with the associated reconciliations and corrections.

### **Section D03. Reconciliation With User Requirements**

The Project Director, in consultation with the Regional Board SWAMP Grant Manager will review project results to determine if the data produced are adequate to address the original questions asked. The intent of the investigators is to provide data that will assist SWAMP in its objective of monitoring surface waters within California, identifying when environmental quality is compromised, and determining the cause underlying these impacts. It is also our intent to publish in the peer-reviewed literature, thus contributing to the growing body of data on pyrethroid pesticides in California waterbodies, and help to establish the extent to which aquatic habitat quality is affected by pesticide use. Data will also be included within the SWAMP database, thereby becoming available to other investigators, and potentially of value to other programs and monitoring efforts.

The primary method of data interpretation will be to establish relationships between the chemical concentration measurements and measures of biological effect as quantified by laboratory toxicity testing results. Further testing of water column samples using toxicity identification evaluation procedures will serve to enhance the validity of chemical analysis results.

This project requires a minimum of 90% completeness. Should collection of the intended samples not be possible, or the integrity of samples collected compromised such that this completeness criteria is unlikely to be met, the Regional Board SWAMP Grant Manager will be notified within 24 hr of this determination. Alternative actions, such as a change in sampling sites or sampling times, will be discussed, documented in project files, and implemented.

All data will be subject to the Quality Assurance assessment described in Section A07 to insure project data quality requirements are met. Any deviations will, depending on severity, result in exclusion of data from project reporting, or at a minimum, flagged with a data qualifier to alert potential data users. If the data quality objectives are met, project findings will be suitable to satisfy the technical goals and intended use.

At the conclusion of the study, the Project Director, Project QA Officer, and Regional Board SWAMP Grant Manager will review all data produced during the project with the intent of identifying any uncertainties of which potential data users should be aware. Uncertainty in the measurements have previously been discussed and documented in this QAPP (Section A07). If any basis for uncertainty in the data exists beyond that already noted, that basis will be discussed by the individuals noted above, and documented in the project final report and/or SWAMP data files as appropriate.

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# ATTACHMENTS

**Attachment 1. CHAIN OF CUSTODY**

Weston lab, UC Berkeley

Project Name: \_\_\_\_\_

Special Instructions/Comments: \_\_\_\_\_

Sampler Name (printed): \_\_\_\_\_

\_\_\_\_\_

Sampler Signature: \_\_\_\_\_

\_\_\_\_\_

ID	Location	Date	Time	Container		Matrix			Preserv.	Intended analyses			
				Type	No.	Wat.	Sed.	Tis.					

Relinquished by:				Received by:			
Printed name	Signature	Date	Time	Printed name	Signature	Date	Time

If samples were shipped frozen via overnight courier, initial to document that they were received in a frozen state \_\_\_\_\_

**Attachment 2. TOXICITY TEST: BATCH COVER SHEET**

**Project** \_\_\_\_\_

**Test start date** \_\_\_\_\_

**Test end date** \_\_\_\_\_

**Species** \_\_\_\_\_

**Age/Size at start** \_\_\_\_\_

**Initial to confirm task done**

<b>Day</b>	<b>0</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b>Day of week</b>					
<b>Temp. display</b>					
<b>Flow check or water change</b>					

**Notes** \_\_\_\_\_

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**Attachment 3. TOXICITY TEST: COMPARISON TO CONTROL**

Station \_\_\_\_\_  
 Start Date \_\_\_\_\_  
 End date \_\_\_\_\_

**SURVIVAL (out of 10)**

Concentration	Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Rep. 8
Survival								

**WATER QUALITY**

	Day 0	Day 1	Day 2	Day 3	Day 4
Day of wk					
Repl. #					
Temp					
D.O.					
pH					
Cond					
Alk					
Hard					
NH3					

Comments \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

**ATTACHMENT 4:  
LABORATORY  
CALIBRATION SHEET FOR  
THE DISSOLVED OXYGEN  
METER**



ATTACHMENT 5:  
BATCH VERIFICATION  
AND VALIDATION FORM  
FOR H. AZTECA 96-hr  
TOXICITY TEST

## BATCH VERIFICATION AND VALIDATION: HYALELLA AZTECA 96-hr TOXICITY TEST

**Batch information:**

Start date \_\_\_\_\_  
 Samples included \_\_\_\_\_  
 \_\_\_\_\_

**Test acceptability criteria:**

		<u>Acceptable</u>	<u>Unacceptable</u>	<u>Comment</u>
Holding time	<48 hr	<input type="checkbox"/>	<input type="checkbox"/>	_____
Water renewal	Exchange at 48 hr	<input type="checkbox"/>	<input type="checkbox"/>	_____
Temperature	Target +/- 1°C	<input type="checkbox"/>	<input type="checkbox"/>	_____
Dissolved oxygen	>4 mg/L	<input type="checkbox"/>	<input type="checkbox"/>	_____
Hardness	Within 50% of initial	<input type="checkbox"/>	<input type="checkbox"/>	_____
Alkalinity	Within 50% of initial	<input type="checkbox"/>	<input type="checkbox"/>	_____
Ammonia	<50% increase	<input type="checkbox"/>	<input type="checkbox"/>	_____
Control survival	>90%	<input type="checkbox"/>	<input type="checkbox"/>	_____

**Accuracy:**

Date of relevant reference toxicity test: \_\_\_\_\_  
 Reference toxicity test within control chart limits? (Yes/No) \_\_\_\_\_

**Precision:**

Field duplicates (1 per 20 samples). Sample numbers \_\_\_\_\_  
 Survival in duplicate 1 \_\_\_\_\_  
 Survival in duplicate 2 \_\_\_\_\_  
 RSD (standard deviation as a percentage of duplicate mean) \_\_\_\_\_

**Corrective action:**

In the event of failure to meet any acceptability criteria for the batch, notify the Project Director. Failure in control survival is automatically cause for retest of the batch. Failure with regards to dissolved oxygen limits is automatically cause for retest of the affected sample.

Name \_\_\_\_\_ Signature \_\_\_\_\_ Date \_\_\_\_\_

## Attachment 6

# SOP 3.4- STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF ALKALINITY

Weston laboratory: University of California, Berkeley

Updated: October 1, 2005

### REQUIRED MATERIALS

- 50 mL graduated cylinder
- Deionized water
- Buret
- Magnetic stirrer and stir bar
- 50 mL beaker
- 0.02 N H<sub>2</sub>SO<sub>4</sub> solution.
- Bromcresol green-methyl red indicator solution
- Hardness indicator solution

### PROCEDURE

1. Place 25 ml sample into 50 ml beaker.
2. Fill buret with 0.02 N H<sub>2</sub>SO<sub>4</sub>.
3. Place stir bar in the sample and begin stirring.
4. Add 2 drops of bromcresol green-methyl red to the sample, turning it blue-green.
5. Note the initial buret reading. Add sulfuric acid titrant dropwise to the sample until the blue-green color is gone and solution becomes clear. (Typically requires about 1.5 ml for the lab's moderately hard water)
6. Note final buret reading and calculate amount of titrant used.
7. Multiply ml titrant times 40 to obtain alkalinity as mg/l CaCO<sub>3</sub>.
8. If alkalinity needs to be expressed as mg/l HCO<sub>3</sub>, divide the above value by 0.8202. This step is not necessary for usual protocols.

**Attachment 7**

**SOP 3.5 - STANDARD OPERATING PROCEDURE FOR THE  
MEASUREMENT OF HARDNESS**

Weston laboratory: University of California, Berkeley

Updated: October 1, 2005

**REQUIRED MATERIALS**

- 50 mL graduated cylinder
- Deionized water
- Buret
- Magnetic stirrer and stir bar
- 50 mL beaker
- Hardness buffer solution
- 0.01 M EDTA solution
- Hardness indicator solution

**PROCEDURE**

1. Place 25 ml of sample into a 50 ml beaker.
2. Add an additional 25 ml of deionized water (to make total volume 50 ml).
3. Fill buret with 0.01 M EDTA.
4. Place stir bar in the sample and begin stirring.
5. Add 1 ml of hardness buffer solution to the sample.
6. Add 2 drops of indicator solution, turning the sample red.
7. Note the initial buret reading. Add EDTA titrant dropwise to the sample until the last hint of red color is gone and solution becomes blue. (Typically requires about 2.5 ml for our lab's moderately hard water).
8. Note final buret reading and calculate amount of titrant used.
9. Multiply ml titrant times 40 to obtain hardness as mg/l CaCO<sub>3</sub>.

## Attachment 8

# SOP 3.6 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF DISSOLVED OXYGEN

Weston laboratory: University of California, Berkeley

Updated: December 4, 2009

## REQUIRED MATERIALS

- YSI Model 55 DO meter
- Associated YSI manual
- Oxygen probe filling solution
- Replacement membranes
- Clipboard with DO calibration records

## PROCEDURE

- Note: See YSI Model 55 operation manual for additional detail if needed.
1. Calibrate the meter prior to analyzing samples. To do so:
    - a. Ensure that the sponge inside the calibration chamber is wet; and insert the probe.
    - b. Turn the instrument **ON** and wait for the DO and temperature readings to stabilize (about 10-15 min.).
    - c. Use two fingers and press the  $\wedge$   $\vee$  keys at the same time.
    - d. Enter the local altitude in hundreds of feet, using the arrow keys to increase or decrease the value (0 at Field Station).
    - e. When desired altitude is displayed press the **ENTER** key.
    - f. The display will show the % saturation. Record value in calibration records.
    - g. Press the **ENTER** key to move to the salinity compensation procedure.
    - f. Enter the approximate salinity of the sample (0-40 PPT) and press the **ENTER** key.
    - g. The instrument will return to measurement mode, displaying mg/L.
  2. After calibration you may toggle from dissolved oxygen as mg/L or % air saturation by pressing the **MODE** key.
  3. If working in a dimly lit area, pressing the **LIGHT** key will illuminate the display area.

4. To take a reading, place the probe in the solution, and gently move it back and forth while waiting for reading to stabilize.
5. When the displayed value stabilizes, record the measurement.
6. After completing a batch of samples (10 maximum), return the probe to the chamber and recalibrate as above, recording the % saturation in the calibration records prior to recalibration.
7. Press the **ON/OFF** key to turn the instrument off.
8. Replace the battery and/or membrane when readings become erratic.
9. Avoid sticking the probe into sediments.

## Attachment 9

# SOP 3.7 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF CONDUCTIVITY

Weston laboratory: University of California, Berkeley

Updated: December 4, 2009

## REQUIRED MATERIALS

- Fisher Accumet XL50 meter with conductivity probe
- Standard solution (100  $\mu\text{S}/\text{cm}$ )
- Deionized water in wash bottle
- Redi-Stor storage solution

## PROCEDURE

1. Calibrate the meter prior to analyzing samples. To do so:
  - a. Remove probe from storage solution, rinse with deionized water using the wash bottle, and place in 100  $\mu\text{S}/\text{cm}$  standard.
  - b. Turn meter on by pressing **STANDBY** button.
  - c. Press the **CHANNEL** key once or twice as needed until only Channel C appears in the display.
  - d. Record the value as  $\mu\text{S}/\text{cm}$  in the calibration records prior to calibrating.
  - e. Press the **CALIBRATE** key and insure the value displayed on the screen as the calibration target is the correct one for the solution in which the probe is inserted.
  - f. Press the **ENTER** key.
2. Place the probe in the sample to be measured.
3. When the reading stabilizes, record measurement. Values about 300-350 are typical for our lab's moderately hard water.
4. NOTE: The meter will automatically switch from  $\mu\text{S}/\text{cm}$  to  $\text{mS}/\text{cm}$  if the reading exceeds 1000  $\mu\text{S}/\text{cm}$ . If an atypical reading is displayed, like 1.24 for example,

confirm that the display is now reading in mS/cm, and if so, convert to  $\mu\text{S/cm}$  before recording value (e.g., 1240).

5. After completing a batch of samples (10 maximum), return the probe to the calibration standard, recording the value in the calibration records prior to recalibration.
6. If drift is ever suspected, the probe may be recalibrated at any time.
7. When done, rinse the probe with deionized water, return it to the storage solution, and press the **STANDBY** key to turn the instrument off.
8. Make sure calibration standard is closed before leaving the instrument. Minimize the amount of time it is kept open.

**Attachment 10**

**SOP 3.8 - STANDARD OPERATING PROCEDURE FOR THE  
MEASUREMENT OF pH**

Weston laboratory: University of California, Berkeley

Updated: December 4, 2009

**REQUIRED MATERIALS**

- Fisher Accumet XL50 meter
- Associated Accumet manual
- pH probe filling solution
- Deionized water in wash bottle
- pH buffers

**PROCEDURE**

- Note: See Accumet operation manual for more detail if needed.
  - Note: The following assumes a one-point pH calibration at pH 7, since waters typically measured in the lab range in pH from about 6.8 to 8.0. A two point curve may be advisable if measuring pH values more distant from 7, and instructions may be found posted near the pH meter.
1. Calibrate the Accumet pH meter as follows:
    - a. Turn the meter on by pressing the **STANDBY** key.
    - b. Insure the probe is in the pH 7 buffer (yellow color).
    - c. Press the **CHANNEL** key once or twice as needed until only Channel B appears in the display.
    - d. Record value in calibration records before calibrating.
    - e. Press the **CALIBRATE** key, and follow instructions on screen.
  2. Rinse the probe with DI water and place it in the sample to be measured.
  3. Wait until measurement stabilizes (may take up to 10 minutes) and record the measurement.

4. After completing a batch of samples (10 maximum), return the probe to the calibration standard, recording the value in the calibration records prior to recalibration.
  
1. When done, rinse the probe with deionized water, return it to the pH 7 buffer, and press the **STANDBY** key to turn the instrument off.

**Attachment 11**

**SOP 3.9 - STANDARD OPERATING PROCEDURE FOR THE  
MEASUREMENT OF AMMONIA**

Weston laboratory: University of California, Berkeley

Updated: October 1, 2007

**REQUIRED MATERIALS**

- Hach colorimeter
- Ammonia analysis vials
- Ammonia salicylate packets
- Ammonia cyanurate packets
- 25 ml graduate cylinder
- Deionized water

**PROCEDURE**

1. Run a 0.5 mg/l ammonia standard solution with every batch of unknown samples.
2. Pour the water sample to be tested in to one of the ammonia testing vials, filling it to the 10 ml mark.
3. Add the contents of one pouch of ammonia salicylate to the sample, and shake.
4. After three minutes add the contents of one pouch of ammonia cyanurate to the sample, and shake again.
5. After 15 minutes, place the sample in to the chamber of the Hach spectrophotometer and cover with the blue cover supplied with the instrument.
6. Press the "read" button and record the value.
7. If the ammonia concentration is greater than 0.6 mg/l, the display will flash, and the sample will have to be diluted and rerun.
8. In most cases a dilution of 5 ml sample to 20 ml deionized water will be adequate, and the resulting meter reading should be multiplied by 5 to get the true concentration.
9. Greater dilutions can be done if the 5:20 ratio is not adequate to bring the concentration to within meter range.

## **Attachment 12**

# **SOP 1.2 - STANDARD OPERATING PROCEDURE FOR COLLECTION OF WATER SAMPLES**

Weston laboratory: University of California, Berkeley

Updated: November 1, 2007

### **REQUIRED MATERIALS**

- Sampling containers appropriate to the intended analytes
- Gloves
- Lab marker and labeling tape
- Sampling pole, bailer or peristaltic pump, as necessary
- Multiparameter meter for water quality measurements
- Cleaning materials if bailer is used
- Ice chest with ice
- Field sampling forms for water samples

### **PROCEDURE:**

1. Gloves should be worn to prevent sample contamination and to protect the sampling person.
2. Water samples should be taken in the midpoint of that portion of the water body with greatest flow. However this point may not be accessible if the water is too deep for wading and no bridge is present. In these cases sampling from a dock may be a good alternative. Shoreline sampling is permissible but the least desirable of the options.
3. Upon reaching the sampling site, water samples should be taken before bed sediment samples or any other sampling that may disturb the substrate or introduce foreign material in to the water column.
4. Label the required sampling containers with sample location, date, time and intended analysis. The exact number and type of containers will vary depending on the analytes of interest. However in all cases, the containers should be pre-cleaned in a manner appropriate to remove any residues of the intended analyte.
5. Sample containers should be rinsed with site water prior to filling for the actual sample unless the analytes of interest include organics, inorganics or bacteria (no rinsing in these cases).

6. If it is possible to reach the water surface, sample containers should be filled by immersing them to 0.1 m below the surface, removing the cap, filling so as to leave minimal air space, and then recapping before withdrawing the bottle.
7. If the water surface is out of reach, a sampling pole is the next best option if the distance to the water permits it, and the bottle to be filled is of a size appropriate for attachment to a pole.
8. A bailer may be the best option in some situations, such as if the distance to the water exceeds the reach of a sampling pole. The bailer should be made of a material suitable for the intended analytes. Stainless steel is appropriate in many cases.
9. If a bailer is used, it is necessary to thoroughly clean it between sampling sites by washing in a soap solution, rinsing with deionized water, rinsing with acetone (if being used for organic analyses), and rinsing again with deionized water.
10. A final sampling option, particularly appropriate if a very high volume of water is needed (>40 L), is use of a peristaltic pump, with water drawn through a Teflon-lined hose.
11. Obtain ancillary water quality parameters as needed for the project (e.g., temperature, dissolved oxygen, pH, conductivity). These measurements may be taken by lowering a probe in to the water body, or by filling a bucket and taking measurements within the bucket.
12. Properly store and preserve the samples. Usually this will involve holding them in an ice chest with ice until return to the laboratory.

## Attachment 13

### SOP 5.1: Liquid-liquid extraction of pyrethroid pesticides from water

Author(s):	<u>Dongli Wang</u>	Date:	<u>12-4-09</u>
Section Leader:	<u>Dr. Michael Lydy</u>	Date:	<u>12-4-09</u>

#### 1.0 OBJECTIVE

To describe the procedures for extracting pyrethroid pesticides from water sample by liquid-liquid extraction and normal phase solid phase extraction clean-up.

#### 2.0 HEALTH AND SAFETY

Lab coat, safety glasses and gloves must be worn at all times. Chemicals utilized in this procedure create possible health risks. Analysts performing this method should obtain and read the MSDS sheets available for all chemicals to be used. Hazard solvents used in this procedure cause possible health risks, therefore, the extraction should be processed in a hood.

#### 3.0 PERSONNEL/TRAINING/RESPONSIBILITIES

Any SIU employee/ student familiar with the equipment, laboratory techniques, and trained in this and references SOPs may perform this procedures. Before preparing samples by this method, each analyst should prepare a series of four replicates (Quad Study) to demonstrate their ability to generate accurate and precise data, or be in the supervision of a trained analyst.

#### 4.0 REQUIRED AND RECOMMENDED MATERIALS

##### 4.1 Pesticide and surrogate standards

Pyrethroids include bifenthrin, lambda-cyhalothrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate, fenpropathrin and deltamethrin.

Surrogates are 4,4'-dibromooctafluoro-biphenyl (DBOFB) and decachlorobiphenyl (DCBP).

##### 4.2 Reagents:

Methylene chloride, hexane, 1N hydrogen chloride (HCl), Acetic acid (HAc), Distilled water

##### 4.3 Instruments:

Nitrogen gas, Disposable Pasteur pipettes, 1000 ml separatory funnels, 1000 ml graduated cylinder, disposable culture tubes (15X85 mm, Fisherbrand). Separatory funnels must be soaked in detergent water over night, and then flushed with tap water, rinsed with acetone and distilled water.

TurboVap II evaporator (Zymark, Hopkinton, MA, USA) with 200 mL Turbovap vials  
Envi-Carb-II/PSA 300/600 mg (6. 0 mL tubes, Supelco, Bellefonte PA, USA)

#### 5.0 PROCEDURE

5.1 Store samples at 4°C free from light till the extraction and analysis. Sample extraction must be finished within 7 days.

5.2 Measure 1000 ml water sample into a 2000 ml separatory funnel, and then spike 25 ng of each of two surrogates (DBOFB and DCBP). Add the matrix spike/ matrix spike duplicate compounds to the two additional aliquots of the sample selected for spiking.

5.3 Add 60 ml methylene chloride to the separatory funnels, and shake the funnels for 2 min, and then let them settle down till two clear layers appear. Drain the bottom layer into vials. Repeat the procedure two additional times. Discard upper layer after washing steps. An additional 60 ml methylene chloride wash will be used to extract the original sampling bottle in order to recover pesticides that may have adsorbed to the glass walls.

5.4 Reduce the volume (~240 ml) of the combined extract to 10 ml under a stream of nitrogen at 40°C and 15

psi using a TurboVap II evaporator. Add 10 ml of hexane, and then continue the evaporation until 5 ml of extract remains.

**Note: TurboVap II evaporator needs to be preheated at least 30 minutes prior to use. Leave the outside cover of the evaporator open after each run, otherwise the accumulated water may cause electrical problems.**

- 5.5 Remove the extract from the TurboVap immediately, transfer it into a disposable culture tube and further reduce to 1 ml under nitrogen gas using Reactivap.
- 5.6 Condition an Envi-Carb-II/PSA cartridge with 3.0 ml hexane, and then transfer 1.0 ml of the extract to the cartridge. Rinse the tube with 0.5 ml hexane three times, the rinsed solution should also be transferred to the cartridge.
- 5.7 Elute analytes from the cartridge with 7.0 ml of 30% methylene chloride in hexane. Collect the eluate with the disposable culture tubes.
- 5.8 Concentrate the solvent to ~ 0.5 ml, completely transfer analytes to 1.5 ml GC vial with hexane. Carefully reduce to near dryness, and add 0.5 ml 0.1% HAC in hexane for the GC analysis.

## 6.0 QUALITY CONTROL CHECKS AND ACCEPTANCE

- 6.1 A Laboratory Control Blank (LCB), Laboratory Control Sample (LCS), Laboratory duplicate (LD), a matrix spike (MS) and a matrix spike duplicate (MSD) are included for every 20 samples (a field duplicate and a blind spike should be also included if required).
  - 6.1.1 The Laboratory Control Blank (LCB) is an aliquot of distilled water of the same volume as the samples (1 L) which is extracted in the same manner as the samples (surrogates should be added prior to extraction). The purpose of the LCB is to demonstrate that reagents and glassware are free from contamination.
  - 6.1.2 The Laboratory Control Sample (LCS) is an aliquot of distilled water of the same volume as the samples (1 L). The LCS is spiked with 50 ng of each of analyte of interest and extracted in the same manner as the samples. The purpose of the LCS is used to verify that the laboratory can perform the analysis in a clean matrix.
  - 6.1.3 The laboratory matrix spike (MS) is one of the twenty samples spiked with 50 ng of each of analyte of interest. It is then extracted in the same manner as the samples. The purpose of the MS is to demonstrate the accuracy of the extraction procedure. Accuracy is usually represented as percent recovery (PR). See Appendix I.
  - 6.1.4 The laboratory matrix spike duplicate (MSD) is prepared exactly the same as the MS. The purpose of the MSD is to demonstrate the precision of the extraction procedure. Precision is usually represented as relative percent difference (RPD). See Appendix I.
  - 6.1.5 The blind spike (BS) is an aliquot of distilled water spiked with unknown amount of analyte(s) of interest. It is then extracted in the same manner as the samples. The purpose of the BS is to demonstrate the accuracy of the extraction procedure. Accuracy is usually represented as percent recovery. See Appendix I.
- 6.2 A surrogate is a compound, which is added to each sample prior to extraction to verify the extraction efficiency of the sample. The compound chosen as a surrogate should be a compound which is unlikely to be found in the samples and does not coelute with target analytes. However, the compound should be similar to the target analytes in order to demonstrate extraction efficiency. DBOFB and DCBP are used as surrogates in this procedure. Extraction efficiency is usually represented as percent recovery of surrogates. See Appendix I
- 6.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDL should be determined for each project individually based on the different cleanup procedure. Reporting limits should be determined for each project individually according to the project design and MDL. Reporting MDL is varied by different cleanup method.

## 7.0 LITERATURE CITED

1. Method 506. Determination of Phthalate and adipate esters in drinking water by liquid-liquid extraction or liquid-solid extraction and gas chromatography with photoionization detection. Revision 1.1, 1995.
2. Method 507 Determination of Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector - Revision 2.1., 1995

3.        Method 508 Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector - Revision 3.1., 1995

#### **Calculations**

##### **Percent Recovery Calculations**

**Percent Recovery (surrogate or BS) = Measured Concentration / Spiked Concentration 100**

**Percent Recovery (MS or MSD) = (conc. of MS – conc. of sample) / Spiked concentration 100**

##### **Relative Percent Difference (RPD) Calculations**

**RPD = (Percent recovery of MS – Percent recovery of MSD) / Average (Percent recovery of MS and MSD) 100**

##### **Method detection limit (MDL) Calculations**

**MDL =  $s * t_{(0.99, n-1)}$**

The practical protocol to determine MDL specifies taking a minimum of 7 replicates of a given spiking concentration in a range of three to five times that of the projected lowest concentration that the detector in the analytical method can measure. Then, the MDL is calculated as follows:  $MDL = s * t_{(0.99, n-1)}$ , where  $s$  is the standard deviation of the 7 replicate measurements and  $t_{(0.99, n-1)} = 3.14$  is a  $t$ -distribution value taken at a confidence level of 0.99 and degrees of freedom  $df = n - 1 = 6$ . The 95% confidence interval estimates for the MDL are computed according confidence level of 0.99 and degrees of freedom  $df$  to the following equations derived from percentiles of the chi-square distribution  $LCL = 0.64 MDL$  and  $UCL = 2.20 MDL$ , where LCL and UCL are the lower and upper 95% confidence limits respectively, based on seven aliquots.

**Qualification detection limit = 3 MDL**

#### Attachment 14

## SOP 5.3 - STANDARD OPERATING PROCEDURE FOR ANALYSIS OF PESTICIDES BY GC-ECD

Lydy laboratory: Southern Illinois University

Updated: November 17, 2007

### REQUIRED MATERIALS

- Hexane
- Volumetric glassware
- Pesticide standards
- Ethyl ether
- Syringes
- Disposable pipettes
- 2 ml vials with septa
- Compressed air
- Ultra High Purity Helium, Nitrogen, and Oxygen Gas
- Capillary Column 1 (DB-5, 0.50 $\mu$ m film, 30m length, 0.35mm I.D.)
- Capillary Column 2 (DB-608, 1.00 $\mu$ m film, 30m length, 0.35mm I.D.)
- HP6890GC with NPD and ECD detectors, autosampler, and supplies

### PROCEDURE

#### Preparing the GC –

1. The appropriate column should be attached to the inlet and the detector of choice. For more information refer to the HP6890 manuals. Only experienced analyst should reconfigure the GC.
2. The GC and Chemstation computer should be turned on and the GC should be allowed to reach initial conditions. (The GC should be left on unless it is not being used for very long lengths of time.) Make sure the appropriate method is loaded on the Chemstation. Methods control all GC parameters. Specific methods are designed for specific analyte mixes, detectors, and columns. An example method for an ECD and a NPD analysis are shown in the Appendix I. To load a new method:
  - Under *View*, make sure that you are in the *Method and Run Control* Screen.
  - Under *File*, *load* the appropriate method.

3. If running the NPD detector, the bead should be allowed to adjust to the appropriate reference energy before each run. To start this process:
  - Under *Instrument* then *Edit Parameters*, hit the *adjust* button.
  - Make sure the adjust offset is at 40pA. Then click the *start* button. This process will take about thirty minutes.
4. Check the 4 mL vials in the autosampler unit to make sure that the solvent vials are full with the solvent which your extracts are in and that the waste vials are empty. The type of solvent may vary; however 1:1 acetone hexane is common.

### Running a Sequence –

5. Run files (computer files containing the data for each run) are stored in the directory named after the date. Before each daily sequence, the new directory path must be entered as follows:
  - Under *Sequence, Sequence parameters*, enter the date in the directory box in the format mmddyy.
6. The sequence table consists of a list of the samples to be run, the methods they will be run by, and the number of injections from the vial. Each line number represents a data file. To keep from over-writing files you must enter each sample on a new line number. To edit the sequence table:
  - Under *Sequence, Sequence table*, enter the samples, the vial (indicating a place on the auto-sampler tray which is marked with numbers accordingly), the method, and the number of injections per vial (always one).
7. Place the 2 ml vials with septa containing the standards and samples in the appropriate place in the auto-sampler tray.
  - The sequence can now be started by either clicking on start sequence in the Sequence table (to run an entire sequence beginning to end) or by clicking on Sequence, then partial sequence and then marking the samples with the space bar that need to be ran (to run a partial sequence after some of the lines of the table have been previously ran).
  - A daily run or sequence should consist of the following:
    - 1) Saturations. A high standard (top level of the curve up to 20 times higher) to remove active sites within the system. (ECD-necessary; NPD-optional)
    - 2) Solvent blanks. A solvent that is only run to demonstrate that no carry over from the saturations or other source is contaminating the run.

3) Calibration standards. A dilution series of known values containing all analytes of interest. Three (or more) calibration levels are mandatory.

4) Samples. The extracts which you wish to analyze.

5) Calibration verification standards (CCV). A calibration standard analyzed after the samples to verify that the calibration was valid throughout the run. CCV's are usually ran at a frequency of every ten samples.

### **Data Processing –**

8. Under *View*, make sure that you are in *Data Analysis*.
9. Under *File*, load the first calibration standard. After the chromatogram appears on the screen, check the baseline that the computer has drawn for each target peak. The baseline should follow a path which would be expected if the analyte was not present. To enlarge small areas of the chromatogram, draw a box around the area of interest with the left mouse button. To return to the full screen, double click the left mouse button. The area above this baseline and below the peak is the peak area. If the baseline is not correct, it can be redrawn manually by the following techniques:
  - To adjust starting and ending points of the baseline, click on *integration*, then *draw baseline*. Next, click on the point where you want the new baseline to start, then double click on the point where you want the baseline to end. The new baseline and peak area should now appear on the screen.
  - To split peaks from the target peaks, click on *integration*, then *split peaks*. Move the cursor to the point at which the peak split needs to go and click on the left mouse button.
10. The report is now ready to be printed. This is achieved by clicking on *Report* then *Print*.
11. The procedure is then repeated for each calibration sample.
12. A calibration curve is then calculated for each analyte using all calibration levels. This can be done by calculating response factors for each analyte at each calibration level. The calibration factor is calculated by taking the amount and dividing by the area. The average response factor is then calculated for each analyte over the different calibration levels. The average response factor for each analyte is then entered in the *Calibration Table* that is under the *Calibration* heading.
13. The calibration curve may be automatically calculated by the computer software. If calibrating by this method, multiple levels are added to the *Calibration table*, each level has the concentrations of a corresponding calibration standard for each analyte

entered within the table. After all necessary adjustments have been made to the chromatogram of the calibration standard (as above), the data is added to the curve by the following steps:

- Go to the *Calibration* menu and select *Calibrate/Recalibrate*. Check the box that says replace and indicate the level of the standard.
- Repeat for remaining levels.
- Go to *Calibration* menu and select *Calibration Settings* and chose either *response factor* or *linear regression* for calibration method. If linear regression is chosen, it is recommended to force the y-intercept through the origin.
- Go to *Calibration* menu and select *Calibration table* and print the table for the run log.

### **Quality Control –**

14. When determining average response factors for a calibration curve, the standard deviation should also be calculated. The standard deviation divided by the average and multiplied by 100 is called the % Relative Standard Deviation (%RSD) or the coefficient of variation. If the %RSD is above 20%, the response factor should be examined to determine if it is representative of the calibration range. High or low points of the curve may need to be reanalyzed or discarded. Linear regression coefficients are provided by the computer software.
15. Sample areas should be higher than the area of the lowest standard and lower than the area of the highest standard. If the sample area is outside of the ranges demonstrated by your standards, it should be reanalyzed or taken as an estimate.
16. If the same calibration curve is frequently ran and adjustments to the instrument have not been made, a continuing calibration verification standard (CCV) may be ran to determine if the instrument is within calibration. Any standard which is part of the calibration curve can be used as a CCV. If the CCV is within 10% of the expected concentration, recalibration is unnecessary. If the CCV is outside of 10%, adjustments have been made to the instrument, or the calibration curve has not been ran within the last two weeks recalibration is necessary.
17. CCVs should also be analyzed at a frequency of every 20 samples and at the end of every analytical run. The CCVs should be within 15% of the expected concentration.

**Calculations –**

Response factor (RF) = Concentration or amount of Standard/ Area of Peak

%RSD = (Standard Deviation of RFs/ Mean of RFs) X 100

CCV percent from expected = (Calculated Conc./ Expected Conc.) X 100

Final Solution Concentration of Sample = Area X RF

Original Sample Concentration =

$$\frac{\text{Final Solution Conc. X Final Solution Volume X Dilution Factor}}{\text{Amount of Sample (Volume for aqueous sample)}}$$

## Attachment 15

# SOP 3.1 - STANDARD OPERATING PROCEDURE FOR TOTAL SUSPENDED SOLIDS ANALYSIS

Weston laboratory: University of California, Berkeley

Updated: November 1, 2007

## REQUIRED MATERIALS

- 934 AH glass fiber filters
- Vacuum filtration apparatus
- Aluminum pans
- Drying oven
- Dessicator
- Analytical balance
- Wash bottle of Milli-Q water
- Filter paper forceps
- 25 ml and 250 ml graduated cylinders

## PROCEDURE

1. To prepare the glass fiber filters, place filters on the filter supports of the vacuum filtration system, with wrinkled side up. Rinse with three successive 20 ml volumes of Milli-Q water. Transfer the filters to aluminum weighing dishes.
2. Dry filters in drying oven at 103-105°C overnight, and place in dessicator until they reach room temperature.
3. Weigh three random filters, redry for a minimum of one hour, and reweigh. If the two weights differ by more than 0.5 mg, re-dry the entire batch of filters. Store filters in dessicator until use.
4. Immediately before use, weigh the filter paper, and record weight on aluminum pan, later copying it to data sheet. Hereafter, only use forceps to handle the filter.
5. Place a pre-weighed filter on the filter support.
6. Vigorously shake the suspended solids sample, and without allowing time for settling, pour the desired amount in to a graduated cylinder. The volume needed will depend on the turbidity of the sample. Highly turbid samples may require only 25 ml; very clear water samples may require up to 500 ml.
7. Transfer the sample from the graduated cylinder to the filter funnel and apply vacuum until all water has passed through the filter. The amount of water filtered should be sufficient to retain a minimum of 1 mg of sediment on the filter. Conversely, it should

- not be so great that the filter becomes clogged, and filtration time exceeds 5 minutes. Record how much water was filtered.
8. Should too much water be used and the filter becomes clogged, discard and repeat with smaller volume.
  9. Once the desired sample volume has passed through the filter, with the vacuum still on, rinse the graduated cylinder and filter funnel walls three times with about 10 ml of Milli-Q water each time.
  10. If there is any large particulate matter on the filter (sticks, leaves) they should be removed with the forceps.
  11. Lift the filter paper from its support, and return to aluminum dish. Write the sample number on the aluminum dish.
  12. Place in drying oven at 103-105°C for a minimum of four hours.
  13. Transfer to dessicator for 30 minutes, then weigh paper and sediment residue.
  14. To calculate the amount of suspended sediment. Subtract the weight of the filter paper from the combined weight of the filter plus sediment, and divide by the volume of water filtered. Adjust units so final result is expressed in mg/L.

**Attachment 16**

**SOP 4.1 - STANDARD OPERATING PROCEDURE FOR  
PREPARATION OF MODERATELY HARD WATER FOR  
HYALELLA AND CHIRONOMUS USE**

Weston laboratory: University of California, Berkeley

Updated: October 1, 2005

**REQUIRED MATERIALS**

- 4- 20 L carboys
- 4 L beaker
- Magnetic stirrer and stir bar
- Sodium bicarbonate
- Potassium chloride
- Calcium chloride anhydrous
- Calcium sulfate dihydrate
- Magnesium sulfate
- Milli-Q purified water
- Airline and air stones
- Plastic weighing boat

**PROCEDURE**

1. Fill the 4 L beaker with Milli-Q purified water.
  
2. Weigh out the following salts in to the weigh boat:
  - a.) Sodium Bicarbonate                      7.68 grams



### Attachment 17

## **SOP 4.3 - STANDARD OPERATING PROCEDURE FOR 4-d WATER TOXICITY TESTING USING HYALELLA AZTECA**

Weston laboratory: University of California, Berkeley

Updated: November 3, 2009

### **REQUIRED MATERIALS**

- 80 ml beakers (5 per sample plus 5 for control)
- Moderately hard reconstituted water
- Temperature controlled bath
- Conductivity meter
- pH meter
- D.O. meter
- Ammonia meter
- *Hyalella azteca* cultures
- 250 ml polyethylene bottles (1 per sample plus 1 for control)
- Disposable pipette with built-in molded bulb
- Brass sieves (355  $\mu\text{m}$ , 425  $\mu\text{m}$ , 500 $\mu\text{m}$ )
- Stainless steel bowl
- Toxicity testing data sheet (1 per sample)
- Dissecting microscope
- 80 mm glass dishes
- Aquarium dip net
- (3) 5-ml pipettman tips
- Airline
- Yeast-cerophyll-trout chow (YCT)
- Labeling tape
- Wash bottle with deionized water
- Turkey baster

### **PROCEDURE**

*H. azteca* is widely used as a standard species for freshwater sediment testing, but no standard EPA protocol exists for use of *H. azteca* to test the toxicity of water samples. Given the fact that the species is about 100-fold more sensitive to pyrethroids than standard water testing species (e.g., *Ceriodaphnia dubia*), use of *H. azteca* may be an appropriate choice when that class of compounds is of concern. For procedures specifically related to *H. azteca* (e.g. culturing of the species, environmental tolerance limits, etc.) the protocol below relies on *H. azteca*-specific

procedures described in the sediment testing manual (EPA, 2000, Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates. EPA 600/R-99/064). For procedures related to acute testing of water samples in general (e.g., test duration, water renewal, number of replicates), the protocol relies on standard acute testing procedures for species such as *C. dubia* and fathead minnow EPA, 2002. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. EPA-821-R-02-012).

### **Harvesting amphipods for use –**

1. One day before test is to start, harvest amphipods from one of the culture tanks. Remove the majority of the maple leaves by hand, then use the dip net to sweep through the aquarium, lightly grazing the bottom. After each pass, transfer contents of dip net to stainless steel bowl filled with moderately hard reconstituted water. Typically about six passes through the aquarium are made.
2. Pour contents of bowl in to 425  $\mu\text{m}$  brass sieve. While immersing the bottom of the sieve in reconstituted water, gently raise and lower sieve in order to rinse fine material through the screen, retaining all but the smallest amphipods.
3. Invert 425  $\mu\text{m}$  sieve over 600  $\mu\text{m}$  sieve, and while holding the rims of the sieves tightly together pour water on to the bottom of the 425  $\mu\text{m}$  screen to wash all amphipods on to the 600  $\mu\text{m}$  screen.
4. Place the 600  $\mu\text{m}$  screen on top of a 500  $\mu\text{m}$  screen, and put both in a stainless steel bowl with the water level near the top but not over the 600  $\mu\text{m}$  screen. Shake the stacked sieves to release and captured air bubbles. Use 5 ml pipettman tips to raise the bottom of the screen off the bottom of the bowl.
5. If there are numerous amphipods trapped by surface tension at the air:water interface, use an open hand to gently tap the surface, allowing the amphipods to break through the surface and swim to the bottom.
6. Place the bowl with the amphipods and screen in the environmental chamber, set for 23°C. Place an airline in the water along side of the screen and begin gently aeration. (Note – do not allow bubbles to collect under the sieve where they will become trapped and block passage of amphipods).
7. Allow the bowl with sieves to remain in the environmental chamber for 6-24 hr as the amphipods sort themselves by size class.
8. The amphipods that pass through the 600  $\mu\text{m}$  screen, but are retained by the 500  $\mu\text{m}$  screen will be 1.8-2.5 mm in length, corresponding to an age of 7-13 days. If used to initiate a test within 1 day, they will be within the 7-14 d of age recommended by EPA. Return the smaller and the larger amphipods back to the culture aquaria from which they were originally taken.

9. For some tests it may be desirable to test at other than 23°C. If a culture has been maintained at the desired test temperature, the amphipods can be collected as described above, and held at that temperature until use. If obtaining amphipods from a 23°C culture for testing at other temperatures, the amphipods should be adjusted to the desired temperature at a rate of 1°C/hr up to 8°C over the course of a day, and then used after 24 h or more at the target temperature. If the shift in temperature exceeds 8°C, then adjustment over a 2-d period is required, with use after 24 h or more at the target temperature.

**Setting up the samples to be tested –**

9. Label 5 beakers with each sample number followed by the replicate number (If sample AD, then AD-1, AD-2...AD-5). Also label 5 beakers for the lab control water.
10. Remove the samples from the refrigerator, and distribute 80 ml to each beaker, with extra set aside for water quality measurements.
11. Add a 1 x 1 cm piece of Nitex screen to provide a substrate for the amphipods, and place the beakers in environmental chamber or water bath at the appropriate temperature.
12. When temperature in the beakers has equilibrated with the surroundings, take water quality measurements for temperature, conductivity, dissolved oxygen, alkalinity, hardness and ammonia. If there is reason to suspect the presence of chlorine (e.g., sample from a POTW) the water should be tested for total residual chlorine.
13. Insure the lights are set for a photoperiod of 16 hr light: 8 hr dark (on at 6 AM, off at 10 PM).

**Starting the test –**

14. Using the amphipods that had previously been sieved, use a turkey baster to transfer about 30 ml of water from the bowl (and associated amphipods) to an 80 mm glass dish. Do this frequently so as to minimize the amount of time the amphipods are out of the desired temperature environment.
15. Using a disposable pipette while viewing the amphipods under the dissecting microscope, transfer 10 amphipods to each test beaker, and then return the beaker to the temperature-controlled environment. Continue until all beakers have received amphipods.

**During the test –**

16. On a daily basis, complete the toxicity testing data sheet, including the measurement of temperature and dissolved oxygen in one replicate per sample.

17. If dissolved oxygen approaches 4 mg/L in a sample, monitor closely, and if it reaches that threshold, begin gentle aeration.
18. Distribute 1ml of YCT mixture to each beaker 4-6 hours prior to renewing sample water to allow test animals to feed.
19. After 48 h remove approximately 80% of the water, and replace it with water from the original sample bottle, previously equilibrated to the desired test temperature.

**Terminating the test –**

20. On the final day of the test, record temperature and dissolved oxygen from one randomly chosen replicate beaker per sample, and remove a water sample for later analysis of ammonia, conductivity, and pH.
21. Remove and discard the small square of screen from each beaker, being sure there are no clinging amphipods. To recover the amphipods, pour the water from each beaker through a 425 µm sieve.
22. Using a wash bottle, rinse the contents of the sieve into a 80 mm glass dish.
23. Examine the dish under a dissecting microscope to find surviving amphipods. Score the test for the number of survivors. Also score the test for the number capable of swimming normally. While most individuals will be actively swimming in the water column, some may require gentle prodding with an instrument (forceps) to induce movement.
24. Pipette out any surviving amphipods as they are located.
25. Record the number of survivors and swimmers on the lab data sheets.

**Test acceptability criteria –**

- Survival in the lab control water must be at least 90%
- Dissolved oxygen should not be less than 4 mg/L.
- Temperature should not vary from the target temperature more than 1°C.

**Attachment 18**

**SOP 6.1 - STANDARD OPERATING PROCEDURE FOR DATA VERIFICATION AND VALIDATION**

Weston laboratory: University of California, Berkeley  
(Modified from SWAMP SOP for Contract Lab Verification and Validation)

Updated: October 15, 2007

**Procedure for data verification (by QA Officer or designee)**

1. Ensure that holding time requirements have been met.
2. If applicable, ensure the raw detector output is properly transcribed for use in data reduction.
3. Ensure that all preparation and analytical values (e.g., aliquot sizes, dilutions) are properly transcribed.
4. Ensure that all formulas used in data reduction are correct.
5. Independently hand calculate at least 10% of sample results to confirm that formulas are being properly applied.
6. Independently hand calculate at least 25% of quality control sample results to confirm that formulas are being properly applied.
7. Ensure correct transcription of at least 10% of electronic data deliverable entries.

**Procedure for data validation (by QA Officer or designee)**

1. Any corrective action determined to be necessary during data verification must be complete before proceeding with data validation.
2. Ensure that all quality control "sample types" are associated with field-collected data.
3. Ensure that the frequency of analysis requirements are met for each sample type.
4. Ensure that method quality objectives are met for each sample type.
5. Ensure that deviations from, additions to, or exclusions from the test method are adequately described for future data interpretation.
6. Ensure that non-standard test conditions relevant to data quality are adequately described for future data interpretation.