



Monitoring Plan

2009

## Investigation of Pyrethroid Pesticides in the American River

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# MONITORING PLAN

Central Valley Water Board

Surface Water Ambient Monitoring Program (SWAMP)

Special Study:

## INVESTIGATION OF PYRETHROID PESTICIDES IN THE AMERICAN RIVER

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# INVESTIGATION OF PYRETHROID PESTICIDES IN THE AMERICAN RIVER

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## Background

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

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

## **Problem Statement**

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

## **Target Audience and Management Decisions**

The Lower American River encompasses the river immediately downstream of Folsom Dam, Lake Natoma to Nimbus Dam and the 23 miles of mainstem river from Nimbus Dam to the confluence with the Sacramento River at Discovery Park. The Lower American River is valued as an area supporting important fish and wildlife habitat and riparian vegetation, and a regional recreational parkway, including fishing opportunities. It is also a major source of drinking water for several municipalities and a critical floodway. A wide variety of urban, industrial, fisheries, environmental, and recreational stakeholders all have a vital stake in the American River and all have a need to understand the health of the River and its complex interrelationships. The current project will provide critical information to many of the interested stakeholders and agencies. For example, management decisions related to pesticide use and water quality impacts are made by the California Department of Pesticide Regulation (DPR), the Regional Water Quality Control Boards (Water Boards), the US EPA, and other agencies. These agencies work together to establish which pesticide products are available for agriculture, urban, and other uses, and permissible application practices for these products.

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

## **Assessment Question**

Information to support management decisions can be obtained by answering the following assessment question:

Do pyrethroid pesticides occur in the water column at acutely toxic concentrations in creek waters and urban storm water catchments discharging to the lower American River, and in the mainstem river itself before, during and after major storm events?

## **Monitoring Goal**

The goal of this study is to assess the potential for aquatic life beneficial use impairment in the Lower American River due to the occurrence and toxicity of pyrethroid pesticides in the water column.

### **Linkage to Beneficial Uses**

The American River provides habitat for aquatic ecosystems that include benthic and water column invertebrates, which form important links in food webs supporting salmonids and many other native fish species. This study focuses on potential impacts to these aquatic invertebrate communities and the ecosystems they support.

### **Spatial Scale**

All sampling will occur within the Lower American River and its tributaries, including creeks, sloughs, and stormwater discharge canals. Four sites along the lower American and at least five tributary sites will be selected to represent the major urbanized areas draining to the lower American River's receiving waters.

### **Temporal Scale**

Samples will be collected over the course of the 2009-2010 wet-season, potentially beginning in late 2009 (depending on finalization of contractual arrangements) and ending in May 2010. All sites are anticipated to be sampled at first flush (rainfall accumulations of at least 0.50 inch over 24 hr in Sacramento) and during two other winter rain events.

### **Indicators and Measurement Parameters**

The Surface Water Ambient Monitoring Program (SWAMP) has outlined a strategy for water quality monitoring of California's surface waters and identified indicators reflective of beneficial uses (SWAMP, 2005). The indicators used to assess pyrethroid pesticide effects on aquatic communities in the lower American River will be:

1. Chemical analyses of whole, unfiltered water column samples.
2. Water column toxicity tests.
3. Water column toxicity identification evaluation procedures specific to pyrethroids.

These indicators will be used in an integrative manner to characterize the level of pyrethroid contamination, the potential for in-stream biological effects and the specific links between contaminants and effects.

Chemical analytes will consist of eight commonly used pyrethroid pesticides: bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, deltamethrin, fenpropathrin, and permethrin. The whole water samples will be extracted by liquid:liquid extraction using dichloromethane, and then analyzed for pyrethroids by GC/ECD. The sampling is expected to yield at least 66 samples for whole water analysis (+ 20 QA = 86). The reporting limit for pyrethroids in water samples is anticipated to be 1 ng/L.

Total suspended solids (TSS) will be measured in whole water samples. These data are important to interpreting pyrethroid concentration data in the context of bioavailability.

All pesticide chemical analyses will be conducted by Dr. Michael Lydy at the Fisheries and Illinois Aquaculture Center, Department of Zoology, Southern Illinois University using SWAMP comparable methods.

The whole water samples from the mainstem river monitoring will be tested for acute toxicity by Dr. Donald Weston at the Department of Integrative Biology, University of California, Berkeley laboratory using *Hyalomma azteca* in four-day, water-only exposures. Mortality and normal swimming behavior will be the measurement endpoints. The sampling described above is expected to yield 36 samples (+ 2 field duplicates = 38). Sample survival <50% of the control will trigger a toxicity identification evaluation (TIE) and the sample will be retested with two TIE procedures specifically developed for pyrethroids. The TIE procedures are limited to up to three of the whole water samples. Since this study is focused specifically on pyrethroids, full-scale TIEs will not be done, but rather several types of TIE-style procedures will be performed that are specifically designed to indicate if pyrethroids could be the cause of toxicity. The Project Team has developed and published on several of these procedures (Weston and Jackson, 2009; Weston and Lydy, in press), and additional procedures are under development. The procedures to be used will consist of any two of temperature manipulation, piperonyl butoxide addition, and addition of engineered esterases. While these procedures have been developed to identify pyrethroid-related toxicity, they have also been tested with an organophosphate pesticide (chlorpyrifos), and can often help identify toxicity attributable to that group of compounds as well.

### **Monitoring Objectives**

The planned study is intended to follow up on the findings of American River sampling during the 2009 rainy season, and in particular to:

- 1) Better define the frequency, magnitude, and duration of pyrethroid-related toxic events in the mainstem American River;
- 2) Identify the specific substance(s) responsible for these toxic events;
- 3) Characterize pyrethroid inputs from many of the major sources of storm water runoff to the river.

### **Monitoring Design**

Sampling sites will be identified in the American River watershed at the following locations:

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

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

To characterize pyrethroid inputs and the potential impacts of these pesticides on aquatic life in the Sacramento-San Joaquin River Delta, sample sites will be selected based on the selection criteria below.

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

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

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

### **Coordination and Review Strategy**

To promote monitoring coordination among agencies and work groups, this Monitoring Plan will be reviewed on multiple levels: 1) internally, through Water Board staff; 2) intra-agency, through DPR or other members of the POD-CWT work team. The Grant Manager will facilitate and coordinate peer review and addressing comments.

Site reconnaissance and selection will be conducted by the UCB Project Director and the Central Valley Water Board Grant Manager. A preliminary list of sampling sites will be developed based on land use patterns and site reconnaissance. The preliminary site list will not be finalized until reviewed by the Water Board staff.

The POD-CWT is comprised of many agency staff and other investigators with interest in contaminant issues as they might effect Delta fish populations. This group will be regularly briefed on project progress and findings as the study proceeds.

### **Quality Assurance**

A project specific Quality Assurance Project Plan (QAPP) will be prepared that is consistent with the EPA 24 Element QAPP Guidelines and the SWAMP Quality

Assurance Management Plan The QAPP will be reviewed and accepted by the SWAMP QA Officer. The QAPP will include criteria for data acceptability, procedures for sampling, testing, and calibration, as well as preventative and corrective measures.

### **Data Management**

All data generated by this project will be maintained as described in the SWAMP-accepted project QAPP. UCB will be responsible for collection of samples and field data. UCB will be responsible for managing chemistry and toxicity data; Southern Illinois University (SIU) will be responsible for transferring analytical chemistry data to UCB in SWAMP format. The UCB Project Director will be responsible for submitting all project data for inclusion into the SWAMP database. Central Valley Water Board staff will be responsible for creating the basic field sampling event (site location, time of sampling, type of samples collected, etc.) in the SWAMP data base, and the UCB Project Director will be responsible for submitting all chemistry and toxicity data associated with that event.

### **Assessment Benchmarks and Data Analysis**

Lower American River watershed water quality will be assessed based on comparison of chemistry measurements with benchmarks indicating potential for biological effects. There currently exist no guideline values or Basin Plan Objectives for pyrethroid pesticides in water. The present study will compare measured pyrethroid concentrations with thresholds for toxicity to aquatic life, and especially *Hyaella azteca* median lethal concentration values (LC<sub>50s</sub>) for short-term (4 d) water exposure, as available in the scientific literature. Dividing measured concentrations by their LC<sub>50</sub> values transforms the data into toxic units, which can be combined to estimate the cumulative effect of all pyrethroids detected, and account for differences in the relative toxicity of each pyrethroid.

### **Reporting**

Data collected from this assessment will be transferred to, and be electronically available from, the SWAMP database. The final project report will be prepared by UCB project staff, and may take the form of a manuscript suitable for publication in a peer-reviewed journal. The report discussion will include an explanation of project context with relevant water chemistry findings, in addition to consideration of occurrence, sources, pathways, and toxicity of pyrethroid pesticides in California's Lower American River.

## Project Schedule

| <b>Activity</b>            | <b>Date/Time</b> |
|----------------------------|------------------|
| Monitoring Plan            |                  |
| Draft                      | November 2009    |
| Final                      | December 2009    |
| Quality Assurance Plan     |                  |
| Draft                      | November 2009    |
| Final                      | December 2009    |
| Sample Collection complete | May 2010         |
| Chemical Analyses complete | July 2010        |
| Reporting                  |                  |
| SWAMP data submission      | February 2011    |
| Draft Final Report         | March 2011       |
| Final Report               | April 2011       |

## **Literature Cited**

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