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Pesticides in Urban Surface Water

Annual Review of New Scientific Findings 2008

Prepared for the
San Francisco Estuary Project

April 2008

PREFACE

This is a report of research performed by TDC Environmental, LLC for the San Francisco Estuary Project. This report was prepared for the San Francisco Estuary Project to fulfill the annual reporting requirement in Task 7.1.1 of its grant agreement with the State Water Resources Control Board (Agreement Number 06-342-552-0) for Taking Action for Clean Water.

Funding for this report has been provided through an agreement with the State Water Resources Control Board. The contents of this document do not necessarily reflect the views and policies of the State Water Resources Control Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ACKNOWLEDGEMENTS

The author appreciates the information and assistance provided by many scientists who are investigating the environmental effects of pesticides in urban surface waters. The members of the project review panel provided invaluable assistance in the preparation of this report:

- Michelle Hladik, U.S. Geological Survey
- Robert Holmes, Central Valley Regional Water Quality Control Board
- Phil Markle, Los Angeles County Sanitation Districts
- Armand Ruby, Consulting Environmental Scientist
- Nan Singhasemanon, California Department of Pesticide Regulation
- Patti TenBrook, U.S. EPA Region 9

Thanks are also due to Laura Speare for technical editing. The author also wishes to acknowledge the contributions of the San Francisco Estuary Project grant management team of Laura Speare and Paula Trigueros.

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SUMMARY

This report is intended to assist California water quality agencies—including municipalities—by summarizing recent pesticide and water quality scientific findings that are relevant to urban surface water quality management. This annual review is prepared by the Urban Pesticide Pollution Prevention (UP3) Project with funding the State Water Resources Control Board.

Recent scientific studies (calendar year 2007 publications) related to the potential for urban pesticide use to affect surface water quality were reviewed to prepare this report. The review focused on identifying new information about pesticides that may adversely affect urban surface water quality. On the basis of the current and previous UP3 Project literature reviews, a set of updated, specific recommendations for monitoring program design and data interpretation are provided. Priority research needs are identified; these would enhance capabilities to measure pesticides of concern, to evaluate pesticides of potential concern, and to interpret surface water monitoring data.

<u>New Information</u>. This year's review includes the following significant new information:

- Updated recommendations for sample collection, storage and analysis for samples that will be tested for pyrethroids.
- Identification of research priorities to address the numerous data gaps related to evaluation of the potential threat posed by use of the insecticide fipronil.
- Additional details regarding pyrethroid-related water quality problems. Notable among this information is that toxicity in wet weather creek water samples has been attributed to pyrethroids, suggesting that pyrethroids could affect organisms dwelling in the water column—not just sediment-dwelling organisms.

<u>Monitoring Recommendations</u>. The UP3 Project recommends that surveillance monitoring of California urban surface waters be conducted. This monitoring should include water and sediment. Monitoring should measure toxicity to standard test organisms as well as the concentrations of specific pesticides that have the potential to cause adverse effects in aquatic ecosystems (e.g., currently used pyrethroids[1], carbaryl, malathion, polyhexamethylene biguanadine [PHMB], and fipronil and its degradates). Specific recommendations for laboratory detection limits, sampling and storage procedures (for pyrethroids only), and reporting of results are provided in Section 5.2.

<u>Research Recommendations</u>. The UP3 Project recommends that filling aquatic toxicity and environmental fate data gaps for the pesticides listed in the paragraph above be research priorities. Completion of toxicity identification evaluation (TIE) method development for pyrethroids and development of TIE methods for fipronil and its degradates are also priorities. Section 5.2 identifies other priority information needs related to identifying and evaluating the potential for pesticides to threaten urban surface water quality.

<u>Management Recommendations</u>. The UP3 Project recommends that managers responsible for water quality protection consider all recommendations in Section 5.2., including a special set of management recommendations designed to assist agencies with interpretation of data collected in monitoring programs and to maximize the value of urban surface water quality-related pesticide research and monitoring programs.

[1] The pyrethroids of greatest interest for urban surface water quality are bifenthrin, cyfluthrin (including beta-cyfluthrin), cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin. Additional pyrethroids are of interest in agricultural areas.

1.0 INTRODUCTION

1.1 Background

The environmental effect of pesticides in urban surface water is a topic of great interest to research scientists, regulatory agencies, municipalities, and the general public. While some key research findings have been noted in the popular press, most research is published only in scientific journals and technical reports that are not commonly read by California water quality agency staff. This report is intended to assist California water quality agencies—including municipalities—by summarizing recent pesticide and water quality scientific findings that are relevant to urban surface water quality management.

This is one of three reports prepared annually by the Urban Pesticide Pollution Prevention (UP3) Project. (The other two reports are a review of California water quality agencies' urban pesticide water quality regulatory activities and an analysis of urban pesticide sales and use trends.) The purpose of the UP3 Project is to help California Water Boards and municipalities prevent pesticide-related water quality problems.[2] The San Francisco Estuary Project (SFEP) has been awarded California water bond grant funds from the State Water Resources Control Board to implement the UP3 Project through mid-2009. TDC Environmental is providing technical support for the project.

1.2 Scope of This Report

This is the fourth annual research and monitoring update prepared by the UP3 Project. It presents the results of the project's ongoing review of pesticide and water quality literature relevant to urban surface waters. It summarizes readily available information about government and university scientific investigations and water quality monitoring programs published during 2007. This report identifies key findings from newly published research relevant to California water quality agency efforts to prevent pesticide-related toxicity in urban surface waters, urban runoff, and municipal wastewater discharges.

This report supplements—and does not repeat—the previous annual research and monitoring updates prepared by the UP3 Project (TDC Environmental 2005, 2006, 2007a), which should also be consulted by those seeking a full understanding of recent relevant scientific findings. The previous reports summarized data demonstrating that use of pyrethroid insecticides in urban areas has been found to cause toxicity to organisms that may ordinarily reside in Northern California aquatic ecosystems receiving urban runoff. The previous reports identified gaps in available data about the effects of urban insecticide use on water quality and made recommendations for monitoring activities. The literature review conducted for this annual update specifically targeted the identified data gaps and monitoring recommendations, as these are particularly important for California water quality agencies.

Since it builds on previous reports, the focus of this report is as follows:

- *The most recent literature* (i.e., published in 2007).
- *New findings*. This update does not include studies with results consistent with previously findings (e.g., reports of elevated diazinon concentrations in urban

[2] In addition to the UP3 Project's statewide work, it does some work specifically in the San Francisco Bay Area to help implement the Diazinon and Pesticide-Related Toxicity in Bay Area Urban Creeks Water Quality Attainment Strategy and Total Maximum Daily Load [Johnson, B. (2005). Diazinon and Pesticide-Related Toxicity in Bay Area Urban Creeks. Water Quality Attainment Strategy and Total Maximum Daily Load (TMDL). Proposed Basin Plan Amendment and Staff report. November.]

runoff or surface water toxicity due to diazinon/chlorpyrifos in samples taken prior to 2005), nor does it address pesticides that are not currently used (e.g., organochlorine pesticides).

- *California focus*. While the report includes literature from around the world, it focuses on California and on urban creeks, as the UP3 Project is supported by California state funds.

This report does not address pesticide sales and use information (e.g., user surveys, pesticide use reporting data). This information is addressed in a separate UP3 Project report on urban pesticide sales and use trends—the next such report is anticipated in mid-2008.

1.3 Data Sources

This report is based on a review of the relevant scientific literature. Information in this report was obtained from a variety of sources. The specific sources that were reviewed have been selected based on their usefulness in identifying relevant literature in previous similar reviews (TDC Environmental 2003, 2005, 2006, 2007a). These include:

- Published scientific literature (e.g., peer-reviewed and other journals). Two methods were used to search the scientific literature (1) keyword searches of multiple subject area scientific literature databases and (2) reviews of the tables of contents for all 2007 issues of the journals that have previously published the majority of relevant articles (i.e., *Environmental Science and Technology, Environmental Toxicology and Chemistry, Journal of Environmental Quality, Journal of Agricultural and Food Chemistry*, and *Science of the Total Environment*).
- Technical reports prepared for local, state, and Federal government agencies and technical comment letters on these reports. Most California local, state, and Federal agencies that publish relevant technical reports participate in the Urban Pesticides Committee and make the UP3 Project aware of relevant publications. Some Federal reports (e.g., pesticide environmental risk assessments) are identified on the basis of *Federal Register* notices. California DPR's electronic surface water updates are used to identify DPR reports.
- Scientific conference presentations and posters. Information is obtained from participation in scientific conferences (notably conferences organized by the Society of Environmental Toxicology and Chemistry) and other, irregular special topic meetings, which are usually organized by state agencies, scientific research organizations, or professional societies.
- Interviews with agency staff and researchers. Scientists often forward their own publications or citations for other publications of interest to the UP3 Project.

1.4 Report Organization

This report is organized as follows:

- *Section 1* (this section) provides the background and scope of the report.
- *Section 2* reviews the status of methods for testing for pesticides in water.
- *Section 3* provides information about pesticide monitoring in California urban surface waters.

- *Section 4* identifies recent major research findings relevant to urban pesticides and water quality.
- *Section 5* gives the conclusions of the review and provides recommendations for future activities based on the latest scientific findings.
- *Section 6* lists the references cited in the body of the report.

2.0 METHODS TO TEST FOR PESTICIDES IN WATER BODIES

2.1 Background

Standard chemical analytical methods[3] exist for only a small portion of the more than 900 pesticide active ingredients registered for use in California. Even when methods are available, they often do not have detection limits low enough to measure environmentally relevant concentrations of pesticides and their degradates in surface waters, urban runoff, and municipal wastewater influent and effluent. Since most California water quality agencies rely on in-house or commercial laboratories for chemical analysis, practical methods must be readily available and robust enough to be implemented by laboratories with diverse analytical capabilities.

A priority for California water quality agencies is development of chemical analytical methods to measure environmentally relevant concentrations of pollutants that threaten California's surface water quality and/or pose compliance risks for municipal wastewater treatment plants and urban runoff programs. With the phase out of most urban uses of the insecticides diazinon and chlorpyrifos, water quality agencies are shifting attention to the pyrethroid insecticides, which have been demonstrated to cause toxicity to organisms in California's surface waters (see Section 4). For pyrethroids, environmentally relevant concentrations are about 1 nanogram/liter (part per trillion) in the water column and 1 nanogram/gram (part per billion, dry weight) in sediment (TDC Environmental 2003; Amweg et al. 2005). In 2007, California analytical capabilities for pyrethroids continued to improve as described below.

2.2 Findings

Chemical Analysis and Sample Handling

Capabilities for measuring environmentally relevant concentrations of pyrethroids in water and sediment are improving; however, additional work is needed to complete development and validation of analytical methods for pyrethroids[4] in environmental water, wastewater, biosolids, and sediment samples. Development of reliable methods for measuring environmentally relevant pyrethroids concentrations—and that can be reproduced by a broad range of laboratories—is nearly complete. The California Department of Pesticide Regulation (DPR), the U.S. Geological Survey (USGS), the California Department of Food and Agriculture (CDFA), and the California Department of Fish and Game (CDFG) collaborated to develop and validate formal analytical methods to detect pyrethroids in water, sediments, and biological organisms. This Pyrethroid Method Development Project successfully validated methods at three agency laboratories (Hladik 2007). The laboratories achieved detection limits appropriate for measurement of environmentally relevant pyrethroid concentrations (for certain pyrethroids these detection limits from one or more of the laboratories were slightly

[3] "Standard chemical analytical methods" is intended to mean methods that are published, peer-reviewed, and extensively validated; have appropriate quality assurance/quality control procedures; are well-accepted by professional analytical chemists; are practical for non-research analytical laboratories; are appropriate for measuring environmentally relevant concentrations in environmental samples; and that do not require equipment that would not normally be available in a commercial analytical laboratory. Such methods include—but are not limited to—U.S. EPA approved methods and methods in the laboratory reference books like *Standard Methods for the Examination of Water and Wastewater* (Eaton et al. 2005).

[4] Urban pesticide market/water quality evaluations indicate that the pyrethroids of greatest interest for urban surface water quality are bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin (TDC Environmental 2007c). Other pyrethroids are also used in manners that may involve discharges to wastewater treatment plants and in agricultural areas.

above the detection limits recommended by the UP3 Project in Section 5.2). Method details are available on the Internet—see www.cdpr.ca.gov/docs/sw/swpyreth.htm for all reports related to this project.

Another analytical method has been developed by pyrethroids manufacturers. One of the requirements that DPR included in its ongoing regulatory action to address water quality problems from pyrethroids (the "pyrethroid reevaluation") was to develop a chemical analysis method for pyrethroids in sediment, with a detection limit no greater than 1 nanogram per gram (dry weight basis). To comply with this requirement, the Pyrethroid Working Group (a consortium of pyrethroid insecticide manufacturers) has developed and validated a method that achieves the required detection limits (PWG 2007).[5] This method uses an instrument that is commonly available in commercial analytical laboratories (gas chromatography-mass spectrometry [GC/MS]), but requires an unusual detector (a negative ion chemical ionization or NICI detector) that it not commonly installed on GC/MS equipment in commercial laboratories.

A Standard Methods Joint Task Group has been established to develop a performance-based method for determination of pyrethrins, pyrethroids, and pyrethroid-like compounds in a variety of water matrices, including freshwater, stormwater, estuarine and saltwater, wastewater influent, and wastewater effluent. Participants include representatives of U.S. EPA, CDFG, a municipal wastewater treatment plant, and a commercial analytical laboratory. The Joint Task Group intends to develop a method that would be suitable for publication in *Standard Methods for the Examination of Water and Wastewater* and that would be appropriate for U.S. EPA to include among methods for compliance monitoring under the Clean Water Act.

Two California commercial laboratories (Caltest Analytical Laboratory in Napa and CRG Marine Laboratories in Torrance) advertise that they are capable of measuring environmentally relevant concentrations of pyrethroids. AXYS Analytical Services, which is outside of California but has worked with California agencies, has also developed the capability to measure environmentally relevant concentrations of pyrethroids.

<u>Special sampling and sample handling procedures are needed to ensure accurate measurements of pyrethroid concentrations</u>. Pyrethroids are challenging to measure accurately in environmental samples. Pyrethroid concentrations in water samples are less than they are in the original water source because pyrethroids tend to adhere to sampling equipment and sample containers. Water samples can degrade while awaiting laboratory analysis. The Pyrethroid Methods Development Project included a preliminary exploration of problems related to sample collection and storage. The laboratories identified some specific procedures that can be used to achieve more accurate laboratory results (Hladik 2007, Hladik 2008):

(1) Pyrethroids in water samples adhere to sample container walls—losses can be significant. The following methods minimize this problem:

- Avoid Teflon when handling samples to be analyzed for pyrethroids.
- Glass containers are preferred over plastic. If plastic must be used (i.e., bottle cap liners), polyethylene (LDPE or HDPE) is preferred over Teflon.

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[5] To obtain a copy of the PWG report that describes the method and its validation in sediment samples, send an e-mail to the DPR public records request e-mail address (publicrecords@cdpr.ca.gov) and request "a copy of the sediment chemical analysis method required by DPR of pyrethroids registrants in accordance with the pyrethroids reevaluation". Please note that there may be some limitations on the commercial use of this method—please contact DPR if you intend to use this method for commercial purposes.

- Shake containers with pyrethroid-containing water samples vigorously for about one minute immediately prior to conducting the laboratory's extraction procedure. The shaking brings pyrethroids that have adhered onto container walls back into solution. (This works best in glass containers.)
- Losses are lower in larger containers (the ratio of surface area to volume of water is lower).
- Keep the water moving—moving water (i.e., in tubing associated with samplers) significantly reduces losses on pyrethroids onto the walls of the container or tubing. When the water is still, losses are greatest.
- Losses to containers do not appear to be a problem for sediment samples.

(2) Water samples can experience significant pyrethroids losses in just two days. To address this problem:

- Laboratories should process water samples collected for pyrethroids analysis within 24 hours.
- Special storage procedures can reduce losses (e.g., adding a "keeper" solvent or extracting the sample prior to storage). The selection of the appropriate storage alternative depends on the laboratory's method for sample preparation and analysis.
- Sediment samples can be stored in the freezer for at least 6 months

Additional details about the procedures recommended above are in the Pyrethroids Methods Development project report (available on the Internet: www.cdpr.ca.gov/docs/emon/surfwtr/caps/calfed_py_md.pdf).

With funding from U.S. EPA, the USGS will be further developing pyrethroid sample collection and handling methods into a standard operating procedure for collection of water and sediment samples for pyrethroids analysis, which is anticipated to be published by the end of 2008. The goal is to produce a formal standard operating procedure for collecting and storing water and sediment samples to be analyzed for pyrethroids. The Standard Methods Joint Task Group described above intends to address sample collection and handling as part of its method development work.

Use of certain solvents could interfere with accurate measurements of concentrations of individual pyrethroid isomers. Some pyrethroid active ingredients are comprised of multiple isomers.[6] In the future, measurements of the concentrations of individual pyrethroid isomers may be desirable because for some pyrethroids, individual isomers have dramatically different aquatic toxicities and environmental fates. Qin and Gan (2007) reported that exposure of pyrethroid-containing samples to certain solvents (which could occur through use of a "keeper" during sample storage or when a sample is extracted for analysis) can cause changes in pyrethroid isomers. If a sample is to be analyzed for individual isomers, special storage procedures and care in solvent selection may be necessary to avoid compromising the analysis.

Methods for measurement of fipronil and its degradates at environmentally relevant concentrations exist, but fipronil and degradates analyses are not generally available from commercial laboratories. The U.S. Geological Survey (USGS) recently developed improved methods for both water column and sediment analyses of fipronil and three degradates. The water column method was has been published (Hladik et al. 2008); a

[6] Any of two or more substances that are composed of the same elements in the same proportions but differ in properties because of differences in the arrangement of atoms.

paper on the sediment method is in preparation. Informal surveys by the UP3 Project have not found commercial laboratories advertising the capability of measuring environmentally relevant concentrations of fipronil and its degradates in water or sediment. Surveyed commercial laboratories all indicated their expectation that fipronil chemical analysis at environmentally relevant detection limits would be technically feasible with current equipment. The surveyed laboratories have not invested the staff time to learn, calibrate, and validate fipronil measurement methods on their equipment due to lack of market demand for fipronil measurements.

Commercial laboratories do not offer methods for analysis of environmentally relevant concentrations of all pesticides currently used in urban areas. Developing methods for polyhexamethylene biguanadine (PHMB) is a priority. The lack of chemical analysis methods with environmentally meaningful detection limits for pesticides and pesticide degradates that have the potential to cause toxicity incidents is a barrier to identification of causes of toxicity and to including these pesticides of concern in monitoring programs. No California commercial laboratory appears to be currently offering analyses for PHMB, a common swimming pool and spa biocide that is highly toxic to aquatic life and is likely to be discharged to creeks or to municipal wastewater treatment plants when pools and spas are emptied.

Toxicity Identification Evaluations (TIEs)

Toxicity identification evaluation (TIE) methods for pyrethroids are progressing well and moving towards standardization. Research teams are developing TIE methods for pyrethroids based on four general lines of evidence: (1) correlations with total pyrethroids concentrations (based on “toxic units” to account for the differing toxicities of individual pyrethroids); (2) increased toxicity with decreasing temperature; (3) increased toxicity with addition of the synergist piperonyl butoxide; and (4) use of an enzymatic procedure for pyrethroid toxicity removal. Publications by researchers using these lines of evidence suggest that it is likely that these Phase I TIE methods will provide acceptable reliability (Phillips et al. 2007; Amweg and Weston 2007; Weston and Amweg 2007). Water quality agencies are successfully applying these techniques to environmental samples (Weston Solutions 2006; Riverside County 2007).

The next step will be to develop Phase II TIE procedures, which require being able to remove a toxicant, recover it, and test it chemically and toxicologically.

3.0 CALIFORNIA URBAN SURFACE WATER PESTICIDE MONITORING PROGRAMS

3.1 Background

Monitoring of urban surface waters and discharges to those surface waters is the only way to determine if a pesticide-related surface water toxicity problem exists. In the mid-1990s, such monitoring identified widespread toxicity in San Francisco Bay Area creeks (which was attributed to diazinon and, to a lesser extent, chlorpyrifos). In recent years, similar monitoring has found widespread toxicity associated with pyrethroid insecticides.

3.2 Monitoring Program Overview

Table 1 (on the next three pages) provides an overview of surface water and discharge monitoring programs for pesticides and surface water toxicity in California urban areas. Funding for these monitoring activities comes from many sources, including municipal, state and Federal governments; California water bonds; and the government agencies and private businesses that participate in group monitoring programs (like the San Francisco Bay Regional Monitoring Program). A relatively complete list of monitoring programs (albeit with few details on the actual monitoring) is available on the California Coastal Water Quality Monitoring Programs Internet site, www.sfei.org/camp/.

This section does not include programs monitoring agricultural discharges, because these are almost always designed to focus exclusively on agricultural pesticide runoff. Two regions (the Central Valley and the Central Coast) are implementing relatively extensive agricultural pesticide monitoring programs that may provide data that could assist with the interpretation of urban monitoring results for mixed agricultural-urban watersheds. For more information on these programs see the following Internet sites:

Central Valley—www.waterboards.ca.gov/centralvalley/water_issues/irrigated_lands/

Central Coast—www.swrcb.ca.gov/rwqcb3/AGWaivers/Index.htm and www.ccwqp.org

3.3 Monitoring Data Availability

In 2005-2007, TDC Environmental worked with the San Francisco Estuary Project to attempt to inventory urban discharge and urban surface water pesticide and toxicity monitoring activities in the San Francisco Bay Area and to identify important urban pesticide monitoring activities occurring elsewhere in California. It was not possible to complete a detailed inventory within the available budget, due to the challenges described below.

Pesticide monitoring plans and results are often not readily available. There is no central repository of urban surface water monitoring or pesticide surface water monitoring data in California (either regionally or statewide). Opportunities exist to create a useful central repository; however, no existing system currently has broad participation of monitoring programs.

An Internet-accessible database would provide the most efficient access to monitoring data. Two databases exist that could potentially serve this function:

Table 1. California Urban Surface Water Pesticide/Toxicity Monitoring Programs

Program	Program Overview
Statewide	
Surface Water Ambient Monitoring Program (SWAMP)	SWAMP is a statewide surface monitoring program managed by the State and Regional Water Boards. Toxicity and some current-use pesticides have been included in various SWAMP monitoring programs. See www.waterboards.ca.gov/water_issues/programs/swamp/ for more information.
California Department of Pesticide Regulation (DPR)	DPR conducts various surface water monitoring projects in California (it receives some assistance from contractors like U.C. Riverside). All DPR monitoring focuses on current-use pesticides. DPR recently initiated a statewide urban surface water monitoring project, with two goals: (1) assessing whether pesticides are present in urban surface waters at levels that have the potential to impact the beneficial uses of those waters and (2) obtaining information on urban runoff pesticide sources (He 2008). DPR monitoring studies are completed on a project basis, often in response to findings by other monitoring programs. For example, DPR is currently completing a marina monitoring project evaluating marine antifouling biocides. See the DPR Surface Water Protection Program Internet site (www.cdpr.ca.gov/docs/sw/index.htm) for more information.
USGS National Water Quality Assessment (NAWQA)	USGS' NAWQA program has monitored surface water quality in the Sacramento and San Joaquin-Tulare River basins and selected Southern California coastal drainages for more than a decade. The monitoring is beginning to include current-use pesticides that the UP3 Project has identified as priorities. See water.usgs.gov/nawqa/ for more information.
Regional	
TMDL Implementation Monitoring	Some California Water Board TMDLs are including pesticides and/or toxicity monitoring as part of their implementation. These involve locally specific monitoring plans that may be conducted by any of the entities involved in the TMDL. For example, the Calleguas Creek Watershed TMDL Monitoring Program (which should be initiated in 2008) includes water column and sediment monitoring for organophosphorous pesticides, pyrethroids, and toxicity. Municipal wastewater treatment plants, urban runoff programs, and agricultural dischargers are slated to conduct this monitoring.
Southern California Coastal Water Research Project (SCCWRP)	SCCWRP is a Southern California joint powers agency that conducts monitoring in Southern California watersheds and coastal waters. Among its largest projects is status and trends monitoring for the Southern California Bight (a region that includes coastal southern California, the Channel Islands and the local portion of the Pacific Ocean). It also has completed pesticides and toxicity-related special research projects with agency, grant, and contract funding. See www.sccwrp.org/ for more information.
Stormwater Monitoring Coalition (SMC)	The SMC is a formal collaboration among water quality regulators (primarily the three Southern California Regional Water Boards), SCCWRP, and most of the municipal stormwater management agencies in Southern California. The SMC's goals are to develop the technical information necessary to better understand stormwater mechanisms and impacts, and to develop the tools that will effectively and efficiently improve stormwater decision-making. Among SMC publications are guidance documents for urban runoff monitoring programs in Southern California. The SMC recently recommended monitoring urban creeks for pyrethroids (SMC 2007).

Table 1. California Urban Surface Water Pesticide/Toxicity Monitoring Programs (Continued)

Program	Program Overview
Regional	
Sacramento River Watershed Program (SRWP)	The SRWP conducts and coordinates monitoring in the Sacramento River watershed. Although its focus is on water bodies affected by agricultural discharges, it does include urban areas. The program maintains a compendium of monitoring programs in the Sacramento River watershed, including monitoring locations and parameters: see www.sacriver.org/monitoring/compendium/ .
San Francisco Bay Regional Monitoring Program (RMP)	The RMP is a collaborative monitoring program conducted by the San Francisco Bay Regional Water Board, municipal wastewater treatment plants, urban runoff programs, other regulated dischargers to San Francisco Bay, and the San Francisco Estuary Institute (SFEI, which manages most of the day-to-day activities of the RMP). Most RMP monitoring focuses on San Francisco Bay, although some special studies of creeks and rivers have been conducted. Routine monitoring includes measurements of various contaminants and toxicity in Bay water and sediment. Although the routine monitoring program does not include most current-use pesticides of concern for water quality, past and current RMP special studies have looked at pesticides and pesticide-related toxicity. See www.sfei.org/rmp/ for more information.
Clean Estuary Partnership (CEP)	The CEP was a cooperative partnership that was established to facilitate efforts to adopt and implement TMDLs in San Francisco Bay Area by providing financial and staff support for technical analysis and stakeholder outreach activities. The official CEP partners were the San Francisco Bay Regional Water Board, the Bay Area Stormwater Management Agencies Association, and the Bay Area Clean Water Agencies (an organization of municipal wastewater treatment plants). The CEP completed limited pesticides and toxicity monitoring in 2004/05 (Ruby 2005) and prepared a monitoring plan for 05/06 (Ruby 2006) that was not implemented due to program restructuring. Pesticide-related CEP reports are available on the UP3 Project web site: www.up3project.org/up3_monitoring.shtml.
Municipal	
Urban runoff (stormwater) programs	Under National Pollutant Discharge Elimination System (NPDES) permits, urban runoff programs are required to complete monitoring of surface waters. Monitoring requirements differ by region and by permittee. Colloquial information suggests that most programs in California are not monitoring for current-use pesticides, but some programs monitor toxicity (usually in receiving waters, occasionally in sediment) and/or organophosphorous pesticides (usually diazinon and chlorpyrifos, for which nearly all urban use has been phased out), or are planning monitoring for pyrethroids in response to new or anticipated permit requirements. Monitoring may occur on an ongoing basis or may involve special studies in one or more watersheds. Special studies like toxicity identification evaluations are most commonly conducted in response to incidents of repeated toxicity.

Table 1. California Urban Surface Water Pesticide/Toxicity Monitoring Programs (Continued)

Program	Program Overview
Municipal	
Municipal wastewater treatment plants	Almost all municipal wastewater treatment plants are required to conduct acute and chronic toxicity monitoring of effluents under their NPDES permits. Requirements for pesticide and toxicity testing are individually determined, but are relatively consistent across the state. Routine acute toxicity monitoring involves species (e.g., fathead minnow, rainbow trout) that are not particularly sensitive to most currently used pesticides that are of concern for water quality; however, most permits require occasional (as often as monthly) chronic toxicity monitoring. The chronic toxicity monitoring may or may not involve species that are sensitive to current-use pesticides. The selection of chronic toxicity species for a municipal wastewater treatment plant depends on an occasional evaluation (commonly once per 5-year permit cycle) of the sensitivity of multiple allowable test species to effluent. Results for required toxicity monitoring must be reported to Regional Water Quality Control Boards; however, these data are not currently compiled or otherwise made readily available. Although almost all treatment plant permits require monitoring for toxic pollutants in discharges, monitoring requirements are based on the Clean Water Act list of “priority pollutants,” which does not include most current use pesticides. Currently used urban pesticides that are included in many treatment plant monitoring programs are copper, tributyltin, lindane and malathion. (Lindane and malathion are measured by the commonly required organochlorine and organophosphorous pesticide analyses). Based on colloquial information, it appears that few municipal wastewater treatment plants appear to monitor for any other current use urban pesticides. Monitoring for pollutants not included in NPDES permits does not have to be reported to regulatory agencies and thus usually is not made public.
Other	
Various entities	A few other miscellaneous public and private entities monitor pesticides and/or toxicity in California surface waters. For example, Stanford University’s Jasper Ridge Biological Preserve completes monitoring in the San Francisquito creek watershed.
Research	
Various entities	Various universities (e.g., U.C. Berkeley and U.C. Davis), non-profits (e.g., SFEI, the Friends of the Russian River) and government researchers (e.g., USGS) conduct grant or contract-funded monitoring of current-use pesticides in urban creeks. Most such projects are short-term in nature. They are usually designed to answer a specific research question or to test a monitoring technique or approach.

Source: Information assembled by TDC Environmental from program web sites, publications, and personal communications with program staff.

- Bay Delta and Tributaries (BDAT) Project and the California Environmental Data Exchange Network (CEDEN). Two related web sites are being set up with the intent of making regional and statewide surface water monitoring data available. The (BDAT) Project site (www.bdat.ca.gov) is currently online and is working to increase its participation. BDAT contains data for the San Francisco Bay-Delta region. More than 50 organizations contribute data to BDAT, including the State Water Board's SWAMP program. The BDAT database includes biological, water quality, and meteorological data. BDAT is the first functioning portion of CEDEN, which will eventually cover the entire state. BDAT and CEDEN are based on voluntary networks of monitoring programs, which must manage their data in a manner that connects to the databases (BDAT/CEDEN provide some support for the necessary data management).
- DPR surface water database. Monitoring programs can voluntarily submit data to DPR for inclusion in its surface water database. The DPR database (www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm) currently contains data from more than 50 studies. DPR accepts data submissions in any form (including hard copies of published reports and print-outs of tabular summaries with supporting documentation), but electronic submissions on disc or by electronic mail are preferred. Data that include at least DPR's minimum requirements (sample date, county, location information, water body name, pesticide name, result, detection limit, and quality assurance/quality control information) are entered into the database.

Internet accessible databases are very convenient for the user, but require extra efforts on the part of the participating monitoring programs. Either of the above databases has the potential to be a powerful resource if most pesticide surface water monitoring programs elect to participate in them.

The UP3 Project found that the majority of programs monitoring pesticides and toxicity in surface waters do not routinely make current monitoring plans and monitoring results readily available to those outside of their agencies, except in required reporting to regulatory agencies. Many monitoring reports are required to be submitted to the relevant Regional Water Board or the State Water Resources Control Board. These required reports are maintained in Water Board records on the basis of the permitting entity or the grant or contract recipient. There are currently no provisions for identifying, separating out, and offering hard copy (e.g., library) or Internet access to the pesticide monitoring data within reports submitted to the Water Boards.

The majority of urban surface water pesticide monitoring plans and reports are not posted on Internet sites or published in professional journals. Some monitoring programs do post plans or reports on the Internet; however, the pesticide-specific information is difficult to find, as it is often not obvious where on the agency Internet site to look, or which report contains the relevant information. Monitoring plans and monitoring data are difficult to find when they are published, as they are often incorporated in reports covering other topics.

Pesticide monitoring program planning is often short term and sometimes ad-hoc. Most monitoring programs plan activities on annual cycles. Consistent, long-term monitoring plans are relatively rare, partly because they can only be conducted by entities with long-term funding sources. This is particularly common for pesticides, which are often monitored reactively (in response to toxicity incidents) rather than proactively. This means that a great deal of pesticide monitoring is funded by short-term grants or contracts. To inventory pesticide monitoring programs, it would be necessary to obtain program-specific information every year. Planning cycles and planning processes are not consistent among programs, further impeding collection of basic information (e.g., which water bodies will be sampled, which parameters will be measured, what toxicity testing will be performed).

Exceptions exist—for example, a few municipal urban runoff program NPDES permits require that pesticide monitoring be planned for the entire term of the permit (usually five years). Also, as noted in Table 1, toxicity monitoring has long been a requirement in municipal wastewater treatment plant NPDES permits. A few pesticide TMDLs incorporate long-term, focused monitoring requirements for dischargers. Usually these cover only a very small number of pesticides (fewer than a dozen). Increasingly, such long-term monitoring requirements for urban runoff and surface waters are including toxicity and sediment monitoring.

The recent initiation of an urban surface water monitoring project by DPR (He 2008) has the potential to fill the need for long-term surveillance for pesticides in California urban surface waters.

Scientists involved in surface water quality monitoring for pesticides and toxicity have no regular communications forum. Although subsets of scientists occasionally meet to discuss monitoring plans and results, there is no regional or statewide forum for scientists to communicate results or to provide topic-specific support for scientists managing pesticides and toxicity surface water monitoring.

4.0 RELEVANT RESULTS OF RECENT SCIENTIFIC STUDIES

4.1 Background

Recent research, monitoring, and technical studies have advanced our understanding of how urban pesticide use can affect California surface water quality and NPDES permit compliance. This research can inform urban water quality monitoring program design, responses to toxicity incidents, and long-term planning for toxicity prevention and control.

4.2 Findings: Pyrethroids

Pyrethroids are causing toxicity to organisms dwelling in California surface water sediments. Explorations of toxicity in sediments from Northern California urban creeks identified pyrethroids as the cause of significant toxicity in sediment (Weston et al. 2005; Amweg et al. 2006). Notable among the findings of these studies is that the toxicity found was more severe and more widespread in urban creeks than in the agricultural water bodies surveyed by the same research team (Weston et al. 2004). The studies used a standard test species, the amphipod *Hyalella azteca*, which is a common resident species in Northern California creeks and rivers. The 2006 annual UP3 Project research and monitoring update (TDC Environmental 2006) described four main findings of published research, which have not been modified by additional studies published in the last two years (see the 2006 report for details):

- The toxicity is severe.
- The toxicity is widespread.
- The toxicity is linked to urban runoff.
- Multiple pyrethroids contribute to the toxicity; bifenthrin is the largest contributor.

Recent findings of pyrethroid-related toxicity in wet weather creek water samples in two separate urban watersheds suggest that the presence of pyrethroids in the water column may be a significant concern. Two Southern California urban runoff programs have identified frequent toxicity to *Hyalella azteca* while conducting routine monitoring of water column samples in wet weather conditions. In both cases, toxicity identification evaluations indicated that pyrethroids were almost certainly the cause of the toxicity (Riverside County 2007; Weston Solutions 2006). Additional monitoring—including chemical analysis for pyrethroids—is planned in both counties.

Urban runoff is more likely to contain environmentally meaningful quantities of pesticides than base flows. Although available data on base flows are limited, these data rarely indicate that pesticide-related toxicity is present in urban creek base flows (Riverside County 2007; Scanlin and Feng 1997, Ruby 2005, San Francisco Bay Water Board 2007, AQUA-Science 2007). Exceptions to this general rule are likely—particularly in association with dry weather discharge events like swimming pool emptying.

Fresh water aquatic sediment acute toxicity data for most—but not all—commonly used pyrethroids are available; however, salt water, water column, and sediment chronic toxicity data are needed. Acute sediment toxicity data for the more sensitive of the two standard freshwater sediment toxicity testing species (*Hyalella azteca*) are available for all of the pyrethroids identified by the UP3 Project as of greatest interest in urban areas except tralomethrin (see Amweg et al. 2005; Maund et al. 2002; these values were summarized in the 2006 annual UP3 Project research and monitoring update [TDC Environmental 2006]).

Chronic sediment toxicity data are not yet available for pyrethroids. Through a regulatory process called reevaluation, DPR is requiring that pyrethroid product manufacturers develop chronic sediment data for most pyrethroids.[7]

Recent findings associating pyrethroids in urban runoff samples with toxicity to a standard freshwater water sample toxicity testing species (*Hyalella azteca*) have raised the need for acute and chronic water column toxicity data for *Hyalella azteca* and other commonly used water column test species (most importantly *Ceriodaphnia dubia*). Very limited data are currently available (see Oros and Werner 2005), which make interpretation of monitoring data challenging.

Since pyrethroids run off into salt water as well as fresh water, aquatic toxicity data for salt water species are needed. Acute toxicity data for one standard salt water sediment toxicity testing organism (the estuarine amphipod *Eohaustorius estuarius*) were recently reported for bifenthrin, cypermethrin, and permethrin (Anderson et al. 2008). Salt water acute toxicity data for other pyrethroids and salt water chronic toxicity data for all pyrethroids are needed. While obtaining remaining data for *Eohaustorius estuarius* are a priority because it is likely to be among the more sensitive organisms, obtaining data for other organisms (e.g., mysids) is also desirable.

<u>The fate and toxicity differences among pyrethroid isomers have the potential to complicate interpretation of environmental data and development of management strategies</u>. Some pyrethroid active ingredients are comprised of multiple isomers.[8] A few pyrethroid active ingredients contain only a single isomer; most of these are also components in another registered active ingredient (i.e., the registered active ingredient "(S)-cypermethrin" is also part of products that contain the registered active ingredient "cypermethrin").

Some pyrethroid isomers are more toxic than others. The environmental fate of isomers can vary (for example, the ability of organisms to break them down can vary). Researchers have been actively exploring the environmental properties of pyrethroid isomers and their differential toxicity to aquatic organisms (Allan et al. 2005; Liu et al. 2004; Liu and Gan 2004; Liu et al. 2005a; Liu et al. 2005b; Qin et al. 2006; Liu et al 2005c; Qin and Gan 2006; Wang et al. 2007; Xu et al. 2008). The isomeric differences can be dramatic—for example, Xu et al. (2008) found that one isomer of lambda-cyhalothrin was >160 times more acutely toxic to zebrafish than another isomer of the same chemical. One of the themes of scientific publications on pyrethroid isomers is the recommendation that pyrethroid isomers be examined individually for their environmental fate and toxicity to non-target organisms.

To date, there is no published evidence to suggest that differential environmental fates of pyrethroid isomers are linked to any identified aquatic toxicity problem. Because available data show a strong correlation between toxicity and pyrethroid concentrations (when expressed in "toxic units"), neither the differences in toxicity nor the differences in environmental fate among pyrethroid isomers currently appear to be a significant element of pyrethroid-related aquatic toxicity problems.

<u>Specialized sampling methods allow straightforward measurement of the bioavailable fraction of pyrethroids in water samples</u>. Many papers have reported that site-specific conditions such as the presence of dissolved organic matter and suspended sediments can reduce the toxicity of pollutants like pyrethroids in surface waters (e.g., Yang et al.

[7] This is just one of a set of data requirements that have been established in this regulatory process.
[8] Any of two or more substances that are composed of the same elements in the same proportions but differ in properties because of differences in the arrangement of atoms.

2006a; 2006b; 2006c; 2007). This year, researchers reported that the pyrethroid concentrations measured via use of solid-phase microextraction (SPME) fibers were well correlated with pyrethroid bioavailability in water samples (Yang et al. 2007).

Similar methods have been used to measure the fraction of pyrethroids in a sediment sample that are in the sediment pore water (Bondarenko et al. 2007); however, the utility of the pyrethroid sediment pore water measurement is questionable. Sediment pore water measurements were found not to correlate with the commonly used indicator of sediment pyrethroid bioavailability, which is organic carbon-normalized pyrethroid concentration in sediments (Budd et al. 2007).

Related findings from previous UP3 Project Annual Updates remain relevant (see TDC Environmental 2005, 2006, and 2007a):

- Likely sources of the pyrethroids causing the identified toxicity are structural pest control applications around buildings (i.e., to control ants) and—to a lesser extent—applications of pyrethroids on lawns and gardens. Applications by both professionals and non-professionals (residents) may contribute to toxicity.
- Outdoor structural pest control applications are of particular interest for water quality.
- The presence of organic matter in sediments moderates pyrethroid toxicity.
- The chemistry of pyrethroids in sediments can change with longer contact time.
- Adverse effects to aquatic ecosystems are likely to occur at concentrations below the LC50.
- Widespread application of synergists in a watershed has the potential to increase toxicity of pyrethroids in sediments.
- Differences in the environmental fates of individual pyrethroids in creek sediments may be relevant to understanding aquatic toxicity patterns.

4.3 Other Findings

New marine antifouling coating biocides are of concern due to their individual and cumulative toxicity to aquatic life. As noted in previous reports, several new biocides that are alternatives to copper and tributyltin—like zinc pyrithione and Irgarol 1051—are very highly toxic to aquatic life. The marine antifouling biocide zinc pyrithione, which has a growing presence in the marketplace, can be converted to the more stable and also very toxic copper pyrithione in the presence of copper, which is commonly present in marinas due to its use in marine antifouling coatings.

Researchers recently explored the aquatic toxicity of marine antifouling biocide mixtures to the brine shrimp *Artemia salina*, generating the disturbing finding that exposure to some biocide combinations caused greater than additive (synergistic) toxicity. Among the combinations with synergistic effects was a mixture of zinc pyrithione and copper pyrithione. Since mixtures of antifouling biocides and their degradates occur in port water and sediments, consideration of cumulative exposures—and potential synergistic toxicity—will need to be made to ensure water quality protection (Koutsaftis and Aoyama 2007).

Use of fipronil has the potential to cause adverse effects in aquatic ecosystems. A 2007 UP3 Project review of scientific information relevant to understanding the potential water quality implications of increased fipronil use concluded that adverse effects are possible, particularly if urban fipronil use increases (Moran 2007). Uncontained above ground urban fipronil applications make fipronil and its degradates available to be washed to storm drains and creeks without any treatment. Improper disposal to gutters and storm drains is also possible. Both improper disposal and washing treated pets can lead to discharges to sewage treatment plants.

Limited available surface water monitoring data show concentrations that are generally lower than most of the available aquatic toxicity data. Due to the lack of sediment toxicity data, it is not possible to determine the environmental relevance of fipronil and degradates sediment concentrations. Available data (both monitoring data and aquatic toxicity data) are too few to determine whether current use patterns and levels may be associated with incidents of acute or chronic toxicity to aquatic organisms or non-compliance with toxicity-related sewage treatment plant permit requirements.

Increased use of fipronil—particularly outdoors around buildings—could occur if fipronil is selected as a substitute for the pyrethroids. Increased outdoor use of fipronil increases the risk of surface water toxicity problems. Available data are insufficient to determine at what use level toxicity problems would occur.

<u>The chemical fate and aquatic toxicity of fipronil and its degradates are not fully characterized. Critical data gaps exist</u>. A review paper published in 2007 by U.C. Davis and DPR scientists summarizes toxicological and environmental fate data for fipronil (Gunasekara 2007). The UP3 Project review of fipronil aquatic toxicity data from this paper and U.S. EPA data sources found that the most important aquatic toxicity data gaps are: data for fipronil's degradates, sediment toxicity data for both fipronil and degradates, and cumulative toxicity data for fipronil and its degradates in mixtures (Moran 2007). Although fipronil degradates are commonly detected along with fipronil in environmental monitoring, little environmental fate and aquatic toxicity data for fipronil degradates are available.

<u>Monitoring findings from previous UP3 Project Annual Updates remain relevant</u> (see TDC Environmental 2005, 2006, and 2007a):

- San Francisco Bay Area urban creek monitoring data show declining diazinon levels and some toxicity (primarily chronic toxicity) in creek water (Ruby, 2005).
    - Diazinon concentrations appear to be decreasing, as expected.
    - Malathion concentrations are of concern.
    - Aquatic toxicity was found on occasion, but it did not have a consistent pattern.
- The USGS National Water Quality Assessment (NAWQA) found pesticides in many streams at concentrations that may have adverse effects on aquatic life or fish-eating wildlife (USGS 2006a; USGS 2006b).[9]
    - Pesticides are frequently present in streams.
    - Urban streams had concentrations that exceeded one or more water quality benchmarks for aquatic life or fish-eating wildlife at 83% of NAWQA monitoring sites.
    - The pesticides most commonly used at the time the monitoring was conducted were detected most frequently in streams.

[9] An excellent review article summarizing USGS's key findings in text and easy-to-read charts (Gilliom 2007) is available on the Internet: http://pubs.acs.org/subscribe/journals/esthag/41/i10/html/051507feature_gilliom.html

  - o In surface water, pesticides occur most commonly in mixtures, rather than individually.

- Unknown toxicity has been identified in various California surface waters and discharges.

<u>Other findings from previous UP3 Project Annual Updates remain relevant</u> (see TDC Environmental 2005, 2006, and 2007a):

- Stress from exposure to disease and/or predators, in combination with pesticide exposures, can adversely affect organisms at concentrations below documented EC50s and LC50s.
- New, potentially environmentally relevant sublethal toxicity endpoints are being identified by researchers.
- The toxicity of a formulated pesticide may be substantially greater than the toxicity of the active ingredient alone.
- USGS data suggest that insecticides are more likely than herbicides to be linked to pesticide-related toxicity in urban surface waters.
- Toxic concentrations of herbicides can appear in urban runoff.
- The insecticide fipronil is highly toxic to aquatic species.
- New urban pesticide products threaten to cause toxicity in municipal wastewater treatment plant effluent and storm drain discharges.
- The environmental fate of pesticides may be different in urban settings than in the agricultural settings for which environmental fate data are generally collected.
- In surface water, the presence of pesticide degradates can be as environmentally important as the pesticide itself.
- Copper-based marine antifouling paint has been linked to elevated copper levels in surface waters with marinas.
- Copper-based wood preservatives may comprise a meaningful source of copper releases into adjacent surface waters.
- Endothall salts differ in aquatic toxicity. The dimethylamine salt (which is the active ingredient in Hydrothol)—is much more toxic to aquatic life than the other chemical form—the dipotassium salt (which is the active ingredient in Aquathol).
- U.S. EPA environmental risk assessments predict aquatic toxicity from ordinary use of various pesticides, including permethrin, cypermethrin, metaldehyde, pyrethrins, carbaryl, malathion, and the synergists piperonyl butoxide and MGK-264.

5.0 CONCLUSIONS AND RECOMMENDATIONS

This section summarizes the information above into key conclusions and provides recommendations based on recent research findings. The conclusions and recommendations below are intended to be viewed together with the conclusions and recommendations of the other two UP3 Project annual reports: the review of California water quality agencies' urban pesticide water quality regulatory activities (TDC Environmental 2007b) and an analysis of urban pesticide sales and use trends (TDC Environmental 2007c). The recommendations below are not directed only at California water quality agencies—U.S. EPA, DPR, and others should play a significant (if not leading) role in their implementation.

5.1 Conclusions

<u>Conclusion 1</u>: *Pyrethroid insecticides are causing adverse effects in aquatic ecosystems receiving urban runoff*. Toxicity to sediment-dwelling organisms from pyrethroids has been documented in most Northern California urban surface waters that have been tested. Water samples collected from urban creeks during storm events have exhibited toxicity attributed to pyrethroids, suggesting that the presence of pyrethroids in the water column may also be a significant concern.

<u>Conclusion 2</u>: *Although several current use pesticides—including malathion, carbaryl, PHMB, and fipronil—have the potential to cause adverse effects in aquatic ecosystems, currently there is little or no monitoring for most of these pesticides in California surface water or wastewater discharges*. Both acute toxicity and chronic toxicity have been reported in surface water and wastewater discharges. It is not known if currently used pesticides contribute to this toxicity.

An urban surface water monitoring project being initiated by DPR is being designed to address the need for surface water (fresh water) monitoring. The DPR monitoring plan includes measurements of malathion, carbaryl, and fipronil in urban runoff and creek water samples (He 2008).

<u>Conclusion 3</u>: *Capabilities for measuring environmentally relevant concentrations of pyrethroids and fipronil in water and sediment are improving; however, additional work is needed to develop and validate analytical methods for pyrethroids and fipronil and its degradates in environmental samples.* Development of analytical methods for pyrethroids and fipronil has been a priority for several years and is nearing completion. The formation of a Standard Methods Joint Task Group to develop a method that would be suitable for publication in *Standard Methods for the Examination of Water and Wastewater* is a major step toward establishing a widely accepted method for pyrethroids. For fipronil, it appears that lack of a market (rather than a technical challenge) is the reason that commercial laboratories are not currently offering analysis of fipronil among their routine services.

<u>Conclusion 4</u>: *Capabilities for measuring other pesticides of concern and pesticide degradates at environmentally relevant concentrations are needed.* The most important current gap is the biocide PHMB.

<u>Conclusion 5</u>: *The results from monitoring of urban surface waters and discharges to those surface waters for pesticides and pesticide-related toxicity are difficult to find.* There is no central repository of urban surface water monitoring or pesticide surface water monitoring data in California (either regionally or statewide). Most monitoring data are not currently combined in any regional or statewide database (this could change if voluntary participation in one of two statewide systems increases). Monitoring plans and

reports are not conveniently compiled on any one Internet site or in any one physical location. Most monitoring programs do not publish their results in professional journals. This means that pesticide monitoring data are not readily available to scientists and water quality and pesticide agencies.

5.2 Recommendations

Monitoring and Chemical Analysis

Recommendation 1: *Improve chemical analytical and toxicity testing capabilities for pesticides in surface water (water column and sediment), urban runoff, and municipal wastewater treatment plant effluent and biosolids*. Standard chemical analytical methods[10] exist for only a small portion of the more than 900 pesticide active ingredients registered for use in California. Even when methods are available, they often do not have detection limits low enough to measure environmentally relevant concentrations of pesticides and their degradates. Ideally, practical pesticide analysis methods with detection limits below the lowest environmentally relevant concentration (e.g., water quality criterion, LC50, EC50) should be available for all registered pesticides and all potentially environmentally significant degradates—and should be validated for surface water (water column and sediment), urban runoff, and municipal wastewater treatment plant effluent and biosolids samples. Creating pesticide chemical analysis methods that are feasible for commercial laboratories is particularly important, since contractors (rather than state agency or university laboratories) perform the chemical analysis of most surface water quality samples collected in California.

While both public and private laboratories have invested in development of pesticide chemical analysis methods, these investments can address only a small portion of the need for pesticide chemical analysis method development. The suggested near-term priority for method development that is not currently being addressed is development of chemical analysis methods with environmentally meaningful detection limits for PHMB. Developing commercial laboratory capacity to measure fipronil and its degradates in environmental samples is also important. Methods for measuring environmentally relevant concentrations of individual pyrethroid isomers are also needed, at least for research purposes to determine if isomer difference are environmentally significant.

Recommendation 2: *Conduct surveillance monitoring of California urban surface waters, including sediment, for toxicity and for specific pesticides that have the potential to cause adverse effects in aquatic ecosystems (e.g., currently used pyrethroids[11], carbaryl, malathion, PHMB, and fipronil and its degradates).* Specific monitoring recommendations are as follows:[12]

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[10] "Standard chemical analytical methods" is intended to mean methods that are published, peer-reviewed, and extensively validated; have appropriate quality assurance/quality control procedures; are well-accepted by professional analytical chemists; are practical for non-research analytical laboratories; are appropriate for measuring environmentally relevant concentrations in environmental samples; and that do not require equipment that would not normally be available in a commercial analytical laboratory. Such methods include—but are not limited to—U.S. EPA approved methods and methods in the laboratory reference books like *Standard Methods for the Examination of Water and Wastewater* (Eaton et al. 2005).

[11] The pyrethroids of greatest interest for urban surface water quality are bifenthrin, cyfluthrin (including beta-cyfluthrin), cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin. Additional pyrethroids are of interest in agricultural areas.

[12] Toxicity test species and detection limit recommendations are based on aquatic toxicity data and (where available) water quality criteria (see section 4, TDC Environmental 2003, Moran 2007, and Oros and Werner 2005) and best professional judgment. The pyrethroids selection is based on evaluation of urban pesticide use (see TDC Environmental 2007c).

- Toxicity monitoring should be conducted with standard aquatic toxicity test species and should (in the near term) include the standard test species most sensitive to pyrethroids (water column—*Oncorhynchus mykiss* and *Hyalella azteca*; sediment—*Hyalella azteca)*. Because aquatic toxicity is a key indicator and monitoring tool in surface waters that can quickly identify the presence of contaminant stressors, it is a recommended element of any surveillance monitoring program. Consideration should be given to completing some tests at actual creek temperature, if that temperature is significantly lower than the laboratory aquatic toxicity test temperature, since the toxicity of some pesticides (e.g., pyrethroids) increases as temperature decreases.
- Pyrethroids monitoring in urban areas should include bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin. (Agricultural monitoring should include additional pyrethroids.) When analysis includes deltamethrin and/or tralomethrin, it is important to clarify with the laboratory whether the method used can distinguish between these two compounds (distinguishing is not necessary as long as the results are properly reported).
- Sediments. Monitoring of pyrethroids in sediments is a higher priority than monitoring for them in the water column.
- Storm events. Monitoring storm events is a higher priority than monitoring base flow conditions. Although available data on base flows are limited, these data rarely indicate that pesticide-related toxicity is present in urban creek base flows.
- Other parameters for sediment samples. Because pyrethroid toxicity is inversely correlated with organic carbon concentration, when monitoring for pyrethroids in sediments, organic carbon concentrations should be measured. With organic carbon concentrations, it is possible to compare monitoring data to aquatic toxicity data for pyrethroids.[13] Sediment grain size should also be measured. Grain size can vary greatly among sampling locations and sampling times. Grain size data will be useful for interpretation of sediment chemistry results, particularly when evaluating larger data sets or comparing data sets among various water bodies.
- Other parameters for water samples. Because the presence of organic carbon and sediment can alter the bioavailability of pyrethroids and other pesticides, measurement of the standard parameters total suspended solids (TSS) and dissolved organic carbon (DOC) is recommended. Although the relationships among TSS and DOC levels and pyrethroid bioavailability have not been quantified—and these relationships may be water-body specific—collecting these data will assist with future data interpretation and may assist with interpretation of aquatic toxicity results.
- Recommended detection limits[14] are as follows:
  - Each individual pyrethroid in water—as close to 1 nanogram/liter as available
  - Each individual pyrethroid in sediment—1 nanogram/gram (dry weight) (0.1 nanogram/gram is preferred, but is not readily available)[15]

[13] Pyrethroid sediment toxicity data are available in Amweg et al. 2005; Maund et al. 2002; these values were summarized in the 2006 annual UP3 Project research and monitoring update (TDC Environmental 2006).
[14] Recommendations are based on available aquatic toxicity data.

- Carbaryl in water—0.5 micrograms/liter
- Malathion in water—0.1 micrograms/liter
- PHMB in water—10 micrograms/liter
- Fipronil and degradates in water—0.002 micrograms/liter
- Fipronil and degradates in sediment—30 nanogram/gram (dry weight)

Monitoring programs should be adjusted every few years to reflect pesticide market changes.

Monitoring programs should include sites that cover a diversity of urban land uses. Available data are insufficient to identify land use characteristics (e.g., land use types and densities) that are most likely to be associated with elevated pesticide concentrations in surface waters.

A long-term surveillance monitoring program for urban areas is needed. DPR recently initiated a statewide urban surface water monitoring project that has the potential to address this need (He 2008).

<u>Recommendation 3</u>: Procedures for sample collection and storage for samples being analyzed for pyrethroids should be checked to ensure they reflect the latest scientific information available at the time the sampling is conducted. Sampling procedures for pyrethroids are slightly different than procedures for other pesticides and other pollutants commonly monitored in urban runoff and municipal wastewater. Different procedures are needed to minimize loses of pyrethroids. Research in progress is the basis for the following recommendations.

For water samples:

- Samples should be collected directly into the sample container that will be taken to the laboratory. Transfers and use of tubing should be avoided.
- If tubing must be used, keep the water moving—moving water significantly reduces losses on pyrethroids onto the walls of the container or tubing. When the water is still, losses are greatest.
- Each sample should be agitated (shaken vigorously) for about one minute immediately prior to conducting the laboratory's extraction procedure to release pyrethroids that have adheres to the container. (This works best in glass containers.)
- Avoid Teflon when handling samples to be analyzed for pyrethroids.
- Glass containers are preferred over plastic. If plastic must be used (i.e., bottle cap liners), polyethylene (LDPE or HDPE) is preferred over Teflon.
- Use the largest convenient containers for sampling. Losses are lower in larger containers (the ratio of surface area to volume of water is lower).
- Laboratories should process water samples collected for pyrethroids analysis within 24 hours.
- Special storage procedures can reduce losses (e.g., adding a "keeper" solvent or extracting the sample prior to storage). The selection of the appropriate storage

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[15] Pyrethroid detection limits may be improved by using a different detector on the laboratory equipment (see Section 2.2 and PWG 2007).

alternative depends on the laboratory's method for sample preparation and analysis.

For sediment samples:

- Sample collection procedures used by U.C. Berkeley are recommended (see Amweg et al. 2006). (Note that these procedures avoid use of Teflon—stainless steel is preferred.)
- Appropriate sediments to collect are from deposition areas that include fine organic material. Gravel should be avoided. Sediment grain size should be measured and reported.
- Sediment samples can be stored frozen for at least six months.
- Ensure that the laboratory is aware that excess sulfur needs to be removed to avoid interferences with analysis of pyrethroids concentrations.

The UP3 Project recommends that water quality agencies provide their laboratories with the Pyrethroids Methods Development project report (available on the Internet: www.cdpr.ca.gov/docs/emon/surfwtr/caps/calfed_py_md.pdf). The methods information in this report may be of interest to the lab, and the information about containers and storage is very important to successful design of sampling programs.

<u>*Recommendation 4*</u>*: Submit all pesticide-related water quality monitoring data to U.S. EPA and to DPR. Consideration should also be given to submitting data to the appropriate local node of the California Environmental Data Exchange Network (CEDEN).* All entities that conduct surface water monitoring in California should submit reports containing pesticide-related data to both DPR and U.S. EPA. Submitting data will help pesticide regulators respond to—and prevent—water quality problems from pesticides, which will help all agencies comply with the Clean Water Act.

Both U.S. EPA and DPR have specific recommendations for the information that should be collected by monitoring programs and included in monitoring data reports. These recommendations are straightforward—most monitoring programs are probably incorporating these recommendations already. Nevertheless, the UP3 Project recommends that monitoring programs consult the two sets of recommendations below when designing surface water monitoring plans:

- DPR: http://www.cdpr.ca.gov/docs/sw/caps/req.htm
- U.S. EPA: See pages 3-4 of "OPP Standard Operating Procedure," which is available on the Internet, see: http://www.epa.gov/oppsrrd1/registration_review/water_quality_sop.htm

Submitting data:

- DPR: Send to Keith Starner, DPR, P.O. Box 4015, Sacramento, CA 95812 (916-324-4167, kstarner@cdpr.ca.gov). The UP3 Project recommends a quick call to Keith before submitting data to discuss submittal formats (any format is acceptable, but electronic submittals are preferred). For more information see: http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm
- U.S. EPA: Please contact Patti TenBrook at U.S. EPA Region 9 (415-947-4223, TenBrook.Patti@epa.gov) for assistance with identifying where to send the data you have collected.

<u>*Recommendation 5*</u>: *Report all pesticide-related toxicity incidents to U.S. EPA and DPR.* Any incident—whether related to aquatic toxicity or human health—should be reported.

Because incident data provide a strong basis for pesticide regulatory agency decisions, providing all data will help U.S. EPA and DPR use their regulatory authorities to protect water quality and prevent pesticide-related noncompliance with water quality standards and NPDES permits.

Recommendation 6: Encourage publication of pesticide monitoring data in professional journals. Data that have been published in professional journals are more broadly accessible and have more credibility for use by regulatory agencies (particularly pesticide regulatory agencies). Since one year's worth of a single program's data may be insufficient for complete interpretation, preparation of regional data reviews every few years is recommended.

Aquatic Toxicity and Environmental Fate

Recommendation 7: Obtain information to fill aquatic toxicity data gaps for pyrethroids and for other commonly used pesticides. The most critical data gaps for pyrethroids include:

- Aquatic toxicity data. Gaps include *Hyalella azteca* LC50 data for tralomethrin in sediment, *Hyalella azteca* and other standard test organism (particularly *Ceriodaphnia dubia*) LC50 data for pyrethroids in water column samples, estuarine organism (particularly *Eohaustorius estuarius* for sediment toxicity) LC50 data for pyrethroids in both sediment and water column samples, LC50 data for individual pyrethroid isomers, and sublethal toxicity data (EC50s) for both fresh water and estuarine organisms in both sediment and water column samples (all pyrethroids).
- Aquatic sediment half-life values for all pyrethroids except bifenthrin and permethrin. (Under the pyrethroids reevaluation, DPR has required manufacturers to generate these data for all of the pyrethroids of greatest interest for urban surface water quality except tralomethrin [for which sales are anticipated to be relatively small]).[16]

The most critical data gaps for fipronil and its degradates are:

- Sediment toxicity data for fipronil and all major degradates.
- Aquatic toxicity data for standard test species for fipronil degradates.
- Chronic toxicity data for standard test species for fipronil and all major degradates.
- Basic environmental fate data—including aquatic sediment half lives—for fipronil degradates.

Since mixtures of fipronil and its degradates are commonly found in the environment, toxicity testing should examine toxicity from exposures to fipronil and its degradates individually and in combinations.

For all pesticides, obtaining sufficient aquatic toxicity data to allow development of water quality criteria in accordance with U.S. EPA methods (U.S. EPA 1985) is desirable.

Recommendation 8: Develop acute and chronic sediment toxicity data for pyrethroids at environmentally relevant temperatures. Pyrethroids have negative temperature coefficients of toxicity, which means that their toxicity increases in colder water. Because ambient temperatures in California surface waters are often lower than the

[16] See http://www.cdpr.ca.gov/docs/registration/reevaluation/chemicals/summary_ai_data_req.pdf

laboratory temperatures used for toxicity testing, the lower temperatures in surface water may result in greater toxicity than would be predicted based on laboratory tests. Preliminary results from a statewide survey of pyrethroids conducted by the Water Boards indicate that more sediment samples are toxic—and that toxic samples show increased toxicity—when tested for toxicity at a colder (more "creek like") temperature of 15°C (as compared to results at the standard 23°C laboratory temperature) (Holmes 2007). In the winter months, temperatures of 5-10°C are common in California urban creeks. Priorities are: (1) obtaining acute and chronic toxicity sediment data for pyrethroids at 15°C and (2) assessing the relationship between temperature and toxicity for a range of temperatures that include temperatures below 15°C (e.g., 5-10°C), to provide a means for addressing the effects of pyrethroids in the winter. Because *Hyalella azteca* is the most sensitive of the standard test organisms, obtaining these data for *Hyalella* is the highest priority. Obtaining these data for both water column and sediment toxicity would be desirable, because both water column and sediment toxicity to *Hyalella azteca* have been observed in California surface waters.

Recommendation 9: Support efforts to complete development and standardization of Toxicity identification evaluation (TIE) methods for pyrethroids. Based on the success of current method development work, funding development of Phase II (toxicant removal and identification) procedures would be appropriate.

Recommendation 10: Support activities to develop toxicity identification evaluation (TIE) capabilities for fipronil in water and sediment samples. Given the potential for fipronil use to increase—particularly its potential use as a substitute for pyrethroids—development of TIE methods is recommended, to ensure that it is possible to determine whether fipronil is causing toxicity.

Research

Recommendation 11: Obtain additional information about the linkage between pyrethroid use and presence in surface waters in urban areas. Such information will allow toxicity reduction programs to more effectively target the causes of toxicity in surface water sediments. Both monitoring and modeling will likely be needed to determine whether any one specific pyrethroid use pattern (e.g., around buildings or on lawns) is the most significant contributor to pyrethroid levels in creek sediments.

Recommendation 12: Encourage and support development of methods to evaluate the potential for pesticides to contribute to adverse effects on ecosystems from exposure to combinations of stressors. Pesticides, in combination with each other and other pollutants, may add to or synergize toxicity to aquatic organisms. Stress from exposure to predators, in combination with pesticide exposures, can adversely affect organisms at concentrations below documented toxicity thresholds. Development of methods to evaluate these cumulative adverse effects is critical to addressing them in pesticide regulatory processes.

Management

Recommendation 13: When incidents of toxicity in municipal wastewater treatment plant effluent, urban runoff, or surface waters occur, evaluate the potential for pyrethroids and other pesticides (e.g., PHMB, fipronil) to be the source of the toxicity.

Recommendation 14: Avoid over-interpretation of non-detect chemical analytical results for pyrethroids. Because commonly used methods (e.g., U.S. EPA Method 1660) cannot detect environmentally relevant concentrations of pyrethroids, non-detect results from chemical analyses by these methods do not mean that pyrethroids are not present at concentrations sufficient to cause aquatic toxicity.

<u>Recommendation 15</u>: *Provide a regular (annual or semi-annual) forum for scientists involved in surface water quality monitoring for pesticides and toxicity to exchange information relevant to method development and monitoring plan design.* With State Water Board grant funding that is now exhausted, SFEI hosted two productive ad hoc meetings of chemists, aquatic toxicologists, and government agency staff to exchange information about recent research findings, challenges, and priorities for monitoring for pyrethroids in California's surface waters. These focused meetings facilitated information transfer among scientists and identified priorities for future research (priorities were based both on scientific challenges of such monitoring and regulatory agencies' key scientific questions for their pesticide risk assessment and risk management functions). Similar meetings, preferably expanded to include other pesticides of concern, would facilitate communication and help both California and Federal agencies ensure that their research and monitoring funds are spent efficiently and effectively.

<u>Recommendation 16</u>: *Use water quality criteria, if available, to interpret surface water monitoring data for pesticides. Develop improved benchmarks to facilitate evaluation of monitoring data for pesticides without water quality criteria*. Water quality criteria developed in accordance with U.S. EPA methods are the preferred values to use to interpret surface water monitoring data. Water quality criteria can be found on the Internet:

- U.S. EPA's Office of Water posts all adopted water quality criteria on the Internet: http://www.epa.gov/waterscience/criteria/
- The Central Valley Water Board maintains a handy compilation of water quality goals, which includes values other than officially adopted U.S. EPA criteria (and lists sources for any alternative values): http://www.swrcb.ca.gov/centralvalley/water_issues/water_quality_standards_limits/water_quality_goals/

When using water quality criteria, select the criteria appropriate to the specific water body and its uses (e.g., drinking water supply, aquatic life habitat, shellfish harvesting).

When water quality criteria are not available, U.S. EPA pesticide benchmarks should be consulted. U.S. EPA's Office of Pesticide Programs (OPP) has established a web page listing "aquatic life benchmarks" for 71 current use pesticides: http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm. These benchmarks were taken from pesticide-specific environmental risk assessments prepared by OPP. Because OPP uses a method to calculate its aquatic life benchmarks that is not consistent with the method used by the U.S. EPA Office of Water to develop water quality criteria, when water quality criteria exist, they should always be used in preference to the OPP benchmarks.

Because water quality criteria do not exist for most currently used pesticides, agencies find interpretation of pesticide monitoring data challenging. Development of water quality criteria—or scientifically robust benchmarks consistent with the Clean Water Act if water quality criteria development is not possible—would help agencies with appropriate interpretation of monitoring data and with selection of priorities for follow-up action based on monitoring results.

Gaps in available aquatic toxicity data (such as those noted in Recommendation 8) can make development of scientifically robust benchmarks difficult. Data gaps often (but not always) cause preliminary benchmarks based on incomplete data sets to be higher (less protective of aquatic life) than water quality criteria. To address this problem, California's Central Valley Water Board is in the process of developing a method to derive pesticide water quality criteria for the protection of aquatic life on the basis of potentially limited aquatic toxicity data (for information see: www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/central_valley_pesticides/criteria_method/index.shtml).

6.0 REFERENCES

Allan, I. J., W. A. House, et al. (2005). "Diffusion of the Synthetic Pyrethroid Permethrin into Bed-Sediments." *Environmental Science & Technology* **39**(2): 523-530.

Amweg, E. L., D. P. Weston and N. M. Ureda (2005). "Use and Toxicity of Pyrethroid Pesticides in the Central Valley, California, USA." *Environmental Toxicology and Chemistry* **24**(4): 966-972. Corrected per erratum in *Environmental Toxicology and Chemistry* **24**(5): 1300.

Amweg, E. L., D. P. Weston, et al. (2006). "Pyrethroid Insecticides and Sediment Toxicity in Urban Creeks from California and Tennessee." *Environmental Science & Technology* **40**(5): 1700-1706.

Amweg, E. L. and D. P. Weston (2007). "Whole-Sediment Toxicity Identification Evaluation Tools for Pyrethroid Insecticides: I. Piperonyl Butoxide Addition." *Environmental Toxicology and Chemistry* **26**(11): 2389-2396.

Anderson, B. S., S. Lowe, et al. (2008). "Relative Sensitivities of Toxicity Test Protocols with the Amphipods *Eohaustorius estuarius* and *Ampelisca abdita*." *Ecotoxicology and Environmental Safety* **69**(1): 24-31.

AQUA-Science (2007). *Acute Toxicity of Sacramento Area Urban Creeks to Ceriodaphnia Dubia.* Prepared for the Central Valley Regional Water Quality Control Board. August 23.

Bondarenko, S., F. Spurlock, et al. (2007). "Analysis of Pyrethroids in Sediment Pore Water by Solid-Phase Microextraction." *Environmental Toxicology and Chemistry* 2587-2593.

Budd, R., S. Bondarenko, et al. (2007). "Occurrence and Bioavailability of Pyrethroids in a Mixed Land Use Watershed" *Journal of Environmental Quality* **36**(4): 1006-1012.

California Regional Water Quality Control Board, San Francisco Bay Region (San Francisco Bay Water Board) (2007). *Water Quality Monitoring and Bioassessment in Four San Francisco Bay Region Watersheds in 2003-2004: Kirker Creek, Mt. Diablo Creek, Petaluma River, and San Mateo Creek*. Surface Water Ambient Monitoring Program, San Francisco Bay Regional Water Quality Control Board, Oakland, CA

Eaton, A. D., L. S. Clesceri et al., Eds. (2005). *Standard Methods for the Examination of Water & Wastewater*. American Public Health Association, American Water Works Association, and Water Environment Federation.

Gilliom, R. J. (2007). "Pesticides in U.S. Streams and Groundwater." *Environmental Science & Technology* **41**(10): 3408-3414.

Gunasekara, A. S., T. Truong, et al. (2007). "Environmental Fate and Toxicology of Fipronil." *Journal of Pesticide Science* 32(3): 189-199.

He, L-M. (2008). Study 249. Statewide Urban Pesticide Use and Water Quality Monitoring. Workplan prepared by California Department of Pesticide Regulation. March 19.

Hladik, M. (2007). *Methods Development for the Analysis of Pyrethroid Pesticides in Environmental Samples.* Final report for CALFED, Recipient Agreement No. ERP-02-P42. Prepared by the U.S. Geological Survey.

Hladik, M., Research Chemist, USGS (2008). Summary of pyrethroid sampling methods information from Pyrethroids Method Development Project, literature review, and U.S. EPA-funded Pyrethroid Sampling Methods Project. Information provided to Urban Pesticides Committee. January 15.

Hladik, M., K. L. Smalling, and K. M. Kuivila (2008). "A Multi-Residue Method for the Analysis of Pesticides and Pesticide Degradates in Water Using HLB Solid-Phase Extraction and Gas Chromatography–Ion Trap Mass Spectrometry." *Bulletin of Environmental Contamination and Toxicology* **80**(2): 139-144.

Holmes, R. W., J. W. Hunt, B. S. Anderson, B. M. Phillips, D. B. Crane, A. Mekebri, and V. Connor (2007). "Statewide Investigation of the Role of Pyrethroid Pesticides in Sediment Toxicity in California's Urban Waterways–Preliminary Data." Presentation at NorCal SETAC Conference, Berkeley CA. May.

Johnson, B. (2005). *Diazinon and Pesticide-Related Toxicity in Bay Area Urban Creeks. Water Quality Attainment Strategy and Total Maximum Daily Load (TMDL)*. Final Staff Report. Prepared by the California Regional Water Quality Control Board, San Francisco Bay Region. November 9.

Koutsaftis, A. and I. Aoyama (2007). "Toxicity of Four Antifouling Biocides and Their Mixtures on the Brine Shrimp *Artemia salina*." *Science of the Total Environment* **387**(1-3): 166-74.

Liu, W. and J. J. Gan (2004). "Determination of Enantiomers of Synthetic Pyrethroids in Water by Solid Phase Microextraction - Enantioselective Gas Chromatography." *Journal of Agricultural and Food Chemistry* **52**(4): 736-41.

Liu, W., J. J. Gan, et al. (2004). "Isomer Selectivity in Aquatic Toxicity and Biodegradation of Cypermethrin." *Journal of Agricultural and Food Chemistry* **52**(20): 6233-8.

Liu, W., J. Gan, et al. (2005a). "Isomer Selectivity in Aquatic Toxicity and Biodegradation of Bifenthrin and Permethrin." *Environmental Toxicology and Chemistry* **24**(8): 1861-1866.

Liu, W., S. Qin, et al. (2005b). "Chiral Stability of Synthetic Pyrethroid Insecticides." *Journal of Agricultural and Food Chemistry* **53**(10): 3814-20.

Liu, W., J. Gan, et al. (2005c). "Enantioselectivity in Environmental Safety of Current Chiral Insecticides." *Proceedings of the National Academy of Sciences* **102**(3): 701-6.

Maund, S. J., M. J. Hamer, et al. (2002). "Partitioning, bioavailability, and toxicity of the pyrethroid insecticide cypermethrin in sediments." *Environmental Toxicology and Chemistry* **21**(1): 9-15.

Moran, K. D. (2007). "Urban Use of the Insecticide Fipronil—Water Quality Implications." Memorandum prepared for the UP3 Project. June 18.

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. San Francisco Estuary Institute Contribution 415. Oakland, CA.

Phillips, B. M., B. S. Anderson, et al. (2007). "Causes of Water Toxicity to Hyalella Azteca in the New River, California, USA." *Environmental Toxicology and Chemistry* **26**(5): 1074-1079.

Pyrethroid Working Group (PWG) (2007). *Residue Analytical Method for the Determination of Residues of Bifenthrin, Cypermethrin, Cyfluthrin, Deltamethrin, Esfenvalerate, Fenpropathrin, Lambda-Cyhalothrin and Permethrin in Sediment*. Prepared by Syngenta Crop Protection, Inc. February 5.

Qin, S., R. Budd, et al. (2006). "Enantioselective Degradation and Chiral Stability of Pyrethroids in Soil and Sediment." *Journal of Agricultural and Food Chemistry* **54**(14): 5040-5045.

Qin, S. and J. Gan (2006). "Enantiomeric Differences in Permethrin Degradation Pathways in Soil and Sediment." *Journal of Agricultural and Food Chemistry* **54**(24): 9145-9151.

Qin, S. and J. Gan (2007). "Abiotic Enantiomerization of Permethrin and Cypermethrin: Effects of Organic Solvents." *Journal of Agricultural and Food Chemistry* **55**(14): 5734-5739.

Riverside County Flood Control and Water Conservation District (Riverside County) (2007). *Santa Margarita Region Monitoring Annual Report Fiscal Year 2006-2007*.

Ruby, A. (2005). Technical Memorandum: Analysis of Bay Area Urban Creeks Monitoring, 2004-05. Prepared for the Clean Estuary Partnership (San Francisco Bay). December.

Ruby, A., (2006). CEP Urban Creeks Monitoring Plan 2005-06. Prepared for the Clean Estuary Partnership (San Francisco Bay) in cooperation with the Diazinon/Toxicity Work Group. February.

Scanlin, J. and A. Y. Feng (1997). *Characterization of the Presence and Sources of Diazinon in the Castro Valley Creek Watershed.* Prepared for the Alameda Countywide Clean Water Program and the Alameda County Flood Control and Water Conservation District. October 30.

Stormwater Monitoring Coalition (SMC), Bioassessment Working Group (2007). *Regional Monitoring of Southern California's Coastal Watersheds*. SCCWRP Technical Report 539. December.

TDC Environmental (2003). *Insecticide Market Trends and Potential Water Quality Implications*. Prepared for the San Francisco Estuary Project. April.

TDC Environmental (2005). *Annual Research and Monitoring Update 2005*. Prepared for the San Francisco Estuary Project. March.

TDC Environmental (2006). *Annual Research and Monitoring Update 2006*. Prepared for the San Francisco Estuary Project. April.

TDC Environmental (2007a). *Annual Review of New Scientific Findings 2007*. Prepared for the San Francisco Estuary Project. June.

TDC Environmental (2007b). *Improving Urban Pesticide Regulatory Activities to Protect Water Quality. Annual Update 2007*. Prepared for the San Francisco Estuary Project. January.

TDC Environmental (2007c). 2007. *Pesticides in Urban Surface Water: Urban Pesticides Use Trends Annual Report 2007*. Prepared for the San Francisco Estuary Project. June.

U.S. EPA Office of Research and Development (1985). *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*. PB85-227049.

USGS (2006a). "Pesticides in the Nation's Streams and Ground Water 1992-2001—A Summary." USGS Fact Sheet 2006-3028. March.

USGS (2006b). *Pesticides in the Nation's Streams and Ground Water 1992-2001*. USGS Circular 1291. March 15; revised February 15, 2007.

Wang, L., W. Liu, et al. (2007). "Enantioselectivity in Estrogenic Potential and Uptake of Bifenthrin." *Environmental Science & Technology* **41**(17): 6124-6128.

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." *Environmental Science & Technology* **38**(10): 2752-2759.

Weston, D. P., R. W. Holmes, et al. (2005). "Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides." *Environmental Science & Technology* **39**(24): 9778-9784.

Weston, D. P. and E. L. Amweg (2007). "Whole-Sediment Toxicity Identification Evaluation Tools for Pyrethroid Insecticides: II. Esterase Addition." *Environmental Toxicology and Chemistry* **26**(11): 2397-2404.

Weston Solutions (2006). *Toxicity Identification Evaluation (TIE) of County of San Diego and Copermittees Chollas Creek Stormwater Sample*. September.

Xu, C., J. Wang, et al. (2008). "Separation and Aquatic Toxicity of Enantiomers of the Pyrethroid Insecticide Lambda-Cyhalothrin." *Environmental Toxicology and Chemistry* **27**(1): 174-181.

Yang, W., J. Gan, et al. (2006a). "Effect of Suspended Solids on Bioavailability of Pyrethroid Insecticides." *Environmental Toxicology and Chemistry* **25**(6): 1585-1591.

Yang, W., F. Spurlock, et al. (2006b). "Effects of Dissolved Organic Matter on Permethrin Bioavailability to *Daphnia* Species." *Journal of Agricultural and Food Chemistry* **54**(11): 3967-3972.

Yang, W., F. Spurlock, et al. (2006c). "Inhibition of Aquatic Toxicity of Pyrethroid Insecticides by Suspended Sediment." *Environmental Toxicology and Chemistry* **25**(7): 1913-1919.

Yang, W. C., W. Hunter, et al. (2007). "Bioavailability of Permethrin and Cyfluthrin in Surface Waters with Low Levels of Dissolved Organic Matter." J*ournal of Environmental Quality* **36**(6): 1678-85.