Quality Assurance Project Plan

Prepared by
Sarah Lowe, SFEI

In collaboration with
Brian Anderson, UC Davis Marine Pollution Studies Laboratory

PRISM GRANT: 04-135-55-20

PROJECT NAME: INVESTIGATIONS OF SOURCES AND EFFECTS OF PYRETHROID PESTICIDES IN WATERSHEDS OF THE SAN FRANCISCO BAY ESTUARY

Project Director: Sarah Lowe (SFEI)
Project Grant Manager: Richard Condit (SWRCB)

San Francisco Estuary Institute, Oakland CA

Version 1.1
July, 2005

GROUP A ELEMENTS: PROJECT MANAGEMENT

1. TITLE AND APPROVAL SHEETS

Quality Assurance Project Plan

For

PROJECT NAME: INVESTIGATIONS OF SOURCES AND EFFECTS OF PYRETHROID PESTICIDES IN WATERSHEDS OF THE SAN FRANCISCO BAY ESTUARY

Proposal Identification Number: 04-135-552-0

Date: March, 2005

NAME OF RESPONSIBLE ORGANIZATION : San Francisco Estuary Institute, Oakland, CA

APPROVAL SIGNATURES

GRANT ORGANIZATION:

Title:	Name:	Signature:	Date*:
Project collaborator	Brian Anderson		
Project Manager	Sarah Lowe		
QA Officer	Donald Yee		

REGIONAL BOARD (SWRCB**):

Title:	Name:	Signature:	Date*:
Contract Manager	Richard Condit		
QA Officer			

* This is a contractual document. The signature dates indicate the earliest date when the project can start.

** If the QAPP is being prepared under the jurisdiction of the State Water Resources Control Board (SWRCB) rather than a Regional Board, substitute the appropriate SWRCB information for the RWQCB information.

2. Table of Contents

Page:

LIST OF APPENDICES

LIST OF FIGURES

LIST OF TABLES

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3. DISTRIBUTION LIST

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4. PROJECT/TASK ORGANIZATION

4.1 Involved parties and roles.

The following agencies are involved in this project as the principal investigators, subcontracting laboratories or information users. Personnel involved in this project art listed in Table 1.

Lead (PI & Program Management)
San Francisco Estuary Institute (SFEI)
7770 Pardee Lane, 2nd floor
Oakland, CA 94621

Collaborating Investigator & Analytical laboratory (Toxicology)
UC Davis – Marine Pollution Studies Laboratory (UCD-GCML)
4500 Highway 1
Monterey, CA 93940

Field Monitoring Logistics
Applied Marine Sciences (AMS)
4749 Bennett Drive, Suite L
Livermore, CA 94550

Analytical laboratory (Trace organics)
Fish and Wildlife – Water Pollution Studies Lab (DFG- MPSL)
2005 Nimbus Road
Rancho Cordova, CA 95670

Analytical laboratory (Trace elements)
Brooks Rand, LLC (BRL)
3958 Sixth Avenue, NW
Seattle, WA 98107

Analytical laboratory (Trace elements and Ancillary measures)
University of California Santa Cruz – Dept. of Environmental Toxicology (UCSCDET)
1156 High Street
Santa Cruz, CA 95064

Table 1. (Element 4) Personnel responsibilities.

Name (Affiliation):	Title:	Contact Information
Sarah Lowe (SFEI)	Project Manager	Tel: (510) 746-7384 Fax: (510) 746-7300 Email: sarahl@sfei.org
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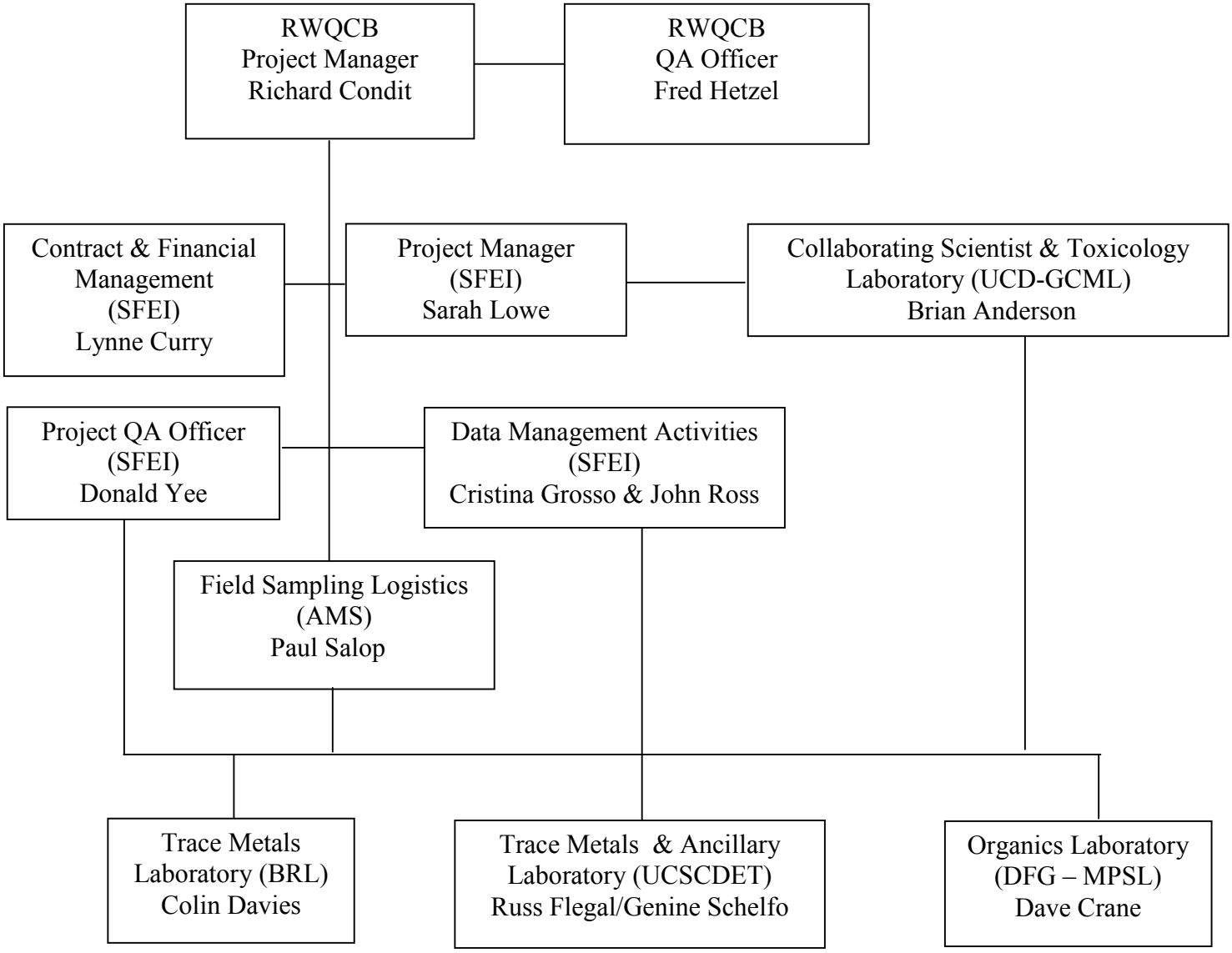
Paul Salop (AMS)	Logistical Coordination (Field Sampling)	Tel: (510) 746-7383 Fax: (925) 373-7834 Email: salop@amarine.com
Dave Crane (DFG-MPSL)	Chemistry Laboratory Manager (organics)	Tel: (916) 358-2859 Fax: (916) 985-4301 Email: dcrane@ospr.dfg.ca.gov
Colin Davies (BRL)	Chemistry Laboratory Manager (Trace metals)	Tel: (206) 632-6206 Fax: (206) 632-6017 Email: colind@brooksrand.com
Russell Flegal & Genine Scelfo (UCSCDET)	Chemistry Laboratory Manager (Trace metals & ancillary measures)	Russell Flegal: PI (831) 459-2093 Genine Scelfo: Proj Mgr. 459-3563 Email: gscelfo@es.ucsc.edu
Richard Condit (SFRWQCB)	Project Grant Manager	Tel: (510) 622-2338 Fax: (510) 622-2460 Email: rjc@rb2.swrcb.ca.gov

4.2 Quality Assurance Officer role
SFEI's QA Officer or designee will conduct an independent QA/QC review of all field-monitoring data produced under task 3.1 of this contract. Don Yee's role does not include generating project information.

4.3 Persons responsible for QAPP update and maintenance.
Sarah Lowe and Brain Anderson will be responsible for maintaining and updating the official approved QAPP. Either person can make changes.

4.4 Organizational chart and responsibilities

Figure 1. (Element 4) Organizational chart.



5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem statement.

The purpose of this project is to evaluate pyrethroids in sediments and their potential impact on benthic organisms. The US EPA is restricting the use of organophosphate (OP) pesticides for home use. As a consequence, the use of alternative pesticides such as pyrethroids is increasing in Bay Area watersheds. Pyrethroids are highly insoluble and are primarily associated with sediments in aquatic systems. Research has shown that greater than 90% of pyrethroid mass entering aquatic systems is associated with particles (e.g. suspended sediments) within 1 hour of application. Sediment-associated invertebrates such as amphipods are the most sensitive benthic organisms to these insecticides.

We suspect that pyrethroids, which are found in tributary sediments, may be inducing toxicity on benthic biota (represented by amphipods) in the San Francisco Estuary and its watersheds.

5.2 Decisions or outcomes.

Combined, the sediment chemistry, toxicity studies, and TIEs performed on the San Francisco Bay tributary samples (task 1 described in section 6.1 below) will provide a weight-of-evidence to help determine if diazinon alternatives used in the watersheds are potentially inducing toxicity to benthic organisms in the tributaries. The results from this study will provide valuable information for environmental managers that could be used to regulate pyrethroid use.

Additionally, this study will develop LC50s for relevant Estuary amphipods for a select few pyrethroids (task 2 described in section 6.1 below).

Finally, sediment TIE methodologies will be developed to determine if pyrethroids are contributing to an observed toxic effect in laboratory amphipod toxicity tests (task3 described in section 6.1 below).

5.3 Water quality or regulatory criteria

This project addresses the narrative “toxicity” water quality objective in the San Francisco Bay Region Basin Plan (Basin Plan, 1995). Some of the most relevant beneficial uses of the San Francisco Estuary, identified in the Basin Plan (Section 2), that are addressed by this proposed project include estuarine habitat, benthic and aquatic invertebrate communities, fresh and salt water fisheries (fish and shellfish), commercial and sport fishing, salmonid fisheries (including spawning and migration), and other rare and endangered species.

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6. PROJECT/TASK DESCRIPTION

6.1 Work statement and produced products.

This project has three tasks to it:

1) Conduct a field study in the early spring of 2006 to determine if sediments entering the San Francisco Estuary from local tributaries are toxic to an ecologically relevant benthic amphipod. Characterize the contaminant levels in the collected tributary sediments including trace metals, PAHs, PCBs, OP pesticides, and diazinon alternative pesticides (specifically pyrethroids), and if the samples are toxic perform Toxicity Identification Evaluations (TIEs) to identify causes.

2) Develop dose-response information (LC50s) for standard EPA sediment toxicity testing species, and ecologically relevant species to the Estuary, for three pyrethroids (cypermethrin, permethrin, and bifenthrin). The species to be evaluated include the amphipods *Eohaustorius estuarius* and *Ampelisca abdita*.

3) Develop and validate TIE procedures for sediment toxicity tests targeting toxicity caused by pyrethroids.

The project will provide quarterly progress reports, during the life of the project. At the end of the project, SFEI will provide a final report on all three components of this project.

6.2. Constituents to be monitored and measurement techniques.

A detailed Field Monitoring Plan has been finalized and already submitted to the RWQCB Project Manager. A copy is included in Appendix A.

1) Field Monitoring (Summary):
   a. Six tributaries of the San Francisco Estuary will be sampled during the early spring (April 2005). The tributaries will be sampled above the tidal reach to ensure that they represent upstream freshwater inputs. When possible, samples will be collected at locations that have been sampled before in other studies (SWAMP, RMP-Episodic toxicity monitoring program, USGS sampling stations, etc.) to maximize information for later interpretation.
   b. The top 1-2 cm of ambient bedded-sediments will be collected using standard RMP grab sampling procedures described in the RMP Field Operations Manual (SFEI, 2001) or using Kynar coated scoops cleaned according to RMP sampling protocol.
   c. Chemical analyses for the full suite of RMP parameters (sediment quality parameters, trace metals, PAHs, PCBs, OP pesticides), pyrethroids, and possibly other diazinon alternatives will be measured in the sediment samples.
   d. Acute sediment toxicity testing using standard EPA laboratory protocols, standard laboratory species (Hyalella) will be performed to screen for potential toxic effects.
   e. If sediments are found to be significantly toxic, and chemistry results show measurable concentrations of toxic contaminants, two tributaries will be resampled in February-March of 2006. TIEs will be conducted to identify possible causes including using methods developed to date for identifying pyrethroids.

2) Acute sediment toxicity dose-response testing using standard EPA laboratory protocols, and ecologically relevant resident species will be conducted on key pyrethroid pesticides for which no dose-response information exists. Amphipods are among the most sensitive taxa to sediment-bound pyrethroids. The genus *Hyalella* resides in the Estuary's watersheds, and is therefore an ecologically relevant freshwater indicator. *Ampelisca abdita* is the dominant resident amphipod species in the Estuary. Both species are used extensively in sediment toxicity monitoring in freshwater and marine systems. *Eohaustorius estuarius* is the RMP sediment test species and is commonly used for toxicity screening of estuarine sediments. All three amphipod species live in different salinity regimes and all have different lifestyles, and therefore potentially different exposure routes to contamination (*Hyalella* is epibenthic, *Eohaustorius* is a free-burrowing detritivore, and *Ampelisca* is a tube-dweller).

a. 10-day dose response toxicity tests will be conducted with cypermethrin, permethrin, and bifenthrin on standard laboratory estuarine species (*Eohaustorius*, and *Ampelisca*) using EPA standard methods. These are the most commonly used pyrethroid pesticides. A minimum of one range finder and two definitive tests will be conducted with each pesticide and test species.

Note: Pyrethroid toxicity to *Hyalella azteca* is not included in this study but some data exist from other studies and that information will be included in the final report (e.g. cypermethrin LC50s for *Hyalella* have been published (Maund *et al.* 2002).

3) TIE procedures will be developed to identify potential toxicity due to diazinon alternatives in sediments. Improvement and development on TIE methodologies specifically for sediment TIEs is the goal of this project component. All TIE experiments will be conducted with the amphipod *Hyalella azteca*. The contractor will have two workshops with researchers conducting TIE development, including other Bay Area researchers to discuss the best approach to further develop TIE procedures for sediments and to make sure that research effort is not duplicated.

6.3 Project schedule

Table 2. (Element 6) Project schedule timeline.

Item	Activity and/or Deliverable	Deliverable Due Date
1	**Contracts**	**- -**
1.1	Subcontract development	Before each award
2	**Monitoring Plan & Quality Assurance Project Plan**	**- -**
2.1	Quality Assurance Project Plan	Feb. 2005
2.2	Monitoring Plan	Dec. 2004
3	**Work To Be Performed**	**- -**
3.1	Field Monitoring: Ambient Sediment Sampling, Analysis and Toxicity Assays (April, 2006)	See 3.4.1 and 3.4.2
3.2	Toxicity Assay Testing (Dose-Response Study)	
3.2.3	Prepare and submit a Toxicity Assay Testing Summary Report	Sep. 2005
3.3	Develop Toxicity Identification Procedures - and validate Approach and Results Via Workshop	
3.3.2	Submit Summary Report of Preliminary Workshop	Apr. 2005
3.3.4	Submit Summary Report of Mid-Point Workshop	Apr. 2006
3.4	**Draft and Final Project Reports**	**- -**
3.4.1	Draft Project Report	June. 2006
3.4.2	Final Project Report	Aug. 2006

6.4 Geographical setting

Location of the six "Upper" freshwater tributary sites sampled in the Field Monitoring task 1 of this project. *Note that the "Lower" sites listed here will be sampled as part of a separate study through the Regional Monitoring Program for Trace Substances (RMP) Episodic Toxicity Monitoring Program and are included here for information purposes only.*

North Bay Tributaries

Suisun Creek Upper: Site 1 (fresh)
(Rockville Rd and Willotta Dr., Suisun City, CA)
Sample the quieter, upstream portion of the Creek

Suisun Creek Lower: Site 2 (tidal)
(Chadbourne Rd. creek overpass just past Jacksnipe Rd., Suisun City, CA)
Sample the downstream side of the overpass

Napa River Upper: Site 1. (fresh)
(1st Street at Copia., Napa, CA)
Sample river below the northwest corner of parking lot

Napa River Lower: Site 2. (tidal)
(John F. Kennedy Park downstream of town., Napa, CA)
Sample off of wharf

Petaluma River Upper: Site 1. (fresh/tidal)
(East Washington St. and Weller, Petaluma, CA)

Petaluma River Lower: Site 2. (tidal)
(Gilardi's Lakeville Marina, Lakeville, CA)

South Bay Tributaries

San Lorenzo Creek Upper: Site 1 (fresh)
(Via Bregani and Madeline, San Lorenzo, CA)

San Lorenzo Creek Lower: Site 2 (tidal)
(Via Murieta and Via Sorrento, San Lorenzo, CA)

Coyote Creek Upper: Site 1 (fresh)
(Murphy Ranch Rd. and Technology Dr., Milpitas, CA)

Coyote Creek Lower: Site 2 (tidal)
(RMP station BW10, N. McCarthy Blvd./ just over the overpass heading south from Dixon Landing Rd., Milpitas, CA)

San Mateo Creek Upper: Site 1 (fresh)
(in Gateway Park, 3rd Ave, San Mateo, CA)
Sample near the steps into the creek

San Mateo Creek Lower: Site 2 (tidal)
(3rd Ave. and J. Hart Clinton Drive, San Mateo, CA)
Sample under the creek overpass.

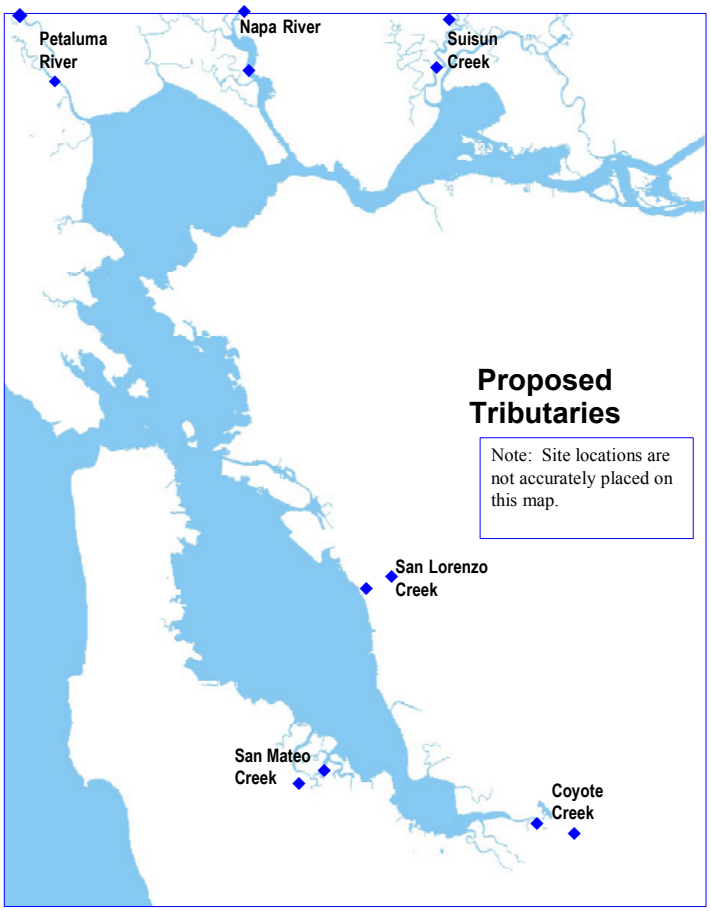

Figure 2. (Element 6) Map of sampling sites for Field Monitoring task.
Note: Only the upstream "Upper" sites will be sampled under this project.

6.5 Constraints
Describe resource and time constraints, if applicable:
Sediment grain size in the targeted tributaries must be visibly fine grained. It is possible that fine grained sediments may not be available at the time of sampling.

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7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Data Quality Objectives
(List measurement or analyses type specific to this project, and specify applicable data quality objectives.)

Measurement or Analyses Type	Applicable Data Quality Objective
Sediment Ancillary (grain size, TOC)	Accuracy, Precision, Contamination, Completeness, Sensitivity
Sediment Trace Elements	Accuracy, Precision, Contamination Completeness, Sensitivity
Sediment Trace Organics	Accuracy, Precision, Contamination Completeness, Sensitivity
Sediment Toxicity	Meet criteria relative to Reference Toxicant tests, Ancillary test condition measures, and Completeness

Accuracy will be determined by measuring one or more Certified Reference Materials or Standard Reference Materials. At least one sample per batch is required. Additional recovery measurements may be determined by laboratory spiking of a replicate sample with a known concentration of the analyte. The target level of addition is targeted to be at least twice the original sample concentration.

Precision measurements will be determined on field and/or laboratory replicates. At least one replicate per batch is required. The relative percent difference between two replicate samples or the relative standard deviation between more than two replicate samples (RPD or RSD respectively) will be less than the DQC listed in Tables 4a-c for each analyte of interest. Following are the calculations:

RPD = ABS (rep 1 - rep 2) X 100/Average (rep 1, rep 2)

RSD = STDEV (all replicate samples) X 100/Average (all replicate samples)

ABS — absolute value
STDEV — standard deviation

Contamination is evaluated by using laboratory and/or field blank samples. At least one blank per batch is required.

Completeness is the number of analyses generating useable data for each analysis divided by the number of samples collected for that analysis.

Method sensitivity is dealt with by the inclusion of the Target Method Detection Limits, employed by the RMP where such values exist.

Suggested Standard Reference Material:

Grain size: NIST 1003b glass spheres (8 to 58 um diameter), constant-density spheres having a range of diameters. Precision and accuracy of the sedigraph (particle size analyzer) is evaluated with a garnet standard reference material (Micromeritrics, Inc.).

TOC: undefined at this time

Trace Elements: NRC MESS-3 or NIST 1646
Trace Organics: NIST 1941a or similar

Field and Laboratory Measurements Data Quality Objectives Tables

Table x. (Element 7) Data quality objectives for field measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limit	Completeness
Not applicable						

Table x. (Element 7) Data quality objectives for laboratory measurements. *See Below*

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
Not applicable						

Table 4a. (Element 7) Data quality objectives for laboratory measurements for Sediment Ancillary Measures (gainsize & TOC).

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material	**Accuracy**	TOC: One per batch Grain Size: NA.	Within 95% confidence interval of the certified value	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	**Precision**	One per batch	RPD or RSD < 20% precision (grain size) 3% (TOC)	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Laboratory control material (LCM)	**Accuracy & Precision**	One per batch of 20 or fewer samples.	Within 20–25% consensus value	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 4b. (Element 7) Data quality objectives for laboratory measurements for Sediment Trace Elements.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.

Certified Reference Material (CRM)	**Accuracy**	One per batch of 20 or fewer samples.	Within 25% of the certified value. Within 35% for Hg, As, Se.	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	**Precision**	One per batch	RPD or RSD < 10%; Hg, As, Se < 35% RSD of last 7 CRMs < 35%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Matrix Spike	**Accuracy**	One per batch of 20 or fewer samples.	Recovery between 50 - 150 % for organics And 70 – 130 % for trace elements	Check CRM or LCS recovery. Review raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Laboratory Control Material (LCM; optional)	**Accuracy & Precision**	One per batch	Within 20–25% of the consensus value	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze LCM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 4c. (Element 7) Data quality objectives for laboratory measurements for Sediment Trace Organics.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material (CRM)	**Accuracy** **Precision**	One per batch of 20 or fewer samples.	As a group: 70% of the analytes within 35% of the 95% confidence interval. Individually: No analyte outside 30% of 95% confidence interval for 2 consecutive analyses. RPD (if n=2) < 35% RSD (if n>2) < 35% RSD of last 7 CRMs < 35%	Review chromatograms and raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	**Precision**	One per batch of 20 or fewer samples.	RSD or RPD < 35%	Recalibrate and reanalyze. If problem persists eliminate source of imprecision and reanalyze.
Matrix Spike	**Accuracy**	One per batch of 20 or fewer samples.	Recovery between 50- 150 % if no CRM limits apply, otherwise use CRM limits.	Check CRM or LCS recovery. Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Surrogate Spike or Internal Standard	**% Recovery** used to adjust sample results	One per sample	Set by analyzing laboratory (reported in QA report). (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCS recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Specialized training or certifications.

No specialized training or certifications is required for this project. This proposals main subcontractor will conduct sediment toxicity, dose-response experiments and TIE analyses: UC Davis-GCML (contact: Brian Anderson). GCML is the RMP's Sediment Toxicity contractor, and the primary toxicology laboratory for the Surface Water Ambient Monitoring Program (SWAMP). In cooperation with CDFG-MPSL, UC Davis-GCML authored the toxicology section of the SWAMP QAPP. Toxicity test methods follow standard US EPA procedures. Sediment spiking and TIE procedures also follow general US EPA procedures. Tasks related to development of TIE procedures specific for pyrethroid pesticides will in some cases require use of novel techniques for which no standardized protocols have been described.

Sediment chemistry for organic contaminants will be analyzed by the RMP subcontract laboratory: California Department of Fish and Game Water Pollution Control Laboratory (CDFG-MPSL-Rancho Cordova, ELAP#-1622, contact: Dave Crane). This lab is one of the RMP's organic chemistry labs and has recently been developing new techniques to measure pyrethroids in ambient sediments. CDFG-MPSL-Rancho Cordova is the primary analytical chemistry laboratory for SWAMP, and was responsible for the sediment chemistry section of the SWAMP QAPP. Laboratory intercomparisons of pyrethroid results between this laboratory and AXYS Analytical Services Ltd. (Oros & Yee's PRISM proposal #0009) will be conducted for four North Bay samples. In general, sediment samples will be collected, homogenized, split into fractions, and sent to the various analytical laboratories using appropriate sample handling protocol outlined in the RMP Field Operations Manual.

Sediment chemistry trace metals and ancillary measures (e.g. grain-size and total organic carbon) will be analyzed by two RMP contractors: Brooks Rand, LLC and the University of California of Santa Cruz - Department of Environmental Toxicology.

8.2 Training and certification documentation.

A complete listing of laboratory accreditation certificates is available directly from the subcontractors.

8.3 Training personnel.

No new training is required for this project.

Table x. (Element 8) Specialized personnel training or certification. N/A

Specialized Training Course Title or Description	Training Provider	Personnel Receiving Training/ Organizational Affiliation	Location of Records & Certificates *
No applicable			

*If training records and/or certificates are on file elsewhere, then document their location in this column. If these training records and/or certificates do not exist or are not available, note this.

9. Documents And Records

AMS has developed Field Sampling Sheets and Chain of Custody forms (COCs) for sample collection (see figure 1), Samples sent to all laboratories will include a COC. Each laboratory generates records for sample receipt and storage, analyses, and reporting.

All documents generated by this project will be stored at SFEI.

Copies of this QAPP will be distributed by the SFEI project manager to all parties directly involved in this project. Any future amended QAPPs will be distributed in the same fashion. All originals of this first and subsequent amended QAPPs will be held at SFEI. Copies of versions, other than the most current, will be discarded so as not to create confusion.

All records will be passed to the SFBRWQCB Project Manager Richard Condit at project completion. Copies of the records will be maintained at SFEI for five years after project completion then discarded, except for the database, which will be maintained without discarding.

APPLIED amarine SCIENCES
4749 Bennett Drive, Suite L
Livermore, CA 94550
925.373.7142, www.amarine.com

Chain of Custody Record:

Project/Cruise:		Date:		Analyses Required					
Site Name/Code	Container Number	Collection Date	Collection Time	Matrix					Comments

Chain of Custody Signatures:

Status	Signature	Date	Time
Relinquished By:			
Received By:			

Shipping Method:

☐ FedX/Airborne Tracking Number:
☐ Pickup by lab
☐ Delivered by AMS

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Figure 3. (Element 9) Example Chain of Custody form used by AMS for this project

Table x. (Element 9) Document and record retention, archival, and disposition information. N/A

	Identify Type Needed	Retention	Archival	Disposition
Sample Collection Records	Not applicable			

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GROUP B: DATA GENERATION AND ACQUISITION

10. SAMPLING PROCESS DESIGN

Field Sampling Design Summary: Six tributaries around the Estuary (see Figure 2, section 6.4) will be sampled. Bedded depositional sediment samples will be collected in the freshwater regions of each tributary (not far above the region of tidal influence). Site selection goals include: 1) Selection of tributaries distributed around the Estuary of variable land-use types; 2) preferably sites that have been studied before so that there is some historical data to refer to (i.e. SWAMP, USGS, Alameda County Sediment Survey, NOAA/EMAP, RMP, other); 3) availability of fine-grained depositional sediments; and 4) safely accessible for sample collection. Sampling will occur in spring (April - 2005), after the winter rains when it is expected that pesticide applications in urban and agricultural settings have resumed.

Please refer to the PRISM Grant # 04-135-55-20 Monitoring Plan already provided to the RWQCB Project Manager (and in Appendix A) for further description of the sampling design and sample collection methodology.

11. SAMPLING METHODS

Sampling methods will be similar to those employed by the RMP and described in the *Field Sampling Manual for the Regional Monitoring Program for Trace Substances* (SFEI, 2001) with the exception that sample collection is performed by scooping only 1-2 cm of sediments directly from the creek bed. A general description follows:

Equipment and Sampling Containers
Preparation of sediment sampling equipment is the responsibility of AMS. An equipment list for sediment sampling is provided in Table 5.

Table 5. (Element 11) Equipment list for sediment sampling.

Quantity	*Description*
8	Insulated plastic coolers for sample storage, pre-cleaned
1	Keys to Alameda and Santa Clara Co watershed access gates
30 (lbs.)	dry ice
1	Insulated plastic cooler for dry ice storage
1 (pr.)	Cotton gloves for dry ice handling
30	Sample collection forms
10	Chain of custody forms
2	Label tape
2	Aluminum foil, 100 square feet
48	Ziploc™ bags, 1 gallon size
2	Sharpie pens, thin and wide
200	Latex gloves, non-powdered
1	Splash-proof eye protection
2	Plastic brushes
3	Five gallon plastic buckets
3	Hydrochloric acid 1%, 4 L amber bottle, reagent grade
3	Methanol, 4 L amber bottle, reagent grade
5	De-ionized/reverse osmosis water, 4 L polyethylene bottle
1	Alconox™ detergent in squirt bottle
3	Teflon™ squeeze bottles, (pre-cleaned) in the laboratory (labeled for distilled water, 1% hydrochloric acid and methanol)
3	Kynar™ coated scoops, (pre-cleaned) in the laboratory
1	Kynar™ coated bucket, (pre-cleaned) in the laboratory
1	Cellular phone with battery charger

The sample containers used for sediment samples and the subcontractor responsible for providing them to AMS are listed in Table 6. Each container is given a permanent sample label written in waterproof ink. At a minimum, each sample label includes station name and code, sample date, LabID, analysis required, and collector's initials.

Sample containers are cleaned and prepared by the analyzing laboratory, or are factory pre-cleaned, and are delivered to AMS at least one week prior to the start of sampling. Sample containers are packed into pre-cleaned ice chests. A container list is prepared before a cruise starts and is used to verify that all samples are properly collected and labeled in the field. At least two personnel verify that the proper sample containers for each station have been filled with sediment and that the labels correspond to the proper station name and code.

Table 6. (Element 11) Container list for sediment sampling.

Sample Type	*Container*
Trace Elements All but Hg & meHg	New 60 ml Nalgene™ polyethylene jar, certified trace metal clean by Nalgene™, pre-cleaned by BRL. Fill 3/4 full with sediments.
Trace Organics	New 100 ml Ichem™, wide-mouth, glass with Teflon™ liner, certified trace organics clean by I-Chem™ and provided by AMS. Fill 2/3 full with sediments. Do not overfill.
Ancillary	New 60 ml Nalgene™ polyethylene jar, certified trace metal clean by Nalgene™ and provided by AMS. Fill 3/4 full with sediments.
Trace Elements Hg and MeHg	New 25 ml Ichem™, wide-mouth, glass with Teflon™ liner, certified trace organics clean by I-Chem™ and provided by AMS. Fill 5 jars per site (¾ full) with undisturbed sediments. Do not overfill.
Archive	Same as trace organics container. Fill 2/3 full with sediments. Do not overfill.
Toxicity	1 L I-Chem™ glass wide-mouth jars, and provided by MPSL. Fill with sediments to top, leave no head-space.

Sampling

It is critical that sample contamination be avoided during collection. All sampling equipment (i.e., compositing bucket and scoops) is composed of a non-contaminating material and are thoroughly cleaned before each use. Sampling personnel wear polyethylene gloves whenever taking or processing samples to avoid contact contamination. In addition, airborne contamination is avoided by keeping sample containers, sample scoops, and compositing bucket appropriately covered (with aluminum foil) when not in use.

Sampling equipment is cleaned at each sampling site using the following methods:
Fill the compositing bucket with a little clean water and add a small amount of Alconox™ detergent to the bucket.
Place all sampling scoops into the bucket and wash thoroughly with the Alconox™ solution. Wash all Kynar™-coated internal parts of the bucket with Alconox™ solution.
Completely rinse the bucket and sample scoops with clean water.
Rinse the bucket, and sample scoops with 1.0 % HCl followed with a rinse of methanol.
Completely rinse the grab, bucket, sample scoops, and coring tubes with de-ionized water.
Cover all cleaned parts with aluminum foil until use.

About 5 liters of fine-grained sediment will be collected from depositional areas in the creeks above the tidal reach. The top 1-2 cm of bedded sediments will be scooped directly into a Kynar™ coated bucket using Kynar™ coated scoops that are carefully cleaned prior to sampling (see above). The composite sample will be homogenized (by careful stirring) and aliquoted into sample containers for all analyses except meHg. Sediment samples for meHg analyses will be placed into five small sample containers directly from undisturbed sediments collected using the scoops. MeHg samples will be kept in the dark, wrapped in bubble wrap, placed in a plastic bag, and stored on dry-ice immediately after collection.

Sample storage and handling will be similar as employed by the RMP (see next section). Chemistry samples will be stored in coolers on dry-ice immediately after collection and toxicity samples will be stored in coolers on wet-ice.

Sediment analyses (for the RMP list of parameters, including pyrethroids) will be performed on all upstream "Upper" samples to characterize contaminant inputs into the Estuary (see Table X). Grain size, and TOC analyses will be performed on all samples.

Sediment toxicity tests will use the 10-d growth and survival protocol for *Hyalella azteca* (U.S. EPA 2000) for all sediments collected in upstream reaches.

If sediments are found to be significantly toxic to amphipods, up to two tributary sites will be resampled and toxicity identification evaluations (TIEs) will be performed. TIEs will be conducted to identify possible causes including using methods developed to date for identifying pyrethroids.

Table 7. (Element 11) Parameter List, Reporting Units, and Target MDLs

Sediment Quality Parameters (USCSDET)	**Reporting Units**
% clay (< 4 µm)	% dry weight
% silt (4 µm–62 µm)	% dry weight
% sand (2 mm > 62 µm)	% dry weight
% gravel (> 2 mm)	% dry weight
% solids (all chemistry labs to report this parameter)	% dry weight
Total Organic Carbon	%
Toxicity Tests — Sediment (UCD-GCML)	**Reporting Units**
(*Hyalella)*	
Sediment Toxicity – (Amphipod) % Survival	%
Sediment Toxicity – (QA/QC measures: sulfide, pH, etc.)	various

Table 7 (continued). Parameter List, Reporting Units, and Target MDLs

Trace elements analyzed in sediment samples: (BACWA-CCSF except where noted) Target Method Detection Limits (MDLs) are in parentheses following the reporting units.	
	Sediment (dry weight)
Aluminum (Al)	mg/kg (200)
Arsenic (As) - BRL	mg/kg (0.2)
Cadmium (Cd)	mg/kg (0.001)
Copper (Cu)	Mg/kg (2)
Iron (Fe)	mg/kg (200)
Lead (Pb)	mg/kg (0.5)
Manganese (Mn)	mg/kg (20)
Mercury (Hg) - UCSCDET	mg/kg (0.00001)
Methylmercury (MeHg) - UCSCDET	µg/kg (0.005)
Nickel (Ni)	mg/kg (5)
Selenium (Se) - BRL	mg/kg (0.01)
Silver (Ag)	mg/kg (0.001)
Zinc (Zn)	mg/kg (5)

Table 7 (continued). Parameter List, Reporting Units, and Target MDLs

Trace organic parameters in sediment (µg/kg): (CDFG-MPSL)		
PAHS (Target MDLs: sediment –5 µg/kg)	**SYNTHETIC BIOCIDES** (Target MDLs: sediment – 1 µg/kg)	**OTHER SYNTHETIC COMPOUNDS**
1-Methylnaphthalene	**Cyclopentadienes**	**PCB congeners (IUPAC numbers):**
2,3,5-Trimethylnaphthalene	Aldrin	(Target MDLs: sediment– 1 µg/kg)
2,6-Dimethylnaphthalene	Dieldrin	8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74,
2-Methylnaphthalene	Endrin	87, 95, 97, 99, 101, 105, 110, 118, 128, 132,
Biphenyl		138, 141, 149, 151, 153, 156, 158, 170, 174,
Naphthalene	**Chlordanes**	177, 180, 183, 187, 194, 195, 201, 203
1-Methylphenanthrene	alpha-Chlordane	
Acenaphthene	cis-Nonachlor	**Pyrethroids:** (note: AXYS to participate in an
Acenaphthylene	gamma-Chlordane	intercomparison of these)
Anthracene	Heptachlor	(Target MDLs: sediment – <1 µg/kg)
Fluorene	Heptachlor Epoxide	Cypermethrin
Phenanthrene	Oxychlordane	L-cyhalothrin
Benz(a)anthracene	trans-Nonachlor	Permethrin
Chrysene		Bifenthrin
Fluoranthene	**DDTs**	Deltamethrin
Pyrene	o,p'-DDD	Piperonyl Butoxide
Benzo(a)pyrene	o,p'-DDE	
Benzo(b)fluoranthene	o,p'-DDT	**Polybrominated Diphenyl Ethers ***
Benzo(e)pyrene	p,p'-DDD	(BDE-IUPAC No., Compound Name)
Benzo(k)fluoranthene	p,p'-DDE	(Target MDLs: sediment – 1 µg/kg).
Dibenz(a,h)anthracene	p,p'-DDT	BDE 17 [2,2',4-triBDE]
Perylene		BDE 28 [2,4,4'-triBDE]
Benzo(ghi)perylene	**HCH**	BDE 47 [2,2',4,4'-tetraBDE]
Indeno(1,2,3-cd)pyrene	alpha-HCH	BDE 66 [2,3',4,4'-tetraBDE]
Dibenzothiophene	beta-HCH	BDE 82 [2,2',3,3',4-pentaBDE]
	delta-HCH	BDE 85 [2,2',3,4,4'-pentaBDE]
	gamma-HCH	BDE 99 [2,2',4,4'5-pentaBDE]
		BDE 100 [2,2',4,4',6-pentaBDE]
	Other Synthetic Biocides	BDE 128 [2,2',3,3',4,4'-hexaBDE]
	Chlorpyrifos	BDE 138 [2,2',3,4,4',5'-hexaBDE]
	Diazinon	BDE 153 [2,2',4,4',5,5'-hexaBDE]
	Endosulfan I	BDE 154 [2,2',4,4',5,6'-hexaBDE]
	Endosulfan II	BDE 183 [2,2',3,4,4',5',6-heptaBDE]
	Endosulfan Sulfate	BDE 190 [2,3,3',4,4',5,6-heptaBDE]
	Hexachlorobenzene	Octa-BDE
	Mirex	Nona-BDE
	Oxadiazon	BDE 209 [2,2',3,3',4,4',5,5',6,6'-decaBDE]
		**** Note the PBDEs will be analyzed under a separate RMP contract for Episodic Toxicity Monitoring and are listed here for informational purposes only.***

12. SAMPLE HANDLING AND CUSTODY

Samples used for chemistry and ancillary analyses are stored on dry ice immediately after sampling. Samples used for toxicity analyses are stored on wet ice immediately after sampling (see Tables 6 and 7 for container and analyte list).

The samples on both wet and dry ice should be checked periodically to ensure that samples are appropriately protected. Ice is added as required. Additionally, coolers containing wet ice should be drained periodically to remove melt water.

A sample record is maintained by AMS for each site. The sample record contains the following information:

- Station name and code
- Collection date
- Arrival and departure time at each station
- Station coordinates (latitude and longitude) from the survey vessel's GPS
- Depth at time of sampling from the ship's depth meter
- A record of every sample bottle filled, with bottle identification code and quantity
- Collecting personnel
- Other remarks (i.e. any conditions that could possibly influence sample analysis or data interpretation or notation of the general performance of equipment involved with the sampling.)

The sample collection form, coupled with a chain of custody record and a laboratory analysis record, allows tracing of the complete history of a sample from time of collection to final entry of data to a computer database.

Samples will be shipped in insulated coolers. All caps and lids will be checked for tightness prior to shipping.

All samples will be handled, prepared, transported and stored in a manner so as to minimize bulk loss, analyte loss, contamination, or biological degradation. Sample containers will be clearly labeled with an indelible marker.

Maximum holding times for specific analyses are listed in Appendix 2.

Ice chests are sealed with tape before shipping. Samples are placed in the ice chest with enough dry or wet ice to completely fill the ice chest. RFA forms are placed in an envelope and taped to the top of the ice chest or they may be placed in a plastic bag and taped to the inside of the ice chest lid. It is assumed that samples in tape-sealed ice chests are secure whether being transported by staff vehicle, by common carrier, or by commercial package delivery.

The receiving laboratory has a sample custodian who examines the samples for correct documentation, proper preservation and holding times.

Contract laboratories will follow sample custody procedures outlined in their QA plans. Contract laboratory QA plans are on file with the respective laboratory.

All samples remaining after successful completion of analyses will be disposed of properly only after written confirmation from the SFEI Project Manager that data have been received, reviewed and validated.

It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

Chain-of-custody procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. A complete chain-of-custody form is to accompany the transfer of samples to the analyzing laboratory and to be forwarded to the SFEI Project Manager with the data reporting package.

(Refer to Appendix 2. For parameters measured in this project, provide information on container, volume, initial preservation, and holding times in the table below. Consult with State Board QA Officer if holding times cannot be met.)

Table 8. (Element 12). Sample handling and custody. Wrap all glass containers in bubble wrap prior to storage and shipping.

Analysis	Method of Storage & Transportation Conditions	Preservative	Holding Time
Trace Elements (except meHg)	Store on dry ice in ice chest	None	1 yr + (-20 °C)
Trace Elements (meHg)	Store in the dark on dry ice in ice chest	None	1 yr (-20 °C)
Trace Organics	Store on dry ice in ice chest	None	1 yr + (-20 °C)
Ancillary	Store on dry ice in ice chest	None	1 yr + (-20 °C)
Archives	Store on dry ice in ice chest	None	1 yr + (-20 °C)
Toxicity	Store on wet ice in ice chest, replenish ice each day	None	14 days (4 °C)

Parameter	Container	Volume	Initial Preservation	Holding Time
Not applicable				

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13. Analytical Methods

(Provide reference to the analytical procedures, including field measurements, that will be used in the study. A simple table of method references for each analyte measured may suffice if using the methods cited in Appendix 3. Appendix 3 provides a list of recommended Target Reporting Limits. You may specify MDLs and QLs if required for your project.)

Table x. (Element 13) Field analytical methods. N/A

Analyte	Laboratory / Organization	Project Action Limit (units, wet or dry weight)	Project Quantitation Limit (units, wet or dry weight)	Analytical Method		Achievable Laboratory Limits	
				Analytical Method/ SOP	Modified for Method yes/no	MDLs (1)	Method (1)
Not applicable							

Table 9. (Element 13) Laboratory analytical methods. See analyte list (Element 11 above) for Target MDLs.

Analysis	Sub-Contractor	Extraction Method	Analytical Method
Sediment Trace Elements	**BRL**		
TEs (Al, Ag, Cd, Cu, Fe, Pb, Mn, Ni, Zn)		SW-846 Method 3051 Mod. Sediment samples are oven-bomb digested with the addition of nitric and hydrochloric acids.	EPA Draft Method 1638. Prepared samples are analyzed by inductively coupled plasma – mass spectrometry (ICP-MS).
% solids		A solid sample is homogenized and an aliquot is measured into a pre-weighed vessel, dried in an oven overnight, weighed again and the percent of the dried solid material is calculated.	BR-1501 Rev.002 (SM 2540G and EPA Method 160.3)
TEs (As)		BR-0050 Rev.003 (Modified EPA 200.2: Nitric acid (HNO3) and Hydrocloric acid (HCl) digestions heating acording to EPA 200.2) or	BR-0050 Rev.003 (Modified EPA 200.9: Stable Temperture Platform Graphite Furnace Atomic Spectroscopy (STP-GFAA))
TEs (Se and As)		BR-0020 Rev.003, modified EPA draft 1632: HNO3:HClO4 digest: reduction with NH2.OH.HCl)	BR-0020 Rev.003, modified EPA draft 1632: Hydride Generation with NaBH4 additon, cryogenic trap precollection and Hydride quartz furnace decomposition, and Atomic absortion detection (HGAAS))
Sediment Quality and Mercury	**UCSCDET**		
Total Organic Carbon		Sample is dissolved in sulfuric acid and CO_2 is measured by coulometric titration. Total organic carbon is determined indirectly from total carbon and inorganic carbon measurements. Total organic carbon is then calcultated by difference, where TOC = TC - TIC.	NOAA Technical Memorandum NOS OMA 25. 1986. A Field Trial of the sediment quality triad in San Francisco Bay.
% solids		A solid sample is homogenized and an aliquot is measured into a pre-weighed vessel, dried in an oven overnight, weighed again and the percent of the dried solid material is calculated.	SM 2540G and EPA Method 160.3
Grain Size %clay (sedigraph)		Organics material removal by digestion (H_2O_2)	Wet sieving, & Sedigraph 5100 quanitification
Grain Size %silt (sedigraph)		Organics material removal by digestion (H_2O_2)	Wet sieving, & Sedigraph 5100 quanitification
Grain Size %sand (digestion, sieve)		Organics material removal by digestion (H_2O_2)	Dry-sieve
Grain Size %gravel (digestion, sieve)		Organics material removal by digestion (H_2O_2)	Dry-sieve
Total Mercury		EPA 1631 mod. UCSCDET (2005-02) Near-total analysis for Total Mercury. HNO3:H2SO4 digestions of freeze-dried samples, oxidation with BrCl. Stannous Chloride (SnCl2) reduction and argon gas capture.	UCSCDET (2005-02) Prepared samples are anaylzed by cold-vapor atomic fluorescence spectroscopy (CVAFS).
Methyl Mercury		UCSCDET 12/22/04: KCl, CuSO4, & H2SO4 digest in methylene chloride solvent	UCSCDET 12/22/04: Argon & mmHg are trapped on Tenax traps and anaylzed by cold-vapor atomic fluorescence spectroscopy (CVAFS).

Table 9. (Element 13 continued) Laboratory analytical methods. See analyte list (Element 11 above) for Target MDLs.

Analysis	Sub-Contractor	Extraction Method	Analytical Method
Sediment Trace Organics	**CDFG-WPCL**	EPA Methods 3500B-3545[(1)] & 3640A (Presurized Fluid Extraction & Gel Permeation Chromatography Cleanup)	
PAHs		3610B and/or 3630C Silica Gel/Alumina Cleanup	8270C Mod GC-MS
PCBs & PESTs (original RMP analyte list)		3620B Florisil Cleanup	8081A Mod & 8082 Mod GC-ECD*
PBDEs (part of the RMP EpTox Contract)		3620B Florisil Cleanup	8082 Mod GC-ECD*
Pyrethroids		3620B Florisil Cleanup	8081A Mod GC-ECD*
Sediment Toxicity & chemistry	**UCD-GCML**		
Sed Tox (H. azteca 10-day solid phase)			EPA 600-R-99-096
Sed Tox (E. estuarius 10-day solid phase)			EPA/600/R-94/025
Clorpyrifos & Diazinon			ELISA Kit assay

*GC-ECD results confirmed by GC-MS (ITD) or MSMS

[(1)] Extraction, cleanup and partitioning methods are modifications of the multi-residue methods for solids described in EPA Methods 3500B-3545, 3640A, 3610B, 3630C, and 3620B from EPA Test Methods for Evaluating Solid Waste Vol. 1B.

EPA Method 8082 Mod GC-ECD reference: Crane, David. 2004. Analysis of Extractable Synthetic Organic Compounds in Tissue and Sediment (Organochlorine Pesticides, PCBs, and PBDEs) - DRAFT, SOP# SO-TISS-SED, Revision #8 (11/5/2004). Ca Dept. of Fish and Wildlife – Water Pollution Studies Lab. Rancho Cordova, CA

EPA Method 8081A Mod GC-ECD reference: Mekebri, Abdou. 2001. Analysis of Lambda-Cyhalothrin in Sediment. SOP# Warrior-SEDT, Revision #1 (2/18/2001). Ca Dept. of Fish and Wildlife – Water Pollution Studies Lab. Rancho Cordova, CA

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14. QUALITY CONTROL

Table x. (Element 14) Sampling (Field) QC. (Not applicable)

Table 10. (Element 14) laboratory Analytical QC .

Group	Parameter	Element 14 Quality Control	Element 16 Instrument Calibration/Frequency
	ELISA	Positive and negative (interference) checks, and 5% checks against laboratory measurement. RPD for Chlorpyrifos and diazinon within 50%	No SWAMP requirement – suggest calibration according to manufacturer's procedures each time device is used (may be more than once during sample run).
	Organic chemicals (PCBs, PAHs, pesticides, pyrethroids, others) in tissue and sediment & semi-volatiles & volatiles in sediment only	Blanks – Laboratory and field blanks. No detectable amount of substance in blanks. Frequencies – Accuracy, precision, recovery, and blanks at 1 in 20 (5%) with at least one in every batch. *MDL study – prior to first use and annually thereafter. Procedure according to 40CFR Part 136.3 appendix B.* *Surrogate spike (similar structure or isotopically labeled) – determined by project manager.* All quality assurance and quality control procedures and criteria specified by selected method.	External calibration with 3 – 5 standards covering the range of sample concentrations prior to sample analysis. At low end, the lowest standard at or near the MDL. Linear regression $r^2 \leq 0.995$ Calibration verification every 10 samples after initial calibration. Standard source different that that used for initial calibration. Recovery 90% - 110%, except for mercury 85% - 115%.
	Trace metals, including mercury in tissue and sediment	Blanks – Laboratory and field blanks. No detectable amount of substance in blanks. Frequencies – Accuracy, precision, recovery, and laboratory blanks at 1 in 20 (5%) with at least one in every batch. Field blanks – initial demonstration. No further blanks collected if no detectable amount. Otherwise blanks collected at 5% of samples. *MDL study – prior to first use and annually thereafter. Procedure according to 40CFR Part 136.3 appendix B.* All quality assurance and quality control procedures and criteria specified by selected method.	External calibration with 3 – 5 standards covering the range of sample concentrations prior to sample analysis. At low end, the lowest standard at or near the MDL. Linear regression $r^2 \leq 0.995$ Calibration verification every 10 samples after initial calibration. Standard source different that that used for initial calibration. Recovery 90% - 110%, except for mercury 80% - 120%.

Group	Parameter	Element 14 Quality Control	Element 16 Instrument Calibration/Frequency
	Monomethyl mercury in tissue or sediment	Blanks – Laboratory and field blanks. No detectable amount of substance in blanks. Frequencies – Accuracy, precision, recovery, and laboratory blanks at 1 in 20 (5%) with at least one in every batch. Field blanks – initial demonstration. No further blanks collected if no detectable amount. Otherwise blanks collected at 5% of samples. *MDL study – prior to first use and annually thereafter. Procedure according to 40CFR Part 136.3 appendix B.* All quality assurance and quality control procedures and criteria specified by selected method.	External calibration with 3 – 5 standards covering the range of sample concentrations prior to sample analysis. At low end, the lowest standard at or near the MDL. Linear regression $r^2 \leq 0.995$ Calibration verification every 10 samples after initial calibration. Standard source different that that used for initial calibration. Recovery 80% - 120%.
	Total organic carbon in sediment and sediment grain size	Blanks – no detectable amount or <30% of lowest sample. Frequency – Accuracy for TOC every 15 samples; Precision one per batch; LCM for TOC 1 in 20 (5%) with at least one in every batch.	No SWAMP requirements. Suggest follow manufacturer's requirements for TOC analyzer. Check weights for balances.
	Toxicity testing sediment	Reference toxicant and negative controls with each test. General water quality measurements – dissolved oxygen, pH, conductivity, and ammonia. All performance criteria outlined in method SOP.	All performance criteria outlined in method SOP.

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Sediment sampling equipment is inspected and cleaned in the laboratory by AMS prior to the start of the sampling event. Scoops and bucket are coated with a non-reactive Kynar coating. This coating is inspected prior to use and if damaged, the equipment is sent for resurfacing. The sampling equipment that are pre-cleaned include:

- Sample scoops
- Compositing bucket
- Wash bottles

Use the following procedures for cleaning sediment sampling equipment:

1. Soak equipment (fully immersed) for three days in a 0.5 % solution of Alconox™ detergent and de-ionized water.
2. Rinse equipment three times with de-ionized water and let dry in a clean place.
3. Rinse equipment with 1.0 % solution of hydrochloric acid, followed by a rinse with petroleum ether, followed by another set of three rinses with de-ionized water. All equipment is then allowed dry in a clean place.

The cleaned scoops are wrapped in aluminum foil and stored in clean Ziploc™ bags until used in the field.

Laboratory instruments and equipment are inspected and maintained by subcontracting laboratory personnel according to laboratory protocol.

Table x. (Element 15) Testing, inspection, maintenance of sampling equipment and analytical instruments.

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
Not applicable				

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Laboratory instruments and equipment will be calibrated and maintained by subcontracting laboratory personnel according to laboratory protocol that is compliant with SWAMP calibration expectations. Documentation for laboratory methods will be provided to contractor prior to analyses.

Table x. (Element 16) Testing, inspection, maintenance of sampling equipment and analytical instruments.

Equipment / Instrument	SOP reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
Not applicable				

17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Supplies and consumables that may be used in this project include reference toxicant chemicals for toxicity testing, test organisms for toxicity testing, bottles of known cleanliness for chemical analyses, etc. All supplies and containers used in this study will be either certified for cleanliness (e.g. IChem jars and reagents), or thorough inspected prior to use (e.g. sampling gloves, and equipment). Laboratories will determine that all supplies and consumables comply with acceptance criteria outlined in their Standard Operating Procedures prior to conducting analyses.

Table x. (Element 17) Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies / Consumables	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Not applicable				

18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

Environmental measurements are not always confined to data generated directly by the organization. In some cases, data from other sources may be used, either as a starting point or to supplement data generated directly. This project used stream gauge data generated by the USGS and available on line (*http://waterdata.usgs.gov/ca/nwis*) to determine when to sample Estuary tributaries, as we wanted to target periods of detectable flow after a spring rain event.

Additionally, in planning where to sample above the tidal range, SWAMP monitoring sites in the region were evaluated as previous sampling information may prove to be helpful in data interpretation and analyses.

19. DATA MANAGEMENT

San Francisco Estuary Institute (SFEI) and each sub-contractor will be responsible for the study's data handling and storage. The data management of this study will be conducted in a similar fashion to the San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP), whose data SFEI has been successfully managing for the past ten years.

Field monitoring results will be transferred to SFEI in Microsoft Excel spreadsheets and compiled into a relational database, which is compatible with the State's Surface Water Ambient Monitoring Program (SWAMP) information management system. To minimize data formatting by SFEI staff, templates and guidelines explaining the structure of the database's tables will be provided to most sub-contractors. Data will be reviewed to ensure that they are consistent with the format of the database and other data records. SFEI's database is backed up on a weekly basis.

Raw data generated to develop LC50s, in the Dose Response study task, and/or to develop TIE Methods will be stored in Excel files and included in the draft and final report. Note: The SWAMP database is not formatted to accept the types of data generated from Tasks 2 and 3 of this project, as these data are not always standardized, and may require interpretation. Data from these tasks (development of dose-response data for specific pyrethroid pesticides, and development of sediment TIE procedures for pyrethroids) will be provided in electronic (Excel) format according to established procedures at MPSL-Granite Canyon. These data will be discussed and interpreted in accompanying MS Word test files. Original raw data sheets and duplicates of these are stored in separate locations at MPSL. Excel data files are stored as original and back-up electronic files.

All dose-response and TIE data are compiled, analyzed, and transmitted by Bryn Phillips (MPSL-Granite Canyon). The TIE data require considerable technical interpretation, and this interpretation is provided in text in MS Word files accompanying all TIE data.

GROUP C: ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS & RESPONSE ACTIONS

SFEI Project Manager will work closely with field sampling crew to assure sample collection is performed according to clean sampling methods described in the QAPP. Periodic discussions between SFEI and the sub-contractors will ensure that the contractual agreements are followed. QA/QC review of the reported results by SFEI will evaluate if DQOs have been met and possible corrective action may be warranted to ensure high quality data is produced.

Quarterly reports to the RWQCB Project Manager ,Richard Condit, will include an update on project status.

If corrective action is warranted, after SFEI has performed QA/QC review of the monitoring data, a subcontracting analytical laboratory may be asked to re-analyze samples that did not meet expected DQOs. Archived samples, maintained by AMS as part of the RMP's sample archive collection, may be used to provide additional sample for reanalysis.

21. REPORTS TO MANAGEMENT

Interim and final reports will be submitted by SFEI to the Project Manager at the RWQCB according to the schedule outline in the Agreement and listed in Element 6, Table 2 *Project schedule timeline.*

Table x. (Element 21) QA management reports.

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Dates(s)	Person(s) Responsible for Report Preparation	Report Recipients
Not applicable				

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

Data generated for the field monitoring component of this project will be reviewed by SFEI QA Officer, or designee, against the data quality objectives cited in Element 7 and the quality assurance/quality control practices cited in Elements 14, 15, 16, and 17. When warranted reanalysis of sample material may be requested of the labs or data will be qualified appropriately.

23. VERIFICATION AND VALIDATION METHODS

Field monitoring data received at SFEI will be processed by SFEI data management staff. Data reporting formats and expectations are written into all sub-contracts. Cover letters and data reports must accompany each data submission, which is verified and validated visually against the original contractual agreement (e.g total number of samples and parameters to be measured, compliance with data quality objectives).

Final validated monitoring data will be made available on the SFEI website for downloading. All Reports will be sent to the RWQCB project manager and upon approval will be posted on the SFEI documents website for downloading.

24. RECONCILIATION WITH USER REQUIREMENTS

(Describe how the project results will be evaluated to determine whether the project's objectives have been satisfied. This element assumes that the data has already met all data quality objectives and other quality issues. The outcome here is whether the data does or does not support the original hypothesis or whether the data does not have the power to make the determination. Describe proposed methods -statistical or scientific- to analyze the data so as to determine possible anomalies or departures from assumptions made when the project was planned. Statistical analyses may include tests for outliers, trends, and dispersion.)

The monitoring task of this project (task 1) will provide an initial screening of Estuary tributaries for a suite of sediment contaminants and toxicity that will be used to evaluate our initial hypothesis. The Dose Response task (task 2) will develop LC50s for toxicity test organisms that can be used to evaluate environmental samples. TIE method development (task 3) will further the current effort to develop reliable processes for pinpointing possible causes for observed toxicity.

You have completed your project QAPP. Please check that you have:

- Appended all relevant forms, SOPs, etc.
- Completed the checklist and included it as an attachment.
- Updated the Table of Contents (to update: use F9)
- Updated List of Figures, List of Tables, List of Appendices
- Deleted all guidance and example text boxes.
- Deleted this text box.

REFERENCES

ASTM. (1992). Designation E 1367: Standard guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. Volume 11.04. American Society for Testing and Materials, Philadelphia, PA.

Field Operations Manual: Regional Monitoring Program for Trace Substances (2001) David, N., D. Bell, J. Gold, San Francisco Estuary Institute, Oakland, CA (www.sfei.org)

Quality Assurance Project Plan for the Regional Monitoring Program for Trace Substances (1999) Lowe, S.; R. Hoenicke; J. Davis. San Francisco Estuary Institute, Oakland, CA (www.sfei.org)

U.S. EPA. (1994) Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. C.I. Weber (ed.). EPA/600/R-94/025. Office of Research and Development, Washington, D.C.

U.S. Environmental Protection Agency. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. Office of Research and Development. EPA 600-R-99-096, Washinton, DC, USA

APPENDIX A: MONITORING PLAN: SUBMITTED TO RWQCB DECEMBER-2004

FIELD MONITORING PLAN

PRISM GRANT: 041355520

PROJECT NAME: INVESTIGATIONS OF SOURCES AND EFFECTS OF PYRETHROID PESTICIDES IN WATERSHEDS OF THE SAN FRANCISCO BAY ESTUARY

Project Director: Sarah Lowe (SFEI)
Project Grant Manager: Richard Condit (SWRCB)

November 30th, 2004

FIELD MONITORING PLAN
PRISM GRANT: 041355520
PROJECT NAME: INVESTIGATIONS OF SOURCES AND EFFECTS OF PYRETHROID PESTICIDES IN WATERSHEDS OF THE SAN FRANCISCO BAY ESTUARY

Project Director: Sarah Lowe (SFEI)
Project Grant Manager: Richard Condit (SWRCB)
Additional Coordination: Brian Anderson (UCD-GCML) and Karen Taberski (RWQCB)

This field monitoring plan covers work to be performed under Task 3.1: *Ambient Sediment Sampling, Analyses, and Toxicity Assays* under this PRISM Grant AND additional work performed by the Trace Substances' Status and Trends Monitoring Program (RMP) Episodic Toxicity Monitoring Program (2004-05). This work constitutes a combined study to investigate sediment contamination, and the potential for sediment toxicity in upper and lower reaches of six tributaries around the San Francisco Estuary, during two sampling events (November 2004 and April 2005).

OBJECTIVE
The purpose of this study is to investigate potential sediment toxicity to both freshwater and estuarine amphipods to sediments from six tributaries around the Estuary whose land uses include varying combinations of urban and agricultural practices. Bedded surface sediments will be collected targeting recently deposited sediments for toxicity and chemical analyses. A suite of California Toxics Rule priority pollutants, sediment grain-size, total organic carbon, and additional pollutants of concern (including pyrethroids and polybrominated diphenyl ethers (PBDEs)) will be characterized for each tributary (see Table 2 for a complete list).

This PRISM grant component (Task 3.1) covers only a portion of the study outlined below: the April 2005 monitoring effort to investigate sediment contamination and potential sediment toxicity to freshwater amphipods in sediments collected at up-stream sites from six tributaries around the Estuary. The number of samples and analyses paid for by the PRISM grant is presented in Table 3 (below).

APPROACH
The San Francisco Estuary Institute will coordinate execution of this work plan. Sub-contractors identified in the original PRISM proposal will provide services for this study to ensure consistency in sampling and analytical methods with the long-term data from the RMP with the exception of CDFG-MPSL, who will be analyzing sediment organic chemicals. We are using this laboratory because the current RMP Status and Trends sediment organics laboratory is presently undertaking an instrumentation change and the CDFG-MPSL is the sub-contracting laboratory for task 2 and 3 for this PRISM grant (Toxicity Dose-Response study and the TIE development) and for another RMP Special Study (Exposure and Effects Pilot Study 2004 – Sediment Dose Response). Having the same laboratory perform the chemical analyses for all these tasks is important for comparing and interpreting our study results.

Table 1. List of Subcontractors for sediment sampling and analyses performed:

1.1 Sediment Chemistry Analyses	
Trace Metals – except Hg, and meHg	BRL
Sediment Characteristics and Trace Metals - Grain size, TOC, Hg, and meHg	UCSCDET
Organics – PAHs, PCBs, Pesticides, PBDEs, and Pyrethroids	CDFG-MPSL
Sediment Toxicity - *Hyalella, Eohaustorius*	UCD-GCML
1.2 Field Work & Logistics	
Field Logistics (Coordination and Sampling)	AMS/SFEI

AMS: Applied Marine Sciences (AMS), Livermore, CA (Mr. Paul Salop)
BRL: Brooks-Rand Ltd., Seattle, WA (Dr. Colin Davies)
UCSCDET: UC Santa Cruz, Santa Cruz, CA (Dr. Russel Flegal, Ms. Genine Scelfo)

CDFG-MPSL: CA Dept. of Fish & Game, Water Pollution Control Laboratory, Rancho Cordova, CA (Mr. Dave Crane)
UCD-GCML: UC Davis- Marine Pollution Studies Lab (MPSL), Granite Canyon, CA (Mr. Brian Anderson, Mr. Bryn Phillips)

PROJECT FUNDING: This is a coordinated study funded by the following projects

1) RMP - Episodic Toxicity Monitoring Program 2004 (Year 1 of sediment toxicity investigations in Estuary tributaries),
2) PRISM – INVESTIGATIONS OF SOURCES AND EFFECTS OF PYRETHROID PESTICIDES IN WATERSHEDS OF THE SAN FRANCISCO BAY ESTUARY (subtask 3.1)

BACKGROUND

The RMP- Exposure and Effects Pilot Study (EEPS) toxicity workgroup met periodically in 2002 and 2003 to discuss the findings from the RMP's toxicity programs and to decide how to adapt the programs to monitor for potential toxicity in the Estuary and it's immediate watersheds in light of recent pesticide management measures (phasing out of diazinon and chlorpyrifos) and shifting pesticide use patterns upstream (i.e., increasing usage of pyrethroids). The workgroup recommended that the Episodic Toxicity Monitoring Program (Ep. Tox. Program) investigate sediment in Estuary tributaries in 2004. In addition, SFEI was awarded a PRISM grant to study pyrethroids in sediments that includes a field investigation to characterize sediment contamination and potential sediment toxicity in several Estuary tributaries. This workplan outlines the combined tasks for the field components of these two studies. Please refer to Appendix A: Related Studies *section below for a brief description of each study.*

WORK PLAN

This project will require execution of the following tasks:

1. *Project management and coordination - SFEI will develop subcontracts, coordinate, track deliverables, and specify appropriate data reporting and quality assurance procedures.*
2. *Sample collection - this task will be done by subcontractors and SFEI staff.*
3. *Sample extraction, quantification, and data reporting - After receipt of samples, the analytical laboratory will analyze samples in accord with conditions agreed to in the contract, including data quality objectives, turnaround time, reporting formats, and specific quality assurance samples and procedures.*

Sampling and toxicity testing strategy

Since estuarine taxa may be more sensitive to some pyrethroids than freshwater taxa, we will sample both above the tidal prism and near the mouth of each tributary and perform ***toxicity tests with freshwater and estuarine amphipod species*** *where appropriate* (Hyalella and Eohaustorius, respectively). *About 5 liters of homogenized* ***fine-grained sediment will be collected from depositional areas in the creeks*** *above the tidal reach and down-stream within the tidal reach. The top 1-2 cm of sediments will be scooped into a Kynar coated bucket using Kynar coated scoops that are carefully cleaned with soap, acid, and methanol similar to the methods employed by the RMP. Sample storage and handling will be similar as employed by the RMP. Chemistry samples will be stored on dry-ice immediately after collection and toxicity samples will be stored on wet-ice. Sediment samples for meHg analyses will be directly allocated into the sample containers from undisturbed sediments collected using the scoops.*

Sediment chemistry (RMP list of contaminants, and pyrethroids) *will be performed in the upstream samples to characterize contaminant inputs into the Estuary (see Table 2). Similar sediment samples from the downstream sites will be collected, but these chemistry samples will be archived. If downstream sediments are toxic, then the same list of analytes will be measured in the archived sediments.* ***Grain size and TOC*** *analyses will be performed in all samples.*

Sediment toxicity tests *will use the 10-d growth and survival protocol for* Hyalella azteca *(U.S. EPA 2000) for sediments collected in upstream reaches, and the 10-d survival protocol for* Eohaustorius estuarius *for sediment collected in the downstream reaches (U.S. EPA, 1994b).*

If sediments are found to be significantly toxic to amphipods, up to two tributary sites will be resampled and toxicity identification evaluations (TIEs) will be performed. TIEs will be conducted to identify possible causes including using methods developed to date for identifying pyrethroids.

Note: SFEI will coordinate additional sample collection with Dr. Daniel Oros for another PRISM grant (#041345520, see Appendix A). A subset of five tributaries will be sampled in April-2005 for ***water and sediment to characterize the ambient concentration of several pyrethroids****. The additional sediment samples will provide an opportunity to compare pyrethroid analyses between two laboratories (AXYS Analytical Services Ltd. (BC, Canada) and CDFG-MPSL).*

Sample locations

Two locations in six tributaries around the Estuary *(see Figure 1) will be sampled. Bedded depositional sediment samples will be collected in the freshwater regions of each tributary (not far above the region of tidal influence) and near the mouths of each tributary within the tidal reach.*

Site selection goals include: *1) Selection of tributaries distributed around the Estuary of variable land-use types; 2) preferably sites that have been studied before so that there is some historical data to refer to (i.e. SWAMP, USGS, Alameda County Sediment Survey, NOAA/EMAP, RMP, other); 3) availability of fine-grained depositional sediments; and 4) safely accessible for sample collection.*

Sampling periods

Field sampling will occur ***twice****. The first samples will be collected after the "first flush" of the wet season in order to capture the potential effects of dry season pesticide usage (****November - 2004****),. The second samples will be collcted in late spring (****April - 2005****), after the winter rains and and coinciding with resumption of fresh pesticide applications in urban and agricultural settings.*

Sampling and Sample Handling

Sample collection, sample handling, and laboratory methods will be the same as those employed by the RMP Status and Trends program and/or compliant with SWAMP protocols. Methods for collection of field samples and sample handling are further outlined in the Field Operations Manual: Regional Monitoring Program for Trace Substances (2001), available on the web at http://www.sfei.org/rmp/reports.htm.

Sampling Equipment

Applied Marine Science (AMS) (Livermore, CA) will coordinate with the laboratory for sample containers and sample handling instructions (contact Paul Salop (925) 373-7142 or [salop@amarine.com]). Each laboratory will be responsible for supplying pre-cleaned/certified containers to AMS at least two weeks prior to each sampling event. RMP Status and Trends sediment and water sampling equipment (e.g. buckets, scoops, cleaning supplies) will be used in this study.

Please see Appendix B for a description of the quality assurance/quality control (QA/QC), and reporting expectations.

Table 2. Parameter List, Target Method Detection Limits (MDLs), and laboratory performing analyses.

Conventional Water Quality Parameters (AMS)	Reporting Units

Salinity (by salinometer)	psu
Temperature	°C
Depth	m

Sediment Quality Parameters (USCSDET)	**Reporting Units**
% clay (< 4 µm)	% dry weight
% silt (4 µm–62 µm)	% dry weight
% sand (2 mm > 62 µm)	% dry weight
% gravel (> 2 mm)	% dry weight
% solids	% dry weight
Total Organic Carbon	%

Toxicity Tests — Sediment (UCDavis-GCML)	**Reporting Units**
(*Hyalella, Eohaustorius estuarius)*	
Sediment Toxicity – (Amphipod) % Survival	%
Sediment Toxicity – (QA/QC measures: sulfide, pH, etc.)	various

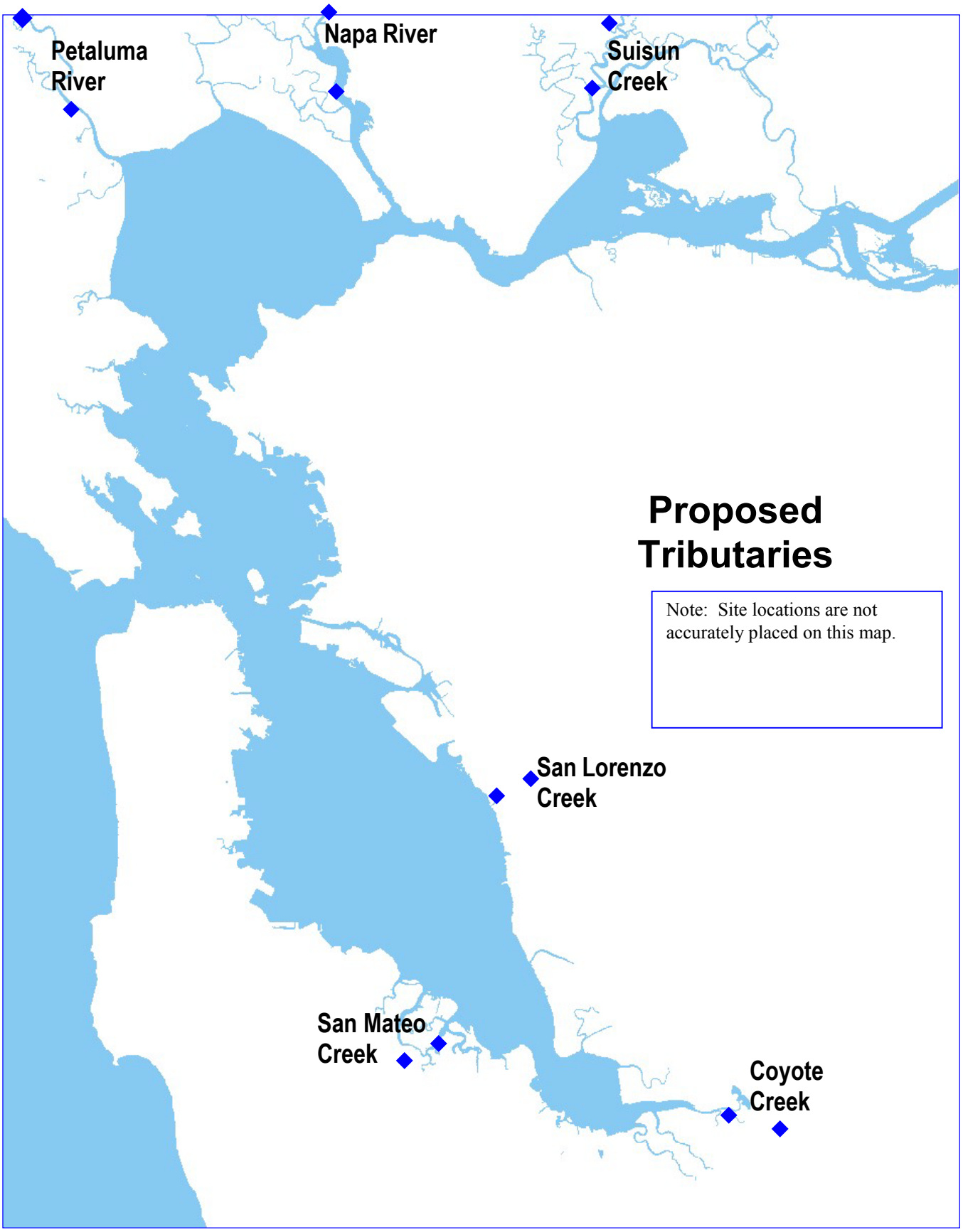
Trace elements analyzed in sediment samples: (BACWA-CCSF except where noted)
Target Method Detection Limits (MDLs) are in parentheses following the reporting units.

	Sediment (dry weight)
Aluminum (Al)	mg/kg (200)
Arsenic (As) - BRL	mg/kg (0.2)
Cadmium (Cd)	mg/kg (0.001)
Copper (Cu)	Mg/kg (2)
Iron (Fe)	mg/kg (200)
Lead (Pb)	mg/kg (0.5)
Manganese (Mn)	mg/kg (20)
Mercury (Hg) - UCSCDET	mg/kg (0.00001)
Methylmercury (MeHg) - UCSCDET	µg/kg (0.005)
Nickel (Ni)	mg/kg (5)
Selenium (Se) - BRL	mg/kg (0.01)
Silver (Ag)	mg/kg (0.001)
Zinc (Zn)	mg/kg (5)

Table 2 (continued). Parameter List, and Target MDLs

Trace organic parameters in sediment (µg/kg): (CDFG-MPSL)

PAHS (Target MDLs: sediment –5 µg/kg)	**SYNTHETIC BIOCIDES** (Target MDLs: sediment – 1 µg/kg)	**OTHER SYNTHETIC COMPOUNDS**
1-Methylnaphthalene	**Cyclopentadienes**	**PCB congeners (IUPAC numbers):**
2,3,5-Trimethylnaphthalene	Aldrin	(Target MDLs: sediment– 1 µg/kg)
2,6-Dimethylnaphthalene	Dieldrin	8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74,
2-Methylnaphthalene	Endrin	87, 95, 97, 99, 101, 105, 110, 118, 128, 132,
Biphenyl		138, 141, 149, 151, 153, 156, 158, 170, 174,
Naphthalene	**Chlordanes**	177, 180, 183, 187, 194, 195, 201, 203
1-Methylphenanthrene	alpha-Chlordane	
Acenaphthene	cis-Nonachlor	**Pyrethroids:** (note: AXYS to participate in an
Acenaphthylene	gamma-Chlordane	intercomparison of these)
Anthracene	Heptachlor	(Target MDLs: sediment – <1 µg/kg)
Fluorene	Heptachlor Epoxide	Cypermethrin
Phenanthrene	Oxychlordane	L-cyhalothrin
Benz(a)anthracene	trans-Nonachlor	Permethrin
Chrysene		Bifenthrin
Fluoranthene	**DDTs**	Deltamethrin
Pyrene	o,p'-DDD	Piperonyl Butoxide
Benzo(a)pyrene	o,p'-DDE	
Benzo(b)fluoranthene	o,p'-DDT	**Polybrominated Diphenyl Ethers**
Benzo(e)pyrene	p,p'-DDD	(BDE-IUPAC No., Compound Name)
Benzo(k)fluoranthene	p,p'-DDE	(Target MDLs: sediment – 1 µg/kg).
Dibenz(a,h)anthracene	p,p'-DDT	BDE 17 [2,2',4-triBDE]
Perylene		BDE 28 [2,4,4'-triBDE]
Benzo(ghi)perylene	**HCH**	BDE 47 [2,2',4,4'-tetraBDE]
Indeno(1,2,3-cd)pyrene	alpha-HCH	BDE 66 [2,3',4,4'-tetraBDE]
Dibenzothiophene	beta-HCH	BDE 82 [2,2',3,3',4-pentaBDE]
	delta-HCH	BDE 85 [2,2',3,4,4'-pentaBDE]
	gamma-HCH	BDE 99 [2,2',4,4'5-pentaBDE]
		BDE 100 [2,2',4,4',6-pentaBDE]
	Other Synthetic Biocides	BDE 128 [2,2',3,3',4,4'-hexaBDE]
	Chlorpyrifos	BDE 138 [2,2',3,4,4',5'-hexaBDE]
	Diazinon	BDE 153 [2,2',4,4',5,5'-hexaBDE]
	Endosulfan I	BDE 154 [2,2',4,4',5,6'-hexaBDE]
	Endosulfan II	BDE 183 [2,2',3,4,4',5',6-heptaBDE]
	Endosulfan Sulfate	BDE 190 [2,3,3',4,4',5,6-heptaBDE]
	Hexachlorobenzene	Octa-BDE
	Mirex	Nona-BDE
	Oxadiazon	*BDE 209 [2,2',3,3',4,4',5,5',6,6'-decaBDE]*


Petaluma River
Napa River
Suisun Creek
Proposed Tributaries
Note: Site locations are not accurately placed on this map.
San Lorenzo Creek
San Mateo Creek
Coyote Creek

Appendix A:

RELATED STUDIES:

PRISM 041355520: Investigations of Sources and Effects of Pyrethroid Pesticides in Watersheds of the San Francisco Estuary.
The purpose of this project is to evaluate pyrethroids in sediments and their potential impact on benthic organisms.

There are three tasks to this project:

1) *Conduct a field study during the spring season to determine if sediments entering the San Francisco Estuary from local tributaries are toxic to three ecologically relevant benthic amphipods. Characterize the contaminant levels in the collected sediments including trace metals, PAHs, PCBs, OP pesticides, and diazinon replacement pesticides (specifically pyrethroids), and if the samples are toxic, perform Toxicity Identification Evaluations (TIEs) to identify causes.*
2) *Develop dose-response information (LC50s) for standard EPA sediment toxicity testing species, and ecologically relevant species to the Estuary, for three pyrethroids (cypermethrin, permethrin, and bifenthrin). The species to be evaluated include the amphipods* Eohaustorius estuarius *and* Ampelisca abdita*. (The rationale for targeted pesticides and species is provided in item 5 below.)*
3) *Develop and validate TIE procedures for sediment toxicity tests targeting toxicity caused by pyrethroids. The TIE methods used will be similar to those proposed in PRISM proposal #0032 "Tools for Surface Water Monitoring", however, that project emphasizes pesticides in water. Both groups will collaborate through ongoing discussions about methods development and validation for both water and sediment samples.*

PRISM 041345520: Development of New Chemical Methods for the Diazinon Replacements*: Pyrethroids (including Deltamethrin), Carbamates, Imidacloprid, and Piperonyl Butoxide.*

There are three tasks in this project:

1) *Evaluation and development of high performance liquid chromatography/mass spectrometry-mass spectrometry (LC/MS-MS) and high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) methods for measurement of the target pesticides,*
2) *Analysis of environmental samples (water and sediment) by LC/MS-MS and HRGC/HRMS. (Field sampling will be coordinated with the RMP's Episodic Toxicity Monitoring Study and PRISM Project 041355520)*
3) *Comparison between LC/MS-MS and HRGC/HRMS methods for both lab and environmental (ambient) samples for some of these pesticides.*

RMP Episodic Toxicity Monitoring Program: Ambient water toxicity monitoring of storm-water runoff events (Oct – May). *Results from this monitoring effort over the past several years has shown that water entering the Estuary during storm events is usually not toxic to mysid shrimp or fish larvae and that pulses of pesticides moving downstream (which are difficult to sample) are toxic to some resident organisms for periods up to several days. Additionally, changing pesticide usage upstream call for adaptive monitoring strategies. We plan to use the 2004 funds to explore the hypothesis that sediments coming into the Estuary through episodic, wet season transport may be contributing to the observed persistent sediment toxicity in several regions of the Estuary, and to redesign the toxicity monitoring effort.*

Excerpt from the most recent RMP Episodic Toxicity Monitoring-Annual Report:

"Aquatic toxicity monitoring programs must be aware of changes in activities (e.g., pesticide use) in the watersheds being studied, and must adapt the monitoring tools (e.g., sampling design, toxicity tests, and chemical analyses) to reflect those changes. For example, knowing that diazinon and chlorpyrifos had been linked to ambient water toxicity in upstream waters, and that OP pesticides can remain dissolved in the water, are very toxic to crustaceans, and are relatively non-toxic to fish, we believe that the currently used approach of ambient water sampling and toxicity testing with A. bahia *is an appropriate monitoring approach. However, the fate and effects of the pyrethroid pesticides are different than the OP pesticides. This suggests that transitions in pesticide use (or use of other chemicals) in the Estuary watershed may need to be reflected in changes in the way we monitor for ambient toxicity. The current water sampling approaches, currently recommended suite of chemical analytes, and toxicity testing with* Ceriodaphnia *and mysids may not be the optimal approach for assessment of the effects of "new" contaminants, such as the pyrethroids, on the San Francisco Estuary aquatic ecosystems." (PERL, RMP Technical Report: Ambient Water Toxicity In The San Francisco Estuary, 2002)*

Appendix B:
DESCRIPTION OF QUALITY ASSURANCE/QUALITY CONTROL, AND REPORTING EXPECTATIONS

Quality Assurance and Quality Control
This study will employ similar laboratory methodologies as the RMP, which is a performance-based program. Laboratories will use current RMP laboratory methods unless new methods are discussed, warranted, and approved by the project manager (or designee). Laboratories will review the 1999 Quality Assurance Project Plan (QAPP) of the RMP available on the web at http://www.sfei.org/rmp/reports/1999_QAPP/99_QAPP.html.

All scientific activities undertaken by laboratories must adhere to quality assurance and quality control (QA/QC) procedures as developed in the QAPP. This will include requirements for documenting chain of custody for samples, proper sample storage and holding times, data validation methods, and analysis of quality control samples, laboratory blanks and spikes, laboratory replicates, and standard reference materials (when available). Laboratories will be required to provide concise and complete reports of analyses of quality control samples to verify that Data Quality Objectives (DQOs) are being met. If DQOs are not being met, re-analysis of samples may be necessary.

DQO's for the pyrethroids will be developed over the coarse of this study and laboratory staff will collaborate with SFEI in developing those objectives.

Reporting of Results
Analytical results, including associated quality control samples, will be provided to SFEI ***no later than 120 days after sample receipt.***

Laboratory personnel will verify, screen, validate, and prepare all data, including QA/QC results, in accordance with the RMP'S QAPP and will provide (upon request) detailed QA/QC documentation that can be referred to for an explanation of any factors affecting data quality or interpretation. Any detailed QA/QC data not submitted as part of the reporting package (see below) should be maintained in the laboratory's database for future reference.

Laboratories will provide electronic copies of the cover letter and tabulated analytical data (including associated QA/QC information outlined below) in the SWAMP database format or a format agreed upon with the RMP's Project/Data Manager or designee.

Each electronic data report package will consist of the following components:

1. *A* ***cover letter*** *(electronic copy) transmitting the data report package. The following topics will be addressed in the narrative:*
    a. *Identify Samples: Include the contract number, study, sample dates, matrix, and total number of field samples being submitted. Note if any of the contracted number of samples were not analyzed for any reason. Include a list of the type of QA samples included in the report package.*
    b. *Clarify linkage between field samples and QA: Provide a list of which QA samples are associated with each set of field samples. Be sure to say if the QA samples are associated by batch or cruise*
    c. *Summarize Methods used: Provide a short summary of the procedures and instrumentation used, including:*
        i. *pre-prep., extraction, and quantification methods (reference EPA methods where applicable). Include electronic copies of your SOPs with your data submission package.*
        ii. *Type and frequency of QA samples run (e.g. blank, duplicate, matrix spike, SRMs). Include: (1) concentrations used for spiked samples or equivalent, and (2)*

concentration range used for generating instrument calibration curves. (Note: You may choose to reference the location of this information in the expanded report.)

iii. *Sample size extracted and what units you are reporting the data in.*

iv. *Indicate if the data have been recovery corrected and if the MDLs were adjusted for sample size extracted. Also indicate if the data are reported in wet or dry weight.*

v. *PROVIDE DATA THAT HAVE NOT BEEN BLANK CORRECTED and clearly identify all blank samples that would be used to blank correct each sample batch. State that the data were not blank corrected in the cover letter and list those parameters that should be blank corrected prior to data usage.*

vi. *A list of qualifier definitions.*

d. *Report on the QA/QC: Do the results meet the data quality objectives (DQOs) outlined in Tables 3 and 4 of the 1999 QAPP? Provide a brief summary table of precision, accuracy, and blank sample concentrations and explain any analytical problems and/or corrective actions taken. Examples of items to include are:*

i. *An explanation of any analyte accuracy and recovery calculations that were outside DQOs outlined in the QAPP.*

ii. *Any contamination of the blanks.*

iii. *Any analyte concentrations that were outside calibrated range.*

iv. *Lost/broken samples.*

2. *Tabulated electronic results in SWAMP database format unless another format is agreed upon with the project manager. Tabulated data will include the following information for each sample (when applicable):*

a. *Sample identification: Unique sample-ID (provided on the COC and available electronically upon request - contact SFEI's Project/Data Manager), site code, site name, collection date, analysis date/s, sample type (field sample or QA/QC), matrix (water, sediment, tissue (include species))*

b. *Analytical methods: pre-prep., extraction, and quantification methods (codes should reference to SOPs submitted with the data submission package).*

c. *Analytical results: Parameter name, result, unit, and method detection limit (MDL) for all target parameters (see Table 1 for naming convention and reporting units). When applicable, state whether the results are reported in wet or dry weight, and submit the appropriate QA/QC data qualifiers with the results.*

d. *Required additional data include:*

i. *% solids*

ii. *Control results (for toxicity tests)*

iii. *Field and lab replicate results*

iv. *Quality assurance information for each analytical chemistry batch:*

1. *SRM results, absolute concentrations measured, certified value, and % recovery relative to certified value.*

2. *Matrix spike results (or similar samples): include target amount spiked for each analyte, actual recovery concentrations, and calculated % recovery.*

3. *Method blank sample results in units equivalent to field sample results (e.g. if the field samples are reported as ng/g, method blanks are given in the same units). Clearly identify those samples recommended for blank correcting the results.*

4. *Field and lab replicate results.*

Waste Disposal
After receipt of samples, laboratories will be responsible for proper storage of samples during the project, and disposal of samples after the project is complete. To the extent that any samples collected, or other materials used, are considered hazardous waste, laboratories will be responsible for disposing of these materials in accordance with all applicable Federal, State and/or Local laws.

Archiving
Whenever possible, laboratories will retain sufficient amounts of sample or sample extract to allow for future re-analysis. Samples or extracts will be archived using appropriate storage techniques. Sample materials will not be discarded until all work described in this contract has been submitted to SFEI, validated, verified and SFEI has paid the final invoice.

TABLE 3. TASK BREAKDOWN BETWEEN THE COORDINATED STUDIES:

1) *EPTOX – RMP Episodic Toxicity Monitoring Program 2004/05*
2) *PRISM – Investigations of Sources and Effects of Pyrethroid Pesticides in Watersheds of the San Francisco Bay Estuary (subtask 3.1)*

Each tributary will be sampled in two locations for two sampling events (November-2004 and April-2005). The six up-stream sites will have a full chemistry analyses. **Only downstream sites that are shown to be toxic to amphipods will have a full chemistry analyses (estimated at 3 down-stream sites per sampling event).** All samples will be analyzed for grainsize and TOC.

	SubContractor	November Sampling	April Sampling		Total
		No. Samples Paid for By EPTOX	No. Samples Paid for By EPTOX	No. Samples Paid for By PRISM	Samples for Combined Study
1.0 Logistics and Sampling	**AMS/SFEI**	12	6	6	24
1.1 Sediment Chemistry					
Trace Elements	**BRL**				
TEs (Al, Ag, Cd, Cu, Fe, Pb, Mn, Ni, Zn)		9	3	6	18
TEs (As)		9	9	0	18
TEs (Se)		9	9	0	18
%solids		9	3	6	18
Sediment Quality and Mercury	**UCSCDET**				
Total Organic Carbon		12	6	6	24
Total Nitrogen		12	12	0	24
% solids		9	3	6	18
Grain Size %clay (sedigraph)		12	6	6	24
Grain Size %silt (sedigraph)		12	6	6	24
Grain Size %sand (digestion, sieve)		12	12	0	24
Grain Size %gravel (digestion, sieve)		12	12	0	24
Total Mercury		9	9	0	18
Methyl Mercury		9	9	0	18
Organics	**CDFG-WPCL**				
PAHs		9	3	6	18
PCBs & PESTs (original RMP analyte list)		9	3	6	18
New analytes - PBDEs		9	9	0	18
New analytes - Pyrethroids		9	3	6	18
Sed TIE (chemistry)		0	0	2	2
1.2 Sediment Toxicity					
Toxicity & chemistry	**UCD-GCML**				
Sed Tox (H. azteca 10d)		6	0	6	12
Sed Tox (E. estuarius 10d)		6	6	0	12
ELISA Clorpyrifos & Diazinon		12	6	6	24
Sed TIE (amphipod toxicity)		0	0	2	2
Sed TIE sample collection		0	0	2	2

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