

QUALITY ASSURANCE PROJECT PLAN

for

Sources of pyrethroid insecticides to Cache Slough during spawning of Delta smelt

Version 1.0

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SWRCB agreement with University of California, Berkeley, #10-066-150

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Section A3. 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	Donald Weston (Univ. California Berkeley)	510-665-3421	1
UCB Project QA Officer	Aundrea Asbell (Univ. California Berkeley)	510-665-3590	1
SWAMP Coordinator	Meghan Sullivan (Central Valley RWQCB)	916-464-4858	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 A4. 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.

4.1 Involved Parties and Roles

The Project Director, Donald Weston, Adjunct Professor, University of California, Berkeley (510-665-3421; dweston@berkeley.edu) will be responsible for overall project oversight and act as primary contact for contractual matters. He or delegated technical staff at UCB will be responsible for sample collection, calibration of field instruments, and sample transport, custody and storage. He and delegated UCB technical laboratory staff will be responsible for toxicity testing of samples in accordance with this QAPP.

Pesticide analyses will be conducted at Southern Illinois University under the direction of Dr. Michael Lydy (618-453-4091; 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

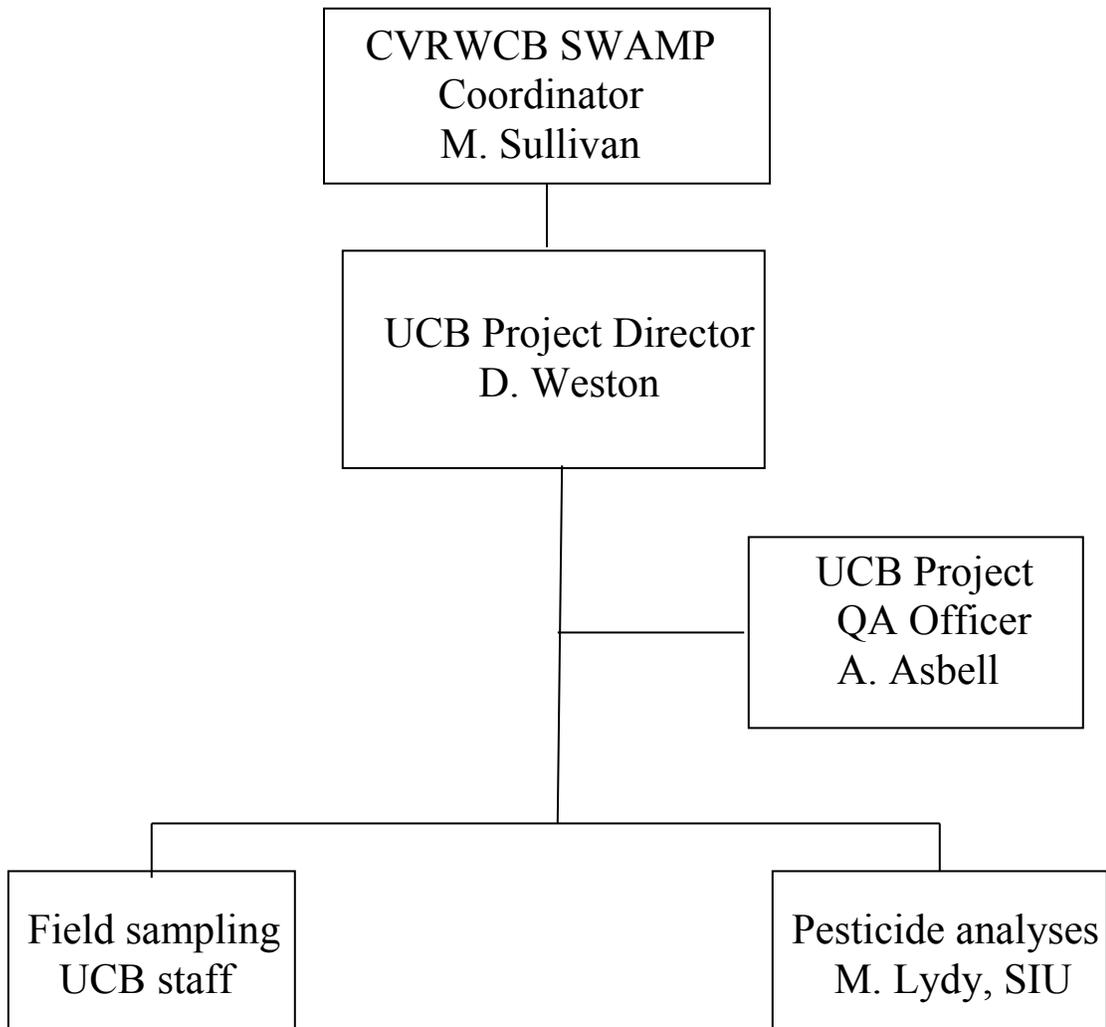
Aundrea Asbell, Staff Research Associate, University of California, Berkeley (510-665-3590; aasbell@berkeley.edu) will serve as the Project QA Officer. She will be responsible for retaining the most current approved QAPP. She will be responsible for implementation of the QA procedures outlined in this QAPP, and monitoring QA performance throughout the project. She will assess compliance of both the prime and subcontractor, and will report to the Project Director should any corrective action be needed. She 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 Manager with concurrence of the Project QA Officer, Regional Board SWAMP Coordinator, 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 A5. Problem Definition

5.1 Problem Statement

The Sacramento-San Joaquin Delta has attracted renewed attention recently because of the decline in populations of several pelagic fish species, notably Delta smelt, striped bass, longfin smelt and threadfin shad. Abundance indices for all four species are at or near record lows, and though the cause(s) for the decline in these Delta populations are not known, toxic contaminants are among the possibilities often suggested. Delta smelt are among the species at risk, and protection of the species, as well as the Delta ecosystem it represents, has become a high priority for management agencies. One of the most critical regions of the Delta for the delta smelt is the Cache Slough area. While spawning is dispersed throughout the Delta in wet years, during dry years the Cache Slough region is the primary spawning grounds for the species. Not only is spawning of the species spatially limited, but it is temporally limited, with adults gathering during the winter months in preparation for the April/May spawn. Smelt larvae remain in the Cache Slough area for several weeks after hatching. In June/July many move out of the Cache Slough complex and spread throughout the Delta, though some remain year around. The spatial and temporal concentration of much of the Delta's delta smelt population within the Cache Slough area makes the species very vulnerable to habitat degradation, including contaminant effects. A single toxic event in February to June affecting delta smelt or their food resources could have significant population consequences.

Pyrethroid insecticides have often been suggested as a potential contributor to the pelagic organism decline. Though data have not yet been collected to carefully evaluate this suggestion, it is based largely on correlative relationships between the decline in fish populations and the concurrent increase in pyrethroid use. There have been several findings from recent studies indicating that a linkage between pyrethroids and delta smelt populations, particularly in the Cache Slough region, deserves closer attention. The goal of this study is to determine the pyrethroid concentration in the water entering the Cache Slough complex from approximately ten waterways that discharge to it.

5.2 Decisions or Outcomes

The Interagency Ecological Program (IEP) formed the Pelagic Organism Decline (POD) work team in response to population declines of pelagic fish species in the Delta. The POD is currently investigating hypotheses related to the role of aquatic contaminants and potential linkage with declining biota abundance. The current project will provide critical information to many of the interested POD stakeholders and member 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 IEP, 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 whether Delta water bodies should 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 enforceable threshold concentrations or Basin Plan Objectives for pyrethroid pesticides in water. The TMDL program has developed thresholds for acute and chronic toxicity using all available toxicity testing data and a modification of EPA protocols to derive criteria. Those thresholds are only for guidance purposes and do not currently have any regulatory basis, but they will be helpful in interpreting the concentration data gathered through this study. In addition, we have published LC₅₀ data for *Hyalella azteca* exposed to a variety of pyrethroids (Weston and Jackson, 2009), and these data will be helpful in identifying those samples in which pyrethroids could present a threat to aquatic life.

Section A6. Project/Task Description

6.1 Work statement and produced products

Sampling sites will be chosen to characterize as many potential sources of pyrethroids to the Cache Slough complex as are accessible for sampling. The following sources have been identified:

1. Ulatis Creek (to be sampled at Leisure Town Road, Hawkins Road, Highway 113, and Brown Rd.)
2. New Alamo Creek (sampled at Leisure Town Road)
3. Old Alamo Creek (sampled at Lewis Road)
4. Upper Haas Slough (sampled by boat)
5. Upper Lindsey Slough (sampled by boat)
6. Shag Slough (sampled at Liberty Island Road)
7. Toe Drain (sampled at West Sacramento and near Liberty Island)
8. Deep Water Ship Channel (sampled at Arcade and Courtland Road)
9. Miner Slough (sampled at Highway 84)
10. Steamboat Slough and/or Sacramento River (sampled at Ryer Island ferry)

The above sites will be sampled during four rain events during the rainy season (Nov.- April), with accumulations of at least 0.5 inches, and preferably more. They will also be sampled on three occasions during the dry season when irrigation runoff could serve as a transport mechanism. We will sample as many of the sites as possible on each occasion, but we may not be able to obtain all samples every time because of access limitations, the timing of rainfall relative to when darkness falls, Ryer Island ferry operation, and other factors. Some of the sites, particularly the creeks, are unaffected by tidal influence so time of sampling with respect to the tidal cycle is irrelevant. Other sites, however, are tidally affected, and while we will try to sample as close to slack low water as possible, this will often not be possible given the number of sites and the brief period of slack low water.

Ulatis Creek is anticipated to be a significant source of pyrethroids, and more intensive sampling in a transect down the length of the creek is anticipated during three rain events in order to establish whether pyrethroids from Vacaville persist all the way to Cache Slough, and to what extent agricultural drains along the creek contribute to its pyrethroid content. This transect sampling will follow a Lagrangian approach in which the same parcel of water is followed as it moves downstream. Ulatis Creek will be divided into 5 reaches of 1.5-2.8 miles in length, with reach boundaries defined by road crossings. The rate of water movement at each end of the reach will be determined, the average value applied to the reach overall, and the time required for water to reach the next sampling point estimated. The same parcel of water will be sampled as it reaches each successive sampling point. In addition the major agricultural drains and other inputs along the creek will be sampled, just prior to the point of discharge. The following samples will be obtained through this transect approach:

ULATIS CREEK

1. Leisure Town Road
2. Byrnes Road
3. Fox Road
4. Hawkins Road
5. Highway 113
6. Brown Road

OTHER INPUTS

1. Agricultural drain at Fox Road
2. Gibson Creek
3. Sweany Creek
4. Agricultural drain at Hawkins Road
5. Agricultural drain at Highway 113
6. Alamo Creek at confluence with Ulatis Creek

Finally, there are approximately 23 agricultural return drains that discharge directly into the Cache Slough complex, and whose contribution would not be captured by sampling of the other sources around the perimeter, as described above. These drains will be sampled on an opportunistic basis since their flow depends on when pumps are turned on, and that in turn is a function of rainfall and/or irrigation activity. If these drains are seen to be discharging while we are in the area, a sample will be taken to characterize the pyrethroid content of that discharge, to the extent access permits.

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 (Wang et al., 2009).

- b) Total suspended solids in water samples will be measured following EPA Method 160.2.
- c) Field measurements are limited to ancillary site characteristics determined during sampling (temperature, dissolved oxygen, pH, conductivity as measured by handheld meters).

6.3 Project schedule and number of test samples

The project is anticipated to yield 111 water samples for analysis of pyrethroid pesticides, plus an additional 30 samples for QA. Chemical analysis will be initiated within approved holding times noted below.

The project timeline is shown below. Some adjustments to draft and final report completion dates are necessary, resulting in small delays relative to the originally planned due dates. This change is necessary since, as a result of early finding, some sampling has been deferred until February 2012 to better characterize rain-related inputs via Ulatis Creek. Report delivery must therefore wait until March 2012.

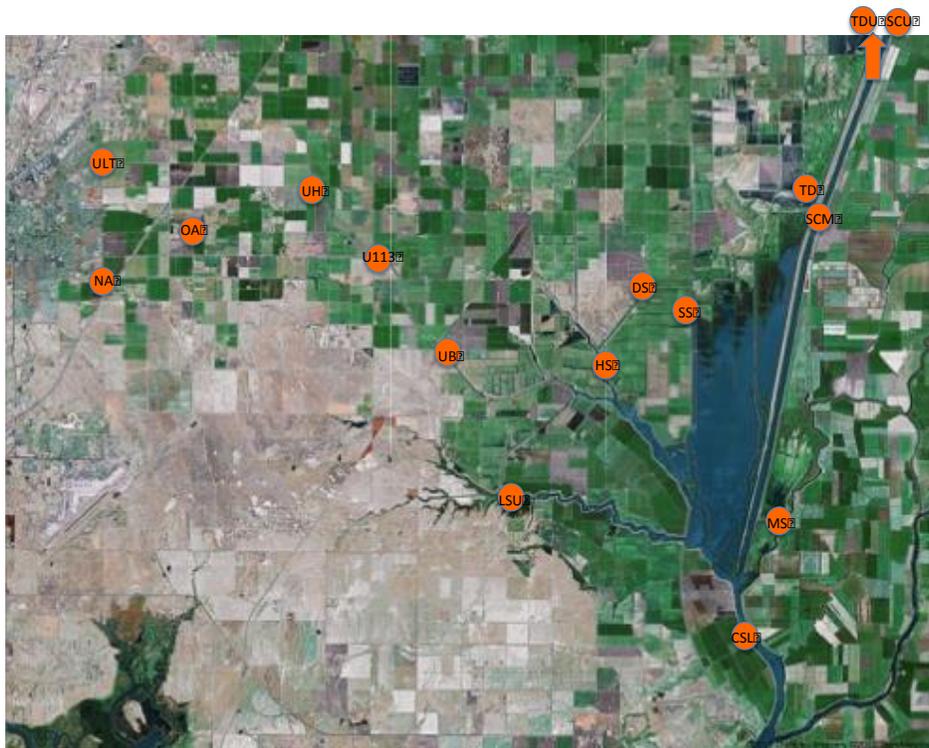
Table 1. Project timeline

Activity	Initiation	Completion	Deliverable	Due date
Project start	4/21/11		None	
Field sampling	4/21/11	2/20/12	Quarterly report	10 th of the month following the quarter.
Laboratory analyses	5/1/11	3/1/12	Electronic data reports	90 days after completion of all analyses
Draft report	1/1/12	3/10/12	Draft report	1/15/12
Final report	3/20/12	3/31/12	Final report	2/28/12

6.4 Geographical setting and sample sites

All sampling will occur in Cache Slough and associated sloughs, and in the waterways that discharge to these waterbodies. The sampling area is bounded by Vacaville to the west, Sacramento to the north, Walnut Grove to the east, and Rio Vista to the south. The location of sites used to characterize inputs to the Cache Slough are shown in Figure 2.

Figure 2. Sampling locations to characterize pyrethroid inputs to Cache Slough area



6.5 Constraints

Some sampling is planned during winter storm events. Sampling of some streams 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 Coordinator will be notified. The SWAMP Coordinator, 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.

Many of the sites have optimal sampling times. For example, some of the sites are tidally affected, and we would prefer to sample these at slack low water. Those influenced by urban runoff during the dry season would be best sampled early in the morning when landscape irrigation runoff is greatest. However, given that we are sampling in any given day all over the northwest Delta, from Vacaville to Sacramento, it is not possible to be at all sites at the optimal time for each one of them. We will plan our sampling route with the general intent to sample the tidal sites at slack water, and the Vacaville sites early in the morning, but precise timing at all sites is not feasible.

A major difficulty with testing for pyrethroids in Delta waters is that analytical detection limits are very near concentrations that are acutely toxic to sensitive aquatic species. To address this concern, we will quantify down to 1 ng/L if the matrix permits. 96-h LC50s to *H. azteca*, one of the most sensitive species to pyrethroids are 1.7 ng/L or greater, depending on the specific pyrethroid.

Section A7. 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
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 discharging to the Delta at the time of the storm event, Sampling sites have been selected so as to optimize representativeness, such as: 1) locating the agricultural samples directly in front of the pump intakes that raise the water over the levees; 2) collecting urban stormwater samples from the sumps at which the storm drains converge prior to Delta discharge; 3) or sampling wastewater treatment plant effluent at the most downstream accessible point, just prior to discharge.

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 (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, permethrin)	LCS within 50-150%	MS/MSD within ±25% RPD: Lab dup. (water) within ±25% RPD	MS within 50-150%.	2-10 ng/L water; 1 ng/g sed.	NA	90%
	Total suspended solids	Lab. Control material 80-120%	MS/MSD /lab dup. within ±25% RPD	MS within 80-120%	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. There are no previously collected data known to be available that are relevant to this project.

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. 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. At least 20% of the total samples in this project will be designated for QA/QC purposes. 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 comprise at least 20% of total project samples. Blanks and spikes will be included in each batch of samples analyzed.

Section A8. 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).

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 A9. Documents And Records

The QAPP original will be held by the Regional Board Contract 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) instrument calibration sheets, 4) 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) or University of Maryland (TOC). 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 Manager, the Project QA Officer, and the laboratory producing the data. Files are backed up to CD monthly, or more frequently if there has been substantial input or modifications to the database.

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 Coordinator.

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 Contract Manager at the completion of the study will consist of manuscripts that have either been published, or are in a format suitable for publication if there has been inadequate time for the 5-10 months that typically are required 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 Coordinator upon request.

Section B10. Sampling Process Design

10.1 Sample process design

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 Contract Manager, SWAMP Coordinator, Project Director, or Project QA Officer.

Sampling sites will be chosen to characterize as many potential sources of pyrethroids to the Cache Slough complex as are accessible for sampling. The following sources have been identified:

- Ulati Creek (to be sampled at Leisure Town Road, Hawkins Road, Highway 113, and Brown Rd.)
- New Alamo Creek (sampled at Leisure Town Road)
- Old Alamo Creek (sampled at Lewis Road)
- Upper Haas Slough (sampled by boat)
- Upper Lindsey Slough (sampled by boat)
- Shag Slough (sampled at Liberty Island Road)
- Toe Drain (sampled at West Sacramento and near Liberty Island)
- Deep Water Ship Channel (sampled at Arcade and Courtland Road)
- Miner Slough (sampled at Highway 84)
- Steamboat Slough and/or Sacramento River (sampled at Ryer Island ferry)

The above sites will be sampled during three rain events during the rainy season (Nov.- April), with accumulations of at least 0.5 inches, and preferably more. They will also be sampled on three occasions during May and June, a period when rain is not expected, but irrigation runoff could serve as a transport mechanism. We will sample as many of the sites as possible on each occasion, but we may not be able to obtain all samples every time because of access limitations, the timing of rainfall relative to when darkness falls, Ryer Island ferry operation, and other factors. Some of the sites, particularly the creeks, are unaffected by tidal influence so time of sampling with respect to the tidal cycle is irrelevant. Other sites, however, are tidally affected, and while we will try to sample as close to slack low water as possible, this will often not be possible given the number of sites and the brief period of slack low water.

Ulati Creek is anticipated to be a significant source of pyrethroids, and more intensive sampling in a transect down the length of the creek is anticipated during three rain events in order to establish whether pyrethroids from Vacaville persist all the way to Cache Slough, and to what extent agricultural drains along the creek contribute to its pyrethroid content. This transect sampling will follow a Lagrangian approach in which the same parcel of water is followed as it

moves downstream. Ulatis Creek will be divided into five reaches of 1.5-2.8 miles in length, with reach boundaries defined by road crossings. The rate of water movement at each end of the reach will be determined, the average value applied to the reach overall, and the time required for water to reach the next sampling point estimated. The same parcel of water will be sampled as it reaches each successive sampling point. In addition the major agricultural drains and other inputs along the creek will be sampled, just prior to the point of discharge. The following samples will be obtained through this transect approach:

ULATIS CREEK

- Leisure Town Road
- Byrnes Road
- Fox Road
- Hawkins Road
- Highway 113
- Brown Road

OTHER INPUTS

- Agricultural drain at Fox Road
- Gibson Creek
- Sweany Creek
- Agricultural drain at Hawkins Road
- Agricultural drain at Highway 113
- Alamo Creek at confluence with Ulatis Creek

Finally, there are approximately 23 agricultural return drains that discharge directly into the Cache Slough complex, and whose contribution would not be captured by sampling of the other sources around the perimeter, as described above. These drains will be sampled on an opportunistic basis since their flow depends on when pumps are turned on, and that in turn is a function of rainfall and/or irrigation activity. If these drains are seen to be discharging while we are in the area, a sample will be taken to characterize the pyrethroid content of that discharge, to the extent access allows.

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. GPS coordinates are taken at every sampling event so as to confirm the correct location and/or to provide guidance for future visits to the site.

Excluding QA samples, field sampling is expected to yield about 111 samples for whole water analysis of pyrethroids.

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

10.2 Variability

Runoff quality is inherently highly variable, and it is precisely for this reason that multiple sampling events are planned. Each input to Cache Slough will be sampled in three winter rain events, and three summer dry season events.

10.3 Bias

One form of bias is proximity to a discharge point, such that a sample drawn from the main waterway of interest is overly biased by a nearby discharge, rather than reflecting conditions in the mainstem with all inputs homogeneously dispersed. When an urban storm drain or agricultural discharge is located near the sampling site, the precise sampling point is selected so as to best characterize the mainstem creek or river, not the incoming drain water (e.g., sampling upstream of drain, on the opposite bank, or as far downstream of the drain as access permits).

Section B11. Sampling Method

11.1 Water sampling

Water sampling 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) and TSS (500 ml jar). The jars will be immersed in the water by hand, and filled just below the water.

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 B12. 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 3. Data generated from samples handled differently than stated in Table 3 will be flagged as such.

Table 3. 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, acidify to pH 2 with 1 N HCl	7 d to extraction, 40 d to analysis
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 labelled 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 act as a keeper solvent preserving the pyrethroids in a hydrophobic solvent (Wang et al., 2009).

Extracted chemistry samples will be sent to subcontracted laboratories 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 Federal Express. 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 B13. 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 organic carbon, total suspended solids, toxicity testing, and pesticide analyses. Method performance criteria are generally discussed elsewhere within this QAPP (e.g., Sections A7 and B14), though an SOP (pesticide analyses) contains additional method specific performance criteria.

13.1 Water quality measurements

Responsible person: D. Weston 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 SWMP Coordinator 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 3.6 - 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)

Field measurements for dissolved oxygen, temperature, conductivity, and pH will be made with a YSI Model 556 meter. The dissolved oxygen meter works 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. The meter will be calibrated the day of use, and calibration data entered on data sheets maintained with each meter.

13.2 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 Coordinator 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 15)

The extraction method for pyrethroids in water will be consistent with EPA Method 3510 (liquid:liquid extraction). Briefly, the water sample (1000 ml) will be acidified to a pH of 2.0 using 1N HCl, which slows degradation of the pyrethroids. The 1000 ml water sample will be placed into a 2L separatory funnel and then spike 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.

An addition 60 ml methylene chloride 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. 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. 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.

13.4 Total suspended solids

Responsible person: D. Weston 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 Coordinator 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 17)

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 month.

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 B14. Quality Control

14.1 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.

14.2 Data quality indicators

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

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

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

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

14.3 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 (You et al., 2004; You et al., in press).

14.4 Total suspended solids

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

Accuracy –A laboratory control material and a matrix spike will be run every 20 samples with results to be 80-120% of expected value.

Precision - Precision will be determined by use of a matrix spike duplicate, 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%.

14.5 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 Coordinator, the Contract Manager, and SWAMP QA Officer. Control actions will be documented in written form in project files.

Section B15. 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 may occasionally require replacement of the solutions within the probes (e.g., KCl) when indicated by meter readings. Spare 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. 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.

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 Coordinator, and be responsible for documentation in interim and final reports.

Section B16. 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, pH, conductivity meter will be calibrated every day of use. 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.

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 Coordinator will be contacted regarding the proper course of action including reanalyzing the sample or sending the samples to an outside laboratory for analysis.

Section B17. 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:

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

Deionized water – Available in an adjacent 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 B18. Non-Direct Measurements

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 B19. 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 sediment and 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.

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.

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 to CD monthly, or more frequently if there has been substantial input or modifications to the database.

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, here 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., ToxCalc or CETIS).

Section C20. 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 Coordinator. 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 Coordinator.

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

Section C21. Reports To Management

Table 4. QA Management Reports

Type of report	Frequency	Due date	Responsible for report prep.	Report recipient
Quarterly report	Quarterly	10 th of the month following the quarter	Project Director	RWQCB SWAMP Coordinator
Electronic data reports	Following sampling	90 days after completion of all analyses	Project Director	RWQCB SWAMP Coordinator
Draft report	Once	3/15/11	Project Director	RWQCB SWAMP Coordinator
Final report	Once	3/31/11	Project Director	RWQCB SWAMP Coordinator

Section D22. 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 A7.

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 D23. 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 D24. Reconciliation With User Requirements

The Project Director, in consultation with the Regional Board SWAMP Coordinator 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 Coordinator 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 A7 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 Coordinator 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 A7). 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.

REFERENCES

Weston and Jackson, 2009

Wang, D., Weston, D.P., Lydy, M.J. 2009. Method development for the analysis of organophosphate and pyrethroid insecticides at low parts per trillion levels in water. Talanta 78:1345-1351.

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:
LABORATORY
CALIBRATION SHEET FOR
THE DISSOLVED OXYGEN
METER**

ATTACHMENT 3:
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 4

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

Weston laboratory: University of California, Berkeley

Updated: October 1, 2005

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 5

SOP 3.7 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF CONDUCTIVITY

Weston laboratory: University of California, Berkeley

Updated: October 1, 2005

REQUIRED MATERIALS

- Fisher Accumet 50 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 mS/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 6

SOP 3.8 - STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF pH

Weston laboratory: University of California, Berkeley

Updated: October 1, 2005

REQUIRED MATERIALS

- Fisher Accumet 50 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 7

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 8

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

Author(s):	<u>Dongli Wang</u>	Date:	<u>4-1-07</u>
Section Leader:	<u>Dr. Michael Lydy</u>	Date:	<u>4-1-07</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 (DBOBF) 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 Add 1N HCl to all the water samples to adjust pH value to ~ 2.0 after the water samples are shipped to the lab, (or prior to shipment if being held on site for some period of time) and then 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 (DBOBF 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 40C 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 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 507Determination 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 9

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 μ m film, 30m length, 0.35mm I.D.)
- Capillary Column 2 (DB-608, 1.00 μ 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 10

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 11

SOP 4.1 - 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.