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Pesticides in Urban Surface Water

Annual Research and Monitoring Update 2006

Prepared for the
San Francisco Estuary Project

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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 2.2.1 of its grant agreement with the State Water Resources Control Board (Agreement Number 04-076-552-0) for the Urban Pesticides Pollution Prevention Project (UP3 Project). Views or information expressed in this report may not necessarily reflect those of the funding agencies.

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1.0 INTRODUCTION

1.1 Background

The presence of pesticides in urban surface water and their environmental effects are topics 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 provide education, outreach, and technical assistance for implementation of the Diazinon and Pesticide-Related Toxicity in Bay Area Urban Creeks Water Quality Attainment Strategy and Total Maximum Daily Load (WQAS/TMDL) (Johnson 2005). The project is structured to mirror the three major elements of the WQAS/TMDL Implementation Strategy: Outreach and Education, Science (Research and Monitoring), and Proactive Regulation. 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 March 2007. TDC Environmental is providing technical support for the project.

1.2 Scope of This Report

This is the second 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 that was published during 2005. 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 update prepared for the UP3 Project (TDC Environmental 2005a), which should also be consulted by those seeking a full understanding of recent relevant scientific findings. The previous report predicted that use of pyrethroid insecticides in urban areas would be likely to cause adverse effects in aquatic ecosystems receiving urban runoff. The previous report also 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 2005).
- *New findings*. This update does not include studies with results consistent with previously findings (e.g., elevated diazinon concentrations in urban runoff or

surface water toxicity due to diazinon/chlorpyrifos), nor does it address pesticides that are not currently used (e.g., organochlorine pesticides).

- *The San Francisco Bay Area*. While the report includes literature from around the world, it focuses on the San Francisco Bay Area and on urban creeks, as the UP3 Project is designed specifically to support the San Francisco Bay Area urban creeks WQAS/TMDL.

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 most recent such report was published in mid-2005 (TDC Environmental 2005c).

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:

- Published scientific literature (e.g., peer-reviewed and other journals);
- Technical reports prepared for local, state, and Federal government agencies and technical comment letters on these reports;
- Scientific conference presentations and posters; and
- Interviews with agency staff and researchers.

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 exist for only a 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, the 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 compliance with National Pollutant Discharge Elimination System (NPDES) permits for municipal wastewater treatment plants and urban runoff programs. With the phase out of most urban uses of diazinon and chlorpyrifos, water quality agencies are shifting attention to the pyrethroids, which have the potential to cause toxicity in California's surface waters and permitted discharges (TDC Environmental 2003). For pyrethroids, environmentally relevant concentrations are about 1 nanogram/liter (part per trillion) in the water column and 1 nanogram/gram (dry weight) in sediment (TDC Environmental 2003; Amweg et al. 2005). In 2005, California analytical capabilities for pyrethroids continued to improve as described below.

2.2 Findings

<u>Capabilities for measuring environmentally relevant concentrations of pyrethroids in water and sediment are improving; however, additional work is needed to develop and validate analytical methods for pyrethroids[1] in environmental water and sediment samples</u>. Some research laboratories have developed methods to measure environmentally relevant concentrations of pyrethroids in surface waters and sediment (e.g., You and Lydy 2004). These research level methods have not proven feasible for all other laboratories to implement for several reasons, including the costly equipment required. Development of reliable methods is important—and is underway. The California Department of Pesticide Regulation (DPR), the U.S. Geological Survey (USGS), and the California Department of Fish and Game are collaborating, with grant funding, to develop and validate formal analytical methods to detect pyrethroids in water, sediments, and biological organisms. A mid-2005 San Francisco Estuary Institute survey of these laboratories showed that they have made great progress toward this goal (Oros and Werner 2005).

Two California commercial laboratories (Caltest Analytical Laboratory in Napa and CRG Marine Laboratories in Torrance) are advertising 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 been developing the capability to measure environmentally relevant concentrations of pyrethroids in water and sediment samples. These laboratories have yet to have the opportunity to demonstrate fully these capabilities for all pyrethroids of interest in various types of environmental water and sediment samples.

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[1] 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 2005b and 2005c).

Sample collection methods for water samples to be analyzed for pyrethroids are being developed. Methods for collection, storage, and laboratory preparation of environmental water samples for pyrethroids analysis are needed. These methods need to address losses by adsorption to sample container surfaces, which may be significant (Lee et al. 2002). U.S. EPA Region 9 is in the process of providing USGS with funding to develop the needed methods.

Toxicity identification evaluation (TIE) methods for pyrethroids are under development; recent progress is promising. U.C. Davis has developed an enzymatic procedure for pyrethroid toxicity removal that can be used to identify pyrethroid caused toxicity in laboratory water and sediment (Wheelock et al. 2004). Work is in progress on two California water bond grant-funded projects[2] looking into development and validation of this and other promising TIE procedures for pyrethroid toxicity identification in surface water and sediment.

Commercial laboratories offer methods for analysis of some other pesticides of concern (e.g., fipronil) but do not offer methods for others (e.g., polyhexamethylene biguanadine [PHMB]). Methods for analysis of environmentally important degradates (e.g., fipronil degradates) are also needed. The lack of chemical analysis methods with environmentally meaningful detection limits for pesticides and pesticide degradates that have the potential to cause toxicity incidents are 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 these analyses.

[2] "Tools for Surface Water Monitoring: Development of TIE Toxicity Testing, and Enzyme-Linked Immunosorbent Assay (ELISA) Procedures for Diazinon and Chlorpyrifos Replacements"—SFEP, AquaScience, U.C. Davis and TDC Environmental; "Investigation of the Sources and Effects of Pyrethroid Pesticides in the San Francisco Estuary"— San Francisco Estuary Institute, U.C. Davis Marine Pollution Studies Lab (Granite Canyon), CDFG, U.C. Santa Cruz, and Applied Marine Science.

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 been limited due to the understanding that monitoring results were unlikely to change until most urban uses of diazinon and chlorpyrifos were phased out. With the completion of the phase outs (in 2004 and 2005), monitoring is needed to evaluate the effects of the phase outs and the adoption of insecticide alternatives in the urban marketplace. Monitoring may also be able to identify other toxicity problems (e.g., chronic toxicity) that were masked by the toxicity due to organophosphorous pesticides.

3.2 Monitoring Program Overview: San Francisco Bay Area

Table 1 (on the next two pages) provides an overview of San Francisco Bay Area surface water and discharge monitoring programs for pesticides and surface water toxicity in urban areas. Funding for these monitoring activities comes from many sources, including municipal, state and Federal governments; California water bonds (primarily grants from the Pesticide Research and Identification of Source, and Mitigation or "PRISM" program); and the government agencies and private businesses that participate in the San Francisco Bay Regional Monitoring Program.

3.3 Monitoring Program Overview: Elsewhere in California

Table 2 (on page 8) reviews surface water and discharge monitoring programs for pesticides and surface water toxicity in urban areas. A relatively complete list of monitoring programs (albeit with few details on the actual monitoring) is available on the new California Coastal Monitoring Programs Internet site, http://www.sfei.org/camp/. SFEI compiled Central Valley pesticide-related monitoring projects (both agricultural and urban) in an appendix to its recent pyrethroids white paper (Oros and Werner 2005).[3]

3.4 Monitoring Data Availability

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.

[3] Available on the Internet: http://www.up3project.org/documents/pyrethroids_white_paper_final.pdf

Table 1. Bay Area Urban Surface Water Pesticide/Toxicity Monitoring Programs

Program	Program Overview
Regional	
Surface Water Ambient Monitoring Program (SWAMP)	SWAMP is a statewide surface monitoring program managed by the State and Regional Water Boards. Activities in each region vary; in the San Francisco Bay Region, SWAMP has concentrated on monitoring watersheds to determine if aquatic life is protected. Toxicity and some current-use pesticides have been included in Bay Area monitoring. See http://www.swrcb.ca.gov/swamp/ and the SWAMP section of http://www.waterboards.ca.gov/sanfranciscobay/Download.htm for more information.
Clean Estuary Partnership (CEP)	The CEP is 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 are 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 interest in pesticides monitoring relates to the development and implementation of the diazinon and pesticide-related toxicity in urban creeks WQAS/TMDL and diazinon and pesticide-related toxicity in San Francisco Bay. 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. It is not known whether the CEP will conduct pesticides monitoring in the future. See http://www.cleanestuary.org/ for more information.
San Francisco Bay Regional Monitoring Program (RMP)	The RMP is a collaborative monitoring program conducted by the 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 http://www.sfei.org/rmp/ for more information.
Municipal	
Urban runoff programs	Under NPDES permits, urban runoff programs are required to complete monitoring of surface waters. In the San Francisco Bay Area, monitoring requirements currently differ for each permittee (the proposed municipal regional permit would make future monitoring requirements consistent). Monitoring for pesticides and/or toxicity in urban creeks has occurred under current permits. For example, Alameda Countywide Clean Water Program, San Mateo Stormwater Pollution Prevention Program, Santa Clara Valley Urban Runoff Pollution Prevention Program, and the City of Palo Alto all planned pesticides or toxicity monitoring in 2004/05.

Table 1. Bay Area 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. 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 the chronic toxicity 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 Bay Area 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.

Table 2. California Urban Surface Water Pesticide/Toxicity Monitoring Programs

Agency/ Program	Overview of Program
California Department of Pesticide Regulation (DPR)	DPR conducts various surface water monitoring projects in California. All of its monitoring focuses on current-use pesticides. Studies are completed on a project basis, often in response to findings by other monitoring programs. DPR does not currently conduct status and trends monitoring. Some projects are conducted by DPR staff; others are completed by contractors (e.g., U.C. Riverside). DPR has not recently conducted many urban surface water monitoring projects. See the DPR Surface Water Protection Program Internet site (http://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 has included some current-use pesticides; however, it has not included most of the urban pesticides of concern listed in this report. (USGS scientists are working to address this issue.) See http://water.usgs.gov/nawqa/ for more information.
TMDL Implementation Monitoring	Some 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 draft monitoring plan includes water column and sediment monitoring for organophosphorous pesticides, pyrethroids, and toxicity (monitoring will not be initiated until the monitoring plan is finalized—anticipated in 2006). 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. It also has completed pesticides and toxicity-related special research projects with agency, grant, and contract funding. See http://www.sccwrp.org/ for more information.
Sacramento River Watershed Program (SRWP)	The SWRP 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 http://www.sacriver.org/resources/wqcompendium/.
Urban Runoff Programs	As mentioned in Table 1, urban runoff programs are required to monitor 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).
Municipal Wastewater Treatment Plants	As explained in Table 1, almost all municipal wastewater treatment plants are required to conduct effluent toxicity monitoring under their NPDES permits. Requirements for pesticide and toxicity testing are individually determined, but are relatively consistent across the state.

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

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 system currently has broad participation of monitoring programs.

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

- 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 (http://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 currently contains data from 49 studies. DPR accepts data submissions in any form, including hard copies of published reports, print-outs of tabular summaries with supporting documentation, and electronic submissions on diskette or by electronic mail. 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. Although the UP3 Project has tried to address this by posting documents on its monitoring and science web page, UP3 Project resources are not sufficient to identify, obtain, digitize, organize, and update a complete record of all relevant monitoring plans and reports, even for the San Francisco Bay Area.

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 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).

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,[4] there is no regional or statewide forum for communication of results or to provide topic-specific support for scientists managing pesticides and toxicity surface water monitoring.

[4] SFEI has hosted one such gathering and is planning a second for scientists that currently have State Water Board grant funding. These ad hoc meetings are being held to fulfill grant requirements to ensure that grantees do not conduct redundant research.

4.0 RELEVANT RESEARCH RESULTS

4.1 Background

In the last year, research 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 toxicity is severe. Nearly all sediments collected from a study of Roseville, California creeks, two-thirds of samples from Sacramento area creeks and more than half of samples from Alameda and Contra Costa County creeks caused toxicity to the test organism (Weston et al. 2005; Amweg et al. 2006). A meaningful fraction of samples (e.g., about half of the Roseville samples) caused nearly complete mortality. Researchers exploring the Roseville creek system found that the test organism (*Hyalella azteca)* was present, but its presence was limited to areas where the influence of urban runoff was relatively small (Weston et al. 2005). Conditions present in the studied areas are not unique; similar land use and pesticide use patterns commonly exist throughout California.
- The toxicity is widespread. Fifteen of the 18 Northern California urban creeks that were tested (on up to four occasions) were toxic on at least one sampling occasion (Amweg et al. 2006). The creeks that were tested were in three counties (Sacramento, Alameda, and Contra Costa). They included creeks in the City of Sacramento (seven creeks that together drain most of the City), Roseville (four creeks), and a total of eight creeks in Oakland, Orinda, Pittsburg, Richmond, San Leandro, and Walnut Creek.
- The toxicity is linked to urban runoff. In two creek systems (Pleasant Grove Creek and its tributaries in Roseville and Kirker Creek in Contra Costa County) samples were collected upstream of urban areas and in urban areas. Upstream samples did not exhibit toxicity and had low pyrethroid levels (Weston et al. 2005; Amweg et al. 2006). Once these creeks entered developed areas, nearly all sediment samples were toxic and contained pyrethroid insecticides at several times the concentration that is lethal for the test species. Study areas were selected to avoid areas receiving agricultural runoff. No study areas had been subject to mosquito abatement treatments with pyrethroids.
- Multiple pyrethroids contribute to the toxicity; bifenthrin is the largest contributor. Sediment pyrethroid concentrations correlated with the observed toxicity in most cases (alternative potential causes, like other pesticides, were also examined and found not to contribute meaningfully to the toxicity). In all of the urban

creeks, bifenthrin was the primary cause of the toxicity. Most of the other commonly used pyrethroids also contributed to toxicity—cyfluthrin, cypermethrin, deltamethrin, and lambda-cyhalothrin were found to contribute to toxicity in one or more samples (Weston et al. 2005; Amweg et al. 2006).

- Toxicity was not found in creeks draining residential areas in Tennessee. None of the sediments collected from 12 Tennessee creeks were toxic; pyrethroids were rarely detectable. The reasons for the difference between California and Tennessee samples are not clear. The authors note differences in climate, types of residential development, and pesticide use practices. Differences in urban runoff management are very likely to contribute to the observed difference. At the California sampling areas, piped storm drain systems efficiently convey urban runoff directly to creeks without any form of treatment. In contrast, the Tennessee areas sampled are not served by storm drain systems; drainage is via overland flow through the large, landscaped lots in the residential area. Flow through vegetated areas has proven to be extremely effective at removing pyrethroids from runoff. For example, a recent study found >99.9% removal of pyrethroids after flowing through a 400 meter vegetated ditch (Bennett et al. 2005).

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. The UP3 Project analyzed data on pesticide use, pesticide sales, and product labels to identify urban use patterns for each pyrethroid that has been found to cause or contribute to toxicity in Northern California urban creeks. While it is not possible to determine exact percentage contribution from each application type, the data suggest that applications by both professionals and over-the-counter purchasers contribute to pyrethroid levels in runoff. Relative contributions by various user categories are compound specific. For example, almost all urban cypermethrin use is by professional applicators (Mumley 2006), but almost all esfenvalerate use is by consumers (TDC Environmental 2005b).

Although most termiticide applications are made by underground injection (where they are unlikely to contribute to urban runoff), pyrethroid applications for pre-construction termiticide control may also contribute to toxicity if a storm event occurs subsequent to application and before foundations are completed and runoff is conveyed to creeks without treatment capable of removing pesticides (Mulley 2006).

Outdoor structural pest control applications are of particular interest for water quality. Of the various uses of pyrethroids, outdoor structural pest control applications are the ones most likely to involve treatment of outdoor impervious surfaces (e.g., pavement and building surfaces), which have much higher pesticide washoff fractions than pervious surfaces (e.g., lawns and gardens). These applications are most likely to be the major source of pyrethroids in urban creeks (Moran 2005).

Aquatic sediment acute toxicity data for most—but not all—commonly used pyrethroids are available. The two standard toxicity testing species used for freshwater aquatic sediments were tested. *Hyalella azteca* have proven to be more sensitive to pyrethroids than *Chironomus tentans*. LC50[5] data have been published for seven pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, and permethrin) (Amweg et al. 2005; Maund et al. 2002). Data are still needed for other

[5] The LC50 is the concentration that kills 50% of the test organisms during the test time period.

pyrethroids—of the other pyrethroids, beta-cyfluthrin and tralomethrin are the highest priorities based on urban use rates.

The presence of organic matter in the sediments moderates toxicity.[6] To reflect the importance of organic matter, toxicity data are expressed as a ratio of the pyrethroid concentration to the concentration of organic carbon in sediments (see Table 3). These LC50s are only slightly above the current analytical detection limits of the most capable research laboratories.

Table 3. Toxicity of Pyrethroids to *Hyalella azteca*

Pyrethroid	Average sediment 10-Day LC50 (µg/g organic carbon)
Bifenthrin	0.52
Cyfluthrin	1.08
Cypermethrin	0.38
Deltamethrin	0.79
Esfenvalerate	1.54
Lambda-Cyhalothrin	0.45
Permethrin	10.83

Source: Maund et al. 2002 (cypermethrin); Amweg et al. 2005 (all others).

Adverse effects to aquatic ecosystems are likely to occur at concentrations below the LC50. Pyrethroids appear to cause various types of sub-lethal toxicity to aquatic organisms at concentrations below the LC50. *Hyalella azteca* growth was significantly inhibited at concentrations roughly one-third to one-half of the LC50s listed in Table 3 (Amweg et al. 2005). Sublethal effects can be subtle; for example, a researcher reported that exposure to relatively low concentrations of esfenvalerate (25-400 ng/l) caused the indigenous Pacific Northwest caddisfly *Brachycentrus americanus* to exit its case prematurely and to exhibit impaired ability to rebuild cases even after removal to an esfenvalerate-free system (Johnson et al. 2005).

Differences in the environmental fates of individual pyrethroids in creek sediments may be relevant to understanding aquatic toxicity patterns. Bifenthrin degrades much more slowly in sediments than permethrin (Gan et al. 2005), suggesting that its persistence (along with its high toxicity and heavy urban use) may be a contributing factor to its common identification as a major contributor to aquatic toxicity in Northern California urban creeks.

Differences in the toxicity and environmental fate of individual pyrethroid isomers may be relevant to understanding aquatic toxicity patterns. Pyrethroids are “chiral compounds,” which means that their structures have a specific rotational direction (like a right or left hand). They are often mixtures of substances with the same chemical formula, but different chirality (these are generally called “isomers”). Recent research has found that pyrethroid isomers can differ significantly in their toxicity to aquatic organisms (Liu et al. 2005a; Liu et al. 2005b). Some isomers degrade at different rates, which can significantly increase the potency of the remaining material (Liu et al. 2005a; Liu et al. 2005b). Measuring isomers individually is challenging. Current laboratory analytical methods are not capable of differentiating most pyrethroid isomers in environmental samples. Isomers are important for other pesticides as well—for example, the toxicity of fipronil isomers differs significantly (Konwick et al. 2005).

[6] Binding to organic materials probably reduces pyrethroid bioavailability.

An updated compilation of background information on pyrethroids was published by the San Francisco Estuary Institute (SFEI). In 2005, SFEI completed a white paper on pyrethroids that includes a great deal of valuable reference material. The paper, *Pyrethroid Insecticides: An Analysis of Use Patterns, Distributions, Potential Toxicity and Fate in the Sacramento-San Joaquin Delta and Central Valley* (Oros and Werner 2005)[7] includes updated summaries of aquatic toxicity data for pyrethroids, a list of pesticide watershed monitoring programs in California's Central Valley, a review of pyrethroids' modes of toxic action, and an evaluation of the potential for pyrethroids to cause adverse effects in surface water ecosystems.

4.3 Findings: Monitoring

San Francisco Bay Area urban creek monitoring data show a recent decrease in diazinon levels and some toxicity (primarily chronic toxicity) in creek water. The Clean Estuary Partnership coordinated with San Francisco Bay Area urban runoff monitoring programs to collect samples to test for pesticides and toxicity in urban runoff in the 2004/05 wet season. It then compiled and analyzed all available Bay Area urban creek monitoring data for pesticides and toxicity in the 2004/05 season to draw the following conclusions (Ruby 2005):

- Diazinon concentrations appear to be decreasing, as expected. Diazinon concentrations were much lower than those observed in Bay Area creeks in the 1990s, when elevated diazinon concentrations were associated with widespread toxicity of creek water to the standard test organism *Ceriodaphnia dubia*. Only one of the 37 creek water samples tested for diazinon exceeded the WQAS/TMDL target concentration of 100 ng/L (Johnson 2005).
- Malathion concentrations are of concern. Malathion was the second most commonly detected pesticide in the 2004-05 urban creek samples. Two samples exceeded the U.S. EPA-recommended chronic water quality criterion of 100 ng/L, and one exceeded the California Department of Fish and Game acute criterion of 430 ng/L (CDFG 1998).
- Aquatic toxicity was found, but it did not have a consistent pattern. More than 25% (16 of 57) of water samples exhibited toxicity. Most of the toxicity was chronic (sublethal), rather than acute. There was no consistent pattern of toxicity—individual samples exhibited toxicity to each of the three standard test species (the fathead minnow *Pimephales promelas*, the small crustacean *Ceriodaphnia dubia*, and the alga *Selenastrum capricornutum*).

Caution should be exercised in interpreting these results as this is a relatively small data set covering only one rainy season. (Note that available sediment monitoring data are summarized in the previous subsection.)

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. The USGS released a new national synthesis of its findings in early 2006. Among its major findings (USGS 2006a; USGS 2006b):

- Pesticides are frequently present in streams. Pesticides and degradates are typically present throughout most of the year in streams draining urban areas.
- Urban streams had concentrations that exceeded one or more water quality benchmarks for aquatic life or fish-eating wildlife at 83% of NAWQA monitoring

[7] Available on the Internet: http://www.up3project.org/documents/pyrethroids_white_paper_final.pdf

sites. In urban areas, the insecticides diazinon, chlorpyrifos, and malathion most frequently exceeded monitoring benchmarks. Frequencies of exceedance declined during the study period. (Note that the study period, 1993-2001, ended prior to the phase out of most urban uses of diazinon and chlorpyrifos).

- The pesticides most commonly used at the time the monitoring was conducted were detected most frequently in streams. Five herbicides commonly used in urban areas—simazine, prometon, tebuthiuron, 2,4-D, and diuron—and three commonly used insecticides—diazinon, chlorpyrifos, and carbaryl—were most frequently detected in urban streams, often at concentrations higher than found in agricultural streams.
- In surface water, pesticides occur most commonly in mixtures, rather than individually. Degradates are common among these mixtures.

While the USGS NAWQA is the nation's most comprehensive water quality monitoring program, it does not monitor for many current use pesticides, including most pyrethroids, PHMB, and fipronil.

Unknown toxicity has been identified in various California surface waters and discharges. Because analytical chemical methods with environmentally relevant detection limits and toxicity identification evaluation methods do not exist or are not widely commercially available for many current use pesticides (e.g., pyrethroids, PHMB), it is not possible to determine whether pesticides are causing or contributing to cases of unknown toxicity. The Sacramento Regional County Sanitation District has experienced chronic effluent toxicity to *Ceriodaphnia dubia* since April 2004 (Maidrand and Bennett 2005); it is not clear if changes in the pesticide market have contributed to this toxicity. The authors of a study identifying unknown toxicity in the Ballona Creek and Dominguez estuaries (Southern California Bight) suspect based on preliminary toxicity identification evaluation results that current use pesticides may contribute to the toxicity (Bay et al. 2005).

4.4 Other Findings

Stress from exposure to disease, in combination with pesticide exposures, can adversely affect organisms at concentrations below documented EC50s and LC50s. While ordinary ecosystems include diseases, typical laboratory toxicity testing systems do not. Researchers explored the link between exposure to pesticides and the effects of a common virus. Juvenile Chinook salmon (*Oncorhynchus tshawytscha*) exposed to sublethal levels of esfenvalerate in combination with a common salmon virus (infectious hematopoietic necrosis virus) were more likely to become ill and were more likely to die sooner than fish exposed to the virus alone. The authors concluded that such joint exposures could compromise survivorship of wild fish populations (Clifford et al. 2005).

The toxicity of a formulated pesticide may be substantially greater than the toxicity of the active ingredient alone. Formulated pesticides contain ingredients other than the active ingredient. These other ingredients are usually called "inert ingredients" to differentiate them from the active ingredient—but they are not necessarily biologically inert substances. An example of the potential importance of other ingredients in formulated products is provided by an investigation of the toxicity of Roundup to juvenile amphibians, which found that the formulated product Roundup had much greater toxicity to frogs than would have been anticipated for exposure to the active ingredient (glyphosate) alone. The toxicity was attributed to a surfactant in the formulated product (polyehtoxylated tallowamine or POEA) (Relyea 2005).

Zinc pyrithione can be converted to the more stable and toxic copper pyrithione in the presence of copper. Zinc pyrithione is a marine antifouling coating biocide that may supplement or serve as an alternative to copper. It is very highly toxicity to aquatic life (U.S. EPA 2004a). In the presence of free copper metal ions (Cu^{2+}), which are commonly present in marinas (because copper is released from copper-containing marine antifouling paints), zinc pyrithione can be converted into copper pyrithione. Copper pyrithione is more stable and more toxic than zinc pyrithione (Grunnet and Dahllof 2005).

Toxic concentrations of herbicides can appear in urban runoff. Although insecticides are more likely to be present at toxic levels in waterways draining urban areas (Hoffman et al. 2000; Gilliom and Martin 2004), a recent study found that levels of herbicides measured in highway runoff can cause toxicity to the standard aquatic plant test species (*Selenastrum*, an alga). The study used runoff from Highway 37, Sonoma County, California, spiked with the highest concentrations of various herbicides (isoxaben, oryzalin, diuron, clopyralid, and glyphosate) measured in previous highway runoff studies, to explore the "worst case" runoff conditions. Diuron (individually) and isoxaben and oryzalin (in combination) produced significant reductions in algal growth (Huang et al. 2005).

Endothall salts differ in aquatic toxicity. Some California municipalities apply endothall-containing products (Hydrothol or Aquathol) to control algae in surface water. According to a U.S. EPA environmental risk assessment for Endothall, one chemical form—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). According to U.S. EPA, "[t]hese salts have dissimilar toxicity properties, with the endothall N,N-dimethylalkylamine salt being far more (2-3 orders of magnitude) toxic (acute and chronic) to aquatic animals than the dipotassium salt." The risk assessment found significant risks to aquatic organisms from use of both forms of endothall. The risk levels of the more toxic form were larger and encompassed more classes of organisms (U.S. EPA 2005b).

Copper-based wood preservatives may comprise a meaningful source of copper releases into adjacent surface waters. The use of copper as a wood preservative has increased in response to the phase-out of chromated copper arsenate preservatives. Copper can leach from preserved wood into the environment. Leaching rates for non-water applications (e.g., decking and fencing) (USFS 2001) are small compared to leaching rates for wood in water (e.g., shoring or piles) (Rice et al. 2002). A recent report estimated that releases in areas with large surface areas of treated wood (e.g., marinas) may be on the same order of magnitude as releases of copper from marine antifouling paint (Process Profiles 2006).

U.S. EPA environmental risk assessments predict aquatic toxicity from ordinary use of various pesticides, including permethrin, cypermethrin, metaldehyde, pyrethrins, and the synergists piperonyl butoxide and MGK-264. Although U.S. EPA environmental risk assessments are based on conservative assumptions and often rely on limited data, findings of significant risks to aquatic organisms indicate that a pesticide has the potential to cause or contribute to adverse impacts on surface water quality. In 2005, U.S. EPA released environmental risk assessments that predicted aquatic toxicity from use of permethrin (U.S. EPA 2005a), cypermethrin (U.S. EPA 2005d), metaldehyde (U.S. EPA 2005c), pyrethrins (U.S. EPA 2005e), and the synergists piperonyl butoxide (U.S. EPA 2005f) and MGK-264 (U.S. EPA 2004b).

5.0 CONCLUSIONS AND RECOMMENDATIONS

This section summarizes the conclusions and recommendations based on 2005 research findings. The findings and recommendations of the 2005 report (TDC Environmental 2005a) and UP3 Project should also be consulted; these still hold true except as updated by new findings in this report. 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 2005b) and an analysis of urban pesticide sales and use trends (TDC Environmental 2005d). 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.

<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.

<u>Conclusion 3</u>: *Capabilities for measuring environmentally relevant concentrations of pyrethroids in water and sediment are improving; however, additional work is needed to develop and validate analytical methods for pyrethroids in environmental water samples (including wastewater samples).* Method development has been a priority for several years and is being pursued by several California laboratories. Because multiple pyrethroids are usually present in urban water bodies, methods need to be capable of measuring all common pyrethroids at once.

<u>Conclusion 4</u>: *Capabilities for measuring other pesticides of concern and pesticide degradates are needed.* The most important gaps are fipronil (and its degradates) and 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 statewidel database (this could change if voluntary participation in one of two statewide systems increases). Monitoring plan 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

Chemical Analysis

Recommendation 1: *Support activities to improve chemical analytical and toxicity testing capabilities for pesticides in surface water (water column and sediment), urban runoff, and municipal wastewater treatment plant effluent*. The suggested near-term priority that is not currently being addressed is development of chemical analysis methods with environmentally meaningful detection limits for PHMB and fipronil (and fipronil degradates). Creating methods that are feasible for commercial laboratories is particularly important, since contractors (rather than agency or university laboratories) perform the chemical analysis of most surface water quality samples collected in California.

Monitoring

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[8], carbaryl, malathion, PHMB, and fipronil and its degradates).* A long-term surveillance monitoring program is needed. Specific monitoring recommendations are as follows:[9]

- 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 *Ceriodaphnia dubia*; sediment—*Hyalella azteca)*.
- Pyrethroids monitoring should include bifenthrin, cyfluthrin (including beta-cyfluthrin), cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin.
- Monitoring of pyrethroids in sediments is a higher priority than monitoring for them in the water column. Because pyrethroid toxicity is inversely correlated with organic carbon concentration, when monitoring for pyrethroids in sediments, organic carbon concentrations should also be measured.
- Recommended detection limits 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)
  - 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—0.1 micrograms/liter
  - Fipronil and degradates in sediment—30 nanogram/gram (dry weight)

The Clean Estuary Partnership designed a monitoring program that—if implemented—would fulfill these recommendations for the San Francisco Bay Area (Ruby 2006).

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[8] The pyrethroids of greatest interest for urban surface water quality are bifenthrin, cyfluthrin (including beta-cyfluthrin), cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin.
[9] 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, TDC Environmental 2005a, and Oros and Werner 2005) and best professional judgment. The pyrethroids selection is based on evaluation of urban pesticide use (see TDC Environmental 2005b and 2005c).

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

Recommendation 3: Compile pesticide-related water quality monitoring data in one readily accessible location. The compilation could be regional (e.g., by Water Board region) or statewide. All monitoring reports for pesticides in surface water should be submitted to DPR for inclusion in its surface water database.[10] Creating an Internet site that contained monitoring plans and final reports would be extremely useful to pesticide and water quality researchers, managers, and regulators. The UP3 Project has compiled some information on its web site[11] and in this report; however, the budget necessary to compile and update a reasonably complete Internet site exceeds UP3 Project resources.

Recommendation 4: 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 (e.g., a multi-year version of the recent Clean Estuary Partnership Analysis of Bay Area Urban Creeks Monitoring, 2004-05) (Ruby 2005).

Management

Recommendation 5: 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 6: 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.

[10] See DPR's Internet site (http://www.cdpr.ca.gov/docs/sw/surfdata.htm) for information on data submittal.
[11] http://www.up3project.org/up3_monitoring.shtml

6.0 REFERENCES

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.

Bay, S. M., T. Mikel, K. Schiff, S. Mathison, B. Hester, D. Young, and D. Greenstein (2005). *Southern California Bight 2003 Regional Monitoring Program: I. Sediment Toxicity*. Southern California Coastal Water Research Project. Westminster, CA.

Bennett, E. R., M. T. Moore, et al. (2005). "Vegetated Agricultural Drainage Ditches for the Mitigation of Pyrethroid-Associated Runoff." *Environmental Toxicology and Chemistry* **24**(9): 2121-2127.

California Department of Fish and Game (CDFG), Office of Spill Prevention and Response (1998). *Hazard Assessment of the Insecticide Malathion to Aquatic Life in the Sacramento-San Joaquin River System*, Administrative Report 98-2.

Clifford, M. A., K. J. Eder, et al. (2005). "Synergistic effects of esfenvalerate and infectious hematopoietic necrosis virus on juvenile Chinook salmon mortality." *Environmental Toxicology and Chemistry* **24**(7): 1766-72.

Gan, J., S. J. Lee, et al. (2005). "Distribution and persistence of pyrethroids in runoff sediments." *Journal of Environmental Quality* **34**(3): 836-41.

Gilliom, R. J. and J. Martin (2004). "The Prevalence of Pesticide Mixtures in U.S. Streams." SETAC 25th Annual Meeting, Portland.

Grunnet, K. S. and I. Dahllof (2005). "Environmental Fate of the Antifouling Compound Zinc Pyrithione in Seawater." *Environmental Toxicology and Chemistry* **24**(12): 3001-3006.

Hoffman, R. S., P. D. Capel, and S. J. Larson (2000). “Comparison of Pesticides in Eight U.S. Urban Streams.” *Environmental Toxicology and Chemistry* **19**(9): 2249-2258.

Huang, X., S. Fong, et al. (2005). "Toxicity of Herbicides in Highway Runoff." *Environmental Toxicology and Chemistry* **24**(9): 2336-2340.

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.

Johnson, K., J. Jenkins, et al. (2005). “Exposure to Esfenvalerate Induces Case-leaving in the Caddisfly *Brachycentrus americanus*.” Poster presentation. SETAC North America 26th Annual Meeting, Baltimore, MD, Society of Environmental Toxicology and Chemistry. November.

Konwick, B. J., A. T. Fisk, et al. (2005). "Acute Enantioselective Toxicity of Fipronil and Its Desulfinyl Photoproduct to *Ceriodaphnia Dubia*." *Environmental Toxicology and Chemistry* **24**(9): 2350-2355.

Lee, S., J. Gan and J. Kabashima (2002). "Recovery of Synthetic Pyrethroids in Water Samples During Storage and Extraction." *Journal of Agricultural and Food Chemistry* **50**(25): 7194-7198.

Liu, W., J. Gan, et al. (2005a). "Enantioselectivity in environmental safety of current chiral insecticides." *Proceedings of the National Academy of Sciences* **102**(3): 701-6.

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

Maidrand, M., and A. Bennett (2005). "Sacramento Regional WWTP Ceriodaphnia Chronic Toxicity Fact Sheet." Informal poster presented at the SETAC 26th Annual Conference, Baltimore. November.

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. (2005). "Sources of Pyrethroids in Urban Runoff," Poster presentation at the 7th Biennial State of the San Francisco Estuary Conference, Oakland, October.

Mumley, T. (2006). "Risk Assessments and Risk Reduction Options for Cypermethrin (Docket No. OPP–2005–0293)." Letter from California Regional Water Quality Control Board to U.S. EPA Office of Pesticide Programs, February 23.

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.

Process Profiles (2006). *Copper Released from Non-Brake Sources in the San Francisco Bay Area.* Prepared for the Brake Pad Partnership. January.

Relyea, R. A. (2005). "The Impact of Insecticides and Herbicides on the Biodiversity and Productivity of Aquatic Communities." *Ecological Applications* **15**(2): 618-627.

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.

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

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

TDC Environmental (2005b). *Urban Pesticides Use Trends Annual Report 2005*. Prepared for the San Francisco Estuary Project. March.

TDC Environmental (2005c). *San Francisco Bay Area Pesticide Retail Store Survey*. Prepared for the San Francisco Estuary Project. September.

TDC Environmental (2005d). *Improving Urban Pesticide Regulatory Activities to Protect Water Quality. Annual Update 2005*. Prepared for the San Francisco Estuary Project. December.

U.S. EPA (2004a). "Zinc Pyrithione Ecological Hazard and Environmental Risk Characterization Chapter for the Reregistration Eligibility Decision (RED) Document (D301371)." Memorandum from K. Montague to R. Petrie, U.S. EPA Office of Pesticide Programs, April 15.

U.S. EPA (2004b). "Screening Ecological Risk Assessment for the Reregistration of MGK-264 Insecticide Synergist.

U.S. EPA (2005a). "EFED Revised Risk Assessment for the Reregistration Eligibility Decision on Permethrin After Error Corrections Comments from the Registrant, Phase I." July 12.

U.S. EPA (2005b). "Environmental Fate and Ecological Risk Assessment for Endothall." April 22.

U.S. EPA (2005c). "Level I Screening Ecological Risk Assessment for the Reregistration of Metaldehyde."

U.S. EPA (2005d). "Revised EFED Risk Assessment for the Reregistration Eligibility Decision (RED) on Cypermethrin After 30-Day "Error Only" Comment Period." October 25.

U.S. EPA (2005e). "Revised Pyrethrins RED Chapter After 60-Day Comment Period." September 9.

U.S. EPA (2005f). "Screening Ecological Risk Assessment for the Reregistration of Piperonyl Butoxide Insecticide Synergist. January.

U.S. Forest Service (USFS) (2001). "Techline Durability: Coatings Minimize Leaching from Treated Wood." Forest Products Laboratory. November.

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.

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.

Wheelock, C. E., J. L. Miller, M. J. Miller, S. J. Gee, G. Shan and B. D. Hammock (2004). "Development of Toxicity Identification Evaluation Procedures for Pyrethroid Detection Using Esterase Activity." *Environmental Toxicology and Chemistry* **23**(11): 2699-2708.

You, J. and M. J. Lydy (2004). "Solid Phase Micro-Extraction of Pyrethroid, Organophosphate and Organochlorine Pesticides in Water and Sediment." SETAC 25th Annual Conference, Portland.