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Pesticides in Urban Runoff, Wastewater, and Surface Water

Annual Review of New Scientific Findings 2010

Prepared for the
San Francisco Estuary Partnership

March 2010

PREFACE

This is a report of research performed by TDC Environmental, LLC for the San Francisco Estuary Partnership (SFEP). This report was prepared to fulfill the annual reporting requirement in Task 7.6.1.1 of SFEP's grant agreement with the State Water Resources Control Board (Agreement Number 09-305-550) for Taking Action for Clean Water. Funding for this project has been provided in part by the American Recovery and Reinvestment Act of 2009 and the Clean Water State Revolving Fund, through an agreement with the State Water Resources Control Board. The contents of this document do not necessarily reflect the views and policies of the State Water Resources Control Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. (Gov. Code, Section 7550, 40 CFR Section 31.20.)

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ACKNOWLEDGEMENTS

The author appreciates the information and assistance provided by many scientists who are investigating the environmental effects of pesticides in urban surface waters, particularly Dr. Donald Weston. TDC Environmental thanks the following reviewers for their assistance with completing this report:

- Gail Chesler, Central Contra Costa Sanitary District
- Jamison Crosby, Contra Costa Clean Water Program
- Preeti Ghuman, Sanitation Districts of Los Angeles County
- Janet O'Hara, San Francisco Bay Regional Water Quality Control Board
- Nan Singhasemanon, California Department of Pesticide Regulation
- Patti TenBrook, U.S. EPA Region 9

Thanks are also due to Athena Honore for editing this report and Paula Trigueros of the San Francisco Estuary Partnership for grant management for the UP3 Project.

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1.0 INTRODUCTION

1.1 Background

This Urban Pesticide Pollution Prevention (UP3) Project report is intended to assist California urban runoff management agencies, municipal wastewater treatment plants (also known as "publicly-owned treatment works" or "POTWs"), the State Water Resources Control Board and Regional Water Quality Control Boards, California Department of Pesticide Regulation (DPR), and U.S. EPA by identifying pesticides used in urban areas that are harming or threatening to harm surface water quality. This group of pesticides is called the "UP3 Project Priority Pesticide List."

Efforts to prevent pesticide-related toxicity in urban surface waters, urban runoff, and municipal wastewater treatment plant discharges should prioritize opportunities to address pesticides on the UP3 Project Priority Pesticide List. The UP3 Project recommends that monitoring programs include UP3 Project priority pesticides or (as applicable) the aquatic toxicity endpoints associated with these pesticides.

Because the list was developed on the basis of a weight-of-evidence assessment of available information, additional information can modify the list. The list should be updated regularly to incorporate new information, which may provide evidence for pesticides to be added to or to be removed from the list.

Because understanding the impacts of urban pesticide use on water quality is complex and time-intensive, the UP3 Project was established in mid-2004 to help California Water Boards, municipal wastewater treatment plants, and urban runoff management agencies prevent pesticide-related water quality problems. The UP3 Project is currently funded (through 2010) by a State Water Resources Control Board grant administered by the San Francisco Estuary Partnership (SFEP). TDC Environmental provides technical support for the project.

1.2 Scope of This Report

This is the fifth science update prepared by the UP3 Project. On the basis of the UP3 Project's ongoing review of pesticide and water quality literature relevant to urban surface waters, this report identifies pesticides used in urban areas that are harming or threatening to harm water quality. This is one of three reports that have been prepared annually by the UP3 Project. The other two reports review California water quality agencies' participation in urban pesticide-related regulatory activities and analyze urban pesticide sales and use trends. (None of these reports was prepared in 2009 due to the suspension of the UP3 Project's grant funding.)

This report supplements—and does not repeat—the previous research and monitoring updates prepared by the UP3 Project (TDC Environmental 2005, 2006, 2007, 2008), which should also be consulted by those seeking a full understanding of relevant scientific findings.

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

- *The most recent literature* (i.e., published in 2008 and 2009).
- *New findings*. This update does not include studies with results consistent with previous findings, nor does it address pesticides that are not currently used (e.g., organochlorine pesticides).

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

This report is informed by—but does not specifically address—pesticide sales and use information (e.g., user surveys, pesticide use reporting data). That information is addressed in a separate UP3 Project report on urban pesticide sales and use trends. The next such report is anticipated in mid-2010.

The scope of this report does not include examination of potential alternatives to pesticides on the UP3 Project Priority Pesticide List. Alternatives may include different pesticides or different pest control methods.

This review is not comprehensive. Information sources were selected on the basis of their usefulness in previous UP3 Project reviews. The scope of this review did not include three classes of pesticides because they have been reviewed or are being reviewed by the State Water Resources Control Board or DPR (State Water Board 2010; DPR 1995): aquatic herbicides, mosquito abatement products, and cooling water system additives.

1.3 Report Organization

This report is organized as follows:

- *Section 1* (this section) provides the background and scope of the report.
- Section 2 describes the methods used to develop the UP3 Project Priority Pesticide List.
- *Section 3* identifies changes to the UP3 Project Priority Pesticide List based on recent scientific information.
- *Section 4* summarizes the updated UP3 Project Priority Pesticide List.
- *Section 5* lists the references cited in the body of the report.

2.0 METHODOLOGY

2.1 Inclusive Approach

The process used in this report to identify pesticides used in urban areas that are harming or threatening to harm water quality, known as the "UP3 Project Priority Pesticide List," was deliberately designed to be inclusive. The intent of this approach was to provide a basis for proactive management of pesticide-related water quality problems.

In this report, "harm to water quality" is broadly defined to include both direct impacts and indirect effects. Examples of direct impacts are aquatic toxicity and exceedance of a water quality standard. Indirect effects include incidents of non-compliance with Clean Water Act permits, interference with municipal wastewater treatment processes, and limitations on biosolids management options.

Since the UP3 Project has the goal of preventing pesticide-related water quality problems, "harming or threatening to harm" is also broadly defined, to include not only pesticides proven to harm water quality—but also pesticides for which a weight of evidence evaluation indicates a meaningful potential for a pesticide to cause harm under certain circumstances. Because of this inclusive approach, the list likely contains some pesticides that are not now harming water quality. These pesticides—which are primarily new pesticides and pesticides that have received little scientific attention—merit careful examination. Each time the list is updated, all pesticides on the list are reevaluated to determine if new evidence supports removing any pesticides from the list.

Harm to water quality sometimes occurs from combinations of pesticides (e.g., pyrethroids) or from chemicals that have both pesticide and non-pesticide uses (e.g., copper). Recognizing this, the weight of evidence evaluation considered not only the potential for a pesticide to alone cause harm—but also the potential for a pesticide to contribute meaningfully toward harm from multiple related sources.

2.2 Information Sources

This report is based on a review of existing information available from reliable sources. The review was not comprehensive. Specific sources were selected based on their usefulness in identifying relevant literature in previous similar reviews (TDC Environmental 2003, 2005, 2006, 2007, 2008). These information sources include:

- Published scientific literature (e.g., peer-reviewed and other journals). A comprehensive review of the tables of contents for all 2008 and 2009 issues of the journals that have previously published the majority of relevant articles (i.e., *Environmental Science and Technology, Environmental Toxicology and Chemistry*) was conducted. Papers from other journals were identified primarily by referral from the author's professional colleagues and ongoing review of science news sources.
- 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.

- Interviews with agency staff and researchers. Scientists often forward their own publications or citations for other publications of interest to the UP3 Project.

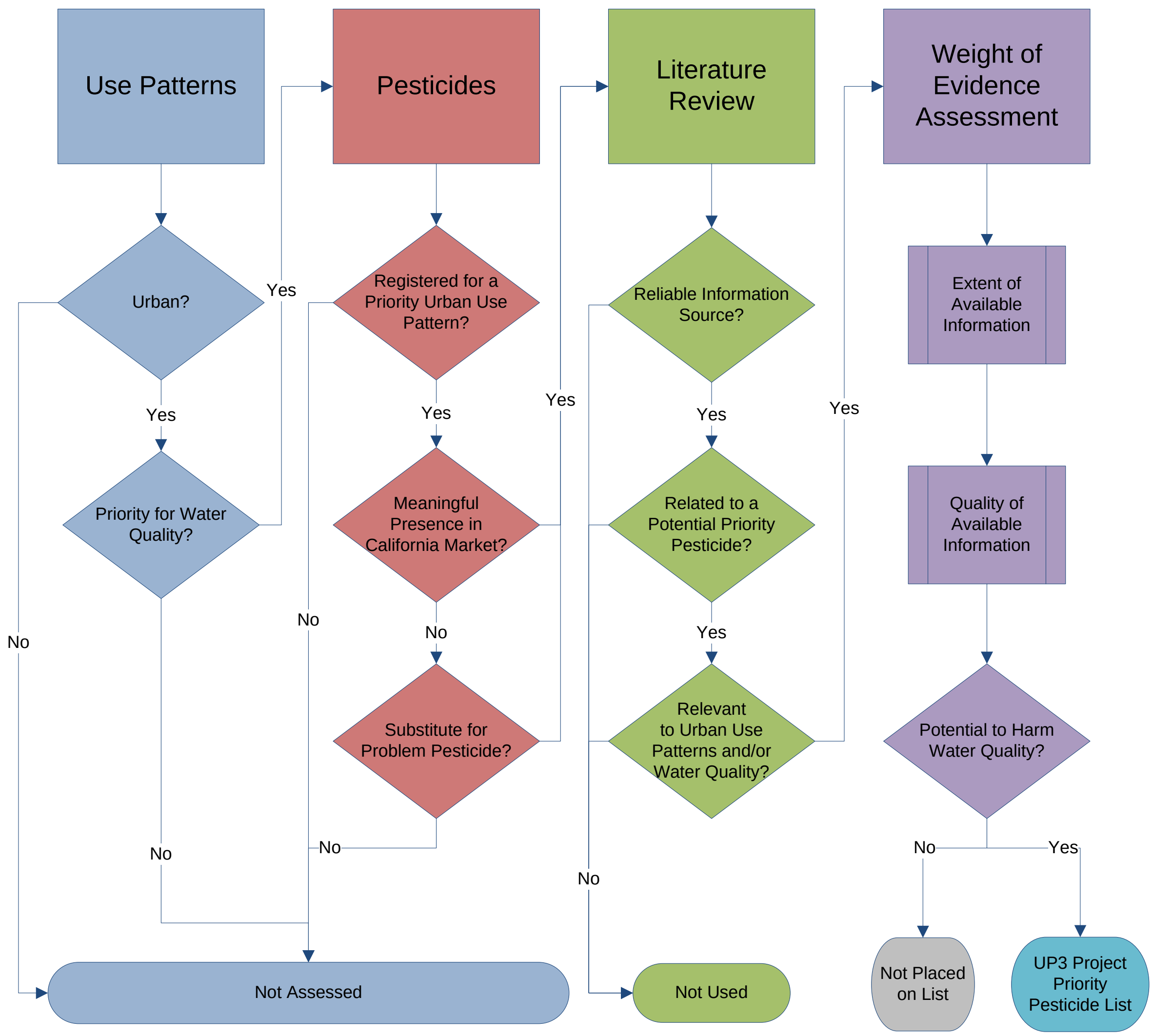
Since this report is an update, it also relies on the literature reviewed for prior similar UP3 Project reports (TDC Environmental 2005, 2006, 2007, 2008).

2.3 Prioritization Process

Consistent with the UP3 Project goal of preventing pesticide-related water quality problems, the prioritization involved a process that is based on pesticide "use patterns." A use pattern is a description of the way that a pesticide is applied in urban areas, such as "outdoors around buildings," "in swimming pools," or "in sewer lines."

The general approach to the process of creating the UP3 Project Priority Pesticide List is outlined in Figure 1.

Figure 1. Prioritization Process



Some—but not all—urban pesticide use patterns have been associated with harm to water quality. These priority use patterns, which are listed in Table 1, were the starting point for the prioritization process.

Because a full review of all registered pesticides has been beyond the scope of UP3 Project reports, each annual review has considered only those pesticides that are the subject of recent government reviews or scientific investigation. Since 2005, several hundred of the approximately 1,000 registered pesticides active ingredients have been screened.

During the review process, pesticides that could potentially be used in a priority use pattern were checked to identify whether they were registered for the use pattern and commonly available in the urban market. Availability was determined on the basis of DPR databases detailing California pesticide registration, sales, and reported use,[1] supplemented by informal retail shelf surveys and interviews with pesticide applicators. New pesticides that appeared to be entering the market as substitutes for pesticides that are proven causes of harm to water quality (outdoor urban insecticides and marine antifouling biocides) were also included, to the extent that information could be identified.

The literature review focused on publications that provided information that could be used to examine the potential for urban use patterns to cause harm to water quality. The most common types of publications reviewed were reports of water quality or discharge monitoring, laboratory measurements simulating discharges, aquatic toxicity testing, and environmental risk assessments. The quality of each piece of information was considered. The weight of evidence assessments, which are individually summarized in Section 3, relied primarily on the characteristics of the use pattern, available monitoring data (if any), and aquatic toxicity.

2.4 Strengths and Limitations of Prioritization Process

The strength of this use pattern-based approach is that it is capable of identifying pesticides with the potential to harm water quality <u>before</u> the harm actually occurs. Another strength is that the approach is tailored specifically to urban areas.

More typical methodologies may start with monitoring data (Pepple 2009) or reported use data (Lu and Davis 2009). These approaches excel at identifying problems that are already present, but are less likely to predict problems that have yet to occur.

Reliance on California's pesticide use reporting system does not work well as the basis for an urban pesticide prioritization. Reporting requirements do not apply to most urban pesticide use, including most of the use patterns listed in Table 1.

Reliance on monitoring data automatically excludes most pesticides from a prioritization process. Few monitoring programs examine currently used pesticides. Laboratories that conduct chemical analysis of surface water, urban runoff, and wastewater samples do not have standard methods to measure most currently registered pesticide active ingredients in environmental water samples. When a standard method exists, detection limits are often not sufficiently sensitive to measure the concentration of the pesticide that can cause aquatic toxicity. To some extent, this shortcoming is mitigated by the increasing inclusion of toxicity testing as a screening method for environmental water samples. However, when toxicity occurs, it can only be linked to a specific pesticide if methods exist to measure the pesticide at the toxicity-causing concentration and if "toxicity identification evaluation" methods exist for that class of pesticide compounds.

[1] http://www.cdpr.ca.gov/dprdatabase.htm

Table 1. Urban Pesticide Use Patterns Most Likely to Threaten Water Quality

Use Pattern	Priority Discharge Pathway			Examples [b]
	Urban Runoff	POTW	Direct [a]	
Outdoors around buildings	X			Outdoor insecticides - DDT, Chlordane, Diazinon, Chlorpyrifos, Pyrethroids
Outdoor broadcast lawn & landscaping treatments	X			Outdoor insecticides - Diazinon, Chlorpyrifos, Pyrethroids
Pet flea insecticides		X		Chlorpyrifos pet flea shampoos
Human body insecticides		X		Lindane head lice and scabies treatments
Impregnated materials (particularly machine washable fabrics)		X		Insecticides (permethrin-treated clothing) and biocides (copper impregnated socks)
Cleaning products		X		Biocides - Triclosan containing soaps, silver ion-generating washing machines
Sewer line or manhole		X		Root control products and manhole cockroach insecticides
Swimming pools, spas, and fountains	X	X		Biocides (Chlorine, Sodium hypochlorite) and algaecides (copper sulfate)
Wood preservatives (particularly wood installed in or adjacent to water)	X		X	Creosote
Marine antifouling biocides			X	Tributyltin, copper oxide
Recirculating cooling water systems additives [c]	X	X		Tributyltin
Aquatic herbicides [c]			X	Copper sulfate
Mosquito abatement [c]			X	DDT, Malathion

[a] Immersed in surface water.
[b] Many pesticides listed in the examples are no longer registered for the use pattern. Some examples reflect uses where U.S. EPA has deferred authority to the Food & Drug Administration.
[c] Not within the scope of this report.

A major shortcoming of this methodology is that it is not comprehensive. Only those pesticides that are the subject of recent government reviews or recent scientific investigation have been evaluated (a few hundred of more than 1,000 registered pesticide active ingredients). Only a subset of all recent literature was reviewed. A full review of all registered pesticides is beyond the scope of UP3 Project reports.

A second major shortcoming to this approach is that information in the literature regarding urban pesticide use patterns, environmental concentrations in urban discharges, and aquatic toxicity in urban discharges is surprisingly limited. Few urban pesticide use patterns have been subject to comprehensive review. Some endpoints have received little attention. For example, the presence of currently used pesticides in POTW biosolids could limit biosolids management options; however, this potential has received little attention in the scientific literature.

Data gaps—particularly limited aquatic toxicity data—hindered the review. For most currently used pesticides, aquatic toxicity data are limited. For some pesticides, just one aquatic species has been tested. Environmental fate data rarely include fate in POTWs.

By focusing on priority use patterns, this approach omits examination of unusual events that may be problematic. For example, this approach does not examine the potential for pesticides to be inappropriately discharged to POTWs in quantities sufficient to cause effluent toxicity incidents.

3.0 CHANGES TO THE UP3 PROJECT PRIORITY PESTICIDE LIST

This section summarizes information from the literature review that provides the basis for modifications to the UP3 Project Priority Pesticide List. The list was last updated in 2008 (when it was termed the UP3 Project "study list"). At that time, it included: pyrethroid insecticides, carbaryl, malathion, polyhexamethylene biguanadine (PHMB), and fipronil.

This section is organized into six subsections, which review the priority urban pesticide use patterns listed in Table 1 in the following groupings:

3.1. Insecticides: outdoors around buildings or general broadcast treatments, pet flea insecticides, human body insecticides, impregnated materials, and manhole treatments

3.2. Indoor biocides: cleaning products and impregnated materials

3.3. Sewer root control products

3.4. Swimming pool, spa, and fountain treatments

3.5. Wood preservatives

3.6. Marine antifouling biocides

As explained in Section 1.2, three of the priority urban pesticide use patterns were not within the scope of this review: mosquito abatement products, aquatic herbicides, and cooling water system additives.

3.1 Insecticides

Pyrethroids

Pyrethroid insecticides remain the highest priority among the pesticides on the UP3 Project Priority Pesticide List because they have been linked to widespread toxicity in California surface waters. On the basis of product availability and outdoor use patterns, the following specific pyrethroids have previously been identified as UP3 Project Priority pesticides: bifenthrin, cyfluthrin (including beta-cyfluthrin), cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, and tralomethrin. Regulatory responses to pyrethroid-related toxicity are underway both at DPR (the pyrethroid "reevaluation") and the Water Boards (designations of surface waters as "impaired" under section 303(d) of the Clean Water Act). Recent information strengthens the identification of pyrethroids as the top priority and (as explained below) provides the basis for adding the following additional pyrethroids to the UP3 Project Priority Pesticide List: cyphenothrin, etofenprox, gamma-cyhalothrin, resmethrin, sumithrin, and tetramethrin.

Pyrethroids continue to cause toxicity to organisms dwelling in California surface water sediments. Sediments from urban streams across California are toxic to a standard aquatic toxicity test species, the amphipod *Hyalella azteca*, which is a common resident species in California creeks and rivers. Numerous investigations have identified pyrethroids as the cause of this toxicity (Weston et al. 2005; Amweg et al. 2006; Holmes et al. 2008; Ruby 2008; Hladik and Kuivila 2008; Weston et al. 2009). While monitoring elsewhere in the U.S. has been quite limited, data from Texas (Hintzen et al. 2009) and Illinois (Ding et al. 2010) show that this problem occurs outside of California.

Notable among the findings of these studies is that the toxicity is more severe and more widespread in urban areas than in agricultural water bodies (Weston et al. 2004; Ng et al. 2008; Weston and Lydy 2010).

Urban streams typically contain mixtures of multiple pyrethroids (Trimble et al 2009). In urban watersheds, bifenthrin is the most frequently detected pyrethroid and is the leading contributor to the total number of toxic units in urban stream sediment samples.

See the 2006 annual UP3 Project research and monitoring update (TDC Environmental 2006) for additional details.

Pyrethroid-related toxicity is occurring in the water column in urban creeks and rivers. Routine monitoring of water column samples collected from urban creeks and rivers during storm events has identified frequent toxicity to *Hyalella azteca* (Riverside County 2007, 2008, and 2009; Weston Solutions 2006 and 2007; Weston and Lydy 2010). Dry weather samples have also exhibited toxicity and/or have contained pyrethroids at levels sufficient to cause toxicity, but less frequently than storm event samples (Riverside County 2007, 2008, and 2009; Weston and Lydy 2010; Weston et al. 2009). Similar concentrations of pyrethroids have been measured in urban stream monitoring by University of California and state agency scientists (He et al. 2009; Oki and Haver 2009). Toxicity identification evaluations indicated that pyrethroids were almost certainly the cause of the toxicity (Weston and Lydy 2010; Riverside County 2007, 2008, and 2009; Weston Solutions 2006 and 2007). In nearly every case, pyrethroid concentrations in the water samples were sufficient to explain the measured toxicity.

After the initial development of this list, gamma-cyhalothrin was approved for the same outdoor urban use patterns as pyrethroids currently on the UP3 Project Priority Pesticide List. Gamma-Cyhalothrin is a component (a single “stereoisomer”) of lambda-cyhalothrin, with similar aquatic toxicity (He et al. 2008; Giddings et al. 2009). This information justifies the addition of gamma-cyhalothrin to the UP3 Project Priority Pesticide List.

Pyrethroids and pyrethroid-related toxicity have been measured in undiluted municipal wastewater treatment plant effluent (Weston and Lydy 2010; U.S. EPA Office of Water 2009). U.S. EPA environmental risk assessments have identified potentially significant risks from pyrethroid sanitary sewer discharges (Panger and Sutton 2006; Rexrode and Meléndez 2005). Due to the discovery of pyrethroid-related toxicity in municipal wastewater treatment plant effluent, several pyrethroids that were not previously included on the UP3 Priority Pesticide List will be added because they are used in manners like pet flea treatment and impregnation into clothing that involve sanitary sewer discharges. These pyrethroids are cyphenothrin, etofenprox, resmethrin, sumithrin, and tetramethrin.

The toxicity of pyrethroids is explained best in terms of the sum of the “toxic units” of the pyrethroids present in the sample. Combined exposures to all pyrethroids need to be evaluated to understand pyrethroid-related toxicity. Sediment toxicity data fit adequately to a concentration addition model based on toxic units, which has been commonly used to interpret pyrethroid monitoring data (Trimble et al. 2009). Calculation of toxic units needs to be normalized on the basis of organic carbon to account for the reduction of toxicity caused by binding to organic matter in sediments (Weston et al. 2005). In water column samples, the presence of both organic matter and particles may cause a measurable reduction in pyrethroid bioavailability in samples with total suspended solids concentrations of 100 parts per million (ppm) or higher and/or dissolved organic carbon concentrations of 20 ppm or higher (Yang et al. 2006a; Yang et al. 2006b). (These concentrations occur in some—but not all—urban creek and river samples e.g., Weston and Lydy 2010; Riverside County 2007, 2008, and 2009).

Fipronil

Recent information strengthens the basis for inclusion of fipronil on the UP3 Priority Pesticide List. A 2007 UP3 Project literature review concluded that fipronil has the potential to harm aquatic ecosystems (Moran 2007). Anecdotal information suggests that fipronil is increasingly used for ant control around buildings, because it is the primary alternative to the pyrethroids. Recent presentations of unpublished monitoring data indicate that fipronil may soon be found in surface water bodies at levels capable of causing toxicity to sensitive aquatic organisms (He et al. 2009; Oki and Haver 2009).

Fipronil degradates are relatively persistent in creek sediments. Fipronil has several environmentally important degradates with aquatic toxicity similar to that of the parent compound. Three fipronil degradates (desthiofipronil, fipronil sulfide, and fipronil sulfone) are relatively persistent in sediments (Lin et al. 2009).

Fipronil and two degradates are highly toxic to the standard sediment toxicity testing organism *Chironomus tentans*. Fipronil, fipronil sulfide, and fipronil sulfone lethal concentrations to 50% of the population were reported to be 0.13, 0.16 and 0.12 µg/g of organic carbon in laboratory sediments (Maul et al. 2008). The toxicity of fipronil and its degradates to *C. tentans* in sediment rivals the toxicity of pyrethroids to *Hyalella azteca* in sediment (LC50s 0.45 – 10.83 µg/g of organic carbon).

Carbaryl and Malathion

The literature review did not identify information that would alter the need to include the inclusion of malathion and carbaryl on the UP3 Project Priority Pesticide List.

3.2 Indoor Biocides

Recent research summarized below provides the basis for addition of three types of biocides that are primarily used indoors to the UP3 Project Priority Pesticide List: copper, silver (including nanosilver), and triclosan.

Copper

Copper impregnated fabrics can discharge copper to municipal wastewater treatment plants. Copper, which is highly toxic to aquatic life, is a frequent cause for impairment of California surface waters (California State Water Board 2006). In response to Clean Water Act Total Maximum Daily Loads (TMDLs) and to strict copper effluent limits in discharge permits, many California POTWs have implemented aggressive copper pollution prevention programs (Weir 2007). Increased use of household products that release copper into sanitary sewer systems could threaten both TMDL implementation and wastewater treatment plant permit compliance. Recently, a new class of fabrics impregnated with copper has entered the market (Weir 2007). While available data about copper discharges from these products are extremely limited, research showed a significant loss of copper when these fabrics are "washed" in a mild detergent solution with sonication (Borkow and Gabbay 2004).

Silver

Growing use of silver biocides has the potential to renew problems with silver in wastewater treatment plant discharges. Ordinary use of silver-containing biocides releases silver to municipal wastewater treatment systems. Silver is highly toxic to aquatic life at low concentrations, is persistent, and can bioaccumulate in some aquatic organisms, such as clams (Luoma 2008). Due to concerns about bioaccumulation and strict silver effluent limits in discharge permits, California POTWs have implemented pollution prevention programs to identify and reduce silver discharges to sanitary sewer systems. Past compliance challenges associated with silver discharges have caused POTWs to be wary of increasing silver use (Pla 2009).

Widespread use of household products that release silver into sanitary sewer systems could increase silver concentrations in POTW influents, effluents, and biosolids (Luoma 2008). Possible impacts include reduction in effluent quality, reduced effectiveness of biological treatment processes, and limitations to biosolids management options.

Nanosilver's special properties can cause different, potentially larger, effects on POTWs than ordinary silver:

- *The quantity and/or nature of silver discharged to POTWs may be affected by the small particle size and large surface area of nanosilver products as compared to other silver biocides*. For example, Benn and Westerhoff (2008) found that for certain products, silver losses during washing were so large that most of the silver in these products would be washed into the municipal wastewater system during the products' lifetimes. Where small particles occur in products, the entire particle could be washed down the drain (Geranio 2009).
- *Nanosilver particles may have extraordinary effects on POTW treatment processes*. In two related studies, Choi and Hu (2008) and Choi et al. (2008) found that silver particles less than 5 nanometers in diameter are uniquely toxic to nitrifying bacteria, which are critical to biological nutrient removal at POTWs.
- *Nanosilver particles may create toxic effects in ecosystems that would not be predicted on the basis of silver concentration alone*. Particle size modifies silver's aquatic toxicity (Griffitt et al. 2008).

Triclosan

Since early this decade, triclosan has been a compound of interest to municipal wastewater treatment plants due to its common presence in POTW effluent, biosolids, and surface waters (Kolpin et al. 2002; Singer 2002). Triclosan appears in a variety of household products regulated by U.S. EPA and the Food and Drug Administration (FDA). Common presence in wastewater effluent can create "pseudo-persistence" of compounds in waters that receive continuous discharges from municipal wastewater treatment plants.

Sensitive aquatic organisms have the potential to experience adverse effects from exposures to triclosan at levels that have been measured in surface waters. Canadian scientists identified potential for hazards to aquatic life from triclosan based on a comparison of environmental monitoring data from the literature to aquatic toxicity data for standard test organisms (Dussault et al. 2008).

In the presence of sunlight and chlorine, triclosan can create dioxins. Buth and colleagues found that in conditions that could occur at POTWs or in surface waters receiving POTW discharges, dioxins could be formed from triclosan (Buth et al. 2009).

Triclosan bioaccumulated in earthworms in fields fertilized with municipal wastewater treatment plant biosolids. USGS researchers found several household chemicals, including triclosan, bioaccumulated in earthworms in biosolids-treated fields (Kinney et al. 2008). Although this finding does not directly link to environmental harm, it confirms the persistence of triclosan in biosolids and its bioavailability when biosolids are reused.

3.3 Sewer Root Control Products

All four pesticide active ingredients that are used to control root intrusion into sewer lines have the potential to cause adverse effects on water quality, as explained below. All four chemicals have been added to the UP3 Priority Pesticide List.

Potential POTW operation interference from root control chemicals. Municipal wastewater treatment plants rely on biological treatment processes. Some pesticides can adversely affect the organisms in the biological treatment processes, which can adversely affect effluent quality. A Stanford University evaluation of the three active ingredients commonly used in California for sewer line root control found that all three—metam sodium, dichlobenil, and diquat dibromide had potential to cause negative effects on treatment plant operations if daily discharges are too large (Yeung and Criddle 2007).

Copper-based root control products. Copper from root control products has been found, in some cases, to contribute significantly to effluent limitation violations by municipal wastewater treatment plants (California DPR 1995). DPR has prohibited sale and use of copper-based root control products in the San Francisco Bay area.

3.4 Swimming Pool, Spa, and Fountain Treatments

Swimming pools, spas and fountains are treated with two types of pesticides—biocides and algaecides. Subsequent to application, biocides and algaecides may be discharged to surface waters when the pool, spa, or fountain is emptied, or when filter backwash is discharged. Swimming pools and spas are typically emptied once every several years. Pools may be drained to the sewer or the storm drain. Discharge to a storm drain releases the water (and any associated pesticide) directly to surface water, typically in a matter of minutes. Discharge to a sewer system sends the water (and any associated pesticide) to a municipal wastewater treatment plant, which in turn discharges to surface water. Individual discharge permits are not required for swimming pool discharges. Although such discharges could cause or contribute to violations of municipal urban runoff or wastewater permits, controlling such discharges is difficult if not impossible, particularly in the residential context (Johnson 2005).

The literature review did not identify information that would modify the inclusion of the swimming pool biocide polyhexamethylene biguanadine (PHMB) on the UP3 Priority Pesticide List. On the basis of the information below, both copper and silver are added to the list.

Copper may be used for algae control or as a biocide—usually in combination with silver—in swimming pools, spas, and fountains. Copper treatment concentrations are 10 to 100 times higher than surface water quality standards. Silver treatment concentrations can be 10 times higher than surface water quality standards. Pool discharges, which usually occur during dry weather, may not be diluted enough to ensure that urban creeks do not exceed water quality criteria (Gouveia 2006). Directing copper and silver-containing discharges to municipal wastewater treatment plants has the potential to affect compliance with effluent limits (Gouveia 2006).

3.5 Wood Preservatives

Use of treated wood in or near water poses the greatest potential for environmentally important copper releases. Three types of wood preservatives are commonly used to treat wood that is installed in or near water—creosote, pentachlorophenol, and copper-containing preservatives. Scientific information summarized below provides the basis for addition of all three categories of wood preservatives to the UP3 Priority Pesticide List.

Pentachlorophenol

Pentachlorophenol is a wood preservative used primarily to treat utility poles and crossarms. Although pentachlorophenol is quite toxic to aquatic life, limited monitoring data are available to assess its presence in urban watersheds. Available data are approach U.S. EPA recommended water quality criteria (Washington State 2004).

All pentachlorophenol products also contain environmentally significant contaminants, including two other Clean Water Act priority pollutants—dioxins and hexachlorobenzene (HCB). The dioxins contamination of pentachlorophenol is of particular interest in the San Francisco Bay area, because according to a screening-level estimate completed by the San Francisco Estuary Institute (Connor et al. 2004), washoff of dioxins from pentachlorophenol-treated utility poles could potentially be the largest source of dioxins to San Francisco Bay, which was formally determined by U.S. EPA, under Clean Water Act Section 303(d), to be impaired due to presence of elevated dioxins levels in fish. Two recent papers suggest that dioxins could potentially be formed from pentachlorophenol in the environment (Gu et al. 2008; Holt et al. 2008).

Creosote

Creosote is a coal tar-based wood preservative. While creosote mixtures vary, they generally consist of a large number of polyaromatic hydrocarbons (PAHs), many of which are toxic to humans and aquatic life. The creosote products of greatest concern for water quality are applied to wood installed in or near aquatic environments, such as creosote-treated wood piers and pilings. These products release PAHs directly into surface waters. PAHs impair 20 California water bodies (California State Water Board 2006).

Fish embryos and larvae are exquisitely sensitive to PAH mixtures. Recent research provides additional information about the hazards that PAHs in creosote pose to fish (Billiard et al. 2008; Carls et al 2008; Heintz 2007; Ownby 2002). The thresholds for toxicity to Pacific herring (*Clupea pallasi*) or pink salmon embryos (*Oncorhynchus gorbuscha*) are in the range of <1 to 10 parts per billion total aqueous PAHs (Heintz et al. 1999; Carls et al. 1999). These concentrations are in well within the range of surface water PAH concentrations estimated by U.S. EPA to occur as a consequence of current creosote use patterns (U.S. EPA OPP 2008).

Copper Compounds

Various copper compounds are used to preserve wood. Copper is a frequent cause of surface water impairment in California (California State Water Board 2006). This copper comes from multiple sources that combine to create urban water pollution problems (TDC Environmental 2004). With the phase out of chromate copper arsenate (CCA), copper-based wood preservatives have grown in market share. Previous UP3 Project reports have summarized information indicating that copper-based wood preservatives may comprise a meaningful source of copper releases into adjacent surface waters (TDC Environmental 2006).

3.6 Marine Antifouling Biocides

Previous UP3 Project reports have summarized numerous studies documenting the potential for marine antifouling biocides—including copper oxides, zinc pyrithione, and Irgarol 1051—to adversely affect water quality (TDC Environmental 2005, 2006, 2007, 2008).

Recent data reinforce previous information linking copper-based marine antifouling paints to elevated copper levels in surface waters with marinas. New reports include investigations of the impacts of biocide-containing paint particles in receiving waters (Turner et al. 2008; Turner, Singh, and Millard 2008; Turner 2010). A DPR survey of copper levels in California marinas found copper levels that frequently exceeded water quality standards in salt water marinas, where marine antifouling biocides are commonly used (Singhasemanon et al. 2009).

New marine antifouling coating biocides continue to be of concern due to their individual and cumulative toxicity to aquatic life. Recent scientific literature does not modify this finding. As noted in previous reports, the new biocides zinc pyrithione and Irgarol 1051 are very highly toxic to aquatic life. DPR's recent marina survey found levels of Irgarol 1051 and its primary degradate M1 above effects thresholds for sensitive aquatic species (Singhasemanon et al. 2009). Data collected by Hall et al. (2009) show Irgarol levels similar to those measured by DPR.

4.0 UPDATED UP3 PROJECT PRIORITY PESTICIDE LIST

Table 2 summarizes the updated UP3 Project Priority Pesticide List. Efforts to prevent pesticide-related toxicity in urban surface waters, urban runoff, and municipal wastewater treatment plant discharges should prioritize opportunities to address pesticides on the UP3 Project Priority Pesticide List.

The UP3 Project recommends that urban water quality monitoring programs include UP3 Project priority pesticides or (as applicable) the aquatic toxicity endpoints associated with these pesticides. Environmental analytical laboratories should strive to develop capabilities to measure environmentally relevant concentrations of all listed pesticides.

Because the list was developed on the basis of a weight-of-evidence assessment of available information, additional information can modify the list. Priority information needs include filling data gaps related to the aquatic toxicity and environmental fate of listed pesticides and other pesticides with urban pesticide use patterns likely to threaten water quality (see Table 1), obtaining monitoring data for priority discharges listed in Table 2, and evaluating the potential for pesticides discharged to POTWs to interfere with biological wastewater treatment processes or biosolids management options. The list should be updated regularly to incorporate new information, which may provide evidence for pesticides to be added to or to be removed from the list.

Inclusion on this list does not mean that a pesticide has been associated with a water quality problem, but rather that the weight of available evidence—including the pesticide's use pattern in urban areas and other available information—indicates the potential exists for the pesticide to cause or contribute to a water quality, permit compliance, or municipal wastewater treatment plant operational problem.

As explained in Section 2, this list is probably not comprehensive. Only pesticides with priority urban use patterns were reviewed. Reviewing all available scientific information for all pesticides with these use patterns was not feasible. The scope of this review did not include aquatic herbicides, mosquito abatement products, or cooling water system additives.

Table 2. UP3 Project Priority Pesticide List

Pesticide	Priority Discharge Pathway			Potential POTW Operational Interference
	Urban Runoff	POTW	Direct*	
Pyrethroid Insecticides				
Bifenthrin	X	X		
Cyfluthrin (including Beta-Cyfluthrin)	X	X		
Cypermethrin	X	X		
Cyphenothrin		X		
Deltamethrin	X	X		
Esfenvalerate	X	X		
Etofenprox		X		
Gamma-Cyhalothrin	X			
Lambda-Cyhalothrin	X			
Permethrin	X	X		
Resmethrin		X		
Sumithrin (d-Phenothrin)		X		
Tetramethrin		X		
Tralomethrin	X			
Other Insecticides				
Carbaryl	X			
Fipronil	X			
Malathion	X	X		
Swimming Pool, Spa, and Fountain Treatments				
Copper and Copper Compounds	X	X		
PHMB	X	X		
Silver	X	X		
Biocides				
Copper		X		
Silver (including nanosilver)		X		X
Triclosan		X		
Sewer Root Control				
Copper Sulfate		X		
Dichlobenil		X		X
Diquat Dibromide		X		X
Metam Sodium		X		X

Table 2. UP3 Project Priority Pesticide List (Continued)

Pesticide	Priority Discharge Pathway			Potential POTW Operational Interference
	Urban Runoff	POTW	Direct*	
Wood Preservatives				
Copper / copper compounds	X		X	
Creosote			X	
Pentachlorophenol	X		X	
Marine Antifouling Biocides				
Copper oxides			X	
Irgarol 1051			X	
Zinc Pyrithione			X	

*Immersed in surface water.
Source: See Section 3.

5.0 REFERENCES

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