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Pesticides in Urban Surface Water

Annual Research and Monitoring Update 2005

Prepared for the
San Francisco Estuary Project

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PREFACE

This is a report of research performed by TDC Environmental, LLC for the San Francisco Estuary Project. This report was prepared for the San Francisco Estuary Project to fulfill the annual reporting requirement in Task 2.2.1 of its grant agreement with the State Water Resources Control Board (Agreement Number 04-076-552-0) for the Urban Pesticides Pollution Prevention Project (UP3 Project). Views or information expressed in this report may not necessarily reflect those of the funding agencies.

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- Bill Johnson, San Francisco Bay Regional Water Quality Control Board
- Raymond Chavira, U.S. EPA Region 9
- Armand Ruby, consulting environmental scientist
- Nan Singhasemanon, California Department of Pesticide Regulation
- Ann Heil and Phil Markle, Los Angeles County Sanitation Districts
- Arleen Feng, Alameda Countywide Clean Water Program
- Laura Speare, UP3 Project Manager

The attached compilation of urban surface water monitoring studies prepared by Nan Singhasemanon (California Department of Pesticide Regulation) is included with its author’s permission.

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1.0 INTRODUCTION

1.1 Background

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

This is one of three reports prepared annually by the Urban Pesticide Pollution Prevention (UP3) Project. (The other two reports are a review of California water quality agencies' urban pesticide water quality regulatory activities and an analysis of urban pesticide sales and use trends.) The purpose of the UP3 Project is to provide education, outreach, and technical assistance for implementation of the Diazinon and Pesticide-Related Toxicity in Bay Area Urban Creeks Water Quality Attainment Strategy and Total Maximum Daily Load (WQAS/TMDL) (Johnson 2004a). The project is structured to mirror the three major elements of the WQAS/TMDL Implementation Strategy: Outreach and Education, Science (Research and Monitoring), and Proactive Regulation. The San Francisco Estuary Project (SFEP) has been awarded California water bond grant funds from the State Water Resources Control Board to implement the UP3 Project through March 2007. TDC Environmental is providing technical support for the project.

1.2 Scope of This Report

This is the first 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. The UP3 Project monitors government, university, and private scientific investigations and water quality monitoring programs. This report identifies key findings relevant to California water quality agency efforts to prevent pesticide-related toxicity in urban surface waters, urban runoff, and municipal wastewater discharges.

Although this is the first annual research and monitoring update prepared for the UP3 Project, it builds on previous related work, particularly a 2003 review of the water quality implications of the shift in urban insecticide use patterns resulting from the phase out of most urban uses of diazinon and chlorpyrifos (TDC Environmental 2003). That report found that use of commonly available insecticides—particularly pyrethroids—as substitutes for diazinon and chlorpyrifos in urban areas may cause adverse effects in aquatic ecosystems receiving urban runoff. That report also identified gaps in available data about urban insecticides and 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:

- <u>*The most recent literature*</u> (*i.e.*, published in 2004).
- <u>*New findings*</u>. This update does not include studies with results consistent with previously findings (*e.g.*, elevated diazinon concentrations in urban runoff or

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

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

This report does not address pesticide sales and use information (*e.g.*, user surveys, pesticide use reporting data). This information will be addressed in a separate UP3 Project report on urban pesticide sales and use trends.

1.3 Data Sources

This report is based on a review of the relevant scientific literature. Information in this report was obtained from a variety of sources:

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

1.4 Report Organization

This report is organized as follows:

- *Section 1* (this section) provides the background and scope of the report.
- *Section 2* reviews the status of methods for testing for pesticides in water.
- *Section 3* describes recent and planned California urban pesticide surface water monitoring.
- *Section 4* identifies recent major research findings relevant to urban pesticides and water quality.
- *Section 5* gives the conclusions of the evaluation and provides recommendations for future activities.
- *Section 6* lists the references cited in the body of the report.
- *The appendix* contains a copy of a useful 2003 California Department of Pesticide Regulation (DPR) review of California urban pesticide monitoring studies (Singhasemanon 2003).

2.0 METHODS TO TEST FOR PESTICIDES IN WATER BODIES

2.1 Background

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

A priority for California water quality agencies is development of chemical analytical methods to measure environmentally relevant concentrations of pollutants that threaten California's surface water quality and/or compliance with National Pollutant Discharge Elimination System (NPDES) permits for municipal wastewater treatment plants and urban runoff programs. With the phase out of most urban uses of diazinon and chlorpyrifos, water quality agencies are shifting attention to the pyrethroids, which have the potential to cause toxicity in California's surface waters and permitted discharges (TDC Environmental 2003). In 2004, California analytical capabilities for pyrethroids improved significantly as described below.

2.2 Findings

<u>Capabilities for measuring environmentally relevant concentrations of pyrethroids in water and sediment are improving</u>; however, additional work is needed to develop and validate analytical methods for pyrethroids in environmental water samples. 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, and permethrin (TDC Environmental 2003, 2004a).

- A previous review of available analytical methods did not identify any commercial laboratory capable of measuring environmentally relevant concentrations of these pyrethroids. Today, two California commercial laboratories (Caltest Analytical Laboratory in Napa and CRG Marine Laboratories in Torrance) are advertising this capability, though it has yet to be fully demonstrated in various types of environmental water and sediment samples.
- Some research laboratories have developed methods to measure environmentally relevant concentrations of these pyrethroids in surface waters and sediment (*e.g.*, You and Lydy 2004). The U.S. Geological Survey (USGS) and California Department of Fish and Game (CDFG) are developing methods to fill gaps in their existing capabilities. The California Department of Food and Agriculture (CDFA) is also working to improve its capabilities—this is particularly important because DPR, which relies on the CDFA laboratory, has been conducting surface water monitoring using pyrethroid detection limits that are higher than environmentally relevant concentrations.

<u>Sample collection methods for water samples to be analyzed for pyrethroids need to be worked out</u>. No agreed-upon methods exist for collection, storage, and laboratory preparation of environmental water samples for pyrethroids analysis. Losses by adsorption to sample container surfaces may be significant (Lee *et al.* 2002).

Toxicity identification evaluation (TIE) methods for pyrethroids are under development; recent progress is promising. U.C. Davis has developed an enzymatic procedure for pyrethroid detection that can be used to identify pyrethroid caused toxicity in laboratory water and sediment (Wheelock *et al.* 2004). Two California water bond grant-funded projects[1] are looking into development and validation of this and other promising TIE procedures for pyrethroid toxicity identification in surface water and sediment.

Methods to measure "free" pyrethroids in solution are being developed. These data are useful, but cannot be compared to toxicity data from the literature. Recognizing that not all pyrethroids in surface water samples will be bioavailable, researchers have developed methods to measure the unbound, dissolved fraction of pyrethroids ("free pyrethroids") in water samples (Liu *et al*. 2004; Yang and Gan 2004). Because pyrethroids have relatively high K_{oc} and K_{ow} values,[2] they are likely to bind to organics and solids in surface waters, reducing their bioavailability—possibly significantly, depending on the characteristics of the individual water body. Research has demonstrated that pyrethroid toxicity in water is inversely correlated with concentrations of suspended solids and dissolved organic matter in water samples (Yang and Gan 2004). The newly developed methods do not measure the "dissolved" fraction as usually defined, because they do not measure pyrethroids bound to organic matter or tiny particles in solution (traditional "dissolved" fraction measurements consider anything that passes through a 0.45 micron filter to be in the "dissolved" phase).

These methods offer the opportunity to explore the effects of other components in a particular pyrethroid-containing surface water sample on the toxicity of the pyrethroids in the sample; however, the data must be interpreted with care. DPR developed a procedure for estimating synthetic pyrethroid "free" concentrations from whole surface water sample chemical analytical data (Spurlock 2003). The interpretation of such "free" concentration data is difficult, however, as it cannot be directly compared to toxicity data from the literature, which is based on "nominal" pyrethroid concentrations,[3] rather than "free" pyrethroid concentrations. The difference between the "free" concentration toxicity and the reported "nominal" or "measured" concentration toxicity data in the literature can be quite significant. "Free" concentration EC50 levels[4] for other chemicals have been reported to be as much as 100-1,000 times lower than "nominal" concentration EC50s reported in the literature (Heringa *et al*. 2004). "Free" concentrations cannot be compared to water quality criteria developed in accordance with U.S. EPA methods.[5]

Researchers are developing enzyme-linked immunosorbent assays (ELISAs) for pyrethroids; however, such methods that are available commercially cannot measure environmentally relevant concentrations of individual pyrethroids. Urban runoff

[1] "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.

[2] K_{oc} and K_{ow} are "partition coefficients." K_{ow} is the ratio of the equilibrium concentration of a chemical in octanol and in water. (Octanol is an organic solvent that is used as a surrogate for natural organic matter.) K_{oc} is the ratio of the equilibrium concentration of a chemical in organic matter ("organic carbon") in soil and in water. These laboratory values are used as indicators of likely behavior of chemicals in the environment. The larger the value of these partition coefficients, the more likely that a substance will adhere to organic matter (like soil and creek sediments) rather than dissolving in water.

[3] The "nominal" concentration is the concentration that should be in the toxicity container, based on the water volume and the amount of pesticide put in the container.

[4] EC50—concentration that causes an effect in 50% of the test organisms during the test time period.

[5] CDFG used U.S. EPA methods to develop water quality criteria for permethrin and cypermethrin (CDFG 2000).

programs have previously found ELISA methods to be a low-cost, convenient alternative for analysis of diazinon. Several ELISA methods have been developed by researchers (*e.g.*, Lee *et al.* 2004; Park *et al.* 2004). Commercially available methods (*e.g.*, EnviroLogix)[6] have detection limits greater than environmentally relevant concentrations and do not distinguish among individual pyrethroids.

[6] The EnviroLogix synthetic pyrethroids microwell place assay is an example of the commercially available ELISA methods for pyrethroids. It was intended for analysis of certain pyrethroids (cyfluthrin, deltamethrin, cypermethrin, and lambda-cyhalothrin) in methanol. It was designed to measure cyfluthrin concentrations of 20 to 80 ppb; other pyrethroid concentrations are approximated with the cyfluthrin calibration. The assay was not designed to distinguish among detected pyrethroids. The assay experiences interferences from other pyrethroids.

3.0 CALIFORNIA URBAN SURFACE WATER PESTICIDE MONITORING

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 activities are anticipated to increase to evaluate the effects of the phase outs and the adoption of insecticide alternatives in the urban marketplace.

TDC Environmental is working with the San Francisco Estuary Project 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. Although that inventory is not complete, this report summarizes currently available information.

3.2 Findings: San Francisco Bay Area

Although colloquial information suggests that some pesticide and toxicity surface water, sediment, and/or discharge monitoring occurred in the Bay Area in 2003/2004, no written reports of such monitoring were identified.

In fall 2004, the Clean Estuary Partnership inventoried San Francisco Bay Area urban creek monitoring plans for the 2004/05 wet season (Ruby 2004). Table 1 (on the next page), which is based largely on the Clean Estuary Partnership inventory, lists monitoring activities planned for the 2004/05 wet season. Organizations planning to monitor current use pesticides and/or toxicity include:

- Urban runoff programs—Alameda Countywide Clean Water Program (ACCWP), San Mateo Stormwater Pollution Prevention Program (STOPPP), Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP), and the City of Palo Alto;
- Clean Estuary Partnership;
- San Francisco Estuary Institute (SFEI);
- San Francisco Bay Regional Water Quality Control Board;
- Universities—Stanford University and University of California, Berkeley.

Funding for these monitoring activities comes from many sources, including municipalities, the state Surface Water Ambient Monitoring Program (SWAMP), California water bond grants (primarily from the pesticide research and identification of source, and mitigation or "PRISM" program), and the San Francisco Bay Regional Monitoring Program (RMP).

Monitoring is generally targeted to past sources of toxicity (organophosphorous or "OP" pesticides), to pesticides of concern based on recent reports (*e.g.*, pyrethroids), or to identify the presence or absence of toxicity. In the 2004/05 wet season, San Francisco Bay Area monitoring programs will include both surface water and sediment samples in creeks and at the estuarine interface.

Table 1. Planned Bay Area Urban Creek Pesticide/Toxicity Monitoring 2004-2005

Agency/ Program	Water Body (# Locations)	Frequency and Type	Relevant Parameters
ACCWP	Castro Valley Creek (1)	Water; 2-3 flow-weighted samples	OP pesticides, aquatic toxicity[1]
ACCWP	Creeks to be selected (8-10)	Water; dry weather grabs (Fall 04, Spring 05)	Diazinon or OP pesticides, aquatic toxicity[2]
STOPPP	Cordilleras Creek Watershed (3)	Water; 3 seasonal time periods (summer, wet season, and spring)	OP pesticides, aquatic toxicity[3]
SCVURPPP	Adobe Creek, San Tomas Creek, Matadero Creek, Barron Creek, Sunnyvale West Channel, Calabazas Creek (10)	Water; 2 seasonal time periods	OP pesticides, aquatic toxicity
City of Palo Alto	San Francisquito Creek (1)	Water; 2-3 storm events and dry weather	OP pesticides
Stanford University, Jasper Ridge Biological Preserve	San Francisquito & Los Trancos Creeks, Bear Creek (3)	Water; 2-3 storm events and dry weather	OP pesticides
SFEI (RMP/PRISM)	Petaluma River, Napa River, Suisun Creek, San Mateo Creek, Coyote Creek, San Lorenzo Creek (12, half freshwater, half near tributary mouth)	Sediment: 1 after first major storm event; 1 in late spring	OP pesticides, pyrethroids; sediment toxicity[4]
SFEI (PRISM)	TBD (probably same as above)	Water and sediment	For method development: pyrethroids, imidacloprid, piperonyl butoxide
U. C. Berkeley (Weston)	Kirker Creek, Lyon Creek, San Leandro Creek, San Pablo Creek, Glen Echo Creek (5)	Sediment	Pyrethroids in sediment, sediment toxicity[5]
Regional Water Quality Control Board (SWAMP)	10 locations from among the following creeks: Codornices, Cerrito, Strawberry, Baxter, Temescal, Arroyo Mocho, Glen Echo, Sausal, Peralta, Lion, and Arroyo Viejo	Water and sediment; 3 events; includes winter samples, but not storm events	OP and carbamate pesticides (water only), pyrethroids (sediment only), and aquatic[3] and sediment toxicity[5]
Clean Estuary Partnership	Corte Madera Creek, Blue Rock Creek, Rheem Creek, Castro Valley Creek, Calabazas Creek, San Francisquito Creek, Belmont Creek (7)	Water; up to 3 storm events	Diazinon, aquatic toxicity,[6] pyrethroids (limited number of samples)

[1] Toxicity testing may be conducted with all three species or on *Ceriodaphnia dubia* only, to be determined.
[2] Toxicity testing may not be conducted on all samples, to be determined.
[3] Includes 3 species chronic testing (*Pimephales promelas* [fathead minnows], *Ceriodaphnia dubia, Selenastrum capricornutum*).
[4] Sediment toxicity testing will use *Hyalella azteca* (fresh water) and *Eohaustorius estuarius* (salt water).
[5] Sediment toxicity testing will use *Hyalella azteca.*
[6] Toxicity testing for acute and chronic toxicity (*Pimephales promelas* and *Ceriodaphnia dubia*).
Source: Adapted from Ruby 2004. Information was updated by TDC Environmental.

No plans to monitor the Bay itself (other than routine RMP monitoring of water column and sediment toxicity), urban runoff discharges (prior to mixing in creeks), or municipal wastewater (other than routine effluent monitoring) were identified. While USGS and DPR have monitored urban surface waters elsewhere in California for pesticides, neither has plans for urban monitoring in the Bay Area this year. Due to the reduction in episodic toxicity in San Francisco Bay associated with Central Valley agricultural runoff, the RMP has directed its special funds for pesticide-related toxicity monitoring into a special study of pesticides in Bay tributaries (see Table 1).

Other monitoring activities relevant to pesticides are undoubtedly occurring in the San Francisco Bay Area. TDC Environmental and SFEP will seek to include these activities and their outcomes in the Bay Area monitoring program inventory that is now underway.

3.3 Findings: Elsewhere in California

In late 2003, DPR completed a review of urban pesticide monitoring studies in California as part of its internal planning process for the protection of urban surface water from adverse effects of pesticides (Singhasemanon 2003). This review identified 36 past or ongoing studies of pesticides in California's urban surface waters, summarized the findings of each study, and provided Internet links to each study report that is available on the Internet. Because this review conveniently summarizes the most important California urban surface water pesticide monitoring completed prior to 2004, it is attached in the appendix.

Other than the monitoring studies listed in the DPR review, no recently published California urban surface water pesticide monitoring studies were identified, except miscellaneous studies with data on organophosphorous pesticides consistent with past monitoring findings. Many studies are currently underway; Table 2 briefly summarizes identified studies that may be of interest to California water quality agencies.

Table 2. Planned California Urban Pesticide/Toxicity Monitoring Studies of Potential Interest to California Water Quality Agencies

Agency/ Program	Study Summary
USGS National Water Quality Assessment (NAWQA)	USGS has monitored water quality in Sacramento's Arcade Creek for more than a decade. In 2004-2005, USGS plans to make Arcade creek a "high intensity" sampling site. It plans to collect water quality samples twice per month, analyzing for nutrients, selected pesticides and volatile organic chemicals, selected major elements, and field measurements such as pH, specific conductance, and temperature.
U.C. Berkeley (Weston) (PRISM Grant)	An investigation of the distribution and toxicity of sediment-associated pesticides in the Sacramento watershed includes monitoring of an urban watershed for pyrethroid pesticides and toxicity.
Friends of the Russian River (PRISM Grant)	The "Russian River Citizens Survey of Pesticides in Urban Creeks" includes monitoring of Russian River watershed urban creeks for selected pesticides and toxicity.
Calleguas Creek Watershed Total Maximum Daily Load Monitoring Program	The Calleguas Creek Watershed Total Maximum Daily Load Monitoring Program is being designed to monitor and evaluate TMDL implementation, to refine the understanding of current loads, and to continue efforts to identify the cause(s) of remaining or future unknown toxicity. The draft monitoring plan includes water column and sediment monitoring for OP pesticides, pyrethroids, and toxicity.
Southern California Coastal Water Research Project (SCCWRP) (PRISM Grant)	A study designed to complete a source apportionment of pesticides in the San Diego Creek/Upper Newport Bay watershed will focus on OP and organochlorine pesticides.

Source: TDC Environmental compilation.

4.0 OTHER RELEVANT RESEARCH

4.1 Background

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

4.2 Findings: Urban Pesticides

Pyrethroids have been linked to toxicity in sediments from California surface waters. An exploration of toxicity in sediments from California's Central Valley identified pyrethroids as a significant cause of toxicity in sediment (Weston *et al.* 2004). While these studies did not include urban surface waters, the findings of pyrethroid-related toxicity in water bodies receiving agricultural runoff suggests that similar toxicity is possible in surface water bodies receiving urban runoff. The study used two standard test species: the amphipod *Hyalella azteca* and midge *Chironomus tentans*. Forty-two percent of the locations sampled caused significant mortality to one test species on at least one occasion. Pyrethroids were detected in 75% of the sediment samples. A comparison of sediment chemical concentrations and toxicity data for the test species suggests that pyrethroids contributed to the toxicity in 40% of samples toxic to *C. tentans* and nearly 70% of samples toxic to *H. azteca*. Two other studies also provided circumstantial evidence linking pyrethroids in agricultural runoff to toxicity in the runoff (Werner *et al*. 2004) and toxicity in surface waters and sediments (Anderson *et al*. 2004). A DPR investigation of agricultural runoff detected pyrethroids and aquatic toxicity; however, because the samples contained several pesticides, it is unclear what caused the identified toxicity (Bacey *et al*. 2004). While similar urban investigations have not been published, several studies are underway (see Tables 1 and 2 in Section 3).

New urban pesticide products threaten to cause toxicity in municipal wastewater treatment plant effluent and storm drain discharges. Washing only one piece of a new brand of permethrin-impregnated clothing could be sufficient to cause toxicity in the effluent of a municipal wastewater treatment plant (Green 2004). Poly hexamethylenebiguanide (PHMB), a new swimming pool biocide, is highly toxic to aquatic life. Discharges of treated pool water to storm drains or municipal wastewater treatment plants have potential to cause incidents of toxicity (Johnson 2004b; Ashby 2004; Martyn 2004b).

U.S. EPA environmental risk assessments estimate environmental concentrations of carbaryl and malathion in excess of water quality criteria. While U.S. EPA did not compare its estimated environmental concentrations to water quality criteria for carbaryl and malathion developed by the California Department of Fish and Game in accordance with U.S. EPA methods (CDFG 1998a, 1998b), its risk assessments predict exceedances of these criteria (U.S. EPA 2000, 2003). The U.S. EPA risk assessments rely on surface water concentration estimates for agricultural areas; they do not estimate surface water concentrations in urban areas. This could underestimate risk, as USGS surface water monitoring data show higher concentrations of carbaryl and malathion in surface waters in urban areas than in agricultural areas (Gilliom *et al.* 1999).

The insecticide fipronil, which has begun to replace certain urban diazinon and chlorpyrifos uses, is highly toxic to aquatic species. "Environmentally realistic concentrations" of fipronil were reported to have adverse effects on reproduction of a common estuarine copepod (Cary *et al.* 2004; Chandler *et al.* 2004).

<u>A contaminant in the root control pesticide metam sodium—n-nitrosodimethylamine (NDMA)—may affect municipal wastewater treatment plant compliance with discharge permits</u>. Applications of metam sodium could release NDMA to surface waters via wastewater treatment plants. Because water quality standards for NDMA have been set at very low concentrations, such releases have the potential to cause or contribute to NDMA effluent limit exceedances for municipal wastewater treatment plants (Martyn 2004a).

<u>Copper-based pesticides may comprise a meaningful source of copper in urban runoff</u>. When it rains, copper from fungicides and wood preservatives can be washed from urban surfaces into storm drains, where it flows (usually without any treatment) into creeks, rivers, and other surface waters. Copper in pool, spa, and fountain algaecides that is not collected in filter systems may be carried into surface waters when the pool, spa or fountain is emptied. A Clean Estuary Partnership (San Francisco Bay) study estimated that copper from these urban pesticides comprises roughly 10% of the copper in urban runoff (TDC Environmental 2004b).

<u>USGS data suggest that insecticides are more likely than herbicides to be linked to pesticide-related toxicity in urban surface waters</u>. USGS NAWQA data show that insecticides are more common and appear at higher concentrations in urban surface waters than in agricultural surface waters (Hoffman *et al.* 2000). Using a tool called the "pesticide toxicity index" (PTI), USGS scientists found that streams in both agricultural and urban watersheds had relatively high PTI values for fish and benthic invertebrates as compared to streams in mixed land-use watersheds or undeveloped watersheds (Gilliom and Martin 2004). Insecticides were the primary contributors to the relatively high urban PTI values. (In agricultural areas, herbicides are more likely to be linked to aquatic toxicity). This analysis suggests that it is appropriate for urban pesticide surface water toxicity reduction efforts to focus on insecticides.

4.3 Findings: Marine Antifouling Paint

<u>Copper-based marine antifouling paint has been linked to elevated copper levels in surface waters with marinas</u>. Investigations conducted in Southern California have found that marine antifouling paint is a significant contributor to elevated copper levels in surface waters with marinas, particularly in the immediate area near marinas. These studies are summarized in a draft Total Maximum Daily Load for the Shelter Island Yacht Basin prepared by the San Diego Regional Water Quality Control Board (Dobalian and Arias 2003). The San Diego data formed the basis for the Clean Estuary Partnership (San Francisco Bay) estimate of copper releases from marine antifouling paint into San Francisco Bay, which identified marine antifouling paint as a potentially significant copper source (TDC Environmental 2004b).

In response to water quality concerns about copper from marine antifouling paint, the Interagency Coordinating Committee (IACC), an existing working group composed of 28 State agencies involved in implementing California's Nonpoint Source Pollution Control Program, formed the Copper Antifouling Paint Sub-Workgroup of its Marina and Recreational Boating Workgroup. The purpose of the sub-workgroup is to assess the degree and geographical distribution of copper pollution caused by copper antifouling paints in California's aquatic environments. In support of workgroup activities, DPR prepared a bibliography of studies on copper antifouling paints (DPR 2004) and compiled California monitoring studies that may be useful for evaluating copper releases from marine antifouling paints (Singhasemanon 2005).

Available data suggest that marine antifouling paint is a significant contributor to copper levels in urban surface waters; however, available data are only sufficient for rough estimates of copper loads in Northern California salt water and in fresh water. Copper releases from marine antifouling paint into surface waters are likely to depend on the specific characteristics of the water bodies (chemistry, temperature, etc.). Neither DPR nor the Clean Estuary Partnership identified any studies of marine antifouling paint copper releases outside of Southern California marinas.[7] Most available data consider only copper releases in the dissolved form, omitting potential long-term partitioning of copper between dissolved and particulate forms in receiving waters.

New marine antifouling coating biocides are very highly toxic to aquatic life. The U.S. EPA risk assessment for zinc pyrithione (zinc omadine) described its very high toxicity to aquatic life (U.S. EPA 2004). Another new biocide, Irgarol 1051, is persistent and may adversely affect aquatic communities (Zamora *et al.* 2004).

4.4 Findings: Cumulative Effects of Pesticides and Other Stressors

Stress from exposure to predators, in combination with pesticide exposures, can adversely affect organisms at concentrations below documented EC50s and LC50s.[8] While ordinary ecosystems include predators, typical laboratory toxicity testing systems do not. Several research groups have been exploring the link between predator-induced stress and the apparent toxicity of pesticides, finding that the presence of predators tends to enhance the adverse effects of pesticide exposures (Relyea 2004b; Relyea 2003; Maul *et al.* 2004).

Pesticides, in combination with each other and other pollutants may add to or synergize toxicity to aquatic organisms. Environmental surface waters typically contain multiple pesticides and other pollutants (Gilliom and Martin 2004). Researchers are exploring the effects that exposures to multiple pollutants have on aquatic organisms. For example, exposures to combinations of diazinon and copper had—at some concentration levels—additive toxic effects on *Ceriodaphnia dubia* (Banks *et al*. 2003). Mixtures of chlorpyrifos, malathion, and carbaryl had additive or greater than additive toxicity on an aquatic invertebrate (*Simulium vittatum* Zetterstedt cytospecies IS-7 larvae) (Overmyer *et al*. 2003). Combinations of diazinon, carbaryl, malathion, and glyphosate had joint effects on the development of larval amphibians (Relyea 2004a). Combinations of malathion and dicrotophos caused greater than additive (synergistic) toxicity to *Ceriodaphnia dubia* (Maul *et al.* 2004).

4.5 Findings: San Francisco Bay

San Francisco Bay is unlikely to be impaired by diazinon,[9] but alternative insecticides in the marketplace—particularly pyrethroids—pose a threat to the beneficial uses of the Bay. The Clean Estuary Partnership is completing a Conceptual Model/Impairment Assessment (CM/IA) of diazinon and pesticide-related toxicity in San Francisco Bay (Ogle 2005). The report presents a conceptual model that describes the current understanding of diazinon in San Francisco Bay, including sources of diazinon to the Bay and the processes that determine the occurrence and concentrations of diazinon in

[7] In 2004, the San Francisco Bay Conservation and Development Commission (BCDC) completed a pilot San Francisco Bay marina water quality study, which included a literature review and sediment monitoring in four Bay Area marinas (but no water column monitoring) (Pap 2004). It did not attempt to evaluate the linkage between copper concentrations in surface waters and marine antifouling paint.

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

[9] It is unclear how the conclusions of this report will affect the formal regulatory status of the Bay on the 303(d) list.

the system. It also evaluates the current effects of diazinon on the Bay's beneficial uses, finding that impairment of San Francisco Bay by diazinon is unlikely. The report explains that reductions in diazinon and chlorpyrifos use in the Bay watershed have reduced releases to the Bay. While these changes have nearly eliminated incidents of episodic toxicity, the report identifies diazinon alternatives—particularly the pyrethroids—as an emerging water quality concern.

4.6 Other Findings

<u>The environmental fate of pesticides may be different in urban settings than in the agricultural settings for which environmental fate data are generally collected</u>. Urban surfaces differ greatly from agricultural soils. While obvious differences include the presence of impervious surfaces, less obvious differences, like differences in soil bacteria, may also be important. For example, the half life of 2,4-D and dicamba were found to be much longer in typical urban landscaping soil than in turf grass planted soil (Gan *et al.* 2003).

<u>In surface water, the presence of pesticide degradates can be as environmentally important as the pesticide itself</u>. The USGS NAWQA program has begun to monitor certain pesticide degradates in surface waters. While it has not specifically studied urban surface waters in this manner, data from agricultural areas shows that pesticide degradates were detected at higher or similar order of magnitude concentrations as parent compounds (Kolpin *et al.* 2004). Some of the detected degradates are more toxic than the parent compounds (Boxall *et al.* 2004). These data suggest that measuring only parent compounds could, for some pesticides, significantly underestimate pesticide loads (Kolpin *et al.* 2004).

<u>Environmental properties of pesticides in sediment are being explored, but cannot readily be predicted from available data</u>. Since available evidence suggests that the presence of pyrethroids in surface water sediment may be of concern, it may be important to understand the environmental fate and bioavailability of pyrethroids in sediment. The potential for pyrethroids to persist and accumulate in sediment is not known. While available environmental fate data suggest that persistence might not be a major problem, a study of the fate of organophosphorous and carbamate insecticides in urban creek sediment provided an important reminder that available environmental fate data for pesticides may not be readily translated to conditions in sediments in urban creeks (Bondarenko and Gan 2004). The researchers found that the persistence of the pesticides was modified by the chemistry of creek sediment, which may be anaerobic and may have characteristics very different from those of standard soils used to estimate environmental fate of pesticides (*e.g.*, redox potential). The presence of sediment inhibited the ability of pyrethroid-degrading bacteria to reduce pyrethroid concentrations in aquatic test systems, suggesting that biodegradation rates may be lower in surface water sediment than in test soils (Lee *et al.* 2004). One possible explanation of the lower biodegradation rate is low bioavailability of sediment-bound pyrethroids; however, another investigation found that pyrethroids in sediment were taken up into sediment-dwelling organisms (Weston *et al.* 2004).

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Conclusion 1: *Recent literature increases the weight of the evidence that use of pyrethroids, carbaryl, and malathion as replacements for urban uses of diazinon and chlorpyrifos may cause adverse effects in aquatic ecosystems receiving urban runoff.* The potential for toxicity in surface water sediment is of particular concern.

Conclusion 2: *Copper-based marine antifouling paints increase copper levels in surface water bodies with marinas. Use of copper-containing urban pesticides (e.g., algaecides, fungicides, and wood preservatives) increases copper levels in urban surface waters* Newer marine antifouling biocide alternatives entering the market (*i.e.*, Irgarol 1051, zinc pyrithione) may also be problematic as they are highly toxic to aquatic organisms.

Conclusion 3: *Combinations of stressors may cause harm to aquatic ecosystems at pesticide concentrations below laboratory toxicity test adverse effects concentrations (LC50s and EC50s) for standard aquatic toxicity testing organisms.* Effects may be additive or synergistic. Cumulative effects can occur among pesticides and between pesticides and other stressors like predators.

Conclusion 4: *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.*

Conclusion 5: *The results from monitoring of urban surface waters and discharges to those surface waters for pesticides and pesticide-related toxicity are difficult to find as they are generally published only in grey literature government agency technical reports.* Since most monitoring data are not combined in any national database (*e.g.*, U.S. EPA's STORET), it is not readily available to scientists and water quality and pesticide agencies.

5.2 Recommendations

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 following are suggested near-term priorities:

- Try methods for chemical analysis of pyrethroids in various environmental water and sediment samples. Since no plans for monitoring pyrethroids in municipal wastewater were identified, method validation is a priority.
- Create standard written procedures for surface water and sediment sample collection, storage, and handling appropriate for samples containing pyrethroids. Methods should be designed to minimize losses of pyrethroids on sampling equipment and container surfaces.
- Develop chemical analysis methods for other pesticides and pesticide degradates that have the potential to cause toxicity incidents, *e.g.*, PHMB.

Recommendation 2: *Conduct surveillance monitoring of California urban surface waters (including sediment) for toxicity and for specific pesticides that have the potential to cause adverse effects in aquatic ecosystems (e.g., pyrethroids, carbaryl, malathion, PHMB, and fipronil).* Toxicity monitoring should be conducted with standard aquatic toxicity test species. The pyrethroids of greatest interest for urban surface water quality are bifenthrin, cyfluthrin (including beta-cyfluthrin), cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, and permethrin. The standard test species most sensitive to pyrethroids are: water column—*Pimephales promelas* and *Ceriodaphnia dubia*; sediment—*Hyalella azteca*.

Recommendation 3: Identify a stable funding source for pesticide-related urban surface water quality monitoring.

Recommendation 4: Encourage publication of pesticide monitoring data in professional journals.

Recommendation 5: When incidents of toxicity in municipal wastewater treatment plant effluent, urban runoff, or surface waters occur, consider the potential for pyrethroids and other new pesticides (e.g., PHMB) to be the source of the toxicity.

Recommendation 6: Continue to discourage use of pyrethroids, carbaryl, and malathion as replacements for urban uses of diazinon and chlorpyrifos.

Recommendation 7: Continue to focus programs intended to prevent urban pesticide-related surface water toxicity on insecticides. USGS data show that insecticides are more likely to be associated with surface water toxicity in urban areas than herbicides.

Recommendation 8: Assess the water quality implications of use of the insecticide fipronil in urban areas.

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APPENDIX. A REVIEW OF URBAN PESTICIDE MONITORING STUDIES IN CALIFORNIA, NOVEMBER 2003 (DPR STAFF DRAFT)

In late 2003, DPR completed a review of urban pesticide monitoring studies in California as part of its internal planning process for the protection of urban surface water from adverse effects of pesticides. This review, prepared by Nan Singhasemanon, identified 36 past or ongoing studies of pesticides in California urban surface waters, summarized the findings of each study, and provided Internet links to each study report that is available on the Internet (Singhasemanon 2003). This review conveniently summarizes the most important California urban surface water pesticide monitoring completed prior to 2004.

A Review of Urban Pesticide Monitoring Studies in California
November 2003
(Regionally and Chronologically Arranged)

Multi-Regional Studies

1) **DPR/CDFA Pest Eradication Monitoring Projects**
    - **Sampling Period:** 1988 - ongoing
    - **Sampling Entity:** DPR
    - **Funding Entity:** CDFA
    - **Study Area:** Various regions in California, including urban areas
    - **Pesticide Analytes:** Various
    - **Descriptions/Findings:** The California Department of Food and Agriculture (CDFA) uses aerial and ground applications of pesticides to eradicate infestations of exotic pests, such as Mediterranean fruit flies and red-imported fire ants in California. The Environmental Monitoring Branch of the Department of Pesticide Regulation (DPR) monitors selected treatments to provide information on pesticide concentrations in various matrices that may include deposition, water, soil, air, foliage, fruits and vegetables. Instead of summarizing each study individually, links are provided.
    - **Links:** 1) Monitoring of metaldehyde and methiocarb for white snail - http://www.cdpr.ca.gov/docs/empm/epests/whgardensnail.htm
    2) Monitoring of spinosad for the eradication of Mexican fruit fly - http://www.cdpr.ca.gov/docs/mexfly/index.htm
    3) Monitoring of methyl eugenol, naled and dichlorvos for the eradication of Oriental fruit fly - http://www.cdpr.ca.gov/docs/empm/epests/orientfly.htm
    4) Monitoring of malathion and diazinon for the eradication of Mediterranean fruit fly - http://www.cdpr.ca.gov/docs/empm/epests/medfly.htm
    5) Monitoring of carbaryl, isofenphos, and diazinon for the eradication of Japanese beetle - http://www.cdpr.ca.gov/docs/empm/epests/japanesebeetle.htm
    6) Monitoring of carbaryl for the eradication of gypsy moth - http://www.cdpr.ca.gov/docs/empm/epests/gypsymoth.htm
    7) Monitoring of bifenthrin, chlorpyrifos, diazinon, fenoxycarb, hydramethylnon, and pyriproxyfen for the management of red imported fire ants - http://www.cdpr.ca.gov/docs/rifa/
    8) Monitoring carbaryl, cyfluthrin, and imidacloprid for the eradication of glassy-winged sharpshooter - http://www.cdpr.ca.gov/docs/gwss/reports.htm

2) **NAWQA – USGS National Water Quality Assessment Program.**
    - **Sampling Period:** 1991-present
    - **Sampling Entity:** USGS
    - **Funding Entity:** USGS
    - **Study Area:** Selected watersheds nationwide. Approximately 11 urban sites across the U.S. including Arcade Creek in California.
    - **Pesticide Analytes:** Approximately 80 pesticides (see http://ca.water.usgs.gov/sac_nawqa/swan.html)

- **Descriptions/Findings:** Hundreds of samples have been taken from 11 urban streams scattered across the country from Florida to Connecticut to Oregon as part of the Pesticides National Synthesis Project. In a recent report on the first cycle of the program, USGS concluded that "urban and suburban areas are substantial sources of pesticides to streams" and that "most urban areas have similar pesticides in streams...and many urban areas may benefit from similar strategies for reduction." USGS periodically release water-resources investigations reports relating to the NWQA program.

  Arcade Creek and the City of Modesto’s McHenry storm drain are two urban indicator sites covered by NAQWA in Northern California. Warm Creek near San Bernardino is a NAQWA urban indicator site in Southern California.

  The NAQWA has Arcade Creek pesticide data dating back to 1996 (see link below). Insecticides used for household, lawn, or garden maintenance were the most frequently detected type of pesticides at the urban sites. Diazinon levels in Arcade Creek were elevated at various times of the year and were frequently above recommended criteria for the protection of aquatic life. Those levels were among the highest in the Nation. However, because of the low discharge of Arcade Creek, pesticide concentrations were greatly diluted upon mixing with Sacramento River water.

  The NAWQA Modesto area storm drain (McHenry and four associated drains) data is from a storm event in February 1995. Fifteen pesticides were detected in the 10 urban samples (see links below). Carbaryl, chlorpyrifos, DCPA, diazinon, malathion, simazine, and trifluralin were detected in all the samples. Benfluralin, disulfoton, EPTC, metolachlor, pendimethalin, prometon, and propanil were also detected. All of the urban samples exceeded the National Academy of Science’s (NAS) and the National Academy of Engineering’s (NAE) recommended guidelines for carbaryl, diazinon, disulfoton, and malathion.

  A non-NAWQA study of the Modesto area is discussed in heading/item number X of this compendium. Note that non-NAWQA investigations are not covered under this heading but are covered individually as special studies elsewhere in this document.

  There does not appear to be an evaluation to date of data from Warm Creek site although data is available in the link below. A pesticide specific report on the Santa Ana Basin is pending according to the NAWQA webpage.
- **Links:** 1) Arcade Creek pesticides data link - http://ca.water.usgs.gov/sac_nawqa/
  2) Modesto urban storm drains site info. link - http://ca.water.usgs.gov/sanj_nawqa/data_sw/tuol_urban.sitetable; pesticide data links - http://ca.water.usgs.gov/sanj_nawqa/data_sw/tuol.urban.1995.pest1.html and http://ca.water.usgs.gov/sanj_nawqa/data_sw/tuol.urban.1995.pest2.html;
  3) Warm Creek data link http://ca.water.usgs.gov/sana_nawqa/sw_warm_ck.html

3) ***Caltrans Construction Sites Runoff Characterization Study 1998-2002*. Caltrans Report CTSW-RT-02-055. September 2002.**
   - **Sampling Period:** Winters 1998-1999 and 1999-2000
   - **Sampling Entity:** Caltrans
   - **Funding Entity:** Caltrans
   - **Study Area:** Road and highway construction areas across the State
   - **Pesticide Analytes:** Diazinon and chlorpyrifos.
   - **Descriptions/Findings:** During four rainy seasons beginning in 1998-1999, Caltrans collected stormwater samples from Caltrans construction sites. The primary objective of this study was to develop baseline water quality data for construction sites. Overall, 120 storm events were monitored at 27 sites. Pesticides analysis took place the first two years of the study. The study's pesticide analysis was dropped in the 2000-2001 monitoring season.

     In 1998-1999, chlorpyrifos was not detected in any samples. However diazinon was found with a mean concentration of 420 ng/L and a detection of 2,400 ng/L of diazinon in the highest concentration sample. In 1999-2000, chlorpyrifos was detected in 2 out of 29 samples. Diazinon was detected in 21 out of 29 samples (particularly frequent at highway construction areas). Peak concentrations for diazinon and chlorpyrifos were 200 and 40 ng/L, respectively. The ELISA method detection limits were at 30 ng/L for both analytes.
   - **Link:** http://www.dot.ca.gov/hq/env/stormwater/special/index.htm, then go to study title for final link.

4) ***Caltrans Statewide Stormwater Runoff Characterization Study*. Caltrans Report CTSW-RT-02-022. July 2002.**
   - **Sampling Period:** Winter 2000-2001 and 2001-2002
   - **Sampling Entity:** Caltrans
   - **Funding Entity:** Caltrans
   - **Study Area:** Caltrans-maintained facilities and roadways
   - **Pesticide Analytes:** Diazinon, diuron, glyphosate, oryzalin, oxadiazon, and triclopyr
   - **Descriptions/Findings:** The characterization study is a multi-year study designed to characterize the quality of stormwater runoff from representative Caltrans facilities and roadways. Monitoring sites were selected to represent "typical" Caltrans operations in all the Districts. Selected sites include commercial vehicle inspection facilities, congested sites, free-flowing sites, highways, maintenance stations, park and rides, rest areas, and toll plaza. This monitoring meets Caltrans' NPDES requirements.

     Diazinon, diuron, glyphosate, oryzalin, oxadiazon, and triclopyr were analyzed for at all the facility types. These pesticides were detected most frequently at the congested, free-flowing, and highway sites. Diazinon was occasionally detected at the remaining facility types. For numerical results and summaries, it is best to click on the link below and go to the study title.
   - **Link:** http://www.dot.ca.gov/hq/env/stormwater/special/index.htm

Sacramento River Watershed-Specific Studies

5) ***Diazinon and chlorpyrifos in urban waterways in northern California, USA*. Bailey, H.C., L. Deanovic, E. Reyes, T. Kimball, K. Larson, K. Cortwright, V. Connor, and D. E. Hinton. 2000. Environ. Tox. Chem. 19(1): 82-87.**
    - **Sampling Period:** 1994-1995
    - **Sampling Entity:** Central Valley Regional Water Quality Control Board (CVRWQCB)
    - **Funding Entity:** University of California and CVRWQCB
    - **Study Area:** urban stream in Sacramento and Stockton areas
    - **Pesticide Analytes:** Diazinon, chlorpyrifos
    - **Descriptions/Findings:** Samples collected from urban streams in the Sacramento and Stockton urban areas, during the precipitation season, were analyzed for diazinon and chlorpyrifos. Concentrations were determined with enzyme-linked immunosorbent assays specific for each pesticide.

      Two hundred thirty-one samples from the two cities were analyzed for diazinon: 85% exceeded California Department of Fish and Game (DFG) water-quality criteria for this pesticide. Chlorpyrifos was measured in 90 of the samples collected from Sacramento and Stockton: 80% exceeded the DFG criterion for this pesticide. Diazinon concentrations ranged from below the detection limit of 30 ng/L to as high as 1,500 ng/L with the median concentration at 210 ng/L. Thirty-six of 47 samples (76.6%) tested for toxicity produced total mortality within 72 h with *C. dubia.* Toxicity identification evaluations on selected samples confirmed that toxicity was primarily due to one or both of these pesticides. Uses of diazinon and chlorpyrifos in urban areas include dormant sprays on fruit trees, professional landscape and maintenance uses, and structural pest control. Pesticide concentrations were lower in a catchment favoring commercial and industrial activities compared with a catchment receiving largely residential inputs. Aerial drift from agricultural applications may play a role in storm-water concentrations.

      A comparative large-scale characterization study was done in the San Francisco Bay Area around the same time period. See *Diazinon in Surface Waters in the San Francisco Bay Area: Occurrence and Potential Impact* elsewhere in this review**.** Concentrations of diazinon and chlorpyrifos were higher in Valley cities than those found in the Bay Area, especially during February. This may be a consequence of aerial transport and deposition during rainfall events.
    - **Link:** No link; however, hardcopy is available. See Nan S.

6) **Sacramento Comprehensive Storm Water Management Program (CSWMP)**
    - **Sampling Period:** January 1989 to present (data from 1995-1997)
    - **Sampling Entity:** Larry Walker & Associates
    - **Funding Entity:** County of Sacramento, Cities of Sacramento, Folsom and Galt
    - **Study Area:** Sacramento/Strong Ranch Slough watershed area.
    - **Pesticide Analytes:** Carbamates (EPA 632) and organophosphates (EPA 8141)

- **Descriptions/Findings:** The goal of the CSWMP is to reduce urban runoff pollutants to the maximum extent possible. Results of the monitoring program are submitted annually to the CVRWQCB as part of the NPDES permit requirement for the County of Sacramento and associated drainages from the cities of Sacramento, Folsom and Galt. The CSWMP's characterization of urban runoff is the most complete for any NPDES stormwater permittee in the watershed.

  Urban discharge monitoring takes place at three sites: Strong Ranch Slough (a concrete-lined channel that provides drainage for 5162 acres of urban watershed); Sump 111 is a stormwater pumping facility with an industrial watershed of 420 acres. It discharges to the American River, less than a mile upstream from the river's confluence with the Sacramento River; Sump 104 is a stormwater pumping facility with an urban watershed of about 2220 acres. It discharges to the Sacramento River, upstream of the "pocket area". Collectively, these three sampling locations are referred to as "discharge sites".

  In the 1995-1996 storm season, benomyl, diuron, chlorpyrifos, diazinon, prometon, Prowl, and simazine. In the 1996-1997 storm season, carbaryl, chlorpyrifos, diazinon, diuron, prometon, Prowl, and simazine were detected.
- **Link:** http://www.sacstormwater.org

7) ***Atmospheric Transport of Pesticides in the Sacramento, California Metropolitan Area, 1996-1997*. M. Majewski and D. Baston. United States Geological Survey. Sacramento. 2002.**
   - **Sampling Period:** January 1996 to December 1997
   - **Sampling Entity:** U.S. Geological Survey (USGS)
   - **Funding Entity:** USGS, DPR
   - **Study Area:** 3 Sacramento area sites (1 urban, 2 ag.)
   - **Objective(s):** To determine the temporal and spatial distribution and trends of selected agricultural pesticides in air during a 2-year period. To determine whether pesticides used in nearby agricultural areas were drifting through the atmosphere into the urban environment.
   - **Pesticide Analytes:** 17 pesticides (insecticides: carbaryl, carbofuran, chlorpyrifos, diazinon, malathion, methidathion; herbicides: alachlor, atrazine, dacthal, EPTC, molinate, pendimethalin, simazine, thiobencarb, trifluralin; and the fungicide chlorothalonil.)
   - **Descriptions/Findings:** Weekly composite, bulk air samples showed a number of pesticides present in the atmosphere throughout the year. The compounds detected most frequently and at the highest concentrations were chlorpyrifos, diazinon, molinate, thiobencarb, and trifluralin. Other compounds such as malathion, carbaryl, and pendimethalin were detected less frequently.

     Molinate and thiobencarb offered the clearest example of pesticides used in agriculture drifting into the urban area. Winter data also suggest that similar drift may be occurring with chlorpyrifos, diazinon, and trifluralin; however, source confirmation of the drifting residues was difficult because many ag. pesticides, including these three, are also heavily used in urban areas. Carbofuran, not considered to be widely used in

the urban environment, was detected at the urban site in about 1/3 of the samples. On several occasions, the concentrations of several pesticides were higher at the urban site than the ag. sites. The residues detected in the urban air are, most likely, a result of both urban and ag. sources.
- **Link:** http://www.cdpr.ca.gov/docs/sw/contracts/usgs024100.pdf

8) ***Toxicants in Surface Waters of the Sacramento Watershed*. Cooke, J., and Conner, V., et al, 1998.**
   - **Sampling Period:** February 1996 to June 1997
   - **Sampling Entity:** CVRWQCB
   - **Funding Entity:** CVRWQCB
   - **Study Area:** Arcade Creek, Sacramento County
   - **Pesticide Analytes:** Not applicable. Report compiled past studies in Sacramento.
   - **Descriptions/Findings:** This report reviewed and summarized available information prior to 1998 on toxicants in surface waters of the Sacramento River watershed. This is an excellent source on urban and agricultural studies on a wide range of water constituents in the watershed. Many of the urban pesticide monitoring data that appear in this report are addressed separately elsewhere in this compendium.
   - **Link:** http://www.sacriver.org/subcommittees/toxics/documents/Toxsurwatr.pdf

9) **Sacramento River Watershed Program (SRWP).**
   - **Sampling Period:** Episodic Events 1996 – present
   - **Sampling Entity:** SRWP? County or CVRWQCB?
   - **Funding Entity:** U.S. EPA and other regional agencies
   - **Study Area:** Sacramento River Watershed
   - **Pesticide Analytes:** Multiple pesticide screens
   - **Descriptions/Findings:** The SRWP was initiated by the Sacramento Regional County Sanitation District using U.S. EPA funds. The SRWP produces annual monitoring reports which contains pesticide monitoring data from one urban site – Arcade Creek.

     The SRWP sampled Arcade Creek monthly in August 1996-July 1997. Samples were toxic to *C. dubia* at all by one sampling time. TIE linked the observed toxicity to diazinon and chlorpyrifos. Chemical analysis verified these pesticides were in the creek throughout the year at levels capable of causing the toxicity. The highest diazinon concentrations measured was in January 1997 (1,170 ng/L) and levels remained high through May (490 ng/L). Chlorpyrifos concentrations ranged from non-detectable to 140 ng/L. In October and November of 1997, carbaryl, chlorpyrifos, diazinon, diuron and glyphosate were also detected. Carbaryl and diazinon were above the U.S. EPA aquatic life criteria.

     The Creek had the largest number of pesticides and the greatest concentrations of any water body monitored by the SRWP 2000 and 2001 programs. Carbaryl, chlorpyrifos, diazinon, diuron, prometon, propazine, prowl, and tebuthruron were all detected in Arcade Creek. Diazinon was detected at levels exceeding the DFG's CCC of 0.05 ug/L in 67% of the samples taken in 2000-2001. Arcade Creek receives diazinon from runoff from landscaping application and aerial deposition from agricultural applications. Chlorpyrifos was not detected at greater than CCC levels in 2001 although it was detected twice.

- **Link:** http://www.sacriver.org/

10) ***Occurrence and Transport of Diazinon in the Sacramento River, CA, and Selected Tributaries During Three Winter Storms, January-February 2000.* Water Resources Investigations Report 02-4101. Sacramento. 2001.**
    - **Sampling Period:** January and February 2000
    - **Sampling Entity:** USGS, DPR, CVRWQCB, UCD
    - **Funding Entity:** DPR
    - **Study Area:** Middle to Lower Sacramento River Watershed
    - **Pesticide Analytes:** Diazinon
    - **Descriptions/Findings:** Diazinon concentrations in the Sacramento River and selected tributaries were monitored during three winter storms in early 2000. Gilsizer Slough @ Bogue Road, located downstream of Yuba City was chosen to represent possible urban sources of pesticides. Land use in the watershed upstream of this site is predominantly residential and commercial.

      Forty-seven samples were collected from Gilsizer Slough and analyzed using ELISA analysis. Only five samples contained diazinon levels lower than the DFG water quality criteria (80 ng/L) for diazinon. Diazinon concentrations ranged from 50 to 2,490 ng/L. Levels detected during the sampling periods were some of the highest among all of the sites sampled.

      This investigation was repeated in January and February 2001 with some minor adjustments to the monitoring protocol. The report on the 2^{nd} year of monitoring is pending.
    - **Link:** http://water.usgs.gov/pubs/wri/wri02-4101/wri02-4101.pdf

11) ***Preliminary Report on Mass Loading of Diazinon to the Sacramento River in the Vicinity of Chico*. D. Brown, Bidwell Environmental Institute. California State University, Chico. September 2001.**
    - **Sampling Period:** February 2001
    - **Sampling Entity:** California State University, Chico
    - **Funding Entity:** DPR
    - **Study Area:**
    - **Pesticide Analytes:**
    - **Descriptions/Findings:** This study investigated the potential for urban organophosphate pesticide (particularly diazinon) loading in the Sacramento River just south of the City of Chico. The Chico urban creeks monitored included Mud Creek, Big Chico Creek, Little Chico Creek, Lindo Channel, and Sycamore Diversion. A storm event from February 8-12, 2001 was monitored. Results showed that eight out of 15 samples from Chico urban creeks contained detectable (greater than 20 ng/L) levels of diazinon. Concentrations ranged from 20 to 185 ng/L. The overall Chico urban area creeks diazinon load appear to have been relatively low compared to the loads

generated downstream in the vicinity of the dormant spray areas of the middle to lower Sacramento River.
- **Link:** No link, but hard copy available. See Nan.

San Joaquin River Watershed-Specific Studies

12) ***Review of the City of Stockton Urban Stormwater Runoff Aquatic Life Toxicity Studies Conducted by the CVRWQCB, DeltaKeeper and the University of California, Davis, Aquatic Toxicology Laboratory between 1994 and 2000.* G. Fred Lee & Associates, El Macero, CA. May 2001.**
    - **Sampling Period:** 1994-2000
    - **Sampling Entity:** CVRWQCB and DeltaKeeper
    - **Funding Entity:** U.S. EPA, CVRWQCB, CALFED, DeltaKeeper
    - **Study Area:** City of Stockton
    - **Pesticide Analytes:**
    - **Descriptions/Findings: This review covers two studies of Stockton area storm runoff toxicity.** The first study is the investigation is represented by the monitoring work done by the CVRWQCB in 1994 (See *Diazinon and chlorpyrifos in urban waterways in northern California, USA* by Bailey et al. 2000). The second study expands on the CVRWCB's work and was supported by the DeltaKeeper beginning in 1996 and is covered here. Storm runoff samples from five Stockton area waterways: Mosher Slough, Five Mile Slough, Calaveras River, Walker Slough-Duck Creek, and the Smith Canal were examined. Of these, Smith Canal and Five Mile Slough receives urban runoff from the City of Stockton.

      All of the runoff samples taken between 1996 and 1999 were toxic to *C. dubia*. Typically, 1 to 2 toxic units of toxicity was found with some samples containing about 4 toxic units. Concentrations of diazinon and chlorpyrifos detected in the samples frequently exceeded DFG's WQC. Samples collected a day after runoff events were in general non-toxic and had low levels of OPs. Based on Toxicity Identification Evaluations diazinon was the constituent primarily responsible for the observed toxicity Some samples had sufficient levels of chlorpyrifos to contribute to the toxicity. Pyrethroids toxicity may also be present based on TIE.
    - **Links:** http://www.gfredlee.com/stockton-txt_0401.pdf**.**

13) ***Toxicity of Urban Runoff in Modesto, CA.* Prepared by the Aquatic Toxicology Laboratory (ATL), University of California, Davis for the City of Modesto. Davis. May 1999.**
    - **Sampling Period:** 1998-2000
    - **Sampling Entity:** UC Davis ATL
    - **Funding Entity:** City of Modesto
    - **Study Area:** City of Modesto

- **Pesticide Analytes:** U.S. EPA 8141 Special Low Level List. Carbaryl, diazinon, and methidathion detected.
- **Descriptions/Findings:** The objectives of this study were to measure and identify potential toxicity to aquatic organisms caused by urban storm water runoff in water samples from Dry Creek in the City of Modesto. Samples were collected from two sites (one urban) on Dry Creek during two storms of the 1998/1999 winter season.

  During both rainstorms, water samples collected at Moose Park (urban site) were more toxic than at Copper Creek (agricultural site). The chemical compound that caused the majority of the observed toxicity to *C. dubia* was identified as diazinon. Diazinon concentrations up to 2,100 ng/L (about five times the LC50 of *C. dubia*) were measured. Low concentrations of carbaryl (up to 200 ng/L) and methidathion (up to 240 ng/L) were also detected. Heavy metals potentially contributed to algal (*S. capricornutum*) toxicity in the study's second storm.
- **Link:** No Link, but hard copy available. See Nan S.

14) ***Diazinon and Chlorpyrifos Loads in Precipitation and Urban and Agricultural Storm Runoff during January and February 2001 in the San Joaquin River Basin, California*. USGS Water Resources Investigations Report 03-4091. Sacramento. 2003.**
   - **Sampling Period:** January to February 2001
   - **Sampling Entity:** USGS
   - **Funding Entity:** USGS, DPR
   - **Study Area:** San Joaquin River Basin
   - **Pesticide Analytes:** Chlorpyrifos and diazinon
   - **Descriptions/Findings:** The storm runoff samples collected at the McHenry storm drain in Modesto had the highest diazinon concentrations found in the study. All nine runoff samples collected there exceeded the DFG CMC (0.08 ug/L). The lowest concentration collected (0.506 ug/L) was more than six times greater than the CMC and the highest concentration collected (0.947 ug/L) was more than 12 times the CMC. Chlorpyrifos detections had similar concentration pattern as for diazinon with a maximum concentration of 0.035 ug/L, but they were more than one order of magnitude less. Seven of the nine samples exceeded the proposed DFG CMC of 0.02 ug/L.

     When rain and runoff concentrations were compared, 68 percent of the diazinon concentration in the runoff could be accounted for by contributions from the rain. Chlorpyrifos, however, had average rain concentrations that were 2.5 times higher than what was detected in the runoff.
   - **Link:** http://water.usgs.gov/pubs/wri/wri034091/wrir034091.pdf

San Francisco Bay Area-Specific Studies

15) ***San Francisco Bay Area Stormwater Runoff Monitoring Data Analysis 1988-1995*. Report prepared by Woodward-Clyde Consultants for the Bay Area Stormwater Management Agencies Association (BASMAA), Oakland, CA. October 1996**
    - **Sampling Period:** 1988 to 1995
    - **Sampling Entity:** BASMAA member municipalities
    - **Funding Entity:** BASMAA member municipalities
    - **Study Area:** San Francisco Bay Area
    - **Pesticide Analytes:** Chlorpyrifos and diazinon
    - **Descriptions/Findings:** This BASMAA report highlights findings of stormwater runoff monitoring programs from 1988 to 1995. Runoff data have been collected by a number of Bay Area agencies for a variety of purposes including characterization of pollutant concentrations from different land-use areas, assessment of compliance with receiving water quality objectives, source identification of pollutants and toxicity, and evaluation of best management practice effectiveness.

      Stormwater runoff is often toxic to the test organism *C. dubia*. For most waterways, the organisms die between 1 to 7 days of exposure to runoff. The commonly used insecticide diazinon has been identified as the cause of the observed toxicity in some residential watersheds. Little pesticide data exists in this compilation; however, the document gives good comprehensive look at stormwater program activities in the Bay Area in this time period.
    - **Link:** No link; however, hardcopy of the report's background section is available. See Nan S.

16) ***DUST Marsh Special Studies*. Reports prepared by Woodward-Clyde Consultants for the Alameda County Urban Runoff Clean Water Program (ACURCWP), Hayward, CA. April 1994, January 1995, December 1996.**
    - **Sampling Period:** 1992 to 1996
    - **Sampling Entity:** Woodward-Clyde
    - **Funding Entity:** ACURCWP
    - **Study Area:** Demonstration Urban Stormwater Treatment (DUST) Marsh
    - **Pesticide Analytes:** Diazinon
    - **Descriptions/Findings:** Alameda County constructed a prototype marsh known as the Demonstration Urban Storm Water Treatment (DUST) Marsh in the early 1980's near Coyote Hills Regional Park. The purpose was to test the effectiveness of artificial wetlands on urban water treatment.

      Toxicity Identification Evaluation (TIE) was conducted on water collected from Crandall Creek following a 1994 storm. TIE identified diazinon as the source of the toxicity. The diazinon concentration in the sample was about 250 ng/L.
    - **Link:** No link; however, hardcopy is available. See Nan S.

17) ***Identification and Control of Toxicity in Storm Water Discharges to Urban Creeks*. Final Report prepared by S. R. Hansen and Associates for Alameda County Urban Runoff Clean Water Program (ACURCWP), Hayward, CA. March 1995.**
   - **Sampling Period:** Winter 1993-94
   - **Sampling Entity:** S.R. Hansen and Associates
   - **Funding Entity:** ACURCWP
   - **Study Area:** San Lorenzo and Alameda Creeks
   - **Pesticide Analytes:** Diazinon
   - **Descriptions/Findings:** One of the earliest urban stormwater studies in California that implicated diazinon in runoff toxicity. Four samples from a 1993 storm, four samples from a 1994 storm, and two samples collected following another storm in 1994.

     TIE determined that OP pesticides were the cause of toxicity. Diazinon was detected in the samples at concentrations ranging from 820 ng/L to 2,900 ng/L. Since diazinon was the primary pesticide in the samples and was present at potentially toxic levels, diazinon was concluded to be the OP pesticide responsible for the toxicity.
   - **Link:** No link. Hard copy being sought. Summary from other reports used to compile current information.

18) ***Diazinon in Surface Waters in the San Francisco Bay Area: Occurrence and Potential Impact.* R. Katznelson and T. Mumley. Report prepared by Woodward-Clyde Consultants and with assistance from the SFBRWQCB for the Alameda Countywide Clean Water Program. June 1997.**
   - **Sampling Period:** 1994 to 1996
   - **Sampling Entity:** Woodward-Clyde Consultants
   - **Funding Entity:** ACCWP
   - **Study Area:** Selected San Francisco Bay Area creeks
   - **Pesticide Analytes:** Diazinon

     Descriptions/Findings: In this large-scale characterization study of diazinon and chlorpyrifos, approximately one hundred and fifty urban storm runoff samples were collected by storm water agencies in the Bay Area between 1994 and 1995.

     Following 1994 and 1995 winter storms, diazinon was found at concentrations ranging from 38 to 590 ng/L in creeks throughout the Bay Area. Table 2.4 in the report at link below shows concentrations of diazinon from 20 urban creeks. The median concentration was 370 ng/L. Overall, 50 percent of the total samples taken exceeded the DFG WQC.

     Forty-four samples were also analyzed for chlorpyrifos. Approximately 75% of these exceeded the DFG WQC. Most values were less than 100 ng/L. These preliminary measurements spawned more intensive studies.

     During the 1995 and 1996 dry seasons, diazinon was detected in 12 of 12 water samples collected from Castro Valley Creek. The concentrations ranged from 40 to 340 ng/L with a median of 65 ng/L. Diazinon was detected in 16 of 18 water samples collected from Crandall Creek. The detection limit was 30 ng/L and the detected concentrations ranged from 58 to 442 ng/L with a median of 220 ng/L. Diazinon was detected in 8 of 9 samples collected at three inlets to Tule Pond in Fremont. The detection limit was 25 ng/L and the detected concentrations ranged from 80 to 3,000 ng/L with a median of 300 ng/L.

A comparative characterization study was done in the Sacramento and Stockton urban areas around the same time period. See *Diazinon and chlorpyrifos in urban waterways in northern California, USA* elsewhere in this review. Concentrations of diazinon and chlorpyrifos were higher in Valley cities than those found in the Bay Area, especially during February. This may be a consequence of aerial transport and deposition during Valley rainfall events.

- **Link:** No link; however, hardcopy is available. See Nan S.

19) ***Sediment Diazinon Special Study.* Report prepared by Woodward-Clyde Consultants for the Alameda County Urban Runoff Clean Water Program (ACURCWP), Hayward, CA. December 1996.**
    - **Sampling Period:** 1995
    - **Sampling Entity:** Woodward-Clyde
    - **Funding Entity:** ACURCWP
    - **Study Area:** Castro Valley and San Leandro Creeks
    - **Pesticide Analytes:** Diazinon
    - **Descriptions/Findings:** Sediment from various locations in Castro Valley and San Leandro Creeks were sampled and analyzed for diazinon. Diazinon concentrations in the top 0.2 cm of muddy bank sediment from Castro Valley Creek and San Leandro Creek ranged from 4,100 to 33,100 ng/kg (ppt). Diazinon in fine sediment collected from the top 8 cm of these streambeds ranged from 2,800 to 55,300 ng/kg.
    - **Link:** No link; however, hardcopy is available. See Nan S.

20) ***Characterization of the Presence and Sources of Diazinon in the Castro Valley Creek Watershed*. Report prepared by ACCWP and the Alameda County Flood Control District (ACFCD), Hayward, CA. June 1997.**
    - **Sampling Period:** 1995-1996 rainy season
    - **Sampling Entity:** ACCWP and ACFCD
    - **Funding Entity:** ACCWP and ACFCD
    - **Study Area:** Castro Valley Creek
    - **Pesticide Analytes:** Diazinon
    - **Descriptions/Findings:** Diazinon concentrations following 12 storm events and non-storm periods were measured in Castro Valley Creek. Diazinon was detected in all samples. The mean concentration for each storm event ranged from 180 to 820 ng/L. The median concentration for a storm event was 310 ng/L. In some cases, values over 150 ng/L persisted for up to one week. Diazinon concentrations during periods of non-storm flows (during sping, when flows were less than 5 cu. ft. per sec.) ranged from 110 to 760 ng/L, with a median of 420 ng/L. Samples collected during longer dry weather periods ranged from 35 to 220 ng/L, with a median of 80 ng/L.

Changes in diazinon concentrations follow the seasonal use pattern. Diazinon applications drop during winter and rise in March, with the heaviest applications during summer and early fall. Diazinon concentrations in storm water were greater when no substantial precipitation preceded a storm. Variations in diazinon concentrations appeared to follow one of two patterns during storm events. A peak concentration occurred early, followed by a substantial decline, or elevated concentrations remained relatively consistent throughout a storm. The early peak concentrations correspond to storms following periods without substantial precipitation. After storms ended, diazinon concentrations remained elevated, dropping by about one half within two days.

Diazinon applied on surfaces during dry weather appeared to accumulate before washing into the creek during storms. The mass of diazinon discharged to the creek increased with increased flow, although diazinon concentrations decreased. Diazinon concentrations were higher in residential and commercial areas compared to those with more open space. Higher levels were not clearly associated with any particular neighborhoods, however, and diazinon samples from adjacent gutters draining separate residences sometimes exhibited very different concentrations. Alameda County concluded that diazinon comes from multiple, sporadic sources. Individual sources may be very localized, and downstream diazinon levels apparently reflect and average of upstream pulses. At any one time, about 2 to 4% of the properties in residential areas could be contributing diazinon to urban runoff. Some consistent discharges may also exist in the watershed because some relatively high diazinon concentrations occurred at certain locations during more than one sampling event.

- **Link:** No link; however, hardcopy is available. See Nan S.

21) ***Volunteer Monitoring in San Leandro Creek, Technical Summary Report, 1995-1998*. Report prepared by URS Greiner Woodward-Clyde Consultants for the ACCWP, Hayward, CA. 1999.**
    - **Sampling Period:** 1995-1998
    - **Sampling Entity:** Citizen volunteer w/ professional guidance.
    - **Funding Entity:** ACCWP
    - **Study Area:** San Leandro Creek Watershed
    - **Pesticide Analytes:** Diazinon
    - **Descriptions/Findings:** Street gutter samples collected from residential areas during a storm exhibited low diazinon concentrations in many areas and high levels in a few areas. Creek samples were more uniform and reflected the average of many different storm water discharges. The data suggest that diazinon applications at discrete, variable, and independent locations are responsible for the diazinon observed in surface water.
    - **Link:** No link; however, hardcopy is available. See Nan S.

22) ***Diazinon/Chlorpyrifos in Central Contra Costa Sanitary District (CCCSD) Sewer System, 1996*. Nan Singhasemanon et al. Department of Pesticide Regulation. EHAP Report 98-05. 1998.**
   - **Sampling Period:** Summer 1996
   - **Sampling Entity:** CCCSD, DPR
   - **Funding Entity:** CCCSD, DPR (jointly funded)
   - **Study Area:** Central Contra Costa County commercial and residential sewer lines
   - **Pesticide Analytes:** Diazinon, chlorpyrifos
   - **Descriptions/Findings:** Goal of the study was to characterize diazinon and chlorpyrifos in CCCSD's sewage system including treatment plant influent and service area sources. Diazinon and chlorpyrifos were detected in all 37 of CCCSD's wastewater influent samples. Mean concentrations of diazinon and chlorpyrifos were 310 and 190 ppt, respectively. A survey of two additional POTWs in the Bay Area shows similar influent concentrations. Residential sampling from five neighborhoods in the CCCSD service area over a one-week period of July 1996 yielded 35 samples. Mean daily concentrations of diazinon were 740, 420, 340, 120, and 110 ppt. Mean daily concentrations of chlorpyrifos were 550, 180, 110, 110, and 80 ppt. Pet groomers, kennels, and PCO's were sampled as commercial sources. Although variable, commercial sources showed the highest concentrations measured. A kennel sample contained 20,000 ppt of diazinon. A pet groomer sample contained 38,000 ppt of chlorpyrifos. Mass load calculations showed that residential contributions likely make up the majority of the two OPs entering the CCCSD treatment plant due to the large flows of residential areas compared to commercial sources.
   - **Link: EH 98-05** and **Executive Summary**

23) ***Diazinon and Chlorpyrifos Quantitative Identification for San Francisco Bay Area Wastewater Treatment Plants.* Prepared by T. Chew, K. Easton, and A. Laponis (CCCSD) in partnership with the San Francisco Bay Area Pollution Prevention Group. 1998.**
   - **Sampling Period:** August 1997
   - **Sampling Entity:** Participating publicly-owned treatment works (POTWs)
   - **Funding Entity:** Participating publicly-owned treatment works (POTWs)
   - **Study Area:** San Francisco Bay Area
   - **Pesticide Analytes:** Chlorpyrifos and diazinon
   - **Descriptions/Findings:** Wastewater treatment plant influents and treated effluents were taken concurrently in August 1997 to 1) compare diazinon and chlorpyrifos levels among Bay Area POTWs; 2) compare different treatment method removal efficiencies; and 3) determine daily mass loads. The nine participating POTWs were located in Contra Costa, Fairfield-Suisun, Hayward, Palo Alto, Petaluma, San Francisco, San Jose, Union City-Fremont, and Vallejo.

     Both diazinon and chlorpyrifos were continually detected in all the POTWs influents. The average diazinon influent concentrations ranged from 288 ng/L at Palo Alto to 1211 ng/L at San Francisco. For chlorpyrifos, concentrations ranged from 30 ng/L at San Francisco to 176 at Contra Costa. Removal efficiencies varied among treatment plants as well as temporally at a particular plant. The best and worst average removal efficiencies for diazinon was 98 and 63 percent. The best and worst average removal

efficiencies for chlorpyrifos was 86 and 18 percent. Effluents discharged often times contained both diazinon and chlorpyrifos at levels higher than LC_{50} values of *C. dubia*.
- **Link:** No link. Hardcopy still being sought. Hardcopy of presentation summary available.

24) ***Diazinon in Dry Weather Flows and Sediments*, 1996-1998, prepared by URS Greiner Woodward Clyde, December 1999.**
- **Sampling Period:** 1998 dry season
- **Sampling Entity:** URS Greiner Woodward Clyde
- **Funding Entity:** ACCWP
- **Study Area:** Alameda County
- **Pesticide Analytes:** Diazinon
- **Descriptions/Findings:** Fifteen urban creeks in Alameda County were sampled during the 1998 dry season. The samples were collected on Sunday afternoons, when gardening activity and pesticide applications were expected to be high.

  Diazinon was detected in 26 (44%) of 59 samples. The detection limit was 30 ng/L. The highest concentration was detected in a sample from Arroyo de la Laguna at 617 ng/L. The three highest median concentrations were 150 ng/L at Cerrito Creek, 137 ng/L at Alameda Creek, and 94 ng/L at Arroyo de la Laguna. Diazinon was below detection limits in four creeks: Codornices, Strawberry Creek, Sausal Creek, and Arroyo Viejo.
- **Link:** No link; however, hardcopy is available. See Nan S.

25) ***Diazinon and Chlorpyrifos in the Upper Petaluma River Watershed*. B. Abelli-Arnen. Prepared by BASELINE Environmental Consulting for the Petaluma Tree Planters. May 1999.**
- **Sampling Period:** October and November 1998
- **Sampling Entity:** BASELINE Environmental Consulting
- **Funding Entity:** Petaluma Tree Planters
- **Study Area:** Petaluma River Watershed
- **Pesticide Analytes:** Chlorpyrifos and diazinon
- **Descriptions/Findings:** Thirty-seven storm-related and dry weather samples were collected from river, creek, and storm drain sampling locations in and around Petaluma. Eight total sites were investigated. The sub-watersheds draining to five of the eight sites are considered primarily urban. All samples were analyzed for chlorpyrifos and diazinon using ELISA techniques (reporting limit of 30 ng/L).

  Results indicate that dry weather flows did not contain considerable concentrations of either OPs. However, approximately 50 percent of the storm-related samples contained potentially toxic concentrations of either diazinon or chlorpyrifos or both. Residential and commercial land uses are dominant in the drainages of the sampling locations with the highest concentrations. The highest diazinon level measured (1,368 ng/L) was at Thompson Creek which drains a primarily suburban residential, commercial, and light industrial watershed. The highest chlorpyrifos level measured (77 ng/L) was at Turning Basin which is in a primarily commercial and suburban residential area. Results from

this study led to the listing of the inclusion of the Petaluma River to the CWA 303(d) list and subsequently to the San Francisco Bay Area Urban Creeks Pesticide TMDL.
- **Link:** Hard copy available. See Nan S.

26) **Diazinon Urban Runoff Study**
- **Sampling Period:** Winter 2001-2002
- **Sampling Entity:** County of Alameda
- **Funding Entity:** DPR
- **Study Area:** Alameda County, paved surface runoff
- **Pesticide Analytes:** Diazinon
- **Descriptions/Findings:** The study investigated the wash-off dynamics of diazinon from paved test-plots and runoff concentrations of diazinon from applications to actual urban (two residential and one industrial) sites. The first portion of the study showed that runoff exhibited a first flush characteristic with a leveling off after the first 1.5 inches of runoff. The average first flush concentration was 2,400 ppb. After 2.6 inches of runoff, only 11% of the total mass of diazinon applied was washed off. The second portion of the study showed that grab samples of runoff from spray areas contained the high concentrations of diazinon (as high as 1,900 ppb), comparable in magnitude to runoff from test plots.
- **Link:** Runoff of diazinon from paved plots and test sites: Summary of results

27) ***Russian river First Flush Summary Report.* Revital Katznelson. Citizen Monitoring Program. State Water Resources Control Board. June 2003.**
- **Sampling Period:** November 2002
- **Sampling Entity:** SWRCB Citizen Monitoring Program (part of SWAMP)
- **Funding Entity:** SWRCB and the Northern Coast Regional Water Quality Control Board
- **Study Area:** Russian River
- **Pesticide Analytes:** Diazinon
- **Descriptions/Findings:** On November 7, 2002, approximately 100 citizen monitors conducted field measurements and collected water samples at 21 urban locations within the Russian River Watershed during the first runoff event of the 2002-2003 rainy season with the assistance of water quality professionals. The first flush was intended to characterize the runoff in different parts of the watershed and identify sources of pollutants.

  Samples from Foss Creek and Cotati Creek exhibited high levels of diazinon. The peak levels from each creek were 780 and 480 ng/L. More than half of the samples taken from the watershed contained diazinon above the study's detection level of 30 ng/L.
- **Link:** http://www.swrcb.ca.gov/rwqcb1/down/russriv/062703RRFFFinalsmall.pdf

28) ***Santa Clara Valley Urban Runoff Pollution Prevention Program FY 02-03 Receiving Waters Monitoring Report.* Prepared by Kinnetic Laboratories, INC. for EOA, INC. for SCVURPPP. July 2003.**
   - **Sampling Period:** September 2002, January 2003, and April 2003
   - **Sampling Entity:** Kinetics Lab. Inc.
   - **Funding Entity:** SCVURPPP
   - **Study Area:** Lower Penitencia Cr. and Coyote Cr. in Santa Clara Valley Watersheds
   - **Pesticide Analytes:** OPs
   - **Descriptions/Findings:** Water samples were collected from five stream sites in the Lower Penitencia Creek watershed and six stream sites in the Coyote Creek watershed. Samples were taken to be representative of dry-weather, wet-wet-weather, and spring periods.

     Diazinon concentrations ranged from 0.02 to 0.05 ug/L (mdl 0.01 ug/L). Diazinon detected in 4 of 21 samples. Eighteen other OPs were not found in any of the samples.
   - **Link:** http://www.scvurppp-w2k.com/bioassessment/Water_Quality_Report_fy02-03.pdf

Southern California-Specific Studies

29) **Los Angeles County Dept of Public Works (LACDPW) Stormwater - NPDES Monitoring Program**
   - **Sampling Period:** Winter 1997/1998
   - **Sampling Entity:** LACDPW
   - **Funding Entity:** LACDPW
   - **Study Area:** Los Angeles County and Santa Monica Bay
   - **Pesticide Analytes:** Chlorpyrifos and diazinon
   - **Descriptions/Findings:** LACDPW manages the stormwater sampling and analysis program for the County of Los Angeles, City of Los Angeles, and 83 other municipalities within the county that are co-permittees in their municipal stormwater NPDES discharge permit. In 1997-98, the LACDPW monitored; eight land use stations including residential, industrial, commercial, transportation, educational and vacant lands; four mass emission stations including Malibu Ck, Ballona Ck, Los Angeles River and San Gabriel River; and receiving water monitoring offshore Malibu Ck and Ballona Ck. The LACDPW attempts to capture a combined 200 station events per year which includes samples during both wet and dry weather.
   - **Link:** http://www.gatekeeper.com/stormwater/

30) ***Aquatic Life Toxicity for the Los Angeles County Stormwater Runoff Samples Collected on March 25, 1998.* G. Fred Lee & Associates, El Macero, CA. December 1998.**
   - **Sampling Period:** March 1998
   - **Sampling Entity:** Los Angeles County Department of Public Works (LACDPW)
   - **Funding Entity:**
   - **Study Area:** Los Angeles

- **Pesticide Analytes:** Diazinon and chlorpyrifos
- **Descriptions/Findings:** The LACDPW collected monthly samples from various streams and rivers in the Los Angeles Area for the March 25, 1998 storm. The focus of the monitoring was on toxicity potentially due to organophosphorus pesticides. Samples from Coyote Creek (City of Long Beach), Ballona Creek (Culver City), and Project 156 (City of Glendale) contained diazinon at the levels of 586, 375, and 298 ng/L, respectively. Chlorpyrifos was detected in Coyote Creek and Ballona Creek at 102 and 50 ng/L, respectively.

  Los Angeles County stormwater runoff is toxic to *Ceriodaphnia dubia*. The OP pesticides diazinon and chlorpyrifos did not account for all of the observed toxicity. The determination of the constituents that caused the remainder of the toxicity in the samples was beyond the scope of this study. From the limited data available it appears that the residential areas in the Los Angeles region contributed higher levels of toxicity to stormwater.
- **Link:** http://www.gfredlee.com/la_aqtox.pdf

31) ***Results of Aquatic Life Toxicity Studies Conducted During the 1997-99 in the Upper Newport Bay Watershed, and Review of Existing Water Quality Characteristics of Upper Newport Bay, Orange County CA and its Watershed.*** **G. Fred Lee and Associates, submitted to SWRCB, SARWQCB, and OC PFRD to meet requirements of the U.S. EPA 205(j) Project. October 1999.**
   - **Sampling Period:** 1997 to 1999
   - **Sampling Entity:**
   - **Funding Entity:** OC PFRD (with U.S. EPA 205(j) grant)
   - **Study Area:** Upper Newport Bay watershed.
   - **Pesticide Analytes:** Benomyl, carbaryl, chlorpyrifos, diazinon, dimethoate, diphenamid, fensul fothion, malathion, merphos, metalaxyl, methiocarb, methidathion, methomyl, methyl trithion, prowl, simazine, stirophos, and trifluralin.
   - **Descriptions/Findings:** This report covers the results of a U.S. EPA 205(j)-funded project devoted to assessing aquatic life toxicity in the Upper Newport Bay watershed in Orange County, California. A total of nine storm events were sampled during the 1997-1999 winter seasons. A total of 6 dry weather low flow samples were also collected. There were approximately 13 sites studied.

     About half of the observed toxicity in the watershed is likely due to the OP pesticides diazinon and chlorpyrifos. Constituents causing the remaining toxicity have yet to be determined. OP pesticide toxicity is likely derived from urban residential use for structural and lawn and garden pest control. There are also high concentrations of diazinon discharged from commercial nurseries during stormwater runoff as well as dry periods. Maximum concentrations of a number of pesticides detected can be found in Table 4-6 in the report link below.
   - **Link:** http://www.gfredlee.com/205j_final.pdf

32) ***Results of Aquatic Toxicity Testing Conducted During 1999-2000 within the Upper Newport Bay Watershed*. Report to the State Water Resources Control Board, Santa Ana Regional Water Quality Control Board, and the Orange County Public Facilities and Resources Department. G. Fred Lee & Associates, El Macero, CA and RBF Consulting, Irvine, CA. January 2001.**
   - **Sampling Period:** 1999 and 2000
   - **Sampling Entity:** RBF Consulting
   - **Funding Entity:** Orange County Public Facilities and Resources Department (under U.S. EPA 319(h) grant.
   - **Study Area:** Upper Newport Bay watershed
   - **Pesticide Analytes:** Benomyl, carbaryl, chlorpyrifos, diazinon, diuron, malathion, methomyl, and Prowl.
   - **Descriptions/Findings:** This paper represents a summary of pesticide and toxicity monitoring results for the Upper Newport Bay watershed for the purpose of defining the sources of selected pesticides and aquatic life toxicity. This report is intended to be a follow up of the 1997-1999 report by the same investigator. Pesticide analysis results for this study can be found in Table 3 in the report link below.

     Under storm runoff conditions there were high levels of *Ceriodaphnia* toxicity at nine of 10 stations. As much as 16 *Ceriodaphnia* acute toxic units were detected. The dry weather sampling that occurred generally showed low levels of toxicity with one exception that also had a measured toxicity unit of 16. The mixed land use nature of five of the sampling stations' drainages confounded the determination of the significance of a particular type of land use as a source of OPs as well as toxicity. However, it appeared that the mixed residential, commercial, and industrial station showed the highest export rates for OPs. The primarily agriculture and nursery stations showed the lowest export rates.
   - **Link:** http://www.gfredlee.com/optox_rev_021801.pdf

33) ***Contributions of Organophosphorus Pesticides from Residential Land Uses During Dry and Wet Weather*. Ken Schiff et al. Prepared by the Southern California Coastal Water Research Project (SCCWRP) for the Irvine Ranch Water District (IRWD) for DPR. June 2003.**
   - **Sampling Period:** December 2000-December 2002
   - **Sampling Entity:** IRWD
   - **Funding Entity:** DPR
   - **Study Area:** Residential neighborhoods, Irvine
   - **Pesticide Analytes:** Diazinon, chlorpyrifos
   - **Descriptions/Findings:** The goal of this study is to quantify the contribution of diazinon and chlorpyrifos in wet and dry weather runoff from residential land uses. In addition, two sub-objectives were identified to help understand and manage contributions of these pesticides from urban watersheds. The first sub-objective attempts to quantify the effectiveness of public education versus a technology-based best management practice (BMP) for controlling OP pesticide contributions from residential land uses during dry weather. The second sub-objective attempted to

quantify the relationship between rainfall characteristics and OP pesticide concentrations during wet weather runoff from residential land uses.

Mean concentrations of OP pesticides were typically greater during dry weather than wet weather at all three neighborhoods. Mean dry weather concentrations ranged from 20 to 572 ng/L chlorpyrifos and from 1,031 to 1,726 ng/L diazinon. Mean wet weather concentrations ranged from 6 to 156 ng/L chlorpyrifos and from 685 to 1,812 ng/L diazinon.

Temporal plots of OP pesticide concentrations during dry weather did not indicate any seasonal patterns, nor was there a noticeable change in concentration following the initiation of the technological or educational BMPs.

There was substantial variability in OP pesticide concentrations both within and among storm events at all three neighborhoods. At least part of the variability in diazinon concentrations was correlated to rainfall quantity and duration.

Mass emissions of diazinon and chlorpyrifos during wet weather far exceeded emissions during dry weather. This was a function of substantially more volume during storm events than during dry weather.

Concentrations of OP pesticides from the test neighborhoods appeared high relative to other residential land uses in nearby watersheds and relative to water quality thresholds recommended by the California Department of Fish and Game.

- **Link:** No link; however, hardcopy of report is available. See Nan S.

34) ***Organophosphorus Pesticides in Stormwater Runoff from Southern California*. Ken Schiff et al. Prepared by the Southern California Coastal Water Research Project (SCCWRP) for DPR. November 2001.**
   - **Sampling Period:** January to April 2001
   - **Sampling Entity:** Southern California Coastal Water Research Project (SCCWRP)
   - **Funding Entity:** DPR
   - **Study Area:** Urban runoff areas, Los Angeles Co.
   - **Pesticide Analytes:** Diazinon, Chlorpyrifos
   - **Descriptions/Findings:** The goal of this study was to characterize diazinon and chlorpyrifos concentrations from different land uses indicative of source categories in urban southern California watersheds. This characterization included analysis of 128 runoff samples from eight different land uses over five storm events. In addition, 41 samples were collected from two sites located at the mouth of large, mixed land use, watersheds during three different storm events.

     Diazinon was consistently detected (93% of samples) during this study whereas chlorpyrifos was not (12% of samples). Agricultural land use had the highest flow weighted mean (FWM) concentration of diazinon (4,076 ng/L), which exceeded the next highest land use categories (commercial, residential) by a factor of 10 to 100 (324 to 99 ng/L, respectively). Open space had the lowest concentration of diazinon (< 20

ng/L). Concentrations of diazinon at replicate land use sites and during replicate storm events at the same site were highly variable. The difference in diazinon FWM concentrations among replicate sites ranged from 1.5 to 45-fold. The difference in diazinon FWM concentrations among storms at the same site ranged from 1.25 to 30-fold. Part of this variability is a response to the temporal patterns observed within a storm event. The majority of land use site-events had peak concentrations prior to peak flow indicating a first flush, but this was not always a predictable temporal trend. Additional sources of variability likely include pesticide usage within the catchment.
- **Link:** Organophosphorous Pesticides in Stormwater Runoff from Southern California

35) ***Shelter Island Yacht Basin Copper Total Maximum Daily Load.* Public Review Draft. San Diego Regional Water Quality Control Board (SDRWQCB). October 2003.**
- **Sampling Period:** mid-1980's to present
- **Sampling Entity:** Various (includes U.S. Navy, Port of San Diego, and SDRWQCB
- **Funding Entity:** Various
- **Study Area:** Shelter Island Yacht Basin (SIYB) in San Diego Bay
- **Pesticide Analytes:** Copper - antifouling paints
- **Descriptions/Findings:** Sporadic sampling of copper at SIYB has been done over many years. At SIYB, the majority of the copper in the water column has been attributed to the use of copper antifouling paints in the marine Basin. Dissolved copper concentrations frequently exceed the California Toxics Rule standards for dissolved copper of 3.1 ug/L for chronic exposures and occasionally exceed the 4.8 ug/L for acute exposures. The SIYB Copper TMDL documented the various copper monitoring studies that took place. The TMDL also contains copper monitoring data references from greater San Diego Bay. Copper sources at the bay level are more varied than the main antifouling paint sources observed at SIYB. Bay concentrations tend to be considerably lower than those observed at SIYB.
- **Link:** http://www.swrcb.ca.gov/rwqcb9/tmdls/tmdl_files/shelter%20island/SIYB%20Staff%20Report.pdf

36) ***1999-2001Chollas Creek Watershed Monitoring*. Prepared by MEC Analytical Systems, Inc. for the City of San Diego for DPR. May 2002.**
- **Sampling Period:** January and February 2001
- **Sampling Entity:** URS Environmental/MEC Analytical Systems Inc.
- **Funding Entity:** DPR, City of San Diego
- **Study Area:** Chollas Creek Watershed, San Diego
- **Pesticide Analytes:** Diazinon, Chlorpyrifos
- **Descriptions/Findings:** Diazinon concentrations exceeded DFG acute water quality criteria (WQC) of 80 ng/L in 17 out of 18 samples during 2 storm events in January and February 2001. Concentrations ranged from 370 to 810. Chlorpyrifos ranged from 20 to 110 ng/L. Spatial observations suggest that chlorpyrifos loading was higher in certain reaches of the Chollas Creek watershed. In contrast, observations of diazinon suggest that loading is more ubiquitous than chlorpyrifos. Statistically significant relationship between toxicity to both *C. dubia* and *H. azteca* to diazinon concentrations were observed. Suspended sediment may have added to the toxicity of test organisms.

The report also contains background on some early pilot monitoring of Chollas Creek for toxicity and related-causes (about 6 storm water samples) in the mid to late 1990's. The highest concentration of diazinon detected was above LC50 values.

- **Link:** 1999-2001 Chollas Creek Watershed Monitoring