MONITORING PLAN

Central Valley Water Board

Surface Water Ambient Monitoring Program (SWAMP)

Special Study:

SOURCES, SEASONALITY, AND TOXICITY OF PYRETHROID PESTICIDES IN THE SACRAMENTO-SAN JOAQUIN RIVER DELTA

OCTOBER 2007 – MARCH 2009

SJSUF to UCB Contract # 22-1509-3942

Version 2.0

December 4, 2007

TRANSPORT OF PYRETHROID PESTICIDES TO THE SACRAMENTO-SAN JOAQUIN RIVER DELTA: SOURCES, SEASONALITY, AND TOXICITY

Project Director: Donald P. Weston[1]
Project Coordinator: Robert W. Holmes[2]

[1] Department of Integrative Biology, University of California, 3060 Valley Life Sciences Building, Berkeley, California 94720-3140;
[2] Central Valley Water Board, 11020 Sun Center Drive #200, Rancho Cordova, CA 95670

Background

Two emerging and potentially converging issues have provided the impetus for the current project and suggest that its completion is a high priority for protection of critical aquatic habitats. First, the Sacramento-San Joaquin Delta has attracted renewed attention recently because of the decline in populations of several pelagic fish species, notably Delta smelt, striped bass, longfin smelt and threadfin shad. Abundance indices for all four species are at or near record lows, and though the cause(s) for the decline in these Delta populations are not known, toxic contaminants are among the possibilities often suggested. Secondly, 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 50% greater than what it was just five 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., in press), 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.

Problem Statement

The presence and toxicity of pyrethroids in sediments of agriculture-affected and urban creeks has been well documented, but there is little data available on sediment concentrations of these compounds throughout the Delta. Given the pelagic habits of the primary fish species of concern, as well as their prey, exposure to water column toxicants is an obvious concern, yet data on pyrethroids in the water column in the Sacramento-San Joaquin Delta is even more limited than that for sediments. Areas of particular concern would be the many sloughs of the Delta, a habitat utilized by Delta smelt for spawning and rearing, and locations of potential pyrethroid-containing effluents. Obtaining information on the importance of the various pyrethroid sources to the Delta, and establishing if these discharges contain pyrethroids at toxicologically significant

concentrations, is critical to protecting aquatic life in general, and specifically to the protection of Delta species that are currently at risk.

Target Audience and Management Decisions
The Sacramento-San Joaquin River Delta is a maze of river channels and islands covering approximately 2,978 square kilometers (CVRWQCB, 2006). The Delta is valued as an area supporting aquatic life and riparian vegetation that provide recreational opportunities, including fishing. The Delta is also the major source of drinking water for over 20 million people, two-thirds of our State's population. A wide variety of interests, such as agriculture, urban, industry, fish and wildlife, environmental, and recreation, all have a vital stake in the Delta and all have a need to understand the health of the Delta and its complex interrelationships.

The Interagency Ecological Program (IEP) formed the Pelagic Organism Decline (POD) work team in response to population declines of pelagic fish species in the Delta. The POD is currently investigating hypotheses related to the role of aquatic contaminants and potential linkage with declining biota abundance. The current project will provide critical information to many of the interested POD stakeholders and member agencies. For example, management decisions related to pesticide use and water quality impacts are made by the California Department of Pesticide Regulation (DPR), the Regional Water Quality Control Boards (Water Boards), the US EPA, and other agencies. These agencies work together to establish which pesticide products are available for agriculture, urban, and other uses, and permissible application practices for these products.

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

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

1. Do pyrethroid pesticides occur in toxic water column concentrations in ambient source, near-field, and Delta channel surface waters of the Sacramento-San Joaquin River Delta?

Monitoring Goal
The goal of this study is to assess the potential for aquatic life beneficial use impairment in the Sacramento-San Joaquin River Delta due to the occurrence and toxicity of pyrethroid pesticides in the water column.

Linkage to Beneficial Uses
The Delta provides habitat for aquatic ecosystems that include benthic and water column invertebrates, which form important links in food webs supporting many 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 legal boundaries of the Sacramento-San Joaquin Delta. Approximately 18 sampling site locations will be selected to include representatives of all major potential pyrethroid source categories to the Delta. The study includes assessment of agricultural, urban stormwater, and wastewater treatment plant sources within the Delta as well as contributions from the Sacramento River and San Joaquin Rivers as they enter the Delta.

Temporal Scale
Samples will be collected over a year, and on multiple occasions during that period to reflect dry and wet weather conditions. All sites are anticipated to be sampled at first flush (0.25 inch in Stockton, 0.50 inch in Sacramento), during two other winter rain events, and at least three times during the dry season. Agricultural discharges will be sampled at least five times during the dry season.

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 Sacramento San Joaquin River Delta will be:

1. Chemical analyses of whole, unfiltered water column samples.
2. Chemical analyses of the dissolved phase and the suspended sediment phase in water column samples.
3. Water column toxicity tests.
4. 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 dicloromethane, and then analyzed for pyrethroids. The samples for phase discrimination will be processed on a continuous flow centrifuge to separate the dissolved and particulate phases, and each phase analyzed separately by GC/ECD for the same pyrethroids. The sampling is expected to yield about 136 samples for whole water analysis (+ 36 QA = 172), 36 samples for dissolved phase pyrethroids (+ 10 QA = 46), and 36 samples for particulate phase pyrethroids (+10 QA = 46). Reporting limits for pyrethroids in water samples are anticipated to be approximately 2.5 ng/L, though may be slightly higher or lower depending on matrix effects.

Deleted:
Deleted:

Total suspended solids (TSS) and total organic carbon (TOC) will be measured in each whole water sample. These data are critical 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. Total organic carbon will be measured in each sediment sample on a CE-440 Elemental Analyzer from Exeter Analytical, following acid treatment to remove inorganic carbon. Total organic carbon in water samples will be determined on a Shimadzu 5000A DOC analyzer. Both organic carbon analyses will be done by the University of Maryland, Horn Point Environmental Laboratory.

The whole water samples from the ambient and effluent monitoring will be tested for acute toxicity by Dr. Donald Weston at the Department of Integrative Biology, University of California, Berkeley laboratory using *Hyalella azteca* in four-day, water-only exposures. Mortality will be the measurement endpoint. The sampling described above is expected to yield 124 samples (+ 6 QA = 130). While the standard temperature for *Hyalella* testing is 23ºC, Delta waters during the winter will be far cooler. Pyrethroids are known to be nearly four times as toxic at 13ºC, relative to 23ºC (Weston, unpublished data). Therefore in order to determine the toxicity of the discharges at ambient temperatures, rather than at an artificial standardized temperature, toxicity tests will be run at a temperature approximating ambient at the time of sample collection (within the range of 13-23ºC in which good *Hyalella* control survival has been shown).

Resampling and retesting may be done if feasible. While complete toxicity testing results will not be available until completion of the 4-day exposure, if high mortality is observed within the first day of the test, the Project Coordinator will be contacted. Resampling and retesting may be done if considered technically justified pending discussions between the University's Project Director and the State's Project Coordinator.

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. In the event toxicity is found in a high proportion of the samples, the TIE procedures are limited to no more than 25 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 Director has developed and published on several of these procedures (Amweg and Weston, in press; Weston and Amweg, 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 enzyme addition. 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 primary objective of this Sacramento-San Joaquin River Delta assessment is to determine if pyrethroid pesticides occur at potentially toxic concentrations within the ambient waters of the Delta and tributary waterways, including within a variety of types of discharges and sources to the Delta. Secondary objectives include examining potential seasonality of pyrethroid inputs to the Delta, and determining whether they are entering in dissolved or particle-bound phases as it could affect their toxicity and transport. The species to be used for toxicity testing (*H. azteca*) is the most sensitive to pyrethroids of all organisms that have been tested, and thus should be a conservative representative of the resident Delta species of concern. TIE-style approaches will be used on toxic water samples to determine the contributions of pyrethroid pesticides to any observed amphipod mortality in Delta water samples.

Monitoring Design

A major difficulty with testing for pyrethroids in Delta waters is that analytical detection limits are often at or even above concentrations that are acutely toxic to sensitive aquatic species. Concentrations capable of causing chronic toxicity are likely far below detectable levels. Thus, even if no detectable pyrethroids were found in Delta waters, it does not mean they were having no toxicological effect. To address this concern, this study will focus on effluents that may contain pyrethroids. Such samples would represent worst case conditions (i.e., highest possible pyrethroid concentrations). If the compounds are not detected in the discharges themselves, then it is unlikely toxicity would remain after release to and dilution within Delta waters.

Sampling sites will be identified in the Sacramento-San Joaquin River Delta to represent the following discharges categories:

1) Eight agricultural discharges
2) Five urban stormwater discharges
3) Three municipal sanitary sewer outfalls
4) Two mainstem river sites (Sacramento River near Freeport/Hood and San Joaquin River near Vernalis)

Sampling at these sites is intended to identify the pyrethroids contributed by each category of discharge, their concentration at the point of discharge, the seasonality of pyrethroid inputs from each discharge category, whether the effluent is toxic, and if so, whether pyrethroids are likely responsible for that toxicity.

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.

Delta Sample Site Selection Criteria
1. Geographic distribution throughout the Delta
2. Urban and agricultural land uses both represented among the discharges
3. Wastewater treatment plant discharges to include, but not limited to, major facilities

4. Stormwater and agricultural discharges sampled to be among the more significant in terms of flow to Delta
5. Flow data available if possible (govt. gauging station or monitored by discharger)
6. Salinity of ambient waters within acceptable range of *Hyalella azteca*
7. Presence of access points to discharges and receiving waterways
8. Confined waterway sites for gradient analysis
9. Evidence of previous data suggesting pyrethroid occurrence or link to toxicity

The selected sites will be sampled on three occasions in the dry season, at the time of the first flush, and during two other storm events. While this schedule will yield six sampling events at each of the eighteen sites, exceptions to this general plan are: 1) the agricultural sites will be sampled an additional two times during the dry season (for total of five dry season samples) because of the probable strong temporal variation in effluent quality, and 2) it may not be possible to sample the urban stormwater sites during the dry season because of low flow.

Sampling during the dry season will consist of a single grab sample at each site on each sampling occasion. Storm sampling will consist of single samples at each site during a storm event, with an attempt to obtain those samples during high flow. Excluding the river samples, all other discharges will be sampled just prior to the point of release to Delta waters, so as to avoid effects of dilution and tidal considerations.

In addition to the samples noted above (for chemical analysis of whole water) each of the eighteen discharges will be sampled on one of the dry season occasions and on one of the storm event occasions for separate analysis of the dissolved and particle-associated pyrethroids. Establishing what fraction of the total pyrethroid that is particle-bound has ramifications as to its bioavailability and potential for mitigation.

Some of the sites will be selected for gradient analysis so as to better quantify the extent of dilution of the effluents in Delta waters. The optimal sites at which this will be done are those where the discharge occurs to a confined body of water (e.g., a slough), with few or no other discharges to that same water body, and with multiple access points along that water body. A maximum of three sites will be established to meet these criteria as best as possible, and on one occasion during a falling tide, water samples will be taken from the water body at various distances from the discharge. These samples will be held for chemical analysis, though not toxicity testing.

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 and member agencies of the POD work team. The SWAMP Project Coordinator (PC) will facilitate and coordinate peer review and addressing comments. Ambient water sampling will not occur prior to the acceptance of the Monitoring Plan by the SWAMP Coordinator.

Site reconnaissance and selection will be conducted by the UCB Project Director (PD) and the Central Valley Water Board SWAMP Project Coordinator (PC). A preliminary list of sampling sites will be developed based on land use patterns, site reconnaissance, and consultation with the POD work team. The preliminary site list will not be finalized until reviewed by the Water Board staff and the POD work team. The current study will be predominately focusing on the potential pyrethroid sources (effluents) to the Delta, and farther up in the system than the POD sites which are mostly in lower Sacramento and San Joaquin Rivers, Delta, and in the San Pablo/Suisun Bay areas.

This project will be coordinated and leveraged with existing relevant investigations including those monitoring efforts already underway through the POD by the UC Davis Aquatic Toxicology Laboratory, a pyrethroid loading study in the San Joaquin River which is underway by the USGS, UCB, and UCD, the Sediment Quality Objective Project commencing in the Delta during Fall 2007 as directed by SWRCB, and the Irrigated Lands Regulatory Program and the Pesticide TMDL Program at the Central Valley Water Board.

1. UC Davis POD Toxicity Investigations including ambient water column toxicity testing and TIEs. This project underway through the 2007 POD workplan – contact: Inge Werner.

2. USGS, UCB, and UCD Pyrethroid Loading Study - quantifying pyrethroid loading to the San Joaquin River via four Westside and three Eastside agricultural tributaries. This work extends from summer 2007 through winter 2008. Pyrethroid loads will be measured in the San Joaquin at Vernalis. Project data will be used to examine loadings to the Delta via the mainstem San Joaquin River - contacts: Joe Domagalski, Donald Weston, and Minghua Zhang.

3. SWRCB Sediment Quality Objectives Development – Delta Phase Project – sampling benthic communities, toxicity, and chemistry from sediments in the Delta. This work will commence Fall 2007 and will provide information related to pyrethroid pesticide occurrence in sediments of select habitats of the delta – contact: Chris Beegan.

4. Irrigated Lands Regulatory Program – Central Valley Water Board. Water quality sampling by agricultural coalition groups including pesticide and toxicity analysis. Contact: Joe Karkoski.

5. TMDL Program – Urban Pesticides – Central Valley Water Board. Pesticide sampling for urban pesticide TMDL analyses. Contact: Petra Lee.

6. CalFed Project – Spatial and Temporal Quantification of Pesticide Loadings to the Sacramento River, San Joaquin River, and Bay-Delta to Guide Risk Assessment for Sensitive Species. Contact: Debra Denton.

The IEP is currently planning for a review of all available data on waterborne contaminants to the Delta and related toxicity information. This review will assess the inputs with regards to risk to pelagic Delta fish species, and that same assessment protocol will be useful for interpreting data from the proposed study.

Quality Assurance

A project specific Quality Assurance Project Plan (QAPP) will be prepared that is consistent with the EPA 24 Element QAPP Guidelines (USEPA, 1998) and the SWAMP Quality Assurance Management Plan (Puckett, 2002). The QAPP will be reviewed and accepted by the SWAMP QA Officer prior to initiating any field sampling for this project. 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 and Central Valley Water Board staff will be responsible for collection of samples and field data. UCB will be responsible for managing chemistry, toxicity testing, and TIE data. Southern Illinois University (SIU) will be responsible for transferring analytical chemistry data to UCB in SWAMP format. The University of Maryland laboratory that analyzes for total organic carbon will submit their data to the UCB PD. The UCB PD will be responsible for submitting all project data for inclusion into the SWAMP database.

Assessment Benchmarks, Data Analysis, and TIE Triggers

Sacramento-San Joaquin River Delta water quality will be assessed based on comparison of chemistry and toxicity measurements with benchmarks indicating potential for biological effects. The study is designed as a screening survey.

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 *Hyalella azteca* median lethal concentration values (LC50s) for short-term (1-4 d) water exposure, as available in the scientific literature. Dividing measured concentrations by their LC50 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.

The benchmarks used to indicate water column toxicity will be: (1) sample mean survival significantly less than control values, as indicated by separate variance t-tests, and (2) sample mean survival less than 80% of the control value. These are the monitoring benchmarks used in the SWAMP program to indicate significant sample toxicity. Arcsine squareroot transformation will be used when necessary to meet the assumptions of normality and homogeneity of variance. Steel's test will be used for comparison to control if these assumptions are not met after transformation.

The toxicity level used to trigger pyrethroid-specific TIE procedures will generally be test amphipod survival less than 50% of the control. These procedures will be conducted on up to 25 toxic water column samples. If no toxicity is observed or toxicity is observed in less than 25 samples, the unused TIE resources will be directed towards additional sampling of effluents or ambient Delta waters.

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 the UCB PD. The report discussion will include an explanation of project context with relevant POD findings, in addition to consideration of occurrence, sources, pathways, and toxicity of pyrethroid pesticides in California's Sacramento-San Joaquin River Delta.

Project Schedule

Activity	Date/Time
Monitoring Plan	October 2007
Quality Assurance Plan Draft QAPP Final QAPP	 November 2007 December 2007
Sample Collection	January 2007 - December 2008
Toxicity Testing and TIEs	January 2007 - December 2008
Chemical Analyses	January 2007 - December 2008
Reporting Draft Final Report Final Report	 February 2009 March 2009
Expected Project Completion Date	March 2009

Literature Cited

Amweg, E.L., D.P. Weston, J. You, and M.J. Lydy. 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. *Environ. Sci. & Technol*. 40:1700-1706.

Amweg, E.L. and D.P. Weston. Whole sediment toxicity identification evaluation tools for pyrethroid insecticides. II. PBO addition. *Environ. Toxicol. Chem.* (in press).

CDPR, 2007. California Department of Pesticide Regulation Pesticide Usage Report (PUR) database. Sacramento, CA.

CVRWQCB. 2006. Water Quality Control Plan for the Sacramento River and San Joaquin River Basins, Fourth Edition. Central Valley Regional Water Quality Control Board (CVRWQCB). Sacramento, CA.

Moran, K.D., *Pesticides in Urban Surface Water: Urban Pesticides Use Trends Annual Report 2007*, prepared for the San Francisco Estuary Project, June 2007.

Oros, D.R., and I. Werner. 2005. Pyrethroid Insecticides: An Analysis of Use Patterns, Distributions, Potential Toxicity, and Fate in the Sacramento-San Joaquin Delta and Central Valley. White Paper for the Interagency Ecological Program. SFEI Contribution 415. San Francisco Estuary Institute, Oakland, CA.

Puckett, M. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program (SWAMP). California Department of Fish and Game, Monterey, CA. Prepared by the State Water Resources Control Board, Sacramento, CA. 145 pages plus appendices.

SWAMP, 2005. Comprehensive Monitoring and Assessment Strategy to Protect and Restore California's Water Quality. State Water Resources Control Board and Regional Water Quality Control Boards, Surface Water Ambient Monitoring Program report. http://www.waterboards.ca.gov/quality.html.

Weston, D.P., J. You, and M.J. Lydy. 2004. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley. *Environ. Sci. & Technol*. 38: 2752-2759.

Weston, D.P., R.W. Holmes, J. You, and M.J. Lydy. 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ. Sci. & Technol*. 39: 9778-9784.

Weston, D.P., J. You, E.L. Amweg and M.J. Lydy. Sediment toxicity in agricultural areas of California and the role of hydrophobic pesticides. In J. Gan, F. Spurlock, P. Hendley and D. Weston (editors), *Synthetic pyrethroids: Fate and Effects*. ACS Symposium Book Series, American Chemical Society, Washington, D.C. (in press).

Weston, D.P. and E.L. Amweg. Whole sediment toxicity identification evaluation tools for pyrethroid insecticides. II. Esterase addition. *Environ. Toxicol. Chem.* (in press).

USEPA. 1998. Guidance for Quality Assurance Project Plans (QA/G-5), EPA/600/R-98/018, Office of Research and Development.