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Pesticides in Urban Surface Water

Annual Review of New Scientific Findings 2007

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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).

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1.0 INTRODUCTION

1.1 Background

The environmental effects 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 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 2009. TDC Environmental is providing technical support for the UP3 Project.

1.2 Scope of This Report

This is the third 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 2006. 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 2005, 2006a), which should also be consulted by those seeking a full understanding of recent relevant scientific findings. The previous reports summarized initial 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 2006).
- *New findings*. This update does not include studies with results consistent with previously findings (e.g., reports of elevated diazinon concentrations in urban 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 and the San Francisco Bay Area*. While the report includes literature from around the world, it focuses on California, the San Francisco Bay Area and on urban creeks, as the UP3 Project is supported by California state funds and 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 next such report is anticipated in mid-2007.

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, 2006a). 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 2006 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[1] 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 diazinon and chlorpyrifos, water quality agencies are shifting attention to the pyrethroids, 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 2006, California analytical capabilities for pyrethroids continued to improve as described below.

2.2 Findings

Chemical Analysis

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[2] in environmental water, wastewater, biosolids, and sediment samples. Some research laboratories have developed methods to measure environmentally relevant concentrations of pyrethroids in surface waters and sediment (e.g., You and Lydy 2004a). 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 that can be reproduced by a broader range of laboratories is important—and is underway. 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 are collaborating, with grant funding, to develop and validate formal analytical methods to

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[1] "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).

[2] 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). Other pyrethroids are also used in agricultural areas.

detect pyrethroids in water, sediments, and biological organisms by the end of 2007 (see http://www.cdpr.ca.gov/docs/sw/swpyreth.htm for the status of this effort).

The Pyrethroid Working Group (a consortium of pyrethroid insecticide manufacturers) has given presentations indicating that it has developed a method to measure environmentally relevant concentrations of pyrethroids in sediments (Dobbs et al. 2007). Although this method has not been made available to the public, it reportedly relies on a method requiring 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.

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 developed the capability to measure environmentally relevant concentrations of pyrethroids in water and sediment samples (Woudneh and Oros 2006a, 2006b). These laboratories have begun to receive monitoring samples, primarily for water column and sediment analyses, but have not yet had the opportunity to demonstrate fully these capabilities for all pyrethroids of interest in municipal wastewater treatment plant effluent and sludge samples.

<u>Typical chemical analysis methods capable of measuring environmentally relevant concentrations of pyrethroids cannot distinguish tralomethrin from deltamethrin</u>. Tralomethrin completely degrades into deltamethrin during chemical analysis using common laboratory methods equipment (gas chromatography) (Woudneh and Oros 2006a; Valverde et al. 2002). Unless a report or paper specifies that chemical analysis methods used were capable of distinguishing these two compounds (e.g., that liquid chromatography[3] was used), it is likely that reported quantities of deltamethrin or tralomethrin are a sum of the two pyrethroids—and could represent one, both, or a mixture of the two compounds.

<u>Methods and materials allowing for routine quantification of environmentally relevant concentrations of individual pyrethroid isomers are needed</u>. Recent research has found that pyrethroid isomers can differ significantly in their toxicity to aquatic organisms (Liu et al. 2005a; Liu et al. 2005b); and fates (Gan et al. 2005). Current low-detection limit chemical analysis methods for pyrethroids are capable of distinguishing many pyrethroid isomers, but procedures to identify and quantify isomers are not developed to the point that they are routine. Among the challenges is that single-isomer standards are not readily available for all pyrethroids. Measurement capabilities will be needed to determine if these differences are environmentally significant.

<u>Sulfur, which is common in sediment, interferes with analysis of pyrethroids concentrations, but can be removed</u>. Laboratories should be aware of this potential interference and remove excess sulfur prior to measuring sediment pyrethroids concentrations (You and Lydy 2004b).

<u>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</u>. In 2003, the U.S. Geological Survey (USGS) published a method that it has used for some monitoring projects under the National Water Quality

[3] Liquid chromatography methods have higher detection limits for pyrethroids than gas chromatography methods (detection limits are higher than the lowest environmentally relevant concentrations).

Assessment (NAWQA) program. This method (Madsen et al. 2003) covers fipronil and four major degradates. It has an initial method reporting limit of >0.010 µg/l for all compounds. There are issues with recovery of fipronil and one degradate from samples that limit data accuracy at low concentrations (Madsen et al. 2003). USGS chemists in Sacramento have developed improved methods for both water column and sediment analyses of fipronil and three degradates. Both improved methods are being prepared for journal publication (Hladik 2007). 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.

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.

Sample Collection and Storage

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 has provided the USGS with funding to develop the needed methods, which USGS plans to test in 2007-2008 (Hladik 2007). The goal of the U.S. EPA-funded USGS work is to produce a formal standard operating procedure for collecting and storing water and sediment samples to be analyzed for pyrethroids.

Sediment sampling procedures exist. Most monitoring programs are using procedures employed by U.C. Berkeley (see Amweg et al. 2006a). Note that these procedures avoid use of Teflon; this is appropriate because pyrethroids have been demonstrated to partition quickly to Teflon surfaces (Wheelock et al 2005).

Water samples collected for analysis of pyrethroids concentrations should be refrigerated and analyzed as soon as possible, preferably within 24 hours of collection—and no later than 3 days after collection. Laboratories involved in developing chemical analysis methods for environmentally relevant concentrations of pyrethroids have explored pyrethroid losses during sample storage. The CDFA laboratory found decreased pyrethroids recovery in four days of holding time for water samples (CDFA 2006). If samples cannot be analyzed immediately, two methods to increase holding time are available. Researchers have found that samples that have been transferred to solid media (e.g., by extracting onto solid phase extraction [SPE] cartridges) can be stored in the freezer for up to one month without significant losses (Hladik 2007). Alternatively, samples intended for liquid-liquid extraction can be spiked with hexane to serve as a "keeper," allowing sample storage in a refrigerator for up to one month (CDFA 2006).

Sediment samples collected for analysis of pyrethroids can be stored frozen for up to one year. No significant losses were found in sediment samples frozen for more than a month (Pyrethroids Method Development Project 2007). The USGS has found that sediment can safely be stored in the freezer for up to one year (Hladik 2007).

<u>Glass containers are preferred for pyrethroids water samples. Samples can be agitated to return pyrethroids to solution</u>. Pyrethroids are known to adhere to the walls of sample containers (Lee et al. 2002). An evaluation of a variety of container types found that glass was the preferred container for pyrethroids water samples. Agitation (e.g., by vigorous shaking or vortexing) was found to be sufficient to cause pyrethroids that had adhered to glass container walls to return to solution (Wheelock et al 2005).

Toxicity Identification Evaluations (TIEs)

<u>Toxicity identification evaluation (TIE) methods for pyrethroids are progressing well and moving towards standardization</u>. In 2007, two California water bond grant-funded projects[4] exploring TIE procedures for pyrethroid toxicity identification in surface water and sediment will be completed. Methods developed from this research (e.g., an enzymatic procedure for pyrethroid toxicity removal [Wheelock et al. 2004, Wheelock et al. 2006]) have already expanded TIE capabilities for pyrethroids (Phillips et al. 2006; Anderson et al. 2006).

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. Preliminary reports from researchers using these lines of evidence (e.g., Phillips et al. 2007; Weston 2007) suggest that it is likely methods under development will be able to provide acceptable reliability.

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.

Development of TIE methods for pyrethroids has proven particularly challenging because method development requires the ability to measure low concentrations of the toxicant, which remains a challenge for pyrethroids. Type of columns, solvents, and flow rates used to extract and elute pyrethroids from sediment and porewater continues to be subject of research in developing TIE methods.

[4] “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—and data from monitoring that is conducted need to be compiled—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.

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/rwqcb5/programs/irrigated_lands/index.html

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

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 11) 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).[5]

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

Table 1. San Francisco 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 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's interest in pesticides monitoring related 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. 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 (stormwater) programs	Under National Pollutant Discharge Elimination System (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 creek water and/or sediments 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 recently conducted pesticides or toxicity monitoring.

Table 1. San Francisco 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 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 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 conducted many urban surface water monitoring projects recently; however, it is currently completing a marina monitoring project evaluating marine antifouling biocides and a Sacramento County urban creek monitoring project. 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 is beginning to include current-use pesticides that the UP3 Project has identified as priorities; however, past monitoring did not include most of the urban pesticides of concern listed in this report. (USGS scientists have and are continuing to expand chemical analysis capabilities to include more pesticides.) 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 (which should be initiated in 2007) 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. 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 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 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, 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.
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.

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.

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 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.

<u>Pesticide monitoring program planning is often short term and sometimes ad-hoc</u>. 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 pesticide monitoring 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.

<u>Scientists involved in surface water quality monitoring for pesticides and toxicity have no regular communications forum</u>. 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 RESEARCH RESULTS

4.1 Background

Recent 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. 2006a). 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 2006a) described four main findings of published research, which have not been modified by additional studies published in the last year (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.

Aquatic sediment acute toxicity data for most—but not all—commonly used pyrethroids are available; however, chronic toxicity data are needed. Acute 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 2006a]). Chronic toxicity data are not yet available for pyrethroids. Through a regulatory process called reevaluation, DPR is requiring that pyrethroid product manufacturers develop these data for most pyrethroids.

Widespread applications of synergists in a watershed has the potential to increase toxicity of pyrethroids in sediments. A series of aerial applications of an insecticide product containing pyrethrins and the synergist piperonyl butoxide (PBO) in the Sacramento area in 2005 offered a unique opportunity to investigate the potential for the synergist to affect creeks in the watershed. Limited sampling of creek waters by the Sacramento-Yolo Mosquito and Vector Control District immediately prior to application, a few hours after application, and about 18 hours after application found relatively low levels of pyrethrins (below the lowest acute aquatic toxicity values), but could not evaluate the effect of the pyrethrins/synergist combination. The District sampling found concentrations of PBO up to 20 µg/l (detected in 50% of the samples, generally in the range of 2-5 µg/l) (Zeigler 2006).

A larger study by U.C. Berkeley scientists used aquatic toxicity testing to explore the potential for the mosquito abatement treatments to affect sediment dwelling organisms (Weston et al. 2006). Previous U.C. Berkeley research found that the presence of the synergist PBO in waters could theoretically enhance the toxicity of pyrethroids in sediment (Amweg et al 2006b). In the Sacramento area, U.C. Berkeley scientists measured post-treatment water column PBO concentrations similar to those measured by the District, and, like the District, found no evidence of direct aquatic toxicity from the pyrethrins or the PBO. However, the U.C. Berkeley team found that measured PBO concentrations were high enough to enhance the toxicity of pyrethroids already present in creek sediments (toxicity to *Hyalella azteca* was almost doubled).

<u>The chemistry of pyrethroids in sediments can change with longer contact time</u>. "Aging" is a well-known phenomenon of sediment chemistry. Recent studies confirm that pyrethroid chemistry in sediments changes as contact time increases, resulting in potential reduction in pyrethroid bioavailability (Bondarenko et al 2006). The Bondarenko paper recommends long contact times (≥30 days) for spiked sediments used in toxicity testing. However, because actual contact times under environmental conditions are unknown—and likely vary, the appropriate contact time to obtain artificially treated sediments that mimic actual environmental conditions cannot yet be determined.

In natural systems, pyrethroids in sediments are subject not only to chemical transformations, but also to biodegradation. Recent studies support previous findings that individual pyrethroid isomers have differing fates in sediments (Qin et al. 2006; Qin and Gan 2006). Because the aquatic toxicities of isomers can differ, these fate differences could be environmentally relevant.

<u>Site-specific conditions can reduce the toxicity of pyrethroids in the water column</u>. The ability of site-specific conditions to affect the toxicity of water pollutants is well known. This effect is the basis for a procedure called a "Water Effects Ratio" that is used to develop site-specific objectives for specific surface waters (U.S. EPA 1994). Both dissolved organic matter and suspended sediments have been shown to reduce the bioavailability of pyrethroids in the water column, thus reducing their effective toxicity (Yang et al. 2006a; 2006b; 2006c).

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

- 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.
- Adverse effects to aquatic ecosystems are likely to occur at concentrations below the LC50.
- Differences in the environmental fates of individual pyrethroids in creek sediments may be relevant to understanding aquatic toxicity patterns.

4.3 Other Findings

<u>Pesticides, in combination with each other and other pollutants, may add to or synergize toxicity in aquatic organisms. Researchers are exploring use of simple models to describe these interactions</u>. Previous research has found that combination of pesticides and other pollutants can cause unexpected adverse effects to aquatic organisms (see

Section 4.4. in TDC Environmental 2005). Recent publications provide additional examples of this effect. For example, the insecticides esfenvalerate and chlorpyrifos, which have somewhat different modes of action, were found to have a slightly greater than additive effect on fathead minnows (*Pimephales promelas*) and aquatic midge larvae (*Chironomus tentans*) (Belden and Lydy 2006). Exposures to environmentally relevant copper concentrations enhanced stresses (measured with biomarkers) on fish exposed to deltamethrin (Parvez and Raisuddin 2006).

Current water quality criteria and pesticide risk assessment do not account for concurrent exposures to multiple pollutants. Developing simple models for such interactions is an important step toward accounting for multiple pollutant exposures in water quality regulatory processes. Common simple models include independent action and concentration addition (sometimes called the “risk quotient addition” or “toxic unit” approach). Recent papers have found that the concentration addition approach may be useful for predicting effects from combinations of triazine and phenyl urea herbicides (Chevre et al 2006), mixtures of organophosphate and carbamate insecticides (Scholz et al 2006), and possibly for mixtures of organophosphate and pyrethroid insecticides (Belden and Lydy 2006).

<u>New, potentially environmentally relevant sublethal toxicity endpoints are being identified by researchers</u>. In surface waters, sublethal exposures to pollutants are much more common than those that cause acute toxicity (note that if acute toxicity is common, the affected species is likely to be absent from an ecosystem). Government regulatory requirements and risk assessments typically focus on a small set of sublethal (“chronic”) toxicity test endpoints (e.g., reproduction and growth). Recent research has shown that pesticides can affect other endpoints that are critical to survival. For example relatively low concentration exposures to endosulfan, glyphosate, iodocarb (IPBC), trifluralin, and 2,4-D adversely affected juvenile coho salmon olfaction, which is critical for predator avoidance and return migration (Tierney et al. 2006).

<u>New marine antifouling coating biocides are very highly toxic to aquatic life</u>. As noted in previous reports, both zinc pyrithione and Irgarol 1051 are very highly toxic to aquatic life and the marine antifouling biocide zinc pyrithione can be converted to the more stable and toxic copper pyrithione in the presence of copper (see Section 4.3. of TDC Environmental 2005 and Section 4.4 of TDC Environmental 2006a). This conversion was recently demonstrated to cause enhanced toxicity to aquatic organisms (Mochida et al 2006). A study evaluating the impact of commonly used "booster" biocides on early developmental stages of marine invertebrates found that environmentally relevant concentrations of chlorothalonil, Sea-Nine 211 and dichlofluanid would represent a threat to marine invertebrates (Bellas 2006).

<u>Environmentally relevant concentrations of the biocide triclosan have the potential to interfere with frog metamorphosis</u>. Veldhoen et al. (2006) discovered that exposure to triclosan interfered with the thyroid hormone-based mechanism that controls metamorphosis of tadpoles into frogs.

<u>One product containing the root control pesticide metam sodium has been reformulated to remove a contaminant—n-nitrosodimethylamine (NDMA)—that may affect municipal wastewater treatment plant compliance with discharge permits</u>. Because water quality standards for NDMA have been set at very low concentrations, municipal wastewater treatment plants are seeking to prevent its discharge to sewer systems. The manufacturer of one commonly used root control product has reformulated the product to reduce NDMA levels (Maguin 2007; Weck Laboratories 2005).

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

- 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).[6]
    - 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.
    - 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 and 2006a):

- Stress from exposure to disease and/or predators, in combination with pesticide exposures, can adversely affect organisms at concentrations below documented EC50s and LC50s.
- 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, which has begun to replace certain urban diazinon and chlorpyrifos uses, 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.

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[6] 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

- 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 2006 research findings. The findings and recommendations of the 2005 and 2006 reports (TDC Environmental 2005, 2006a) 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 2007) and an analysis of urban pesticide sales and use trends (TDC Environmental 2006b). 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 (particularly 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. Laboratory reports do not always clarify whether the method used is capable of distinguishing tralomethrin and deltamethrin (most methods are not).

<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

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. 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. In general, creating 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.

Recommendation 2: *Ask laboratories to clarify whether data reported for deltamethrin and tralomethrin represent these individual pyrethroids or the sum of both chemicals.* Although typical chemical analysis methods capable of measuring environmentally relevant concentrations of pyrethroids cannot distinguish tralomethrin from deltamethrin, laboratory reports often list only one of these two pyrethroids.

Monitoring

Recommendation 3: *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[7], carbaryl, malathion, PHMB, and fipronil and its degradates).* A long-term surveillance monitoring program is needed. Specific monitoring recommendations are as follows:[8]

- 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)*. 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).

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[7] 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.

[8] 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).

- <u>Monitoring of pyrethroids in sediments is a higher priority than monitoring for them in the water column</u>. Because pyrethroid toxicity is inversely correlated with organic carbon concentration, when monitoring for pyrethroids in sediments, organic carbon concentrations should also be measured.
- <u>Recommended detection limits</u>[9] 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)
  - 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)

The Clean Estuary Partnership designed a monitoring program that—if implemented—would fulfill these recommendations for the San Francisco Bay Area (Ruby 2006). Monitoring programs should be adjusted every few years to reflect pesticide market changes.

<u>Recommendation 4</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:

- Glass containers are preferred.
- Samples should be collected directly into the sample container that will be taken to the laboratory. Transfers and use of tubing should be avoided.
- Samples collected should be analyzed quickly—preferably within 24 hours of collection and definitely no later than 3 days after collection, unless appropriate steps are taken to extract or preserve the sample.

For sediment samples:

- Sample collection procedures used by U.C. Berkeley are recommended (see Amweg et al. 2006a). (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.
- Ensure that the laboratory is aware that excess sulfur needs to be removed to avoid interferences with analysis of pyrethroids concentrations.

[9] Recommendations are based on available aquatic toxicity data.

<u>Recommendation 5</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 the California Department of Pesticide Regulations 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 phone: (916) 324-4167e-mail: 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 some formats are more convenient). For more information see: http://www.cdpr.ca.gov/docs/sw/surfdata.htm
- U.S. EPA: Please contact Patti TenBrook at U.S. EPA Region 9 (415-947-4223, TenBrook.Patti@epamail.epa.gov) for assistance with identifying where to send the data you have collected.

<u>Recommendation 6</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.

<u>Recommendation 7</u>: *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).

<u>Aquatic Toxicity</u>

<u>Recommendation 8</u>: *Obtain information to fill aquatic toxicity data gaps about pyrethroids.* The most critical data gaps include:

- <u>Aquatic toxicity data</u>. Gaps include *Hyalella azteca* LC50 data for tralomethrin, LC50 data for estuarine organisms (all pyrethroids), LC50 data for individual pyrethroid isomers, and sublethal toxicity data (EC50s) for both fresh water and estuarine organisms (all pyrethroids).

- Aquatic sediment half life values for all pyrethroids except bifenthrin and permethrin.

Recommendation 9: Characterize the influence of ambient surface water temperatures on pyrethroid toxicity. Laboratory tests of field samples are conducted at standard laboratory temperatures, which are warmer than typical surface waters. Most pyrethroids are more toxic at lower temperatures. The lower temperatures in surface water may result in greater toxicity than would be predicted based on laboratory tests.

Recommendation 10: 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.

Management

Recommendation 11: 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 12: 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.

Recommendation 13: 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.

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