Describing the Behavior and Effects of Pesticides in Urban and Agricultural Settings

ACS SYMPOSIUM SERIES **1168**

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Sponsored by the
ACS Division of Agrochemicals

American Chemical Society, Washington, DC

Distributed in print by Oxford University Press

Library of Congress Cataloging-in-Publication Data

Describing the behavior and effects of pesticides in urban and agricultural settings / Russell L. Jones, editor, Bayer CropScience. Research Triangle Park, North Carolina, Mah Shamim, editor, U.S. Environmental Protection Agency, Washington, DC, Scott H. Jackson, editor, BASF Research Triangle Park, North Carolina ; sponsored by the ACS Division of Agrochemicals.
pages cm. -- (ACS symposium series ; 1168)
Includes bibliographical references and index.
ISBN 978-0-8412-2974-7
1. Pesticides--Environmental aspects. I. Jones, Russell L. (Russell Lawrence), 1951- II. American Chemical Society. Division of Agrochemicals.
QH545.P4D47 2014
363.738′498--dc23
2014031546

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48n1984.

Distributed in print by Oxford University Press

PRINTED IN THE UNITED STATES OF AMERICA

Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department

Preface

Studies of the behavior and effects of pesticides in the environment have been conducted for decades and have been the subject of numerous symposia at American Chemical Society meetings. Originally most of this work focused on agricultural settings, but in the past three decades there has been increasing interest also in non-agricultural uses of pesticides. In the past few years, increasing attention has been paid to uses in residential settings.

This ACS Symposium Series volume consists of 13 book chapters from authors making presentations at two symposia at the American Chemical Society 246th National Meeting and Exposition in September 2013 in Indianapolis, Indiana. All deal with agricultural and non-agricultural uses of pesticides. Ten of these book chapters are from authors making presentations at the symposium entitled Assessing Potential Ecological and Human Health Effects from Fertilizer and Pesticide Use in Urban Environments, while the remaining three are from modeling papers from the symposium entitled Environmental Fate, Transport, and Modeling of Agriculturally Related Chemicals.

The book chapters cover a number of different topics related to non-agricultural uses of pesticides, including: transport mechanisms associated with residential applications and associated modeling of these processes; modeling of storm water discharges from residential subdivisions; bioassessments performed on urban streams; monitoring of large rivers receiving water from urban areas; residues entering POTW (publicly owned treatment works, i.e., sewage treatment plants); analytical methods; and aspects related to the regulation of non-agricultural uses of pesticides. The three papers dealing with modeling of agricultural uses of pesticides consider screening assessments for considering potential movement to ground water, the sensitivity of model parameters used in assessing potential movement to surface water, and refined assessments for surface water catchments

We thank the AGRO Division of the American Chemical Society for including these two symposia in their 2014 fall meeting. We also thank the authors for the careful preparation of the book chapters and their cooperation with the review process. As a result, we believe that this ACS Symposium provides useful information on recent developments in a number of areas related to describing the behavior and effects of pesticides in urban and agricultural settings.

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Editors' Biographies

Russell L. Jones

Russell L. Jones (Ph.D., University of California Berkeley) is currently a Fellow in Environmental Safety at Bayer CropScience in Research Triangle Park, NC, specializing in the behavior of crop protection products in soil and water. Research interests include the development of management practices for preventing movement of crop protection products to ground and surface water, design and conduct of field research studies, and the application of environmental modeling to risk assessment. He has authored or co-authored over 100 papers and 140 presentations at scientific meetings.

Mah Shamim

Mah Shamim (Ph.D., Howard University) has been a Section Head and Branch Chief in Environmental Fate and Effects Division, Office of Pesticide Programs, United States Environmental Protection Agency since 1993. She manages multi-disciplinary teams of scientists involved in performing ecological risk assessments, endangered species assessments, and drinking water assessments to be used in dietary human risk assessments. Prior to joining the EPA in 1991, she served as a Senior Staff Fellow at the National Heart, Lung and Blood Institute, the National Institutes of Health (1989 – 1991) and as a Research Fellow at the National Institute of Diabetes and Digestive and Kidney Diseases (1983 – 1989). Her research interests included development of oligonucleotide probes for site-specific cleavage of target DNA; design, development, and synthesis of potent and selective antagonists to adenosine receptors; and the study of insect pheromones as channels of communication for insects. She is the recipient of numerous Agency awards including the EPA Excellence in Management Award.

Scott H. Jackson

Scott H. Jackson (Ph.D., Union University) is currently stewardship manager in the stewardship and sustainability group at BASF in Research Triangle Park, NC. He is responsible for managing risk assessments for human health, ecotoxicology, and spray drift as well as designing and supervising studies intended to monitor surface water, ground water and soil systems for environmental quality. He has authored or co-authored over 80 papers and 120 presentations at scientific meetings. He has organized or co-organized many symposiums at national meetings.

Chapter 1

Runoff of Phenylpyrazole Insecticide Fipronil from Concrete Surfaces

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Fipronil is a phenylpyrazole insecticide first registered in U.S. in 1996 and in California, is exclusively used for urban structural pest control and landscape maintenance. Although commonly found in urban waterways, runoff potential of fipronil from urban surfaces was seldom assessed, and with different physicochemical properties, conclusions obtained from pyrethroid runoff may not be applicable to fipronil. We conducted a field study by placing concrete blocks in real environment, treating the surfaces with fipronil, and analyzing surface runoff after simulated or natural precipitation. Isopropanol-wetted sponges were simultaneously used to wipe concrete surfaces for runoff prediction. The results showed during repeated precipitations fipronil residue could remain on the concrete for up to 3 months, and fipronil could still be detected in natural rainfall-induced runoff even 7 months after fipronil treatment. Compared to pyrethroids, fipronil has better water transferability. The wash-off in Day 1 was 2.1 ± 0.7 % of applied amount, higher than 0.8 ± 0.5 % for bifenthrin and 0.7 ± 0.5 % for permethrin. However, fipronil is less persistent, and the runoff half-life was 17.2 d. Unlike pyrethroids, 81.1-96.7 % of runoff fipronil was dissolved in the aqueous phase, implying the potential for long-distance transport and better bioavailability. The surface wiping method successfully measured fipronil on concrete, and the same linear model developed for pyrethroids could be also used on fipronil, even for different precipitation schemes and after different periods of post-treatment exposure.

Introduction

Fipronil was introduced into U.S. in 1996 and in California is almost exclusively used for structural pest control (*1*, *2*). With mode of action different from other common insecticides such as pyrethroids, organophosphates and carbamates, fipronil showed low insect resistance, and its use rapidly increased especially in urban and residential areas (*1*). In 2011, licensed California applicators used 28,785 kg fipronil, compared to 300 kg in 2000 (*2*). This rapid increase has caused fipronil contamination in urban waterways and aquatic toxicity (*3–5*). For instance, fipronil could be detected in almost all urban runoff samples from southern California (*3*). The 90th percentile concentrations at the four sampling sites were 176-472 ng/L, which were above EC50 (0.14 μg/L) for mysid shrimp (*6*).

Urban areas feature impervious surfaces such as concrete which are used to drain surface runoff fast. However not until recently studies have found these surfaces can affect pesticide persistence and runoff behaviors in urban areas (*7–11*). For instance, permethrin on concrete could continuously desorb into water for over 300 h, and the runoff persistence extended longer as permethrin residence time on concrete increased (*8*). Jorgenson and Young treated commercial formulated pyrethroids on concrete slabs and during a 60 min rainfall, and depending on different pesticide formulations, 0.8- 60 % of applied pyrethroids were washed-off (*9*).

While most of these studies addressed pyrethroids, little is known about fipronil (*11*). In a different pesticide class, fipronil is treated at rates different from pyrethroids, and may also display different persistence and runoff potential. In a preliminary bench-top study we treated small concrete disks with different pesticides and washed the surfaces immediately after treatments, more fipronil was recovered in the wash-off water than pyrethroids (*7*). However, if the concrete left in outdoor for 56 days, less fipronil was left on concrete than many pyrethroids such as bifenthrin, permethrin and cyfluthrin.

The objective of this study is to measure fipronil levels in concrete runoff after extended outdoor exposure and during different precipitation schemes. By comparing with pyrethroids, the results will improve the understanding of current-use pesticide runoff, which is essential for a comprehensive contamination mitigation plan. We also used a wiping method that successfully predicted pyrethroid runoff in previous studies, and tested its applicability for fipronil.

Materials and Methods

Chemicals

Termidor (9.1 % suspended concentrate, BASF, Research Triangle Park, NC) is the primary formulated fipronil product in California and was selected in this study. The concentration of active ingredient in the product was measured at 10.1 ± 0.8 % before the experiment. Chemical standards of fipronil (98.9%, Environmental Protection Agency National Pesticide Standard Repository, Fort Meade, MD), phenoxy $^{13}C6$-labeled cis-permethrin (^{13}C-permethrin, 99%, Cambridge Isotope Laboratories, Andover, MA) and (rac-cis)-Z-bifenthrin-d5 (d5-bifenthrin, Toronto Research Chemicals, Toronto, Ontario, Canada) were purchased from different sources. All solvents in GC/MS or pesticide grade were purchased from Fisher Scientific (Pittsburgh, PA), and all glassware was baked at 400 °C for 4 h before use to remove contamination residues.

Concrete Prepare and Fipronil Treatment

Preparation of concrete surfaces was described elsewhere (*10*). Each hardened concrete slab has a surface area of 60 × 40 cm and set at around 2˚ slope. A copper tube was connected at the lower end of concrete surface and runoff water from individual concrete slab was collected into a 1-L amber glass sample bottle.

Fipronil was applied in a diluted solution by mixing 2.25 mL fipronil concentrate in 500 mL water. Mixed solution (50 mL) was sprayed on each concrete slab using a Marson MC air-brush sprayer (Swingline, Lincolnshire, IL) with controlled pressure at 40 psi. The application rate was 9.12 $\mu g/cm^2$ for all concrete slabs, which was close to the label instructions.

Runoff Induced by Simulated and Natural Rainfalls

Concrete slabs were divided into eleven groups and each group was subject to one of three types of simulated or natural precipitation (*10*). For single-time precipitation event, 5 groups of slabs (4 replicates in each group) were treated with fipronil at the same date on July 1, 2010, and received the same simulated rainfall but 1, 7, 20, 47 or 89 days after treatments. The simulated rainfalls were generated by an automated rainfall simulator, and the precipitation was controlled at 26.2 mm/h for 15 min (*10*, *12*). For repeated precipitation event, one group of treated slabs (4 replicates) received the 15 min 26.2 mm/h rainfall repeatedly on day 1, 7, 20, 47 and 89.

Another 5 groups of slabs received natural rainfalls. Different groups were treated with the same amount of fipronil but at different time of the year (i.e., April 1, July 1, August 17, September 28 and November 1, 2010), and runoff water during the same two rainfalls on November 8 and November 20, 2010 were collected. The two rainfalls are the first and second flushes for treated concrete, except for April 1 treatments which also encountered three minor rain showers in April.

The runoff water was transported to the analytical lab within 4 h after sample collection, stored at 4 ˚C and the extraction was finished within 3 days. For concrete receiving simulated precipitation, the runoff water was individually filtered through a glass-fiber filter paper (pore size 0.7 μm, Whatman, Florham Park, NJ) to separate the aqueous phase and suspended fine particles. The filtrate was extracted in a separation funnel using methylene chloride and the extract was cleaned up using a florisil cartridge (Grace, Deerfield, IL). The particles retained on the filter membrane were extracted in a sonication bath using methylene chloride-acetone (1/1, v/v) and the extract was loaded onto a florisil cartridge for cleanup. For natural rainfall runoff, the collected water was extracted in separation funnels without pre-filtration using the same method as mentioned above. Fipronil concentrations were analyzed using a gas chromatography/tandem mass spectrometry (GC-MS/MS). Detailed information on sample extraction and instrumental analysis can be found in elsewhere (*10*, *13*).

Sponge Wiping for Fipronil Runoff Prediction

For concrete receiving simulated precipitation (both single-time and repeated), we prepared extra two slabs for each group and tested a previously developed sponge wiping method to measure runoff-transferable residues. This method was successfully used for pyrethroid runoff prediction, but no other pesticides. To test its applicability for fipronil, the two slabs were treated and then exposed to the same precipitation schemes as mentioned above. Instead of collecting concrete runoff, the surface of each slab was wiped individually before each precipitation event by using a Versalon™ nonwoven sponge (10 × 10 cm, 4-ply, Kendall Healthcare, Mansfield, MA) freshly added with 10 mL isopropanol. The wiping movement was confined within a 20 × 20 cm stainless steel frame and the wiped surface on each day did not overlap. The collected wiping sponges were extracted and cleaned-up using the same method as for the filter membranes, and the final extracts were analyzed on a GC-MS/MS to quantify fipronil and three fipronil degradates.

Quality Controls

The reproducibility of results and possible cross contamination in this study were assessed using a series of protocols. First, the method recoveries and detection limits (MDL) for fipronil were determined in a preliminary experiments following modified EPA method 40 CFR, Part 136, Appendix B (n=4). The quantification limit was set at 5.0 $ng \cdot L^{-1}$. Second, every sample was spiked with decachloropiphenyl before extraction as surrogate and ^{13}C-*cis*-permethrin before instrumental analysis as internal standard. The surrogate recoveries were 78.4 ± 15.5%, 91.4 ± 25.0%, 74.3 ± 13.0% and 70.0 ± 30.7% for filtrate, filter membrane, whole water and wiping sponge respectively. Third, concrete slabs without fipronil treatments were prepared as field controls and lab cross-contamination was assessed by including 1 blank for every 20 samples.

Results and Discussion

Fipronil Runoff through Simulated and Natural Rainfalls

We tested three precipitation scenarios, which respectively represented three different runoff types that may occur in the real environment: treated concrete receiving the first irrigation/rainfall but after different periods, scheduled recurring irrigations, and concrete treated at different time but received the same winter storms. During simulated single-time and repeated precipitation, fipronil residue was detected in all runoff water even 89 days after treatments. For instance, during repeated precipitation, fipronil concentrations in the fifth runoff on Day 89 were 0.18 ± 0.06 µg/L (Table I). Persistent runoff was also seen for concrete receiving natural winter rainfalls (Table II). For April 1 treatments, after >7 month outdoor exposure and 3 rain showers, fipronil was still found in the two November runoff, and the concentrations were 0.10 ± 0.04 µg/L and 0.02 ± 0.00 µg/L respectively.

We previously used a bench-top setup evaluating fipronil wash-off from concrete, and found water-transferable residues could persist on concrete surfaces even 112 d after summer outdoor exposure (*7*). Later in 2012, Thuyet et al. (*11*) used a simulated rainfall system to study fipronil wash-off profile during a continuous 1-h rainfall, and the rainfall was applied within 14 days after treatments. So far no field studies have been done to evaluate long-term fipronil runoff potential. This information is especially critical to U.S. west coast states with Mediterranean weather, where fipronil is most heavily used during the summer while the rainfalls will not start until winter. For instance, in Riverside County, CA in 2010, 429 kg (active ingredient) of Termidor was used from June to August, which was 47 % of entire 2010 use (*2*). During the winter rainfall runoff, only $9.49 \pm 4.03 \times 10^{-3}$ % of fipronil treated on July 1st was recovered in the two winter runoff, significantly lower than what have been previously seen for bifenthrin ($4.92 \pm 1.05 \times 10^{-2}$ %) and permethrin ($3.81 \pm 2.56 \times 10^{-2}$ %) (Table II).

By fitting the results into a first-order model, we found the dissipation half-life (DT50) of fipronil runoff potential was 17.2 d. This value was shorter than 21.8 d for permethrin and 30.1 d for bifenthrin, indicating less persistence of fipronil on concrete due to photolysis and reactions with concrete basic groups (*10*). Due to the rigid structure of concrete, methods could not been developed to extract fipronil from concrete, but previous research in soil and water all found bifenthrin and permethrin have much better resistance to base-catalyzed or photolytic decomposition than fipronil. For instance, in water at pH 9 and 20 ºC, the half-lives of permethrin and fipronil were 242 and 32 d respectively (*1*, *14*). The photolysis half-life of fipronil in aqueous solution was 0.33 d also shorter than 276-416 and 51-71 d for bifenthrin and permethrin respectively (*14*, *15*). Shorter half-life of fipronil on concrete required frequent treatment on concrete to maintain satisfying pest controls. For instance, Greenberg et al. found 7 d after initial application, bifenthrin treated houses still showed 87 % ant reduction, higher than 70 % for fipronil treated houses (*16*). After 28 d, the ant reduction efficacy continued to reduce to 48 % for fipronil, also lower than 66 % for bifenthrin.

Table I. Concentrations of fipronil in the runoff and percentage as the initial application rate. The runoff was induced by simulated single-time or repeated precipitation.

Runoff (d)	*One-Time Precipitation*		*Repeated Precipitation*	
	Concentration (μg/L)	*%*	*Concentration (μg/L)*	*%*
1	590.48±204.62	2.11±0.71	590.48 ± 204.62	2.11±0.71
7	48.32±20.72	0.17±0.07	22.61±4.92	0.09±0.02
20	15.47±5.08	0.05±0.02	3.78±1.40	$1.41 \pm 0.50 \times 10^{-2}$
47	20.41±7.13	0.06±0.02	0.90±0.20	$0.24 \pm 0.06 \times 10^{-2}$
89	10.92±6.60	0.04±0.02	0.18±0.06	$0.07 \pm 0.02 \times 10^{-2}$

Table II. Concentrations of fipronil in the runoff and percentage as the initial application rate. The runoff was induced by two natural rainfalls on November 8 and November 20, 2010.

Treatment date	*November 8*		*November 20*	
	Concentration (μg/L)	*%*	*Concentration (μg/L)*	*%*
Apr. 1	0.10±0.04	$1.73 \pm 0.91 \times 10^{-4}$	0.02±0.00	$1.09 \pm 0.19 \times 10^{-4}$
Jul. 1	1.85±0.65	$3.79 \pm 1.30 \times 10^{-3}$	0.81±0.42	$5.70 \pm 3.20 \times 10^{-3}$
Aug. 17	20.13±9.97	$3.10 \pm 1.05 \times 10^{-2}$	6.97±4.65	$4.97 \pm 3.37 \times 10^{-2}$
Sept. 28	25.02±4.04	$5.38 \pm 0.34 \times 10^{-2}$	13.35±3.77	$8.97 \pm 2.79 \times 10^{-2}$
Nov. 1	938.94±191.77	2.32±0.50	190.78±66.94	$1.36 \pm 0.48 \times 10^{-2}$

Validation of Surface Wiping for Multi-Residue Runoff Prediction

We previously developed a surface wiping method to measure runoff-transferable amounts of pyrethroids on concrete (*13*). The similar method was used to estimate multiple pesticide risks, including pyrethroids, fipronil, organophosphates and organochlorines, to humans in indoor environment but for outdoor runoff prediction, only two pyrethroids bifenthrin and permethrin were included, so more pesticides are needed to test method universality (*17*, *18*).

In this study we included fipronil and three common fipronil degradates (desulfinyl fipronil, fipronil sulfide, fipronil sulfone). Compound residues on the wipes were expressed as wiping-extractable concentrations on concrete, and the concentrations in the runoff were expressed as concentrations on concrete that were runoff transferable. The results showed wiping and runoff-extractable fipronil levels were in the same order of magnitude. For instance, for concrete receiving repeated precipitation on Day 89, the wipe measured fipronil concentration on concrete at 5.29 ± 1.89 μg/m^2, close to 10.37 ± 5.16 μg/m^2 runoff-transferable levels. As shown in Figure 1A and Table III, strong positive correlation was found for pesticide concentrations on the wiping sponge and in the runoff water, with the *Pearson*'s correlation coefficients determined at 0.90.

In Figure 1, runoff-transferable pesticides were plotted against the wiping-extractable concentrations, and a linear regression was used to fit the results. The same linear curve was used but different compounds were included (Figure 1A-D). For all four scenarios, strong positive correlation and good model fitting were observed (Table III). The model-fitting parameters were almost identical under all four scenarios, and with more compounds included, the model showed better fittings , with the regression slope closer to 1 (Table III). In Figure 1D, which included 74 plots representing six compounds, two precipitation schemes, three pesticide formulations and five post-treatment time points, the slope was at 1.03 ± 0.05. Good model-fitting results indicate the surface wiping method is capable of predicting all pyrethroid, fipronil and fipronil degradate runoff, and the identical regression curve shows the same quantitative equation is available for different compounds, application methods and environmental conditions.

This study expanded previous surface wiping method by including compounds other than pyrethroids. Currently, pesticide runoff loading is estimated by collecting water from drainage outlets, measuring pesticide concentrations, and multiplying the values by runoff volume during the entire rainfall event. However, this method only gets samples when contamination already occurs, and does not account for variations of pesticide concentrations during an extended runoff event, or provide information on the source of contamination. All these drawbacks could be supplemented by this simple, portable and easy-to-use surface wiping method. However, it was also noticed that some points in Figure 1 showed large standard variations especially for wiping results. This was probably caused by the relative small areas used for wiping and lack of repeatable wiping movements. This variation indicates necessary method improvement, such as using different types and volumes of solvents, and developing robust tools for repeatable wiping movements.

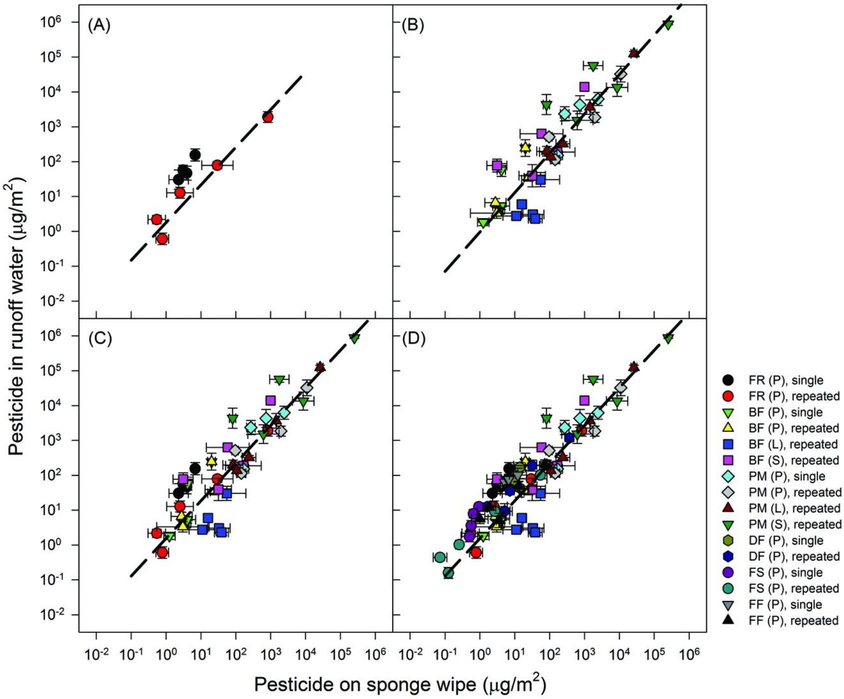

Figure 1. Regression of bifenthrin (BF), permethrin (PM), fipronil (FR) and three fipronil degradates (i.e., desulfinyl (DF), sulfide (SF) and sulfone (FF)) in runoff water and on sponge wipes. The concrete slabs were treated with pesticides in ready-to-use solid (S), ready-to-use liquid (L), or professional concentrate (P) formulations, and received single-time or repeated precipitation at 26.2 ± 2.7 mm/h. Pesticide amounts in the runoff water and on the wipe were expressed as concentrations on concrete surfaces. The regression was conducted for (A) only fipronil, (B) only bifenthrin and permethrin[a], (C) fipronil, bifenthrin and permethrin, and (D) fipronil, bifenthrin, permethrin and three fipronil degradates. Reproduced with permission from ref. (13). Copyright 2012 American Chemical Society.

Table III. Parameters derived from regressions in fitting average concentrations of fipronil, bifenthrin and permethrin in the winter rainfall runoff to a first-order decay model. The regression was conducted using (A) only fipronil, (B) only bifenthrin and permethrin, (C) fipronil, bifenthrin and permethrin, and (D) fipronil, bifenthrin, permethrin and three fipronil degradates (i.e., desulfinyl fipronil, fipronil sulfide, fipronil sulfone).

Regression	*a*	*b*	R^2	*Pearson's r*
A	1.08 ± 0.19	0.25 ± 0.23	0.81	0.90
B[a]	1.13 ± 0.11	-0.02 ± 0.28	0.78	0.90
C	1.08 ± 0.07	0.19 ± 0.16	0.83	0.91
D	1.03 ± 0.05	0.31 ± 0.10	0.85	0.92

[a] Jiang and Gan (*13*).

Comparison to Pyrethroids

Fipronil is also a non-ionic hydrophobic pesticide, but with higher water solubility (1.9 mg/L at 20 ºC) and lower octanol-water partition coefficient (lgKow at 4.0) than bifenthrin (<1 μg/L and lgKow >6.0) and permethrin (6 μg/L and lgKow=6.1, (*19*)). Consequently, fipronil may display different environmental persistence, runoff potential, and ecological risks. As both pyrethroids and fipronil are major pesticide classes used in urban areas, a close comparison will be critical for comprehensive contamination assessment and mitigation.

All concrete surfaces were flushed with water 1 d before treatments to remove deposited particles, and collected post-treatment runoff was filtered through 0.7 μm glass-fiber paper to separate the aqueous and solid phase. The results showed almost all runoff fipronil (81.1-96.7 %) was found in the filtrate, implying dissolving in the water phase is the primary route for fipronil runoff movement (Table IV). This is significantly different from pyrethroids in similar formulations. For instance, for concrete treated with professional formulations and receiving repeated precipitation, 85.1 ± 7.0 % of fipronil runoff on Day 89 was in the aqueous phase, much higher than 12.6 ± 2.8 % for bifenthrin and 12.2 ± 5.3 % for permethrin (Table V, (*13*)). For fipronil, the major partitioning in water phase is because of less particle erosion from concrete surfaces and lower hydrophobicity than pyrethroids. Dissolving in the water phase implies unlike pyrethroids, fipronil will be difficult to get removed through sedimentation process after entering the environment, and will consequently facilitate its long distance transport and increase the bio-accessibility.

Table IV. Percentage of fipronil in runoff aqueous phase (<0.7 µm)

Runoff (d)	*Single-time*	*Repeated*
	% of runoff in the filtrate	*% of runoff in the filtrate*
1	94.4 ± 3.2	94.4 ± 3.2
7	96.7 ± 0.9	96.7 ± 0.8
20	92.8 ± 1.4	83.7 ± 4.2
47	88.3 ± 2.3	81.1 ± 7.0
89	83.9 ± 10.7	85.0 ± 7.0

With better water solubility and shorter persistence, more fipronil was washed off than pyrethroids if the rainfalls occurred shortly after treatments. For instance, for concrete treated on November 1st, 2010, 2.3 ± 0.5 % of treated fipronil was washed-off after 7 days, significantly higher than 0.2 ± 0.1 % for bifenthrin (*10*). However, for July 1st treatment, fipronil runoff percent was only $3.8 \pm 1.3 \times 10^{-3}$ %, smaller than $8.3 \pm 2.1 \times 10^{-3}$ % for bifenthrin. The same thing was also observed during simulated precipitation. During repeated precipitation, 2.1 ± 0.7 % of applied fipronil was found in Day 1 runoff, significantly higher than 0.8 ± 0.5 % and 1.5 ± 0.8 % for bifenthrin and permethrin respectively (Table I, (*10*)). However, on Day 89, only $6.8 \pm 2.1 \times 10^{-4}$ % of applied fipronil was detected in the water, much lower than $7.0 \pm 1.2 \times 10^{-3}$ % for bifenthrin and $6.6 \pm 0.9 \times 10^{-3}$ % for permethrin. In total 5-time runoff, 2.2 ± 0.7 % of applied fipronil was recovered, higher than 1.0 ± 0.5 % and 1.7 ± 0.8 % for bifenthrin and permethrin respectively. This indicates fipronil on concrete is more likely to be washed off than pyrethroids. Therefore, to mitigate the contamination, greater attentions should be paid to avoid concrete contact with water especially shortly after treatments.

Table V. Percent of fipronil, bifenthrin and permethrin partitioning in runoff aqueous phase (<0.7 µm) during repeated precipitation. Concrete was treated with professional formulated pesticides.

Runoff (d)	*Fipronil*	*Bifenthrin*[a]	*cis-Permethrin*	*trans-Permethrin*
1	94.4 ± 3.2	8.0 ± 5.7	2.4 ± 1.1	3.5 ± 1.2
7	96.7 ± 0.9	10.1 ± 1.6	6.1 ± 2.3	8.8 ± 1.0
20	83.9 ± 4.2	8.1 ± 2.6	7.9 ± 2.6	8.1 ± 2.9
47	81.1 ± 7.0	14.9 ± 4.0	9.9 ± 2.8	11.6 ± 3.2
89	85.1 ± 7.0	12.6 ± 2.8	11.9 ± 5.3	12.3 ± 5.2

[a] Bifenthrin, *cis*- and *trans*-permethrin data was obtained from r (*13*).

In 2012, California Department of Pesticide Regulation published a new regulation to standardize residential outdoor pesticide application and protect urban surface water habitat (*20*). According to this regulation, pesticides should not be applied prior to or during precipitation, and braodcast treatments are not allowed on any drainage surfaces such as driveway, sewer, curbside gutter, etc. Fipronil was not included in this regulation, but similar statements have been added to the labels of fipronil products sold in California. The results from the present work showed compared to pyrethroids, fipronil has higher mobility with water. This research also expanded previous surfacing wiping method by including both pyrethroids and fipronil, and both pesticide parent and degradation compounds, but other common urban-use pesticides such as carbamates should be tested in future studies.

Acknowledgments

The authors thank California Department of Pesticide Regulation for the funding support.

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Chapter 2

Factors Affecting Residential Runoff Transport of Pyrethroids

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Replicated runoff studies investigating the transport of pyrethroids applied to suburban residences were conducted at a full scale test facility in central California over two years. The first year of results showed losses from historic practices mainly from applications made to impervious surfaces (such as driveways or walls adjacent to driveways) as a result of runoff generated by simulated or natural rainfall. Revised application procedures according to new product labeling specifying spot applications to impervious surfaces reduced runoff losses of pyrethroids by a factor of 40 compared to historic practices. The second year of testing examined the effect of formulation on washoff from driveways or walls adjacent to driveways. Differences in runoff losses between five pairs of product formulations under field scale conditions were considerably less than in small scale laboratory experiments. Also in one pair, one formulation gave higher washoff in laboratory experiments and the other formulation gave higher washoff under field conditions. Therefore, laboratory studies assessing the effect of formulation on runoff losses may not always be predictive

of behavior under actual use conditions so field studies remain important for understanding runoff losses from residential pesticide treatments.

Introduction

Pyrethroids are a class of insecticides widely used to control a range of pests in urban settings, especially after the withdrawal of most urban uses for organophosphate insecticides. California is an area where pyrethroids are used extensively and have been detected in urban creeks (*1–3*).

When the work described in this report was being planned, there was a variety of opinions on the source of the residues including applications to lawns, applications to impervious surfaces such as driveways, and spills resulting from poor handling practices. Understanding the source of the residues is essential for the development of effective management practices. Management practices had been required by EPA on pyrethroid product labels (the most important was the requirement that applications to impervious surfaces be limited to crack and crevice applications), but there was no information on the effectiveness of these management practices. Also, small scale experiments had been done on washoff by other researchers (*4–7*) as well as the Pyrethroid Working Group (PWG, the industry task force sponsoring the work reported in this chapter) (*8*). This work showed that formulation could significantly affect the amount of washoff in small scale experiments. Therefore, the PWG decided to conduct field scale experiments to study washoff of pyrethroids in a simulated residential setting. The first year of these experiments (Pathway Identification Study) concentrated on assessing the contribution of the applications to various surfaces on the amount of pyrethroid losses in runoff and determining the effect of the management practices required by the new product labels. The second year (Washoff Dynamics Study) examined the effect of formulation. This chapter summarizes the results of both studies.

Description of the Experimental Site

The study site was located on a research farm in central California near Porterville. A summary description of the site follows but more detailed information is presented elsewhere (*9*). The soil at the site is a Tulunga loamy sand soil, but was modified with a clay loam soil to increase runoff. Each of the 6 simulated house lots at the site consisted of a stucco front wall 2.4 m in height without overhanging eaves, 2-car painted aluminum garage door, driveway, street curb, and front lawn with a typical residential sprinkler irrigation system. Each driveway had a slope of 6 percent towards the street curb. Runoff water reaching the curb flowed down the curb until the end of the lot where it was directed into a sampling shed where the volume of runoff water was measured and composite samples were collected. Figure 1 provides a diagram of a house lot. A rainfall simulator covering all 6 house lots provided the ability to generate simulated rainfall events on all lots simultaneously. The lots were in an east-west orientation with the house walls facing south, since the southwest sides of houses typically receive the most intense rainfall in central California (F. Spurlock, California Department of Pesticide Regulation, personal communication).

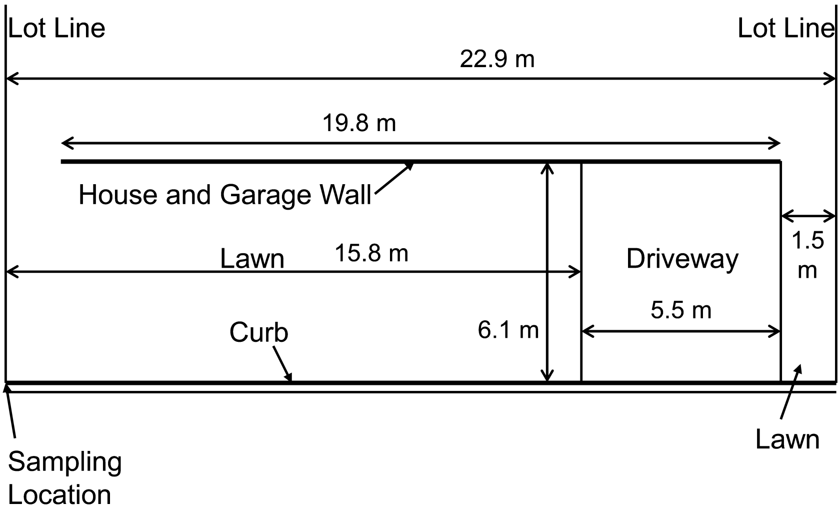

Figure 1. Diagram of a house lot.

Pathway Identification Study

Study Design

The pathway identification study compared runoff over a one year study period from two different sets of application procedures (historical and revised), with each set of application procedures replicated on three house lots. To determine the source of the residues within the house lots, five different pyrethroids were applied, each to different surfaces. The lawns were treated once at the start of the study, but the other four surfaces (driveway, garage door and adjacent wall over the driveway, the house wall adjacent to the grass, and the lawn adjacent to the house wall) were treated at the start of the study and then every two months. Normal irrigation practices were followed and the rainfall simulator was used to provide rainfall events typical of Sacramento to the site between October and March. The volume of runoff water was measured and samples of the runoff were analyzed to determine the losses of each pyrethroid.

Application Procedures

Table Isummarizes the applications used in the Pathway Identification Study. Different application procedures, historic or revised, were used only on two of the five surfaces, the driveway and the garage door and adjacent wall over the driveway. The same application practices were used on the other three surfaces, although adjustments were necessary when the amounts of spray solution or granules applied differed between the products.

Table I. Applications in the Pathway Identification Study

Surface	*Application Procedure*
Driveway	
Historic	1.5 m band adjacent to the garage door across the width of the driveway
Revised	Only the expansion joint between the top of the driveway and the garage was treated
Garage Door and Adjacent Wall	
Historic	0.6 m band across the length of the driveway
Revised	Only the approximately 0.3 m portion of the stucco wall above the driveway on each side of the garage door was treated, but not the garage door itself
Lawn	
Historic and Revised	The entire grass lawn was treated with a drop spreader since granular products were applied to the lawn
Grass Perimeter	
Historic and Revised	The grass perimeter treatment consisted of an application to the lawn 1.5 m wide beginning at the house wall
House Wall	
Historic and Revised	The stucco wall above the grass was treated with a 0.6 m band starting at the bottom of the stucco wall.

Product Selection

Eight different products were selected for use in the study. Five products each with different active ingredients were applied to each house lot so that the surface from which the pyrethoid originated could be determined. For the two surfaces with different historical and revised application procedures, the same product was used so as not to confound the interpretation of the runoff from these surfaces. For each of the other three surfaces, different products were applied to the house lots with historic and revised application procedures. Assisting in the selection of the products were preliminary results of a formulation washoff study conducted with a number of products (these preliminary results are available in supplementary information on-line (*9*).

Table II lists the products used in the Pathway Identification Study. A product used in a previous PWG study (*8*) was used for the driveway. The two products used to treat the lawn were the two most used in California. The product used to treat the garage was one of the products with higher washoff in the PWG formulation washoff study. The products used on the grass perimeter and the portion of house wall next to the lawn were products with contrasting behavior on concrete in the PWG formulation washoff study.

Table II. Products Applied in the Pathway Identification Study

Surface	*Historic Practices*	*Revised Practices*	*Amount Applied[1] (g)*	
			Historic	*Revised*
Lawn	DeltaGuard G (deltamethrin)	Talstar PL granular (bifenthrin)	1.74	5.83
Grass Perimeter	Demand CS (λ-cyhalothrin)	Warrior (λ-cyhalothrin)	2.12	2.15
House Wall	Wisdom TC (bifenthrin)	Prelude (permethrin)	0.88	17.5
Garage Door	Tempo Ultra SC (β-cyfluthrin)	Tempo Ultra SC (β-cyfluthrin)	0.66	0.09
Driveway	Cynoff WP (cypermethrin)	Cynoff WP (cypermethrin)	1.70	0.08

[1] Average amount applied for each application to each of the three house lots.

Irrigation and Rainfall

Lawns were irrigated with residential lawn sprinklers that were installed, maintained, and operated by a local lawn service according to their standard residential practices.

Simulated rainfall events occurred in October through March if needed to supplement natural rainfall. A one in five year event occurred each month in October through March and an additional one in two year event occurred each month in November through March. While the site was located in Porterville, the rainfall events were determined from records for Sacramento (approximately 350 km northwest of Porterville) and based on historical rainfall data for the specific month.

Study Results

Initial applications were made to all five surfaces on August 2, 2011 and to the same surfaces except for the lawn on October 4, December 6, February 2, April 3, and June 5. During the year-long study period, there were 187 lawn irrigation events and 34 rainfall events totaling 320 mm (8 simulated events totaling 150 mm and 26 natural events totaling 170 mm). During the same period of time, Sacramento experienced 48 rainfall events, totaling approximately 340 mm of rainfall. A total of 1683 runoff samples were collected and 1182 of these samples were analyzed. Samples not analyzed were largely collected several weeks from the last application, when pyrethroid concentrations had declined significantly.

This chapter summarizes the losses during the entire study period. Losses for the six periods after each application are provided elsewhere (*9*). The losses expressed in grams of pyrethroid from the individual surfaces over the year-long study period are summarized in Figure 2 for both application procedures. Table III provides a breakdown of the losses from each surface for both application procedures as a percent of the total losses for both historic and revised application procedures. Figure 3 provides the losses expressed as a percent of applied material for each of the surfaces for both historic and revised application procedures.

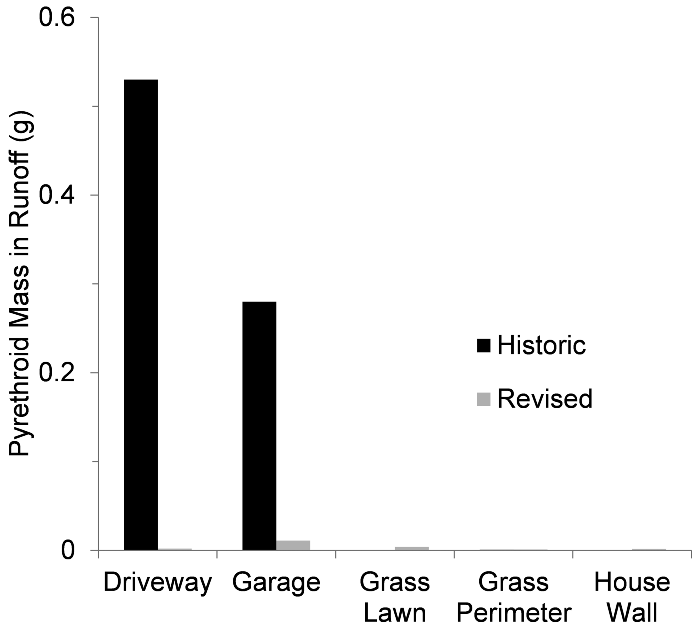

Figure 2. Average losses for each surface expressed in grams over the year-long study period.

As shown in Figure 2 and Table III, the applications to driveway and the garage door and adjacent wall are the source of essentially all (99.75 percent) of the residues in runoff from the applications made with the historical application procedures. With the revised application practices, losses from both of these surfaces are dramatically reduced, as shown visually in Figure 2. With the revised practices, the wall adjacent to the garage door and over the driveway is the source of most of the residues, with the rest of the residues split among the other four surfaces.

The reductions in the residues on the two surfaces (driveway and garage door and adjacent walls) with different application procedures in the historical and revised house lots were a combination of two factors; reduced amounts applied in the house lots receiving the revised applications, and less of the applied material running off as shown in Figure 3. For the driveway, about 30 times less spray solution was applied in the house lots receiving revised applications, and when combined with the reduction in the percent of applied running off, the losses from the house lots receiving the revised applications were a factor of 265 less than from the house lots receiving the historic applications. For the garage door and adjacent walls over the driveway, the house lots using the revised applications received about 7 times less spray solution and losses were a factor of 25 less than from the house lots receiving the historic applications.

Table III. Runoff Losses by Surface

Surface	*Percent of Total Losses*	
	Historic Practices	*Revised Practices*[1]
Driveway	65	10
Garage Door	35	54
Lawn	0.087	21
Grass Perimeter	0.11	5.0
House Wall	0.052	9.8

[1] Note that the overall losses with the revised practices are about a factor of 40 lower than with the historic practices

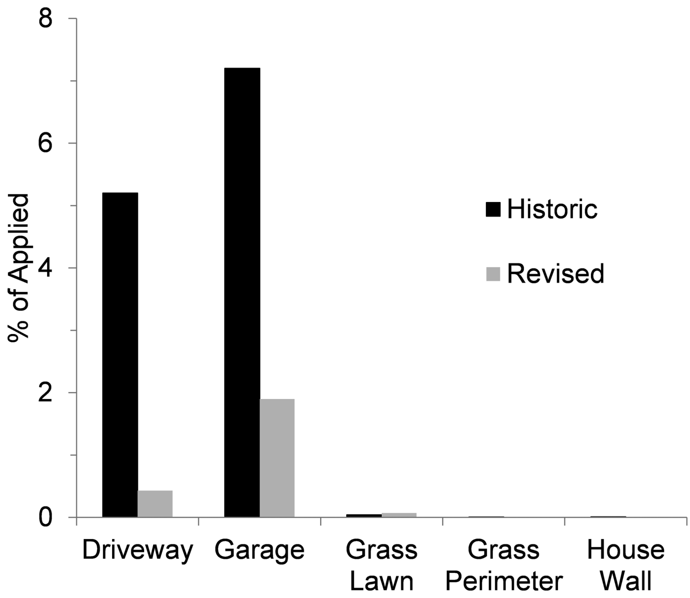

Figure 3. Average losses for each surface expressed as a percent of applied over the year-long study period.

The results from the three surfaces not receiving different application practices in the historic and revised house lots are summarized in Table IV. The applications to a specific surface were the same except for adjustments in the lawn and house wall surfaces needed to account for different amounts of product applied. Therefore, differences between the historic and revised house lots reflect differences in the products applied rather than differences in application procedures.

For the grass perimeter, two different products containing the same active ingredient were applied at the same rate to the different sets of house lots. The product applied to the revised house lots had significantly less washoff in experiments conducted with concrete slabs. There were no significant differences in runoff losses between the two products, indicating that the washoff experiments on concrete are not predictive of relative washoff on lawns.

Table IV. Losses from the Surfaces Not Receiving Different Application Practices

Surface	*Overall Losses from Specified House Lots*			
	Mass (g)		*Percent of Applied*	
	Historic	*Revised*	*Historic*	*Revised*
Lawn	0.00072	0.0041	0.041	0.070
Grass Perimeter	0.00090	0.00098	0.0071	0.0076
House Wall	0.00043	0.0019	0.0081	0.0018

Note that the losses arise from the use of different products since the application procedures were the same except for changes needed for the applications to the lawn and house wall to adjust for the different amounts of product applied.

The lawns in the two different sets of house lots received applications of two different granular products, each with a different active ingredient, a different application rate, and a different granule (gypsum in the historic house lots and sand in the revised house lots). The application rate for the product applied to the revised plots was higher than for the product applied to the historic plots. Earlier Koc measurements indicated that the active ingredient applied to the historic plots was significantly higher than the active ingredient applied to the revised house lots (704,000 versus 237,000) (*10*). However, recent unpublished Koc measurements conducted by the PWG indicate that the Koc of active ingredient applied to the revised house lots is higher (1,641,000 versus 1,245,000). There are no data available on the relative sorption to grass. Therefore, the reason for the higher losses when expressed as a percent of applied has not been identified.

The house walls in the two different sets of house lots received applications of different active ingredients applied at different rates. The application rate of the product applied to the revised set of house lots was about twenty times that of the other product, but this product also had significantly less washoff in experiments conducted with concrete slabs. The losses from house wall are also influenced by the flow through the lawn to the street curb, which is influenced by the Koc of the active ingredient. Earlier Koc measurements (*10*) indicated that both products had essentially the same Koc but recent unpublished Koc measurements conducted by the PWG indicate that the Koc of product applied to the set of revised house lots was significantly higher. The end result of all of these factors was that the washoff of the product applied to the revised plots was less when expressed as a percent of applied and more when expressed as mass.

Washoff Dynamics Study

Study Design

The Washoff Dynamics Study compared the washoff of different product formulations over a six month study period, using the driveway and the wall above the driveway, the two surfaces responsible for the majority of pyrethroid runoff in the Pathway Identification Study. The same site and basic procedures used to conduct the Pathway Identification Study were used in the Washoff Dynamics Study. The study was conducted over the period when rainfall was likely to occur since losses in the Pathway Identification Study were greater in runoff from rainfall than from irrigation events.

The basic study consisted of comparisons of five different pairs of product formulations of contrasting washoff behavior as measured in laboratory studies. One of these product comparisons was conducted on the wall next to the garage door above the edge of the driveway, according to current label directions. These surfaces received three pyrethroid applications, spaced two months apart.

The other four product comparisons were made with single broadcast applications to sections of concrete located in the middle of the driveway, away from the portion of the driveway receiving water from the lawn irrigations. Note that the broadcast driveway applications are now not allowed under current labels, but these tests were performed to show the different washoff behavior of these formulations on concrete. Each of the product pairs was replicated in three of six house lots, although the division of the house lots for the driveway applications was not the same as the division of the replicates for the applications to the house wall over the driveway. Two of the pairs applied to the driveway were followed by a major rainfall event approximately two weeks after application and the other two pairs applied to the driveway were followed by a major rainfall event about a month after application.

While this study focused on the effect of formulation on washoff, formulation can also impact the amount of active ingredient that is needed to provide effective insect control and the interval between applications. This information also needs to be considered when assessing overall runoff losses. The type of formulation can also influence the amount of volatile organic carbon (VOC) emissions.

Product Selection

Ten products, grouped as five product pairs of higher and lower washoff products, were selected using the preliminary results of a formulation washoff study conducted with a number of products (these preliminary results are available in supplementary information on-line (*9*)). These product pairs are listed in Table V. Four of the product pairs were different formulations of the same active ingredient, while the fifth product pair consisted of two products with different active ingredients. The two cypermethrin products were chosen for the wall above the driveway because, in addition to being included in the formulation washoff study, they had been included in the building material washoff study (*8*), which included applications to stucco, the material used on the wall above the driveway. The differences in the washoff among the product pairs ranged between a factor of 2.4 to 170 in the formulation washoff study. Such differences should be readily measurable under field conditions.

Table V. Products Applied in the Washoff Dynamics Study

Surface	*Lower Washoff Product*	*Higher Washoff Product*
House Wall above Driveway	Cynoff EC (cypermethrin)	Cynoff WP (cypermethrin)
Driveway Pair 1	Talstar Professional Demand CS (bifenthrin)	Wisdom TC (bifenthrin)
Driveway Pair 2	Prescription Treatment brand Cy-Kick CS (cyfluthrin)	Tempo Ultra SC (β-cyfluthrin)
Driveway Pair 3	Warrior Insecticide with Zeon Technology[1] (λ -cyhalothrin)	Demand CS (λ-cyhalothrin)
Driveway Pair 4	Prelude (permethrin)	Suspend SC (deltamethrin)

[1] Not registered for residential use but included to provide a useful comparison for this experiment.

Irrigation and Rainfall

The irrigation and rainfall during the Washoff Dynamics Study followed the same procedures as in the Pathway Identification Study. The one exception was that the size of the simulated rainfall event was increased to 18 mm in October to provide a significant washoff event for the first set of applications.

Study Results

From the time of the first application on October 3, 2012 through the end of runoff sampling on May 9, 2013, a total of 34 rainfall events (simulated and natural) occurred, totaling approximately 311 mm of rainfall. Ten simulated events totaling approximately 190 mm and 24 natural events totaling approximately 121 mm occurred. A total of 513 runoff samples were analyzed.

The first set of applications occurred on October 3, 2012 and was followed by a simulated rainfall event on October 17 (2 weeks following application). The magnitude of this rainfall event was approximately 18.3 mm. There were two small natural rainfall events of 1.5 and 0.3 mm on October 11 and October 14, respectively. Therefore the first small rainfall event occurred eight days after the application.

A second group of applications to the driveways occurred on October 18, 2012 (1 day after the simulated rainfall event in mid-October). This second application event to the driveways was followed by a simulated rainfall event on November 15 (28 days following application). The magnitude of this rainfall event was 22 mm. There were three natural rainfall events of 0.5, 0.8, and 2.3 mm that occurred on October 22, November 9, and November 10, respectively. Therefore, the first small rainfall event of any significance occurred 23 days after application.

The second and third applications to the wall above the driveway occurred on December 5 and February 5. Rainfall events of 28 and 10 mm occurred on December 12 and February 8, respectively.

Runoff losses from the driveway, expressed as percent of applied, are summarized in Table VI across the entire study period for each of the four product pairs. This approach was taken because the overall loss of pyrethroids is the best measure on impact on urban streams, rather than concentrations in runoff in individual events (the effect on a receiving body is more related to the mass of pyrethroid entering than the concentration of pyrethroid entering and may involve several events because pyrethroids present in runoff may accumulate in the sediment). Individual events are also highly variable due to differences in the size of the event and the time between application of the product and the rainfall event.

In each of the four driveway-applied pairs, the amount of pyrethroid lost from the higher washoff product in each group was higher than the lower washoff product. However, in one case, the difference between the two products was negligible. Much smaller differences were observed in the Washoff Dynamics Study than in the formulation washoff study. The largest difference between product pairs in the Washoff Dynamics Study was less than a factor of five while the difference was greater than a factor of up to 160 for the same product pair in the laboratory setting. This difference could be the result of a number of factors including the longer time between application and rainfall events for most of the rainfall events and the absence of wind and solar radiation during the time between application and the rainfall events in the laboratory setting. For example, photolysis could be contributing to degradation in the field setting. Also sunlight could result in higher surface temperatures on the concrete. There is also increased potential for degradation on the alkaline concrete or increased binding to concrete during the longer times between application and most rainfall events in the field experiments. In addition, the smaller scale of the formulation washoff study might have magnified differences that were dampened in the larger size of treated area in the Washoff Dynamics Study. While the time between application and rainfall events was expected to have an effect on the amount of pyrethroid mass in runoff water based on results from other studies (*4*, *6*), the effect is not clearly evident in this study.

Runoff losses from the wall above the driveway are summarized in Table VII. As with the results for the driveway, the data were summarized across the entire study period. The findings from this surface are in contrast to the findings in the formulation washoff study, showing that some critical factors may not be sufficiently represented in the laboratory setting. The low washoff product (from the formulation washoff study) was the higher washoff product in this Washoff Dynamics Study. Potential explanations offered earlier for the driveway experiments are also applicable here. In addition, the stucco material was vertical in this study (parallel to rainfall) whereas it was at a five degree angle from horizontal during the formulation washoff study. This difference affects the impact of rainfall on the surface and may affect the ability of the pyrethroid to be transported by rainfall.

Table VI. Results from the Driveway Applications

	Pair 1	*Pair 2*	*Pair 3*	*Pair 4*
Days to Initial Rain	8[1]	8[1]	23[2]	23[2]
Loss (% of Applied)				
Lower Washoff Product	1.22	0.79	0.15	0.96
Higher Washoff Product	1.25	2.69	0.27	4.60
Ratio (higher/lower)				
Washoff Dynamics	1.02	3.39	1.82	4.78
Formulation Washoff[3]	2.37	2.24	33.9	168

[1] This was a minor rainfall event and the pyrethroid losses in the event 14 days after application were an order of magnitude higher. [2] This was a minor rainfall event but losses were similar to that observed in the event 28 days after application. [3] From the preliminary results of the formulation washoff study (available in supplementary information on-line (*9*)).

Table VII. Results from the Applications to the Wall above the Driveway

Loss (% of applied over entire study)	
Lower Washoff Product	0.54
Higher Washoff Product	0.22
Ratio (higher/lower)	
Washoff Dynamics	0.41
Building Material Washoff (painted stucco)[1]	5.9
Formulation Washoff (concrete)[2]	85

[1] Results reported elsewhere (*8*). [2] From the preliminary results of the formulation washoff study (available in supplementary information on-line (*9*)).

Conclusions

Broadcast applications to impervious surfaces with a direct pathway to street drains have the greatest potential to generate runoff that may reach urban streams. Applications to concrete driveways sloping to the street are especially vulnerable. Switching from broadcast applications to spot (crack and crevice) applications can greatly reduce overall washoff losses; a 40-fold reduction was observed in our experiments.

The product formulation can affect washoff of active ingredients, especially from impervious surfaces. Formulation effects on washoff potential are complicated, since laboratory studies are not necessarily predictive of behavior under actual use conditions. Formulation can also affect the amounts of active ingredient or the number of sprays per season needed to achieve and maintain insect control as well as the extent of VOC emissions.

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Chapter 3

Determining Critical Factors Controlling Off-Site Transport of Pyrethroids in the Urban Environment

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Identifying critical factors that control the off-site transport of pyrethoids in the urban environment is critical to the safe and effective use of pyrethroids in the control of insects for home and business owners. This work uses a data mining approach to extract critical event variables from an urban study site that had been operational for a year (August, 2011 – August, 2012). Six applications occurred for four surfaces (driveway, garage door, grass perimeter, and house wall) and one application to the grass lawn following historic and revised practices. A Multivariate Adaptive Regression Spline (MARS) modeling approach was used to statistically model the percent of pyrethroid mass applied (percent washoff) from all surfaces. This approach yielded accurate models for all surfaces, with the driveway surface having the simplest model of percent

washoff. The MARS modeling approach allows very dynamic changes in variables to represent complex behavior at the sites—integrating many variables to calculate percent washoff. For all surfaces, a near-post application period (around 14 days for all surfaces except the grass lawn, which had an extended multiple month period post application) controlled washoff particularly during low intensity lawn sprinkler events. During natural and simulated rainfall events, the dynamics of washoff included multiple types of characterizing runoff factors (from 10, 20, 30, and 60 min maximum runoff rates), the rainfall amounts, days since the previous application of a pyretheroid, among other factors. In addition, a number of other often minor factors were included by the MARS models for each surface for the calculation of percent washoff that warrant further investigation.

Introduction

Pesticide transport due to runoff is a major concern, and a well-studied one in farming and rural contexts, but is not so well understood in urban environments. Urban areas contain diversity of surfaces, both constructed and natural, creating a range of potential runoff conditions. In suburban areas, these pathways are different still, and can often be relatively short. This potentially sends constituents like pyrethroids directly into receiving waters. An example of this would be small lawn areas adjacent to curbs that flow directly to street drains. In addition, urban areas in California receive both natural rainfall and lawn irrigation. Complicating matters, urban chemical application patterns are more complex than those seen in agricultural areas. All these factors contribute to the unique challenges of managing pyrethroids in an urban environment. Because of this inherint unpredictability, it is critical that transport pathways be managed appropriately.

Pyrethroids are a class of insecticides used to control a wide range of pests. Pyrethroids are used extensively in California and have been detected in urban environments (*1–3*). Pyrethroids can be applied to grass, driveways, vertical walls, and garage doors. The Pyrethroid Working Group (PWG; a task force of pyrethroid registrants) has sponsored studies on off-target washoff of pyrethroids (e.g., (*4*, *5*)), including the field study upon which this work is based: a study tracking chemical flow from common surfaces in the urban environment under natural conditions (*6*). Davidson, et al. (*6*), summarized the primary washoff results of this study from a surface application perspective, including both historic and revised application practices. The objective of this work is to mine the fine temporal resolution data available from the Davidson, et al., study, define variables representing critical processes that could influence washoff of pyrethroids, and model the system and individual surfaces statistically, in order to understand critical processes influencing off-target washoff of pyrethroids from diverse surfaces in the urban environment.

Materials and Methods

Basic Study Design

The primary study design is discussed in Davidson, et al. (*6*)—an open access journal article and summarized here. The study was conducted at a full-scale test facility in central California, USA. Six replicate house lots were built to model typical front lawns and house fronts of California residential developments and consisted of stucco walls, garage doors, driveways, and lawn sprinkler systems. Each of the six lots also included a rainfall simulator to generate artificial rainfall events. Different pyrethroids were applied to five surfaces (Table I)—driveway, garage door and adjacent walls, lawn, lawn perimeter (grass near the house walls), and house walls not adjacent to concrete. The volume of runoff water from each house lot was measured, sampled, and analyzed to determine the mass of pyrethroid lost from each surface. Broadcast applications were made to the lawns once, and perimeter applications were made every two months. Applications to three of the house lots were made using the application practices typically used prior to recent label changes (historic), and applications were made to the other three house lots according to the revised application procedures (revised). On the three surfaces not affected by the change in application procedures (lawn, lawn perimeter, and house wall not adjacent to concrete) products with contrasting washoff behavior were used.

Table I. Surfaces and pyrethroids applied

Surface	*Historic (Lots 1, 3, 5)*	*Revised (Lots 2, 4, 6)*
Lawn	Deltamethrin *(DeltaGuard G)*	Bifenthrin *(Talstar PL)*
Grass Perimeter	λ-cyhalothrin *(Demand CS)*	λ-cyhalothrin *(Warrior)*
House Wall	Bifenthrin *(Wisdom TC)*	Permethrin *(Prelude)*
Garage Door	β-cyfluthrin *(Tempo Ultra SC)*	β-cyfluthrin *(Tempo Ultra SC)*
Driveway	Cypermethrin *(Cynoff WP)*	Cypermethrin *(Cynoff WP)*

Experimental Site

The experiment site was located on an experimental farm in central California near Porterville. This site contained a Tulunga loamy sand soil, which is a preferred soil for building homes in the area. To increase runoff, a clay loam soil with greater clay content was brought in and applied as a base layer (10–15 cm) on top of the existing soil. The site consisted of six identically assembled simulated house lots (pictures of the site are shown in Figure 1). Each house lot was 22.9 m in width, with the length of the house and two-car garage facade wall measuring 19.8 m. The width of the concrete driveway was 5.5 m, and the distance between the concrete curb and house wall was 6.1 m. The placement of the driveway provided two separate sections of grass lawn. The section on the west side of the driveway was approximately 15.8 m wide, and the section on the east side was approximately 1.5 m wide. Both sections of the lawn were treated the same throughout the study. During construction, the lots were graded with driveways sloping (6%) from the house to the street, according to normal practice in many suburban areas of California. The garage doors were made of painted aluminum panels that were fixed and nonoperational. House exterior walls were approximately 2.4 m tall, constructed of a sturdy substrate, and covered in typical California polymer, modified stucco, using local California contractors following techniques and material arrangements typical of California construction. Particular attention was focused on accurately reproducing the transition area between the stucco wall and slab foundation. The six lots were side-by-side in an east-west orientation with the facade walls facing south.

Professional landscape contractors installed the residential irrigation systems using typical components (Figure 2a). The sprinkler heads were arranged in the corners of the larger lawn section (west side of each driveway) and then every 4.0 m along the perimeter of the larger lawn section, giving eight sprinkler heads. On the small lawn section (east side of each driveway), the sprinkler heads were positioned at the midpoint of each side, giving four sprinkler heads. The rainfall simulator consisted of nozzles on cross-beams mounted on risers located approximately 6.1 m above the ground (so that the drops reach terminal velocity) spaced at 6.1 m intervals just outside the curb and wall (Figure 2b). Each nozzle covered a radius of approximately 6.1 m, the same as the depth of the house lots, and produced a random distribution of rain droplets, closely mimicking natural rainfall patterns (Figure 2c).

Runoff water from each site flowed down the curb and at the west end of the plot, made a 90° turn into a 37.9 L stainless steel collection basin located below a sampling shed (Figure 2d). The sheds were approximately 2.4 m x 2.4 m and housed the runoff collection basin, refrigerator, an Isco 6712 autosampler (placed inside a refrigerator with its temperature monitored by a Campbell Scientific Incorporated [CSI] CS107 temperature probe), CSI CR1000 data-logging system, and various other electronic components. Water from the collection basin was pumped to a 5680 L concrete tank, where it was collected and stored until it could be transported off-site. Each house lot also had a rain gauge and soil moisture and soil temperature probe attached to the CR1000 in the shed. Over the duration of the study, meteorological data were collected for the sampling site by a weather station.

(a) Garage door and driveway

(b) Curb and channel routing runoff to collection

(c) Garage door, driveway, and expansion joint

(d) Elevated view of the site

Figure 1. Images representing the experimental site design. (see color insert)

(a) Lawn irrigation sprinklers

(b) Rainfall simulator on cross beams

(c) Simulated rainfall event

(d) Flow of runoff water to collection system

Figure 2. Irrigation and rainfall system operation, rainfall splash, and directed flow to the collection system. (see color insert)

Pyrethroid Selection

Eight products were selected for use in the study: two products with contrasting washoff behavior for each of the three surfaces (lawn, lawn perimeter, and the house wall above grass) and one product for each of the two surfaces (driveway and garage door and adjacent walls) receiving different application practices (Table I). A more complete discussion of these applications is detailed in Davidson, et al. (*6*). Different active ingredients had to be chosen for each of the five surfaces in both sets of plots (historic and revised treatment practices) in order to determine the source of pyrethroids in the runoff water.

Application Procedures

Calibrated applications of all five products were made on 2 August 2011 to all 6 house lots and repeated (except for the broadcast application to the lawn) on 4 October, 6 December, 2 February, 3 April, and 5 June. All application rates were at the maximum label rate for the given product and specific concentration. Lawn: Applications of the lawn products were made using a drop spreader, and any material landing on the driveway or street curb was swept back onto the lawn. Grass perimeter: The pyrethroid was applied to the grass in a band 1.5 m wide, measured from the wall outward. Wall above grass: The pyrethroid was applied to the vertical wall above the grass in a band measuring 0.61 m high. The application stopped approximately 10 cm (horizontally) from the section of wall above the concrete driveway to prevent washoff water containing pyrethroids from this surface from running down the driveway. Garage door [and wall above driveway]: The pyrethroid was applied differently for the historic and revised application practices. For both practices, it was applied to the wall directly above the concrete driveway in a band 0.61 m high, starting at the surface of the driveway. In the treatment representing use according to historic application practices, the pyrethroid was also applied to the garage door in a band 0.61 m high starting at the surface of the driveway. In the treatment representing the revised application practices, the garage door was not treated. Driveway: The pyrethroid was applied differently for the historic and revised application practices. Historic practices had pyrethroid applied to all of the upper part of the driveway in a band 1.5 m wide, beginning at the wall or garage door. Revised practices treated only the expansion joint between the garage door and the driveway.

Irrigation and Simulated Rainfall

The lawns of the six house lots were managed by a local lawn service, including mowing and setting the irrigation schedule. The irrigation schedule was adjusted to match both the duration and the number of days per week for a typical lawn in central California. Typically, an irrigation event lasted anywhere from 8 to 15 min and applied from 3.4 to 6.4 mm of water, depending on the needs for maintaining the health of the lawn.

A rainfall simulator was used to supplement natural rainfall and to produce storm events representative of Sacramento (CA, USA) during the period of

October to March. The rainfall intensity was set at approximately 12.7 mm per hour, with the duration of each event varying to meet the desired rainfall amount. Using a 15-yr rainfall record for Sacramento, 1-in-5-yr and 1-in-2-yr rainfall events were determined. The 1-in-5-yr rainfall event in October through March varied from 9.7 mm to 22 mm, and the 1-in-2-yr rainfall event ranged from 9.7 mm to 16 mm in November to March. The intent was to have a 1-in-5-yr event in October through March and an additional 1-in-2-yr event in November through March, with either natural or simulated rainfall.

Runoff Sampling and Monitoring

The runoff volume from each house lot was measured and recorded at the collection point down-gradient from the lot. Runoff was defined as the water leaving the house lot and entering the collection device. A 38 L stainless-steel collection basin contained flow rate measuring equipment for both bulk and fine flow volumes. Event-based sampling was performed for irrigation and rainfall (natural or simulated) events, with a refrigerated autosampler triggered to collect water samples when a runoff event occurred through an autosampler intake in the stainless steel collection basin after a predetermined volume. Approximately one composite sample was collected for each lawn irrigation event into a 1 L glass bottle. When a rainfall (either natural or simulated) runoff event occurred, a series of up to 12 composite samples was collected into 1 L glass bottles. Samples were refrigerated during collection and remained refrigerated until study personnel retrieved samples from the autosamplers, at which time samples were immediately capped with Teflon-lined lids. Samples were then preserved with formic acid and methanol to maintain a pH below 6 and reduce sorptive loss to the glass during storage, respectively. Samples remained refrigerated from the time of collection until they were shipped to the analytical laboratory.

Sample Analysis

Residues of bifenthrin, cypermethrin, beta-cyfluthrin, delta- methrin, lambda-cyhalothrin, and permethrin were extracted from water samples by adding methanol and sodium chloride to each sample, then partitioning the mixture twice with hexane. Additional procedures and data quality control measures are detailed in Davidson, et al. (*6*). The targeted (method) limits of quantitation for residues in water samples were 2.0 ng/L for bifenthrin, cypermethrin, beta-cyfluthrin, and lambda- cyhalothrin; 4.0 ng/L for deltamethrin; and 20.0 ng/L for permethrin.

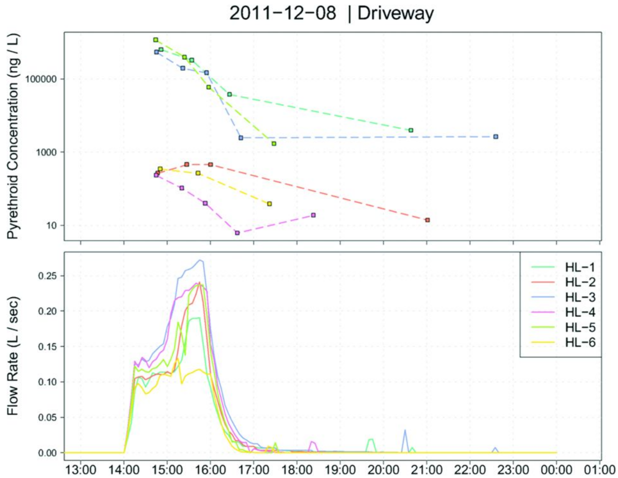
Because of the high volume of runoff samples, it was neither feasible nor necessary to analyze all samples for the duration of the study. However, all samples collected in the two weeks following an application, as well as all samples collected during large rainfall events, were analyzed. If significant residues were still present beyond the two-week period after application, additional samples were analyzed. Typically, an individual sample concentration greater than 100 ng/L from any house lot prompted the analysis of additional runoff samples (from all house lots to maintain a consistent comparison).

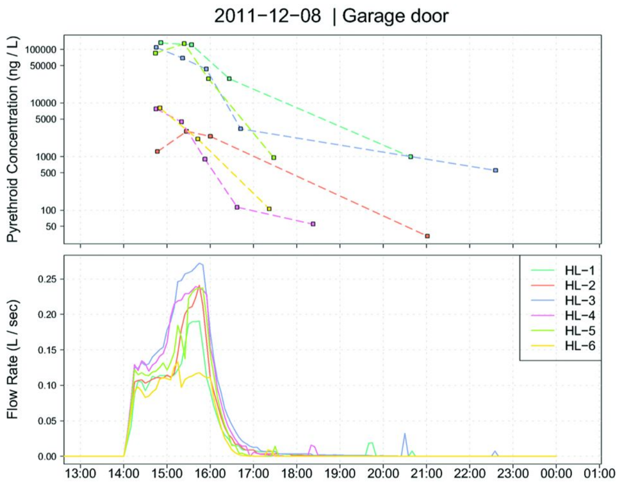
5-Minute Resolution Dataset

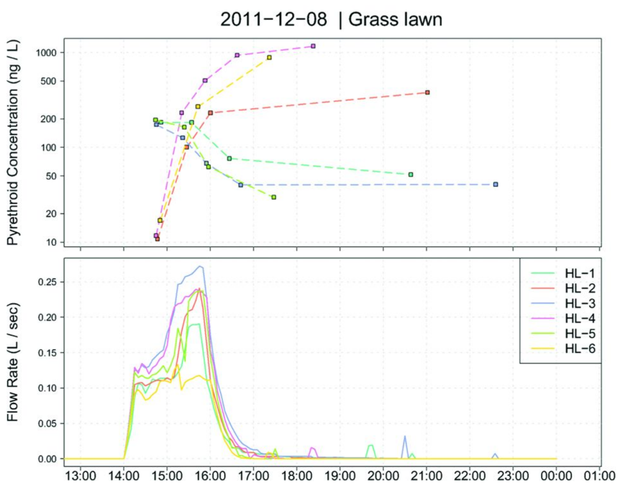
A 5-minute temporal resolution dataset was created from the data collected by site instrumentation. The previous work of Davidson, et al. (*6*) evaluated the resultant data using an overall study length / application period approach. A complete set of data was created at this 5-minute resolution to permit the creation of variables for the same time scales that are indicative of the processes representing critical factors controlling off-target washoff of pyrethroids. This included rainfall, irrigation, and meteorological variable summaries, runoff rates and volumes, assigned sample concentrations and calculated mass loads, among others. In order to bridge gaps in monitored data, estimated concentrations were calculated using an average of concentrations measured previous to the gap in data and after the gap in data. The exception to this was when the next samples were collected from plots directly after application or after a significant rainfall indicating a change in the dynamics of the site. In those cases, the previous concentration was used. This met with the practicalities of sample collection; the costs of analysis, the dynamics of the chemical evolution in runoff at the site; the site configuration, including very low sprinkler depth irrigation events; and the requirements of the modeling, which was a complete time series.

The dynamics of this dataset are exemplified in Figure 3a-3e for runoff discharge and pyrethroid transport. This is indicative of the variability of individual plot runoff from a rainfall event with slightly different runoff discharge rates from the same event at the site. In general, the washoff response differed by surface on orders of magnitude for this single event (with driveway > garage door > grass lawn > house wall > grass perimeter, approximately, for this example). These orders of magnitude differences were the case for both historic and revised practices under rainfall and irrigation conditions found in Davidson, et al. (*6*). In some instances, the chemograph response to the rainfall-runoff process differed between the historic and revised practices—for example, Figure 3d where the historic and the revised practices for the grass lawn show completely different washoff response.

This 5 minute dataset was mined for critical factors, which represent the influencing variables for transport phenomena on a daily basis. The primary reason for this approach is that it attempts to preserve the influence of critical factors on washoff without losing processes by averaging out responses or being lost in statistical data noise. For this work, a critical example is the number of events occurring on a short timescale of sprinkler irrigation overflows lasting, in general, less than 20 minutes, which would be lost in the noise of the dataset without characterizing variables. These characterizing variables are discussed below.


2011−12−08 | Driveway
Pyrethroid Concentration (ng / L)
100000
1000
10
Flow Rate (L / sec)
0.25
0.20
0.15
0.10
0.05
0.00
HL−1
HL−2
HL−3
HL−4
HL−5
HL−6
13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 00:00 01:00


2011−12−08 | Garage door
Pyrethroid Concentration (ng / L)
100000
50000
10000
5000
1000
500
100
50
Flow Rate (L / sec)
0.25
0.20
0.15
0.10
0.05
0.00
HL−1
HL−2
HL−3
HL−4
HL−5
HL−6
13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 00:00 01:00


2011−12−08 | Grass lawn
Pyrethroid Concentration (ng / L)
1000
500
200
100
50
20
10
Flow Rate (L / sec)
0.25
0.20
0.15
0.10
0.05
0.00
HL−1
HL−2
HL−3
HL−4
HL−5
HL−6
13:00 14:00 15:00 16:00 17:00 18:00 19:00 20:00 21:00 22:00 23:00 00:00 01:00

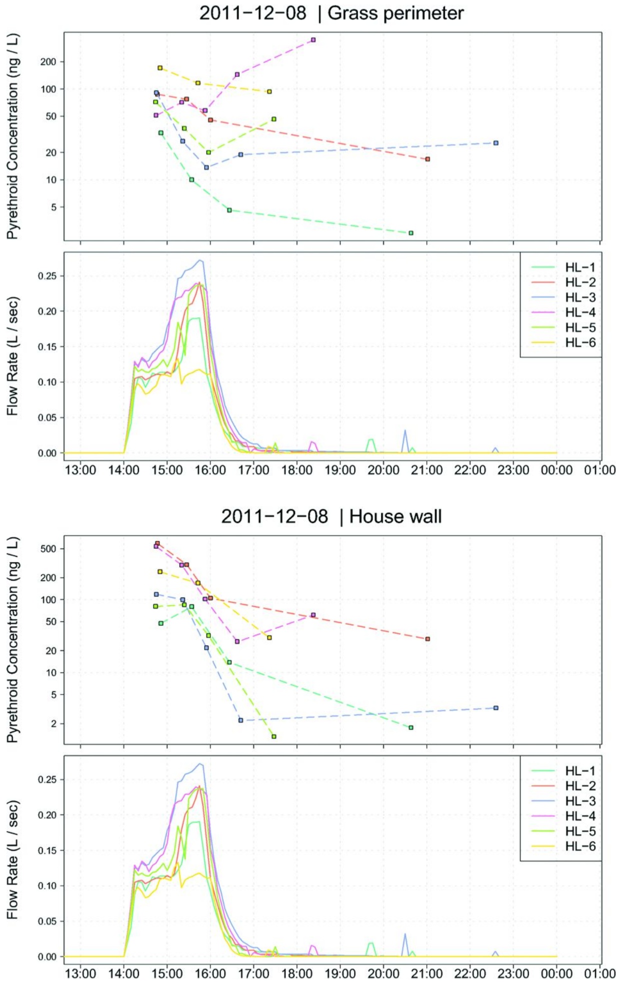


Figure 3. Driveway (a), grass perimeter (b), garage door (c), grass lawn (d), and house wall (e) event on 12/08/2011 showcasing 5 minute resolution flow and pyrethroid transport. (see color insert)

Data Analysis: Characterizing Variables

There are six primary collections of characterizing variables and one primary target collection. These include the following characterizing variables: application, rainfall, runoff, time, experiment, and weather, with the primary target being mass loss (via percent washoff). The variables representing these collections are shown in Figure 4. Many of these variables are self-explanatory. Rainfall and runoff variables were structured to really identify critical factors. This included creating a four-factor version of precipitation and runoff rates at 10, 20, 30, and 60 minute intervals. These variables serve as a method of fingerprinting the types of events that cause off-target washoff of pyrethroids.

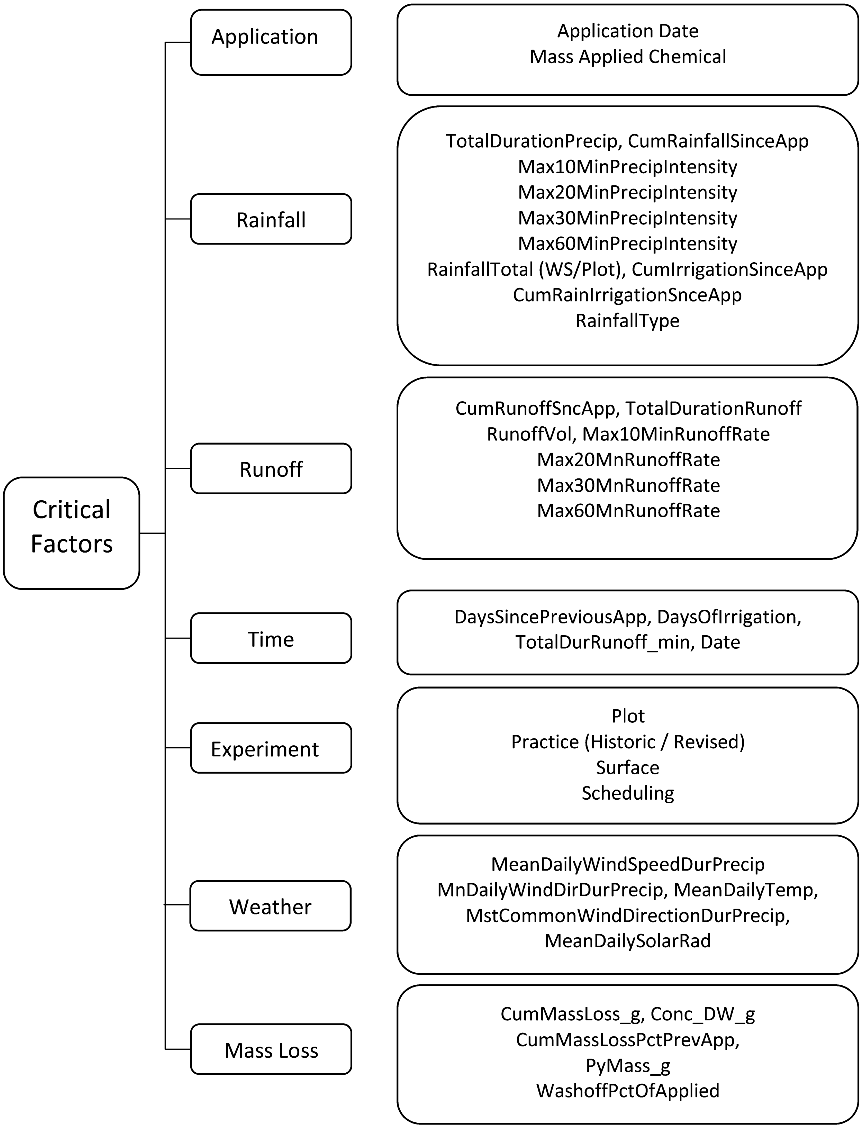


Figure 4. Critical factors (variables) included in the analysis.

For example, a small event associated with a timed lawn sprinkler irrigation event will have much greater values of 10 and 20 minute intensity variables and a reduction in values at 30 and 60 minutes for both rainfall and runoff rates. This becomes a significant differentiator for larger rainfall events which could have greater values for all four factors. Event specific variables were determined including rainfall total (RainfallTotal) and rainfall duration (RainfallDuration). Additional variables were defined to represent the accretion of time and other variables affecting off-target washoff. These include variables such as cumulative rainfall since application (CumRainfallSinceApp), cumulative irrigation since application (CumIrrigationSinceApp), cumulative runoff since application (CumRunoffSncPApp), days since previous application (DaysSincePreviousApp). With this approach to the characterization of the dynamic events driving off-target washoff of pyrethroids, critical factors can be identified through a statistical modeling approach.

Statistical Modeling

All statistical analyses were conducted using R (*7*). A Multivariate Adaptive Regression Splines (MARS; (*8*, *9*)) modeling approach was used as the primary approach to data analysis for this work. This approach has many benefits over other approaches. MARS is intended for high-dimensional problems. Additive effects are captured well by MARS, and the algorithm can include both numerical and categorical variables. As time progresses after an application event, additive processes may drive the percent washoff after an application event, which can be easily captured by the MARS methodology. Finally, the results of the model construction are easy to understand, which permits understanding of critical factors driving the off-target washoff of pyrethroids from the diverse surfaces.

The set of potentially influential parameters as well as the target response variable (the percentage of pyrethroid mass applied) were transformed, where necessary, to best approximate normality through a custom *R* function based on the Shapiro-Wilk normality test (*10*). Because the MARS model framework does not allow missing data, missing data were imputed using a *k*-nearest-neighbors algorithm (function knnImputation in the package DMWR, with $k = 10$).

A separate model was created for each surface since different transport phenomena may govern different surfaces. This approach allowed different critical factors for each surface. Data from each surface was split into training and testing portions of the dataset (75% and 25%, respectively) such that the distribution of the percentage of pyrethroid mass applied was consistent between the two portions (function createDataPartition in the CARET package). This process ensured that the training data were balanced across the phenomena occurring across the study period that influenced off-target washoff including larger rainfall events, smaller irrigation overflow events, both wet and dry seasons, and other phenomena influencing the percent washoff. A MARS model was optimized using the training data by varying the number of pruned terms (nprune) and the degree of terms in the model (degree), with the selection criterion being the most parsimonious model within one standard error of the best generalized cross-validation score (GCV; through the train function of the package CARET, with method = *earth*, and selectionFunction = *oneSE*).

To evaluate the performance of each model, several analyses were performed. First, the observed values of the testing dataset were plotted against the values predicted by the optimized model. Second, the relative importance of each variable in the optimized model was estimated using 1) the number of subsets including the variable created during the pruning pass, 2) the decrease in the residual sum of squares when the variable is included in the model, and 3) the decrease in GCV when the variable is included in the model (using the evimp function of the package EARTH). Third, the root mean squared error and the mean absolute error were calculated by comparing predicted values for the whole dataset (not just the testing set). Fourth, a significance of each MARS model was calculated by an F-test against the null model (model using only an intercept). The 'effective number of parameters' were used as the degrees of freedom for the MARS model. This value was calculated as: number of MARS terms + penalty * (# of MARS terms -1)/2, where the penalty was set to 2. The MARS modeling approach does not lend itself to calculating the significance of individual terms of the model. Finally, for each estimated data point, its composition was broken into components attributable to each factor by summing the hinge terms including that factor. To assess whether factors selected by the MARS methodology may be representative of another, correlated factor, the degree of correlation between potentially influential factors was calculated. For correlations between continuous variables, the Pearson correlation coefficient was used. For relationships between factor and continuous variables, Kruskal-Wallis tests were conducted, and for relationships between factors, the chi-squared metric was calculated.

Results

Model Performance

The results of all MARS model predictions alongside actual results are shown in Figure 5-9 for each surface and plot within each surface. The model summary statistics including the mean absolute error (MAE), the root mean square error (RMSE), and the normalized root mean square error (NRMSE) are shown in Table II. The statistical MARS models accurately predict the transport of pyrethroids as a combination of critical factors for all surfaces. For the transformed washoff as a percent of pyrethroid applied (as percent of previous application, from now on percent washoff), there was no difference between historic and revised practices for any of the surfaces in the MARS models except for the grass lawn (discussed below and in later sections of the document). This is due to the data transformation, which has leveled response such that the difference in magnitudes between the practices is not contributing to changes in the critical factors in the other surface models. Selected variables are different between surfaces. Analysis results of each surface model versus a null model resulted in the following statistics: Driveway, $p = 0.063$, Garage door, $p = 0.008$, Grass lawn, $p = 0.008$, Grass perimeter, $p = 0.003$, House wall, $p = 0.040$. All model results were highly significant with the Driveway model having the lowest null model test result; however, this surface is the surface with the greatest variability in runoff and peak washoff lowering the value of this statistic compared to the results of the other surfaces. In general, investigation of the results of the modeling showing predicted and actual percent washoff results through the study period (Figure 5-9) show that the modeling represents both the peak, event-based concentrations alongside the transport caused by the shorter duration lawn sprinkler irrigation events, which would be lower energy intensive events than those caused by natural and simulated rainfall. For the duration of the field study, the dry lawn sprinkler irrigation season began and ended the study period, with a wet season of rainfall in between. Both periods for all surfaces are well represented by the statistical modeling, with only the grass lawn having significant modeling issues by the end of the study period, particularly for the historic plots (1, 3, 5). These plots had random responses in transport across the plots near the end of the study period. Interestingly, the revised application plots (2, 4, 6) were modeled more accurately. The MARS model for this surface captures this response by having a critical factor indicating that these plots were revised application plots. This is likely a difference between deltamethrin and bifenthrin since the grass lawn was applied to only once for both compounds for the duration of the study period.

Model predicted versus actual plots are shown in Figure 10. There are two primary features of the model predicted versus actual graphics by surface. The first is the magnitude of the scales for the surfaces of driveway and garage door versus the surfaces of grass lawn, house wall, and grass perimeter. Both the driveway and the garage door involve applications to impervious areas, which by definition are at the theoretical end of the spectrum of environmental fate and transport (off-target), since application is completed on impervious surfaces without much of a pervious surface in the flow pathway. These surfaces have much greater mass flux after application compared to the other surfaces. From Figure 10, all surfaces have accurate actual versus predicted relationships, particularly driveway and garage door with a few notable events related to the December 8, 2011, rainfall, where historic practice plots (1, 3, 5) are all under-represented by the model for both surfaces (Figure 5and6). The second feature is the notable presence of predicted values when no actual values were measured in samples or based on flows from the plots. This is present for all surfaces but is more significant for the grass lawn, house wall, and grass perimeter—surfaces with pervious surfaces and lowest magnitudes of pyrethroid mass load. Most of these responses come from periods of record for the plots that are missing data. This occurred particularly during the dry sprinkler irrigation season.

MARS model statistics by individual plot, summarized for historic and revised practices (plots 1, 3, 5 and 2, 4, 6), are shown in Table II. Overall, the MARS models show very low values for all statistics for all plots and surfaces, indicating good agreement between predicted and actual percent washoff. The magnitude of percent washoff does increase the error in model fit with the transformed variable by surface and by plots, as values are generally increased for historical practices compared to revised practices as shown by the means for those respective surfaces when combined. When evaluated with normalized statistics (NRMSE), the grass lawn, grass perimeter, and house wall all have increased error compared to the garage door and the driveway. However, this slight increase in error is negligible when compared to the overall difference in magnitudes of transport (in untransformed units) between the driveway and garage door and the grass lawn, grass perimeter, and house wall. While comparisons between surfaces and plots can be made with even more depth, the intention of Table II is to showcase a number of statistics that reinforce the general quality of model fit for all plots and surfaces regardless of practice. While some plots and surfaces have elevated error values (e.g., plot 6 – grass perimeter), these error values are not indicative of a significant problem with the modeling for any surface, rather reflective of differences caused by the experimental variability contained within this complex study. This general quality in model fit statistics ensures the repeatability of the modeling to represent the environmental fate and transport off these varied surfaces.

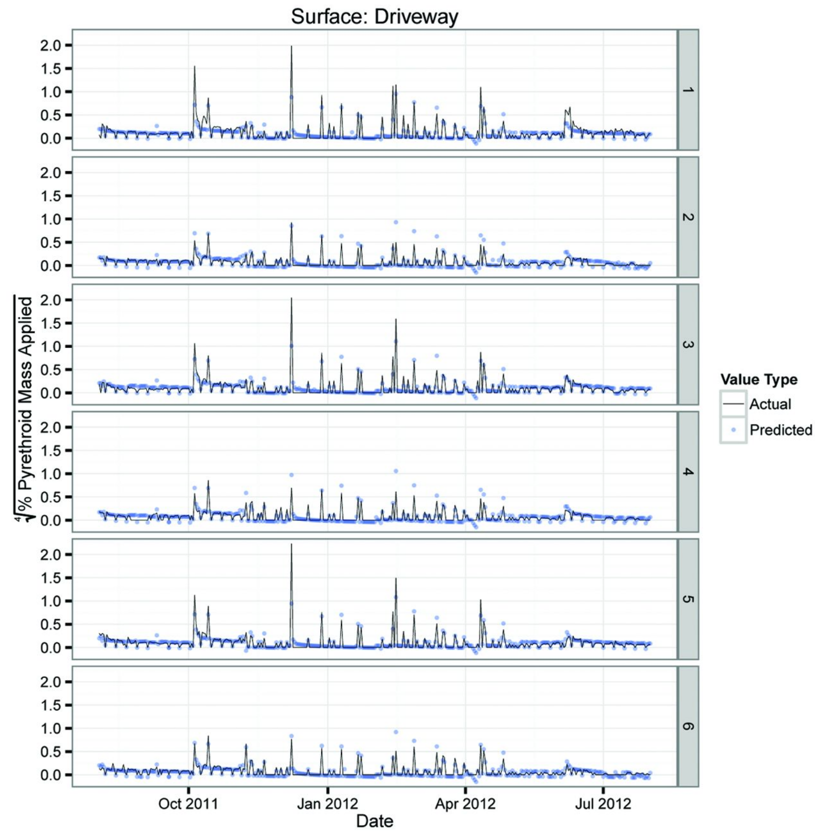


Figure 5. Actual percent washoff (of previous mass applied) vs MARS modeled values for driveway in transformed units.

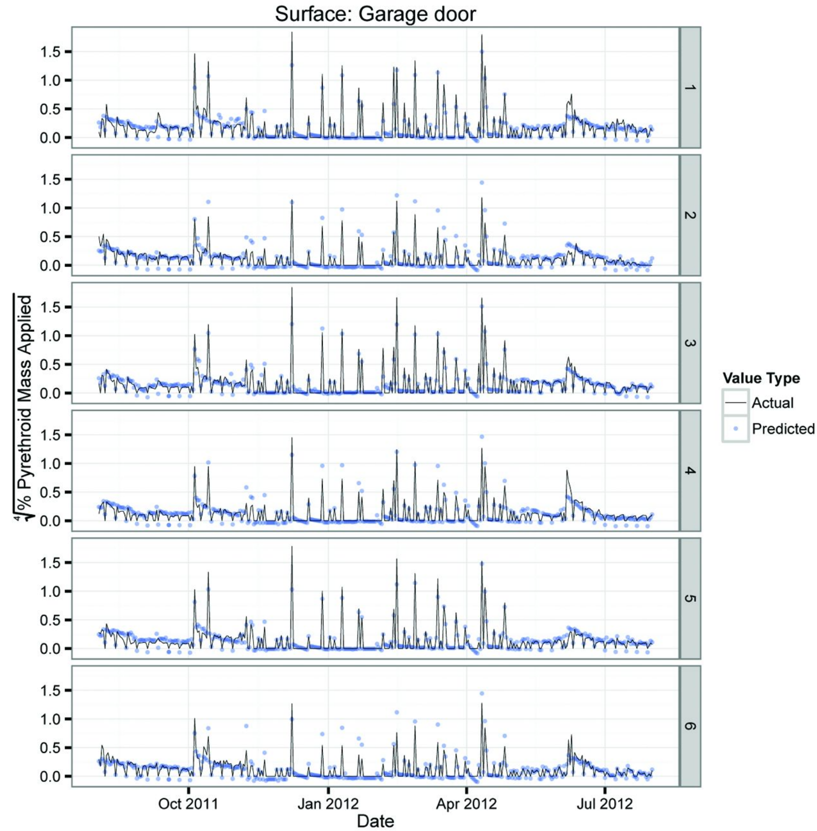


Figure 6. Actual percent washoff (of previous mass applied) vs MARS modeled values for garage door in transformed units.

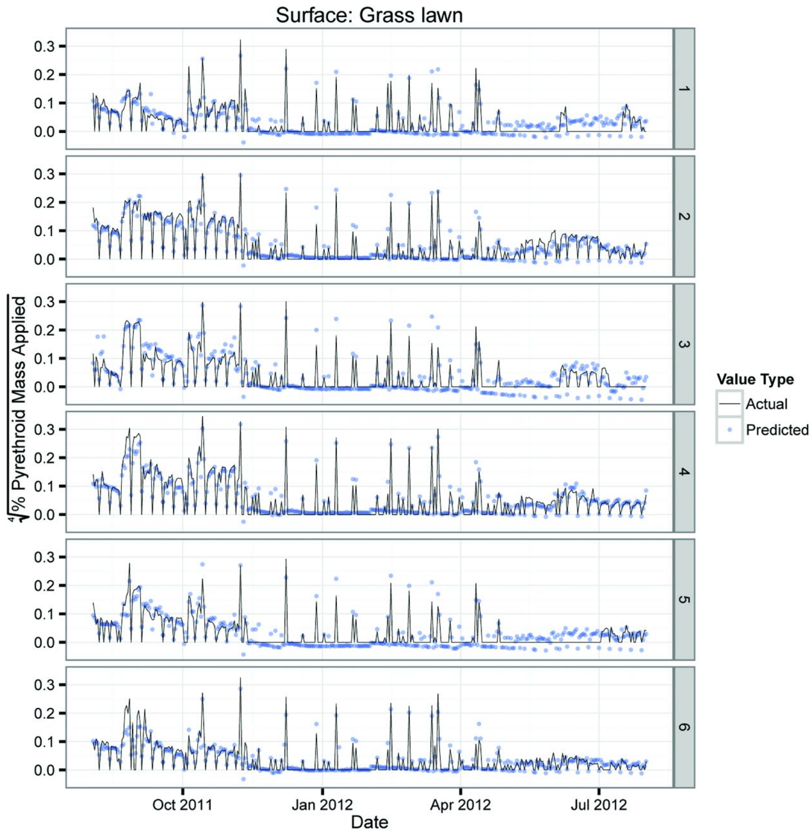


Figure 7. Actual percent washoff (of previous mass applied) vs MARS modeled values for grass lawn in transformed units.

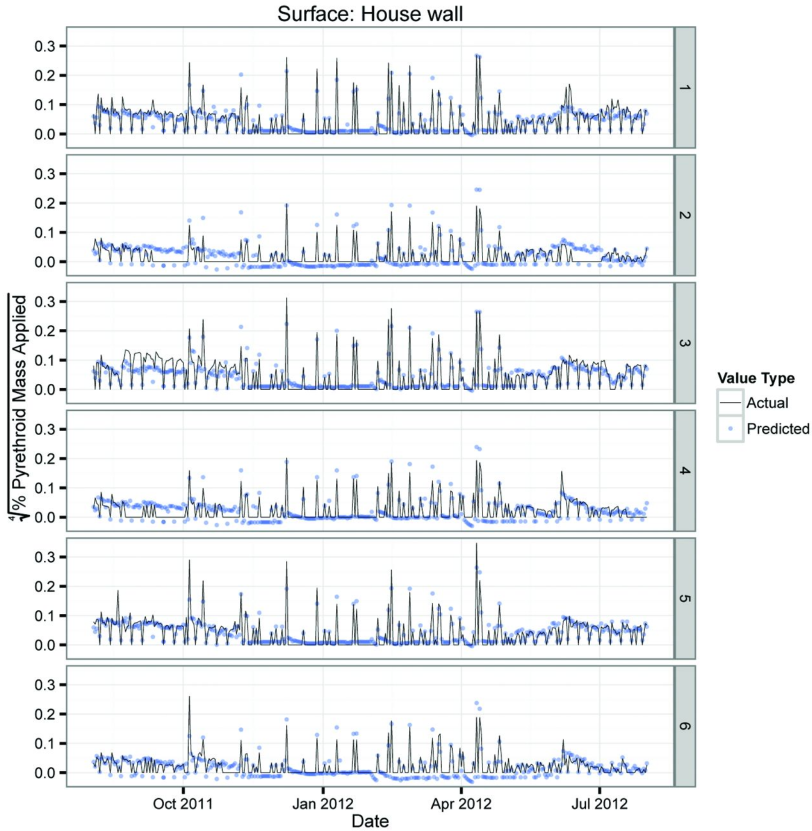


Figure 8. Actual percent washoff (of previous mass applied) vs MARS modeled values for house wall in transformed units.

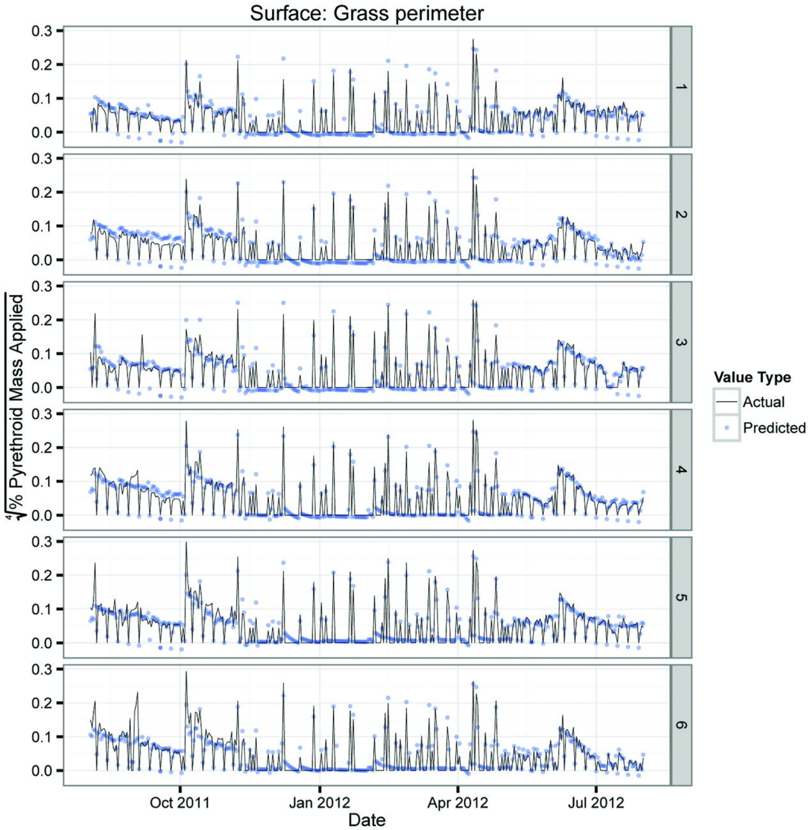


Figure 9. Actual percent washoff (of previous mass applied) vs MARS modeled values for grass perimeter in transformed units.

Table II. Surfaces and pyrethroids applied

Surface	*Plot 1*	*Plot 2*	*Plot 3*	*Plot 4*	*Plot 5*	*Plot 6*	*Mean (Historic)*	*StDev (Historic)*	*Mean (Revised)*	*StDev (Revised)*
MAE Statistic										
Driveway	0.0509	0.0372	0.0413	0.0391	0.0389	0.0355	0.0437	0.0052	0.0373	0.0014
Garage door	0.0544	0.0435	0.0476	0.0466	0.0426	0.0442	0.0482	0.0048	0.0448	0.0013
Grass lawn	0.0171	0.0133	0.0176	0.0139	0.0171	0.0122	0.0173	0.0002	0.0132	0.0007
Grass perimeter	0.0099	0.0109	0.0108	0.0096	0.0118	0.0135	0.0109	0.0008	0.0113	0.0016
House wall	0.0135	0.0173	0.0170	0.0151	0.0118	0.0126	0.0141	0.0022	0.0150	0.0019
RMSE Stastic										
Driveway	0.1103	0.0566	0.0835	0.0604	0.0920	0.0505	0.0953	0.0112	0.0558	0.0041
Garage door	0.0978	0.0652	0.0793	0.0700	0.0734	0.0727	0.0835	0.0104	0.0693	0.0031
Grass lawn	0.0235	0.0186	0.0239	0.0198	0.0215	0.0204	0.0230	0.0010	0.0196	0.0007
Grass perimeter	0.0140	0.0138	0.0168	0.0147	0.0178	0.0214	0.0162	0.0016	0.0166	0.0034
House wall	0.0199	0.0225	0.0229	0.0201	0.0181	0.0177	0.0203	0.0020	0.0201	0.0019
NRMSE Stastic										
Driveway	4.94%	2.54%	3.74%	2.71%	4.12%	2.26%	4.27%	0.50%	2.50%	0.18%
Garage door	5.31%	3.54%	4.30%	3.80%	3.98%	3.94%	4.53%	0.57%	3.76%	0.17%

Continued on next page.

Table II. (Continued). Surfaces and pyrethroids applied

Surface	*Plot 1*	*Plot 2*	*Plot 3*	*Plot 4*	*Plot 5*	*Plot 6*	*Mean (Historic)*	*StDev (Historic)*	*Mean (Revised)*	*StDev (Revised)*
Grass lawn	6.81%	5.39%	6.91%	5.73%	6.23%	5.90%	6.65%	0.30%	5.68%	0.21%
Grass perimeter	4.69%	4.62%	5.63%	4.92%	5.97%	7.17%	5.43%	0.54%	5.57%	1.14%
House wall	5.71%	6.46%	6.57%	5.77%	5.21%	5.09%	5.83%	0.56%	5.77%	0.56%

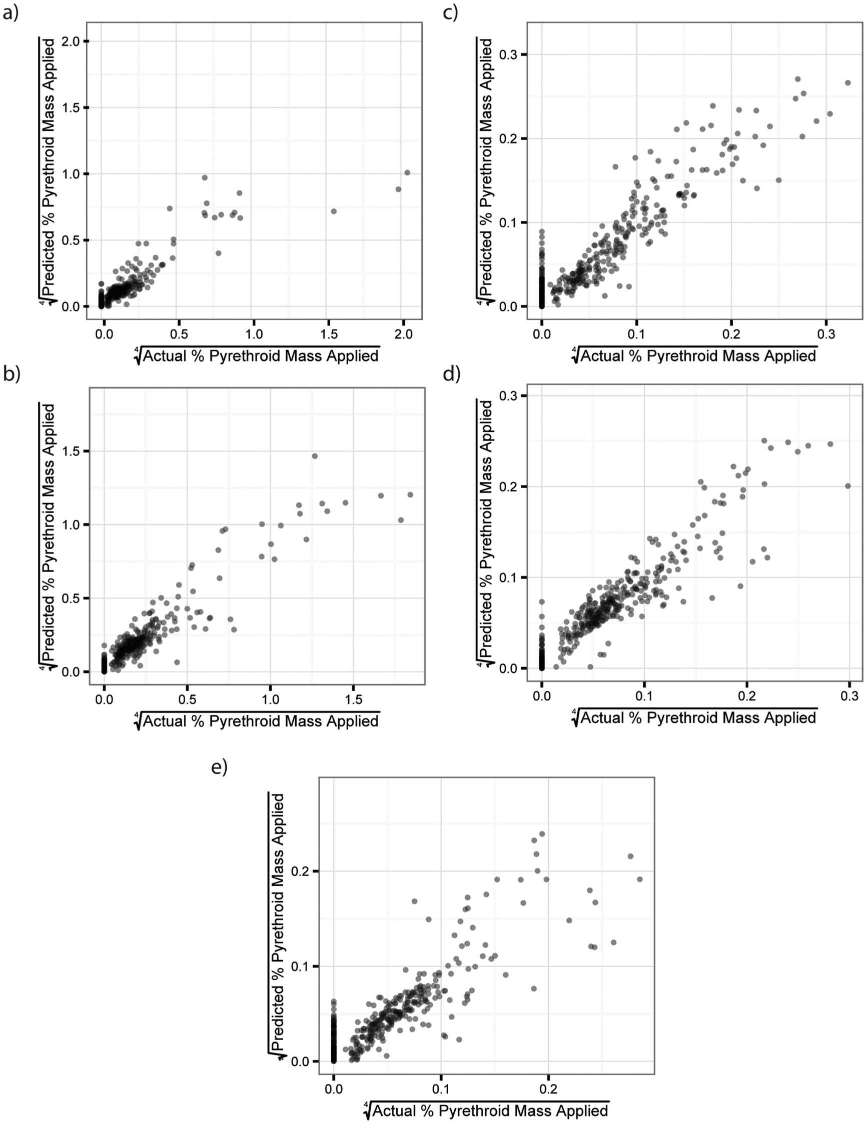


Figure 10. Driveway (a), garage door (b), grass lawn (c), house wall (d), and grass perimeter (e) predicted versus actual graphs.

Critical Factors (MARS Models) by Surface

The MARS model approach is based on the creation of hinge functions that allow nonlinear changes in response for a variable based on values of the variable used in prediction. This includes zeroing the value, decreasing it over time, or rapidly increasing the value and influence of the variable in the calculation of response (percent washoff, in this instance). This is the exact type of response that is required for this type of complexity in response where multiple environmental and study variables are combined to get a single response as the study progresses. Described in Table III are the untransformed variables used in the MARS modeling (named critical factors henceforth) for each surface. An example of the way these factors are combined across values of the parameter is shown for the driveway in Figure 11. The nonlinear response for flow (bottom row, Figure 11) is split between 10, 30, and 60 min maximum flow rates. This includes a sharp increase and then lower sloping increase in contribution for the 60 min rate, a flat response for the 30 min runoff rate with a very sharp increase after exceeding 0.46 (in transformed units), and finally a flat response for the 10 min rate until 0.48 when the response sharply decreases. This response aids in accommodating the complex hydraulics associated with the combined low-level sprinkler irrigation rates and the simulated and natural rainfall hydraulics, which can span both that type of response to flooding of the site from heavy rainfalls. The days since previous application (log10plus1 transformation) has a very flat response, which decreases at different rates and is very similar to a one-phase decay with plateau equation. This is in contrast to the slowly increasing values of previous mass applied (tenth root transform). Rainfall and weather station rainfall have very different responses based on value to differentiate between rainfall and lawn sprinkler irrigation. For the driveway, the inclusion of the cumulative runoff since application (fourth root transform) rapidly increased until it plateaued, which is an expected response particularly for chemical applications completed on impervious surfaces. The cumulative rainfall (square root transform) since application had a lower response for all values but generally increased over time. The combination of all of these factors and using the hinge function of the MARS modeling approach allow us to calculate the percent of pyrethroid washoff in very efficient ways.

The MARS modeling approach is to overfit the percent washoff data and then reduce the variables to create as compact a set of hinge functions / variables as possible. Shown in Table III are the factors contributing to the calculation of percent washoff for each surface. There are significant similarities for all of the surfaces for critical factors within all factor groupings: rainfall, runoff, time, experiment, weather, and application. The models with the least to most complex set of factors are the following: driveway (9), house wall (11), grass perimeter (14), garage door (15), and grass lawn (16). While the combination of factors by value was discussed for the driveway, a look at the driveway factors indicate that there is a representation of different types of runoff, long (duration) and short time (event) spans related to application, rainfall, and runoff, and the previous mass applied. This simpler model may be related to the driveway having the most simple transport mechanics, with direct application and transport distinguished by the difference between 10, 30, and 60 min runoff rates and the cumulative effects of multiple rainfall events and irrigation amounts on the percent washoff. Model results (Figure 5) are shown for both wet and dry seasons. The garage door (Figure 6) had the most complex model of the surfaces including most of the factors used in the driveway model and the duration of rainfall and runoff, windspeed, and the duration of irrigation. These factors may represent the complexities of the application to a vertical surface and the influence of irrigation for this surface. The grass lawn was the only surface to have a distinguishing characteristic for the revised versus the historic practices, which is also the only surface to show a significant difference in percent washoff between those plots (Figure 7, plots 1, 3, 5 vs 2, 4, 6). The model also distinguishes the response for plot 3, particularly. This plot was the only historic plot to have a significant transport series of events in June and early July of 2012. The model performed poorly during this period of time for the historic plots due to the lack of transport for deltamethrin after almost a year since application, whereas response was modeled very well for this period for bifenthrin. In addition, this model is the only model to have a rainfall intensity (60 min max intensity) factor to represent the requirement for a longer duration significant rainfall to create transport from this surface. Cumulative rainfall, runoff, and days of irrigation were factors used to account for the longer time since the initial application to the surface. The house wall (Figure 8) had the second simplest model with, accounting for irrigation rainfall type, 10 min maximum flow rate, flow duration, and windspeed, which may be indicative of direct sprinkler spray against the house wall. Some early events were not captured by the modeling for some revised plots, but other replicated plots did have actual transport for those same missing periods of record for the surface, which were accurately modeled. Finally, the grass perimeter (Figure 9) was the only MARS model to focus on both cumulative irrigation and cumulative rainfall and irrigation as critical factors in the transport / percent washoff process, both primary components in enabling transport of the grass lawn near to the walls of the house lot (influenced by the additional water flow from the vertical surface). Plots 4, 5, and 6 were also selected as model factors, due to the greater peak percent washoff in October of 2011 compared to the other plots.

In order to show the response over time for the surfaces, the MARS model results were compiled on a daily basis subdivided into their primary components so that a visual inspection can show the dynamic changes modeled by the MARS modeling approach. These are shown for significant portions of the data for each surface. Due to the nature of the hinge functions of MARS models, dynamic changes can occur from one day to the next based on the dynamics of the input data. The dynamic charts for the MARS modeling are created by summing all values of the hinge functions by factor values (transformed) plus the intercept of the model. Each chart was created for each surface and plot. The individual variable values are shown by factor and intercept on a daily basis. Often variables were combined to subtract values from the intercept to calculate a percent washoff value for the day. This is common in statistical modeling; however, it may seem opposite to the reader. Examples are shown for the driveway (Figure 12 for plots 3 and 4) and garage door (Figure 13 for plots 3 and 4) for a section of the year transitioning from the application period 2—dry (irrigation) season October 4, 2011, through December 4, which was the start of the wet season had no lawn sprinkler irrigation events and was instead dominated by rainfall events. The second section of the year is the rainfall dominated (wet) season of the year from February 2 through April 2 of application period 4.

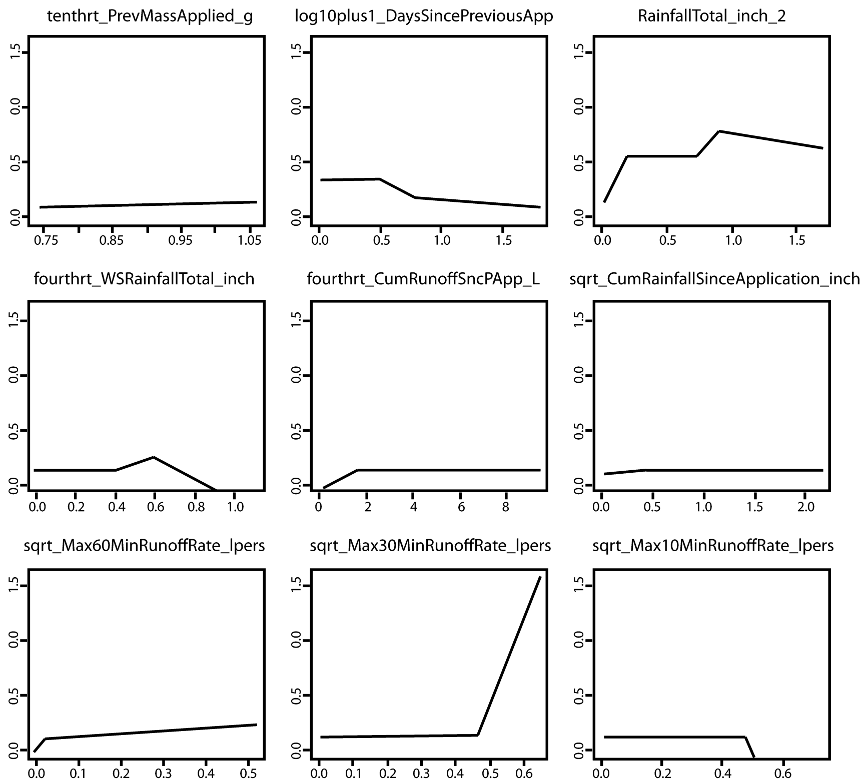


Figure 11. Structure of the Driveway MARS model hinge functions for each variable.

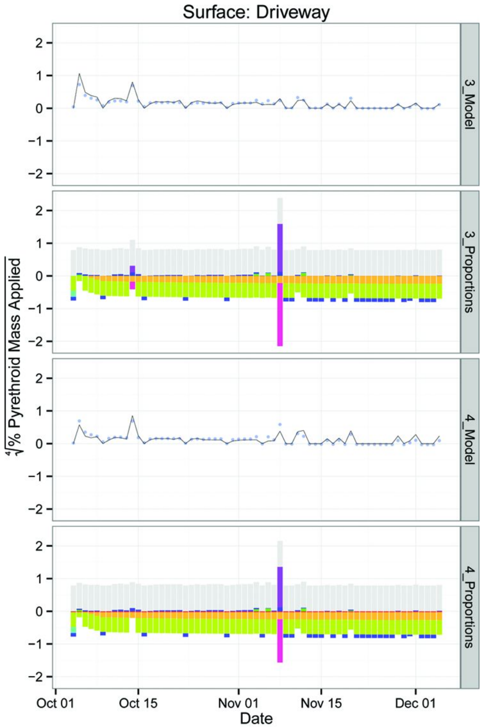
Table III. MARS Model critical factor variables by surface

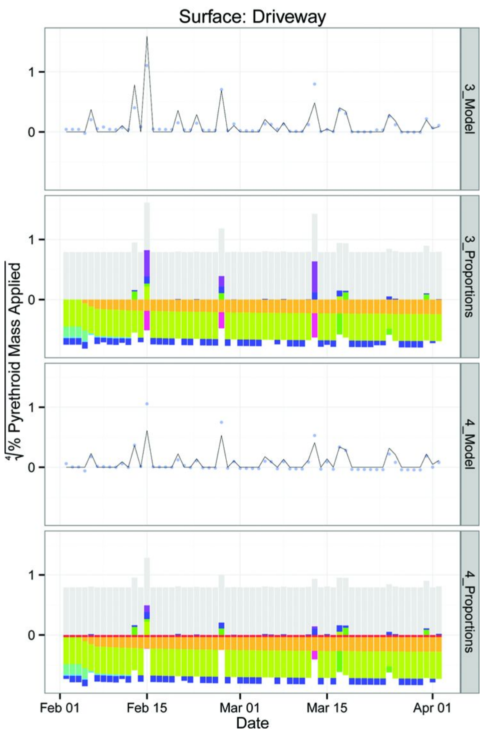
Driveway	*Garage Door*
CumRunoffSncPApp_L	ConcDataTypeSample
WS_RainfallTotal_inch	CumIrrigationSinceApplication_inch
DaysSincePreviousApp	CumRunoffSncPApp_L
RainfallTotal_inch	WS_RainfallTotal_inch
CumRainfallSinceApplication_inch	DaysSincePreviousApp
Max10MinRunoffRate_lpers	RainfallType
Max30MinRunoffRate_lpers	RainfallTotal_inch
Max60MinRunoffRate_lpers	CumRainfallSinceApplication_inch
PrevMassApplied_g	Max10MinRunoffRate_lpers
	Max20MinRunoffRate_lpers
	Max60MinRunoffRate_lpers
	MeanDailyWindSpeedDurPrecip_mpers
	TotalDurationPrecip_min
	TotalDurationRunoff_min
	PrevMassApplied_g
Grass Lawn	***House Wall***
AppTypeRevised	ConcDataTypeSample
DaysOfIrrigation	CumRunoffSncPApp_L
CumRunoffSncPApp_L	WS_RainfallTotal_inch
WS_RainfallTotal_inch	DaysSincePreviousApp
DaysSincePreviousApp	RainfallTotal_inch
Plot3	RainfallTypeLawn.Irrigation
CumRainfallSinceApplication_inch	CumRainfallSinceApplication_inch
CumRainIrrigationSinceApplication_inch	Max10MinRunoffRate_lpers
Max10MinRunoffRate_lpers	MeanDailyWindSpeedDurPrecip_mpers
Max30MinRunoffRate_lpers	TotalDurationRunoff_min
MeanDailyWindSpeedDurPrecip_mpers	PrevMassApplied_g
TotalDurationPrecip_min	
TotalDurationRunoff_min	

Continued on next page.

Table III. (Continued). MARS Model critical factor variables by surface

Grass Lawn	*House Wall*
Max60MinPrecipIntensity_inpermin	
PrevMassApplied_g	
Grass Perimeter	
ConcDataTypeSample	
CumIrrigationSinceApplication_inch	
DaysSincePreviousApp	
RainfallType	
Plot4	
Plot5	
Plot6	
RainfallTotal_inch	
CumRainIrrigationSinceApplica-tion_inch	
Max60MinRunoffRate_lpers	
Max30MinRunoffRate_lpers	
MeanDailyWindSpeedDurPre-cip_mpers	
TotalDurationRunoff_min	
PrevMassApplied_g	


Surface: Driveway
3_Model
3_Proportions
4_Model
4_Proportions
∜% Pyrethroid Mass Applied
Oct 01
Oct 15
Nov 01
Nov 15
Dec 01
Date


Surface: Driveway
3_Model
3_Proportions
4_Model
4_Proportions
∜% Pyrethroid Mass Applied
Feb 01
Feb 15
Mar 01
Mar 15
Apr 01
Date

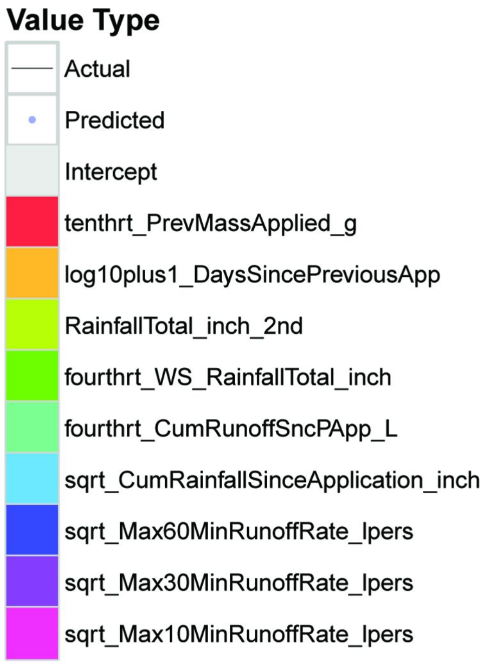
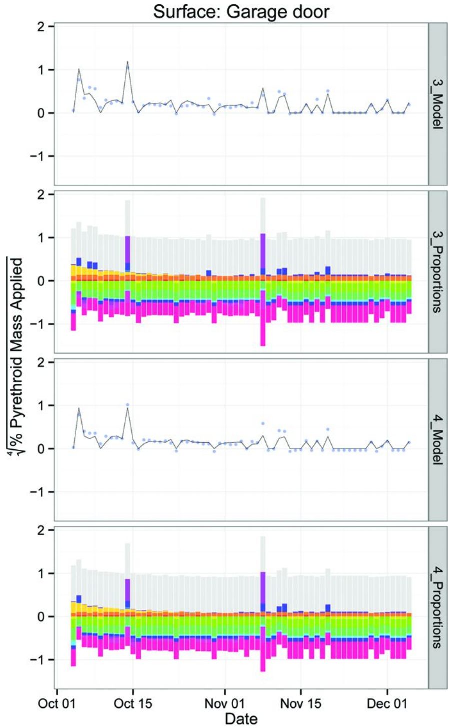


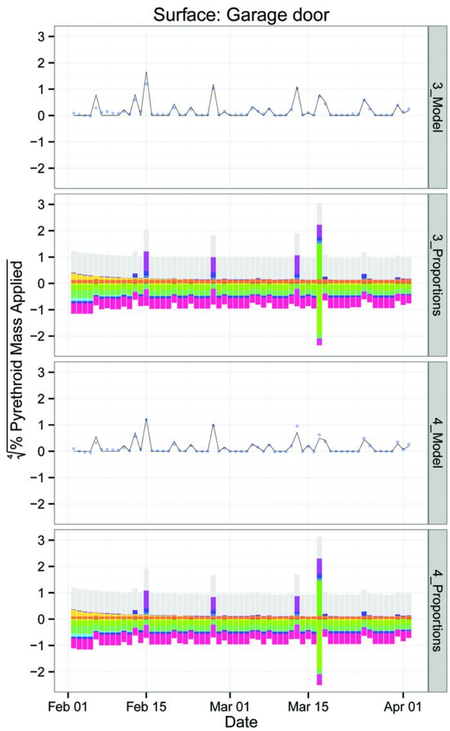
Figure 12. Dynamic assignment of values for calculating percent washoff from the MARS model for Driveway. (see color insert)

First, the intercept is the primary positive value in the model with the other factors adding or subtracting from this value. For the lawn sprinkler irrigation section of the study (application period 2), there is a suppression of the intercept value by event rainfall total (square transform) and a gradual increase in the value of days since previous application (log10plus1 transform). The first event (on October 5) was handled by a very small suppression of all factors showing the influence of the time since first application and the gradual decrease in mass occurring over time. A drop in rainfall on the 7th day of the non-irrigation day of the weekly application schedule is shown by an additional drop in percent washoff. The MARS model calculates a day with very low or no maximum 60-min runoff (square root transform) as a low level negative contribution. In Figure 12, these days are marked with a small blue contribution appearing every seven days, which drop the total percent washoff to the zero value it should be when irrigation is not occurring. This is the primary mechanism for ensuring no percent washoff occurring when there is no rainfall. As soon as significant rainfall occurs, the rainfall variable is suppressed and the maximum 60, 30, and 10 min flow rates (e.g., November 8) are used to calculate the percent washoff. As the site transitions into the dry portion of the year, this lack of rainfall becomes a critical factor in ensuring that the MARS model does not predict mass transport on non-rainfall days. The event occurring on November 7 differs significantly from other events (both very small rainfall events and random lawn sprinkler irrigation events) occurring later in the application period. This counterpoint between runoff rates is critical since the November 7 event still does not yield a significant amount of percent washoff. Two additional events followed November 11 and 12, 2011. The influence of rainfall total (square transform) is reduced to contribute to the percent washoff. Days since previous application (log10plus1 transform) is continuing in an increasing trend to reduce the percent washoff, and the 60 minute runoff rate (square root transform) contributes to the percent washoff, with the weather station rainfall also contributing to the washoff on November 12. Interestingly, the general difference in magnitude of washoff between plot 3 (historic larger application) and plot 4 (revised targeted, lower application) is handled by the model by using the previous mass applied as a general reducing factor, which is what a pesticide transport model would do with a difference in the mass applied.

When evaluating model performance for the driveway during application period 4 (wet) season (Figure 12b), multiple events occurred after application on February 2. In addition, random lawn sprinkler irrigation events were also completed during longer periods between events. The larger rainfall events (February 15, February 27, March 13, and March 17, 2014) showed similar responses as the larger events shown in Figure 12a for the end period of application 2 during the transition from irrigation to the wet season. The events of February 15, February 27, and March 13 include a mixture of 10, 30, and 60 min runoff rate (square root transform) based contributions to percent washoff with the event on March 17 having a different response but very accurate model results compared to actual for the historic plot. A bigger difference is shown with the revised plots where the complex flow interaction was suppressed but still occurring for the events on February 15 and March 13. The model results were overestimated for plot 4 (revised) in Figure 12b compared to the actual percent washoff; however, for both surfaces, the additional very small rainfall and random irrigation events were very accurately modeled using a combination of days since application (log10plus1 transform) and rainfall (squared transform) and max 60 min runoff rate (with previous mass applied, tenth root transform, for the revised plot).

For the garage door (Figure 13), the MARS model is far more complicated. In the first two weeks of the model after application, there are factors representing the impact of a recent application for both seasons. This decreasing trend is then mixed with characteristic event mechanics including maximum 10, 20, and 60 min flow rates (square root transform). Additional factors are used to map out the washoff response and differentiate between irrigation events and rainfall events and very light rainfall events (noted by rainfall type). These results are very similar across both seasons. The complexity of response for the garage door includes factors that are gradually increasing (cumulative irrigation since application, fourth root transform), that are gradually decreasing (days since application, log10plus1 transform), and that are included to model percent washoff based on certain conditions on a day (mean daily windspeed during precipitation). Results were similar for the other surfaces, exchanging other factors as discussed previously and shown in Table III.


Surface: Garage door
3_Model
3_Proportions
4_Model
4_Proportions
∜% Pyrethroid Mass Applied
Oct 01
Oct 15
Nov 01
Nov 15
Dec 01
Date


Surface: Garage door
3_Model
3_Proportions
4_Model
4_Proportions
∜% Pyrethroid Mass Applied
Feb 01
Feb 15
Mar 01
Mar 15
Apr 01
Date

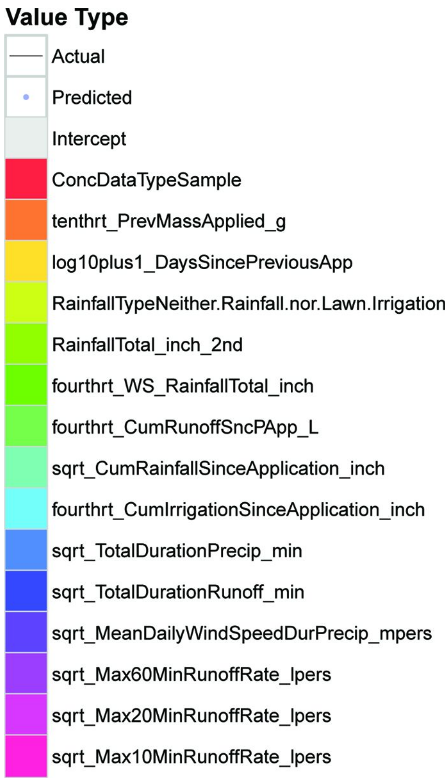


Figure 13. Dynamic assignment of values for calculating percent washoff from the MARS model for Garage door. (see color insert)

For the house wall and grass perimeter, results were similar to those of the driveway and garage door (not shown) – just with slightly different factors selected by the MARS model approach to map differences between environmental factors driving percent washoff. For the house wall, the post application period lasts about 14 days including the days since previous mass applied (log10plus1 transform) in a rapidly decreasing trend, the previous mass applied (tenth root transform), and the cumulative runoff and rainfall since application (fourth root and square root transforms, respectively). Rainfall-based percent washoff events are described by including the total duration of runoff (square root transform) as a primary driver, possibly due to the length of time that contributions from this edge of the plot surface take to reach the sampling system (a delayed reaction), and the rainfall total (squared transform). Lawn sprinkler rainfall events are distinguished by a lack of duration of runoff, a greater 10-min flow rate (square root transform), and the rainfall total (squared transform). The magnitude of the 10 min runoff and rainfall are then used to modulate the modeled percent washoff. Other variables are also included when certain conditions are met for this surface, including the rainfall type (lawn irrigation, categorical variable), the weather station rainfall (fourth root transform), and mean daily windspeed during precipitation (square root transform). The post application period for the grass perimeter showed general decreasing trends for approximately 30 days including days since previous application (log10plus1 transform) and rainfall total (squared transform). A general increasing negative trend existed for cumulative irrigation since application (fourth root transform). The only surface with this variable in it showing the exhausting of this surface over a number of applications, for both the dry irrigation season but also the wet rainfall season (where a few lawn sprinkler irrigation events occurred between larger rainfall events). Rainfall-based percent washoff events were describing using a combination of total duration of runoff (square root transform), maximum 30 and 60 min runoff rates (square root transform), and rainfall total (square transform).

Since the grass lawn is the only surface that has had a single application for the entire study period, it is useful to evaluate the model results (Figure 14 for the revised plot only for scale). The primary period after application is extended for the grass lawn from the beginning of August through the beginning of November based on days since previous application (log10plus1 transform), cumulative runoff since application (fourth root transform), maximum 10 and 30 min runoff rate (square root transform), mean daily windspeed during precipitation (square root transform), total duration of runoff (square root transform), and the maximum 60 min precipitation intensity (tenth root transform), among others. Rainfall events and lawn sprinkler irrigation events are complexly partitioned among the factors used by the MARS model for the grass lawn. In general, there is a long-term negative effect due to the days since previous application (log10plus1 transform) and the cumulative runoff since application (fourth root transform). Rainfall event-based percent washoff are still calculated based on differing contributions of runoff rates and weather station rainfall totals. For lawn sprinkler irrigation events, the maximum 60 min precipitation intensity (tenth root transform) is used to lower the model's calculated percent washoff in addition to differing runoff rates and days since previous application (log10plus1 transform). Minor other factors contribute such as the duration of runoff, cumulative rainfall and irrigation since application (square root transform), days of irrigation (untransformed), and mean daily windspeed during precipitation (square root transform).

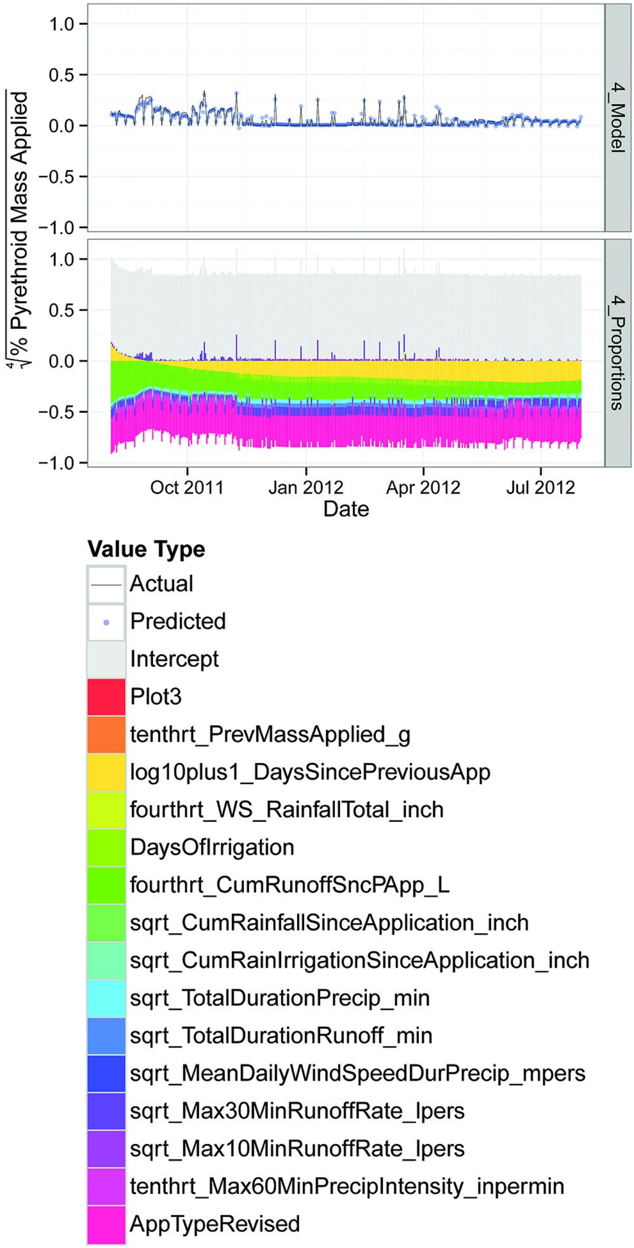


Figure 14. Dynamic assignment of values for calculating percent washoff from the MARS model for revised application lot 4 for the Grass lawn. (see color insert)

Discussion

The complexity that MARS modeling can capture bridges the gap between extremely sophisticated computational modeling of the environment and experimental field studies. This complexity leads to the identification of not only critical factors and interactions for a surface, but also unexpected responses in the experiment. Model results were representative of the actual values for all surfaces. The model results were not limited during prediction of the percent washoff for any surface, so that the results of the MARS modeling could be understood. Limiting the results would have improved the percent washoff estimates for all of the surfaces since, in some cases, the model predicted negative values (which could have been limited to 0). The MARS modeling approach has not been applied in this context (to the authors' knowledge), so it was critical to understand the full functionality of the approach in modeling a very complex set of pyrethroid application surfaces within the complex California urban environment, which includes both rainfall and significant lawn sprinkler irrigation events.

Statistical models are significantly different from numerical or computational models. Real-world complexity is difficult to describe in computational models and can be difficult to inject into most statistical models. The MARS modeling approach bridges this gap in that the computational overhead for the approach is not significant and that it brings insight into the results from a field study by representing both complex dynamics alongside macro trends. These insights can be used to further complete studies to characterize specific transport dynamics. Primarily, the approach identified well known critical factors, identified interesting interactions as possible characterizing variables (for example, the influence of different runoff flow rates), and, finally, identified some variables which may be ignored in modeling and field studies.

While we understand that runoff occurs uniquely per event, the simple characterization available from the MARS modeling approach allows for the understanding of some of these transport phenomena. For example, runoff rate and the time evolution of the process drive the capabilities of transport in radically different ways. Luo et al. (*11*) discussed the creation of a new mathematical model to describe the persistence and transferability of the pyrethroid washoff mechanism from concrete surfaces using a semi-mechanistic approach. This approach allowed both wet and dry periods to affect the washoff mechanism from concrete by using two modeled pools representing the washoff potential of the concrete and that transferred in runoff water. By using this process, Luo et al (*11*) accurately modeled both the immediate post application period and also longer-term periods up to 238 days for bifenthrin, in particular. It could be argued that this two-pool theoretical framework was represented for all of the surfaces modeled using the MARS modeling—with an immediate post application period and a dynamic event-based washoff process mixed with longer term trends. In addition, the incorporation of extra parameters for differing surfaces may be indicative of both the scale and complexity of the site and the complex interactions with rainfall and lawn sprinkler irrigation, the accumulation of dust during the dry season (which may provide another surface to transfer pyrethroid residue for transport), and other environmental factors. The mixture of both vertical and horizontal surfaces along with pervious and impervious surfaces, including the longer transport distances shown in Figure 2 (a and b), creates a very complex transport environment. The mixture of differing flow rates as critical factors in modeling washoff may be indicative of the energy required to not only wet all surfaces but also to entrain available particulates and wash out built up particulates from various crevices or micro pooling areas at the site.

It may be that the additional factors included in many of the models are indicative of critical factors that need to be included in the development of computational models or the design of field experiments. For example, the mean daily wind speed during precipitation appeared in all models except for the driveway. While wind speed may be included in models as part of the evapotranspiration process, the wind speed here may be indicative of the physical washing action of rainfall hitting these surfaces. It may also be indicative of a certain type of rainfall event (or lack thereof, for lawn sprinkler irrigation). The site serves as a sort of wind block so that, when wind speeds become significant, rainfall can be pushed into the vertical surfaces at the site in addition to accumulating near the grass perimeter and the along the garage door. The influence of the wind on washoff of vertical surfaces and perimeters around vertical surfaces may be something significant to consider in further experimentation. Finally, many of the critical factors included in this work require that data at resolutions of less than an hour (including many 10 min variables throughout the surface models). The processes occurring to transport pyrethroid residues offsite from target application areas are incredibly complex and best represented by sub hourly resolution data, and computational approaches occurring at the daily scale or coarser may be biased when estimating pyrethroid washoff.

Conclusion

Data from a complex urban environmental study site were mined for over 30 variables to identify critical factors influencing the off-target washoff of pyrethroids from 5 surfaces. These data were transformed for normality using an automated process. They were then used to construct Multivariate Adaptive Regression Spline (MARS) models to calculate the percent washoff from various surfaces under both historic and revised application scenarios. This approach yielded accurate models for all surfaces, with the driveway surface having the most simple model of percent washoff. From partitioning the dynamic responses (hinge function values) of these models, complex behavior was extracted. Results indicated that a post-application period of approximately 14 days for the all surfaces except the grass lawn represented an initial washoff condition, while transport for the rest of time between application events was modulated by some of these initial variables, but also additional dynamic variables representing rainfall events and different characteristics of flow. Other variables that may be critical for certain washoff events were also included by the MARS models for a number of surfaces. In addition, the MARS modeling approach identified non-replicated differences in some plot response for a few surfaces which will be investigated in further work.

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Chapter 4

Review of Modeling Approaches for Pesticide Washoff from Impervious Surfaces

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Pesticide uses on impervious surfaces and subsequent offsite transport significantly contribute to pesticide detection and aquatic toxicity in urban watersheds. This review evaluates the various methods that currently exist to model pesticide washoff from impervious surfaces. Empirical equations successfully describe pesticide washoff by calibration to a single rainfall event, but lack consistent parameterization with varying set time and repeated rainfall. Partitioning coefficients determined from experimental data could significantly improve PRZM capability in predicting pesticide washoff from impervious surfaces. Highlighted in this review is a new semi-mechanistic approach which incorporates the time-dependence of washoff potential during the dry period after application and washoff dynamics during a runoff event. This review aims to provide information to guide model selection and model development for pesticide registration, regulation, and mitigation for urban pesticide uses.

Introduction

Pesticide transport in urban watersheds is a function of stormwater hydrology, various processes that control transport in watercourses, and the dynamics of pesticide release and washoff from treated surfaces. While stormwater modeling and pesticide transport in runoff have been extensively investigated, relatively few studies have evaluated pesticide washoff from urban landscapes, especially from impervious surfaces. Impervious surfaces are primary sources of overland flow generation in the urban environment. Impervious surfaces are often directly treated with pesticides in structural pest control applications, paved area applications, and incidental overspray or drift (*1*, *2*). Previous studies suggest that impervious surfaces are the dominant contributors to pesticide movement off-site in urban areas (*3–5*). Compared to other surfaces such as turf and bare soils, limited knowledge is available on the dynamics of pesticide buildup and washoff on impervious surfaces. The California Department of Pesticide Regulation (CDPR) recently adopted new regulations to protect water quality in urban areas by restricting pyrethroid application amounts and certain contact areas (*6*). Thus, there is an emerging research need for improved washoff modeling capabilities to evaluate the effectiveness of the regulations and extrapolate the effect of mitigation practices to different conditions.

The physical processes and modeling approaches of urban pollutant washoff and runoff have been reviewed in previous studies (*7–13*). Most of the reviews focus on pesticide transport in overland flow, concentrated flow and/or pipe flow over urban landscapes. This chapter reviews existing modeling approaches for simulating pesticide washoff from impervious surfaces, and introduces a semi-mechanistic model developed based on washoff experiments data. The models discussed here are classified as empirical or mechanistic (or semi-mechanistic) approaches. The empirical models are based on statistical analysis and data fitting and do not explicitly simulate mass transfer from pesticide-treated surfaces to the overlying water layer. These models use regression equations to mimic the observed washoff loading curves as function of time or runoff volume. The mechanistic models formulate pesticide mass fluxes based on the concentration gradients across the boundary layer of treated surface and runoff water. These models also explicitly describe the dynamics of water runoff and degradation on pesticide washoff loss.

Characterization of Pesticide Washoff

Most studies investigating pesticide washoff from impervious surfaces are small-scale experiments, such as those on concrete cubes and slabs, with pesticide spikes and simulated or natural rainfall (*3*, *4*, *14–17*). Runoff water samples are analyzed for pesticides (active ingredients and/or degradates) to estimate mass flux and persistence for off-site transport. The amount of pesticide available to runoff extraction is defined as "washoff potential", M_P (kg/m^2, or user-defined unit of mass/area), at a given time after application referred to as "set time" or "incubation period" (Figure 1a). In addition to degradation, the decrease in washoff potential over time may be associated with transport to inaccessible domains of the concrete matrix, called irreversible adsorption (*14*). Washoff potential is unlikely to be directly measured; instead, it is operationally indicated by "washoff load", i.e., cumulative mass of pesticide released to water over the duration of a rainfall event, M_W (mass/area). Washoff load is determined by experiments with flowing water (runoff induced by natural or artificial rainfall) or static water (immersion for a given equilibration period). Washoff load can be measured at given time intervals during a washoff event, $M_W(t)$, or only at the end of the event as "total washoff load". For the former case, washoff load is usually plotted with cumulative time or runoff, referred as a "washoff profile" (*3*) or "load characteristic curve" (*18*) for a pesticide in a given experimental configuration (Figure 1b). Two time systems are presented in Figure 1: t_d accounts for the duration of the dry period since the last pesticide application, and t describes the washing time.

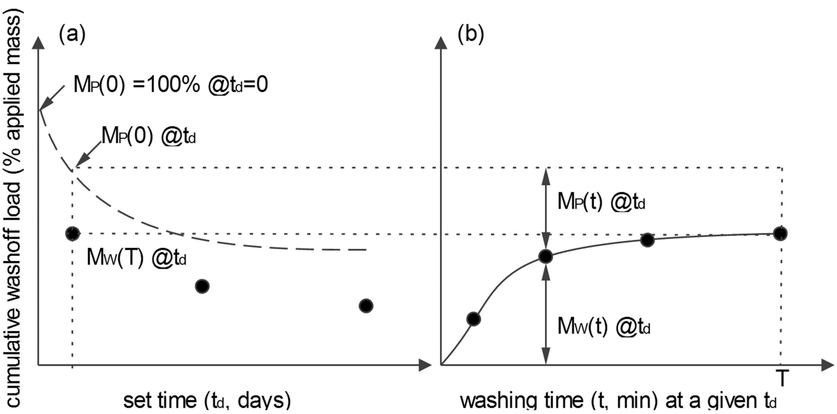


Figure 1. (a) Washoff potential, $M_P(0)$ (dashed line) and total washoff load, $M_W(T)$ (dots) are presented at a given set time t_d. (b) Cumulative washoff loads, $M_W(t)$ (dots) and washoff profile (solid line) measured during washing time t (t=0~T). Note: Dotted lines included to connect $M_P(0)$ and $M_W(T)$ in the two panels.

Published washoff experiments for pesticides from impervious surfaces have been reviewed previously (*19*, *20*). According to measure washoff loads, $M_W(T)$, usually only a small portion of applied mass could be detected in the runoff, even with a short set time, suggesting a rapid initial dissipation. With a longer set time, however, extended "tailing" or slow release from concrete surfaces was also typically observed. This behavior suggests the potential for further transport to non-target areas (Figure 1a). The surfactant components of some formulated pesticide products are influential in washoff from concrete surfaces. The effects of chemical properties (such as soil partitioning coefficient and soil metabolism half-lives) and environmental settings (including rainfall intensity and surface conditions of concrete and other media such as asphalt, vinyl siding, stucco, wood siding, etc.) were inconsistent. Pesticide washoff profiles generally follow a convex, advanced-type curve (Figure 1b), and thus can be characterized by a steep initial washoff rate followed by a steadier rate.

In summary, pesticide buildup and washoff, as demonstrated in Figure 1(a) and 1(b), respectively, should be considered in model development for simulating pesticide washoff loads from impervious surfaces. The term of "buildup" is taken from early studies of urban non-point source loads of suspended solids, heavy metals, chlorides, nutrients, and hydrocarbons. In those studies, buildup is considered as a natural accumulation of pollutant available for washoff. More recent modeling studies typically included model implementation for degradation and application of chemicals in buildup simulation.

Empirical Equations for Washoff Profiles

The most popular modeling approaches for predicting pesticide washoff from impervious surfaces are based on empirical equations, including exponential functions or power-law functions of runoff volume. Since the empirical equations are applied to each individual rainfall event with a given set time (t_d), the associated washoff potential and washoff load are only dependent on the washing time (t). Therefore, t_d does not appear in the following equations.

The exponential function follows from the assumption that the rate of pollutant washoff is proportional to the washoff potential during a rainfall event (*18*),

$$\frac{dM_P(t)}{dt} = -k_1 \cdot r \cdot M_P(t) \tag{1}$$

$$\begin{aligned} M_P(t) &= M_P(0)\exp(-k_1 \cdot r \cdot t) = M_P(0)\exp(-k_1 R)] \\ M_W(t) &= M_P(0) - M_P(t) = M_P(0)[1-\exp(-k_1 R)] \end{aligned} \tag{2}$$

where k1 = the washoff coefficient (mm^{-1}), r = the runoff rate (mm/hr), and R = the cumulative runoff depth (R = r*t, mm).

Eq. (2) is the integrated form of Eq.(1), where a constant runoff rate is assumed. A similar exponential relationship is obtained for time-dependent rates. The exponential function for washoff prediction has been used in the hydrological simulation program – FORTRAN (HSPF) (*21*), early versions of the storm water management model (SWMM) (*22*), the storage, treatment, overflow, runoff model (STORM) (*23*), and site-specific modeling studies (*24–27*). The washoff coefficient k_1 is related to pollutant characteristics and the shear stress at the flume bottom (*28*, *29*). The coefficient value determines the shape of washoff profile predicted by the exponential function (Figure 2). In the early version of SWMM, for example, the default k_1 value was set as 0.18 mm^{-1} (*18*), indicating 90% washoff under 12.7 mm (or 0.5 inch) runoff, i.e., 1-exp(-0.18*12.7)=0.9.

The exponential function in Eq. (1) implies the independence of predicted pollutant concentration on the runoff rate,

$$C(t) = -\frac{dM_P(t)}{A \cdot r \cdot dt} = \frac{k_1}{A} M_P(t) \tag{3}$$

where A = the area of study surface, and A*r*dt is the total runoff volume in the corresponding units.

The result is referred to as an event-mean-concentration (EMC). EMCs are widely used in watershed-scale transport modeling, especially for total maximum daily load (TMDL) projects. Concentrations in urban runoff may vary with runoff rate, as observed in previous studies (*12*, *30*). The standard adjustment to overcome this limitation is to introduce a power (n, dimensionless) of runoff intensity to Eq. (1),

$$\frac{dM_P(t)}{dt} = (k_2 \cdot r^n)M_P(t) \tag{4}$$

with k_2 as a new washoff coefficient which has different units and values than k_1 in Eq. (1). In this case, the resultant concentration will also be proportional to $r^{(n-1)}$, so the concentration may increase or decrease with runoff rate according to the value of n.

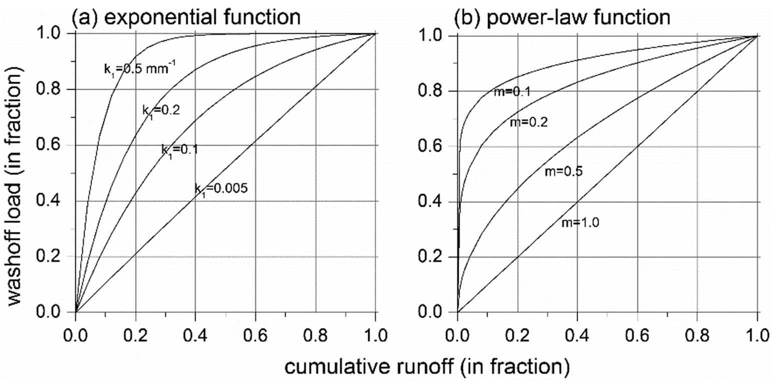


Figure 2. Demonstration of washoff profiles based on (a) exponential function, Eq. (2); and (b) power-law function, Eq. (6) with k_4=1.

The mechanism of the power-law model is associated with the simulation of a diffusion process for a planar system. The early portion of the washoff profile could be formulated as,

$$M_W(t) = (k_3 \cdot t^m)M_P(0) \tag{5}$$

where k_3 and m are the linear and exponent characteristics of the diffusion process, respectively (Figure 2). A value of m=0.5 suggests a diffusion process that follows Fick's laws. With m<1, the power-law function generates convex, advanced-type washoff profiles consistent with those observed for pesticide washoff from concrete surfaces (Figure 1). With m close to 0, the profile suggests rapid initial washoff followed by a more steady state, or "type A" profile (*3*), while large m values indicate "type B" profile with relative steady washoff rate over the duration of the experiment. Again the simple relationship of R=r*t can be introduced to Eq. (6) for the prediction of pollutant washoff by runoff depth,

$$M_W(t) = (k_3 \cdot r^{-m}R^m)M_P(0) = (k_4R^m)M_P(0) \tag{6}$$

Eq. (6) has been widely used in the urban pollutant runoff models such as SWMM and more recent modeling studies (*31*, *32*). Similar functions have also been successfully used to predict in-stream pollutant loadings, including pesticides at watershed scale (*33*, *34*). Model efforts were applied to estimate the exponents (m) from commonly available properties. In HardSPEC, a first-tier model for estimating aquatic exposure resulting from herbicides applied to hard surface developed by the UK Pesticide Safety Directorate (*35*), for example, the exponents in power-law function are formulated as functions of pesticide solubility (for soluble mass) or specific gravity (non-soluble mass).

Transport Modeling with Impervious Scenarios

In addition to empirical equations, physically-based modeling approaches have also been used to predict pesticide washoff over impervious surfaces. Model equations were originally developed based on transport mechanisms in soils. For example, USEPA developed Tier 2 modeling scenarios for its regulatory model PRZM (Pesticide Root-Zone Model) for applications on impervious surfaces (*36*). PRZM assumes instantaneous chemical equilibrium between water, air, and soil/concrete matrix during a rainfall event. When applied to impervious surfaces, PRZM transport equation can be simplified,

$$\frac{\partial}{\partial t}[C_w(\theta + K_d\rho_s + \alpha K_H)] = -C_w[K_s(\theta + K_P\rho_s) + \frac{Q}{A_w \cdot z} + \frac{X_e K_d}{A_w \cdot z}] \qquad (7)$$

where z = the interaction depth of the impervious surface layer containing pesticide potentially available to water extraction and all the following variables are defined within this depth; Cw = the dissolved concentration (g/cm^3); θ = the volumetric water in the soil (dimensionless); α = the volumetric air contents in the soil (dimensionless); ρ_s = the bulk density (g/cm^3); K_H = the dimensionless Henry's constant; K_P = the lumped, first-order decay constant (d^{-1}) for the solid phase; K_d = the lumped, first-order decay constant (d^{-1}) for the dissolved phases; Q = the total runoff volume (cm^3/day); A_w = the drainage area (cm^2); X_e = the erosion loss (g/day).

In addition to the processes presented in Eq. (7), PRZM also simulates dispersion and diffusion in dissolved and vapor phases as well as degradation in the vapor phase. The washoff flux was adjusted according to the availability of chemical residues in the dissolved phase for runoff extraction, which is assumed to be decreasing with the interaction depth z. Soil-related properties (soil adsorption coefficient, soil aerobic metabolism half-life, and soil photolysis half-life) are applied to a hypothetical impervious surface characterized by high curve number (CN2=98), small incorporation depth (0.1 cm) and zero partitioning coefficient to concrete (K_d=0).

The PRZM-based modeling approach for impervious surfaces can be further improved by introducing an effective pesticide partition coefficient for impervious surfaces (K_d*) to replace the soil K_d in Eq. (7). Values of K_d* can be directly incorporated in PRZM simulations. For other models, K_d* can be expressed as the product of K_{OC} (soil partitioning coefficient normalized by organic carbon, OC, content) and a "surface coefficient" representing the OC content equivalent for each impervious surface. This was also accepted by the HardSPEC model with a "surface coefficient" of 0.02% for concrete and 1% for asphalt based on herbicide washoff experiments (*35*).

For demonstrating the model capability, PRZM with USEPA impervious modeling scenario was tested for nine pesticides commonly used in urban areas (Table 1). Washoff measurements were taken from CDPR-supported experiments under controlled rainfall of approximately 25mm/hr for 1 hour (*3*, *4*, *16*, *20*). Pesticide washoff loads were measured from pre-washed concrete surfaces at various set times. The following three simulation settings were involved in the test, [1] K_d=0 as suggested by USEPA, [2] reported K_d values from soil adsorption studies, and [3] K_d calibrated to the measured washoff loads at 1 day after application (DAA), and applied to data with a longer set time. Input parameters were mainly retrieved from registration data (*37*) (Table 1). Pesticide degradation on the impervious surfaces during dry periods was simulated with soil photolysis half-life (SPHOT) (*38*). It's worthy to note that K_d and other physiochemical properties are retrieved for the active ingredients, while K_d* were determined for the pesticide products with formulations specified in the experimental documentations. Even with the same active ingredient, pesticide products with different formations could be associated with different K_d* values. As expected, the simulations with K_d=0 significantly overestimated the measured data of all tested pesticides. Predicted mass losses were up to 46% of applied mass, while the measured data ranged from 0.006% to 20.8%. By using reported K_d values in soils, PRZM generally underestimated washoff loadings measured at 1DAA (Figure 3a), except for two chemicals with relatively high mobility (imidacloprid and malathion, K_d<2 mL/g for both). With a longer set time, conservative estimates were obtained for some pesticides, mainly due to their persistence as indicated by large SPHOT values used in PRZM for representing terrestrial dissipation.

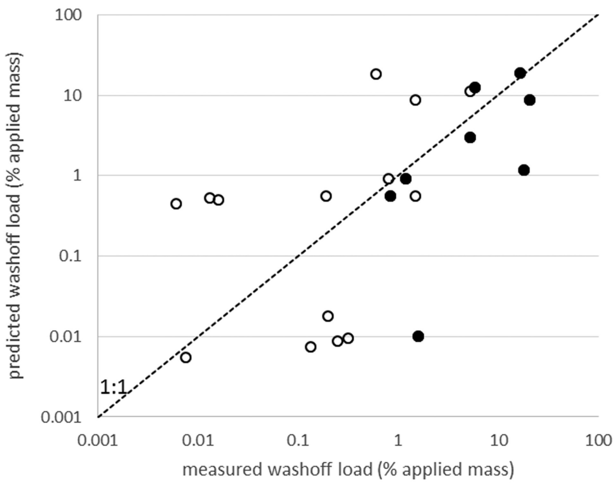
Simulation results with calibrated K_d values (Figure 3a) were between those with K_d=0 and reported soil K_d: predictions overestimated observations at >1DAA within 1 magnitude for most of the tested pesticides. Except for imidacloprid and malathion, which are associated with relatively high mobility, calibrated K_d* values (Table 1) were smaller than the corresponding soil K_d. This finding was consistent with previous studies for pyrethroids (*38*, *41*, *42*). This suggests that adjustments are required before using a K_d value measured in soil adsorption studies to transport modeling on impervious surfaces. Based on the data in Table 1, the ratio of K_d/K_d* showed an increasing trend with the corresponding K_d value ($p<0.001$).

Table 1. Tested pesticide products with PRZM inputs

Pesticide	*MW*	*HENRY*	*VP*	*SOL*	*SPHOT*	K_d	K_d*
Bifenthrin	422.9	7.2E-3	1.4E-7	0.001	104	3925	20
Beta-cyfluthrin	434.3	5.3E-7	1.6E-8	0.0012	5.6	23	0.8
Carbaryl	201.2	2.7E-9	1.2E-6	11.3	3421	3.2	0.9
Esfenvalerate	419.9	6.3E-7	1.5E-9	0.001	1391	38.8	30
Fipronil	437.2	8.5E-11	2.8E-9	1.9	34	10.7	5
Imidacloprid	255.7	6.5E-11	1.0E-7	514	39	1.9	5
Lambda-cyhalothrin	449.8	1.8E-7	1.6E-9	0.01	274	1960	15
Malathion	330.4	1.2E-8	3.4E-6	125	118	1.0	1.3
Permethrin	391.3	7.5E-8	4.5E-8	0.07	289	63.3	40

Parameters: MW = molecular weight (g/mol). HENRY = Henry's law constant (Pa m^3/mol). VP = vapor pressure (mPa). SOL = water solubility (ppm). SPHOT = soil photolysis half-life (day). K_d = soil partitioning coefficient (mL/g). K_d* = calibrated partitioning coefficient on impervious surfaces (mL/g). Notes: Chemical properties are mainly taken from CDPR Pesticide Chemistry Database (*37*). For data not reported in the CDPR database, other data sources are used: SOL of bifenthrin, beta-cyfluthrin, and esfenvalerate from the IUPAC FOOTPRINT pesticide properties database (*39*), and SPHOT of beta-cyfluthrin from a USEPA publication (*40*).

(a)



(b)

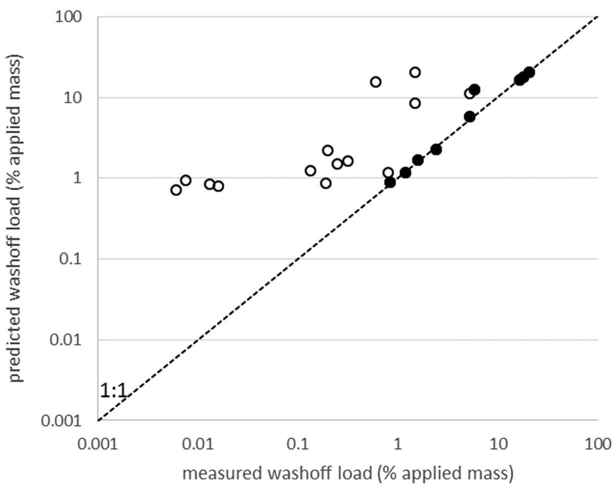


Figure 3. PRZM-predicted pesticide washoff loads from impervious surfaces relative to measurements (3, 4, 16, 20), (a) with repeated soil K_d (partitioning coefficient), and (b) with K_d calibrated to measurements at 1DAA (days after application). Open circles for data at 1DAA (days after application) and closed circles for those >1DAA.

A Semi-Mechanistic Model Based on Experimental Data

Implication and Research Gap Based on Model/Data Review

The review and investigation of existing modeling approaches and experimental data suggest that the basic concepts of fate and transport processes and their modeling implementations, such as chemical dissipation half-lives and mass transfer coefficients (MTC's) (as a function of portioning coefficient and boundary layer depth), are also mathematically applicable for predicting pesticide washoff from impervious surfaces. However, adjustments are required to better predict measured washoff data. First, pesticide washoff from impervious surfaces cannot be simulated with the commonly reported chemical properties for pesticides such as soil partitioning coefficient and soil metabolism half-lives. New parameters should be defined and determined from measured data. The effective partitioning coefficient value of a pesticide on concrete could be significantly lower than that in soils (Table 1). Secondly, the effective dissipation rate of washoff potential shows a decreasing trend with set time. As mentioned previously, the loss of washoff potential during the dry period after application is attributed to pesticide degradation and irreversible adsorption to concrete matrix. This is further confirmed by fitting the total washoff losses into a pseudo-first-order kinetics (*15*, *20*), and suggests that the transferability of a pesticide from impervious surfaces to runoff water after application is initially high, but decreases quickly over time. Systematical simulations for the time-dependence of the effective dissipation rate constant are not available in modeling approaches by empirical equations or by PRZM.

Finally, the effective MTC also changes during a rainfall event. Using the power-law function as an example, most experiments reported a non-Fickian washoff profile ($m \neq 0.5$) (*20*), indicating a varying MTC with washing time. The major challenge in applying empirical equations is that the calibrated model parameters (k_1 in Eq. (2) and m in Eq. (6)) vary with set time to reproduce measured data. Washoff profiles must be described as bi-phasic or multi-phasic processes (*14*, *16*, *26*, *27*, *43*). For example, Thuyet et al. (*16*) applied power-law functions to fit washoff profiles of imidacloprid from concrete surfaces, and the results indicated that the regression coefficients must be calibrated separately for each of the washoff profiles with various set times. Similarly, power-law exponents (m values) were estimated for measured washoff data of commonly used insecticides from 21 controlled rainfall events with R_2 ranging from 0.86 to 1.00 (*20*). Small m values were observed with a short set time for all tested pesticides. There was a general trend toward increasing m values with increasing set time and with repeated rainfall.

In summary, new model development will address the above implications and research gaps in predicting pesticide washoff from impervious surfaces. This can be realized by formulating new parameters for pesticide dissipation rate constant, mass transfer coefficient, and their time dependence.

Model Equations and Evaluation

A semi-mechanistic model was developed for pesticide washoff from impervious surfaces by describing washoff potential dynamics during dry periods and washoff profiles during rainfall events. Detailed information on model development and applications were documented in the previous publications (*19*, *20*). This review highlights the key equations and features in the model.

Pesticide washoff potential as a function of set time was simulated by pseudo-first-order kinetics with a time-varying parameter, $K_P(t_d)$ (d^{-1}), as the effective rate constant of the overall loss of pesticide washoff potential. Analysis of experimental data suggested that K_P is associated with the washoff potential for each rainfall event. A linear relationship between K_P and the washoff potential was assumed,

$$K_P(t_d) = K_P(0) \cdot M_P(0)|_{t_d} \tag{8}$$

where $K_P(0)$ is the initial rate constant immediately after pesticide application. Eq. (8) demonstrates that the rate of decline of washoff potential decreases over time, which was consistent with the results from the experimental data analysis.

Washoff profiles were simulated using an equation similar to Fick's second law, with the effective mass MTC varying with time, $D^*(t)$ (s^{-1}). At a given set time t_d, the washoff load as a fraction of the washoff potential (F) was estimated as,

$$F|_{t_d} = \frac{M_W(t)}{M_P(0)} = 1 - \frac{M_P(t)}{M_P(0)} = \begin{cases} \sqrt{\dfrac{4\tau}{\pi}}, & F \le 0.52 \\ 1 - \dfrac{8}{\pi^2}\exp\left(-\dfrac{\pi^2\tau}{4}\right), & F > 0.52 \end{cases} \tag{9}$$

where τ is a characteristic dimensionless time,

$$\tau = \int_0^t [D^*(t)]dt \tag{10}$$

According to the analysis of washoff profiles, the early portion of the washoff profiles followed a power-law function and the following equation was assumed for the dynamics of D*,

$$D^*(t) = D^*(0) \cdot t^n \tag{11}$$

$$\text{where } n = -2s \cdot M_P(0)\,|_{t_d}$$

where s is a slope factor representing the assumed relationship between the exponent n and the washoff potential. The power-law function in Eq. (11) provided a simple mathematical form to describe the dynamics of pesticide release from concrete, which have previously been described as bi-phasic or multi-phasic processes (*14*, *16*, *26*, *27*, *43*). Eq. (11) was applied to pyrethroids, suggesting a decreasing trend of the effective mass transfer coefficient during the rainfall event ($n<0$). For relatively soluble chemicals (carbaryl, imidacloprid, fipronil, and malathion), n was expressed as $1 - 2s \cdot M_P(t_d,0)$ with a value between -1 and 1. Positive n values indicate that D* increases within a washoff test, as observed in the data analysis on measured washoff profiles with $m>0.5$ (Figure 2b).

The semi-mechanistic model has been applied to a large set of experimental data with nine insecticides commonly used in urban environment (Table 1). One set of model parameters $D^*(0)$, $K(0)$, and s was assigned to each pesticide product for all experiments with that product. Model parameters were calibrated based on experimental data from the first rainfall events, and validated with data with a longer set time. Calibrated models and their performance in predicting pesticide washoff from impervious surfaces were documented in the previous studies (*19*, *20*). Modeling results for selected pesticides are demonstrated in Figure 4. In summary, with appropriate calibration the model was capable to capture the dynamics in washoff profiles from concrete surfaces for insecticides with wide ranges of chemical properties (Table 1) and set time (1.5 hours to 238 days). For overall model performance, resultant relative RMSE (root mean square error) values were less than 10%, and NSE (Nash-Sutcliffe efficiency) coefficients were larger than 0.98 for tested pesticides.

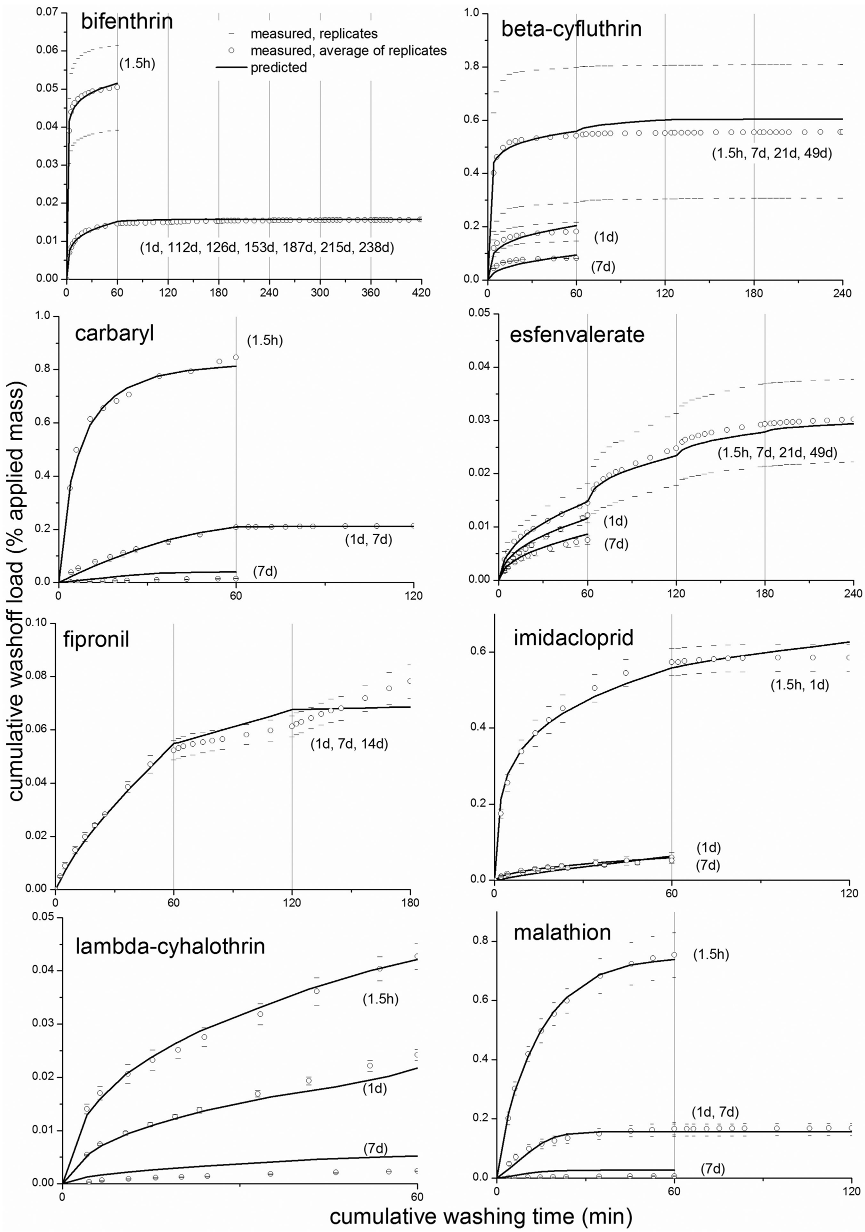


Figure 4. Predicted and observed cumulative washoff loads of selected pesticides. Shown in parentheses are set times (multiple set times indicate related rainfall events). Adapted with permission from reference (20). Copyright 2014 ACS Publications.

Summary and Suggestions

This chapter reviewed modeling approaches for predicting pesticide washoff from impervious surfaces, including empirical equations (SWMM as a representative model), a chemical transport model (PRZM), and a semi-mechanistic model. Washoff module in SWMM is based on regression coefficients which are supposed to be parameterized for each individual rainfall events, but do not have direct physical meanings. PRZM and the semi-mechanistic model are designed for more consistent simulations for each pesticide by introducing physically-based processes in washoff simulation. SWMM and the semi-mechanistic model provide sub-daily simulation, while PRZM only reports daily (or event total) results. Since the majority of washoff losses are observed during the early stage of a rainfall event, PRZM parameters calibrated to total washoff loads actually reflect the initial washoff mass flux. Both the empirical equations and the semi-mechanistic model are designed to simulate total (dissolved and adsorbed) pesticide runoff, by incorporating the contribution of particle-bound washoff into the calibrated parameters. PRZM with USEPA impervious modeling scenario only simulates dissolved pesticide. However, the effective K_d value (K_d* in Table 1) were usually calibrated with measured data of total concentrations, so that the predictions would be consistent in terms of total washoff mass.

Both SWMM and PRZM require runoff data supplied by other models, such as the kinematic wave approach for SWMM and SCS curve number method for PRZM. Systematic evaluations on the effects of rainfall intensity and runoff rate on pesticide washoff loads are not available. Increased rainfall intensity may have complicated effects on pesticide washoff loads. However, most of the existing models only simulate one of those effects, i.e., higher runoff rates, and would always predict increased washoff loads under higher rainfall intensity. This is not consistent with recent washoff experiments on insecticides where a significant relationship between rainfall intensity and washoff loads were confirmed (*3*, *4*). Therefore, an urban scenario for the semi-mechanistic model is suggested to be developed for regulation evaluation according to the local conditions such as representative weather conditions (intensity, duration and frequency of rainfall) and impervious surface properties (*19*, *20*). The scenarios could also serve as guidelines for the washoff experiments and model calibrations to determine the required model input parameters.

SWMM was initially designed for urban pollutants other than pesticides. Applications to urban pesticide evaluation require secondary development, such as the additional module to handle episodic chemical applications. Improved SWMM was applied to California urban community in Orange County, and satisfactorily simulated in-stream pyrethroid concentrations as daily and max 6-hr means (*44*). PRZM with an impervious modeling scenario has been used by USEPA and others in the risk assessment of urban pesticide uses on endangered species (*38*, *45*, *46*). By incorporating with EXAMS, the model conservatively estimated pesticide concentrations in urban streams. Determination of effective partitioning coefficients for pesticides on impervious surfaces is suggested for future studies. The semi-mechanistic model has been shown to reproduce pesticide washoff profiles for a range of set times and for repeated runoff events with a single calibration (*19*, *20*). The model is being incorporated into hydrological simulators of overland flow for pesticide risk assessments at urban community scale. For example, researchers from the Stone Environmental, Inc., have coupled the model into SWMM. More details of their development and applications are provided in other chapters of this book (*47*). In addition, integration with overland flow simulation by kinematic wave equations was also proposed for the development of a spatially high-resolution modeling system for evaluating urban pesticide regulation and mitigation efforts (*48*).

Acknowledgments

The author would like to acknowledge scientists of California Department of Pesticide Regulation for their valuable discussion and comments, and the book editors and two anonymous reviewers for critical reviews. The author would like to sincerely thank Dr. Thomas Young, Dr. Brant Jorgenson, and Dr. Dang Quoc Thuyet (University of California, Davis), and Dr. Jay Gan and Dr. Tim Jiang (University of California, Riverside) who provide experimental data for pesticide washoff from concrete surfaces.

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Chapter 5

A Modeling Approach for Predicting Pyrethroid Residues in Urban Water Bodies for Use in Environmental Risk Assessments

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An urban residential pesticide exposure modeling approach using the Storm Water Management Model (SWMM) has been developed and validated in a high density residential watershed in southern California. The approach incorporates pyrethroid wash-off characteristics from pervious and impervious surfaces, neighborhood characteristics, and local pyrethroid application practices. This modeling approach was extended to the Southeast, South Central, Northwest, North Central, Northeast, and Mid-Atlantic US through parameterization of local use practices, along with local weather and irrigation characteristics. Application of the SWMM modeling approach to a broader population of regional conditions has provided aquatic exposure estimates important for developing a comprehensive higher tier ecological risk assessment for pyrethroids at the national scale.

Introduction

The use of pyrethroid insecticides in urban residential environments has become more common for the control of outdoor pests as the use of pesticides based on older chemistry (e.g. the organophosphates) has declined. The use of pyrethroids in outdoor residential applications is regulated through product labels developed by the product registrants and the US Environmental Protection Agency (US EPA) or California Department of Pesticide Regulation (CDPR). A recent comprehensive review of pyrethroid labels showed that residential applications can occur on a variety of outdoor use sites, from foundation perimeter treatments, and hard surface applications, to lawn and ornamental applications (*1*). These types of use sites occur throughout a typical residential neighborhood and can vary in terms of their hydrologic interaction with each other and the urban stormwater systems designed to swiftly transport runoff from residential areas. Clearly, pyrethroid uses in an urban residential environment are more complex than for pyrethroids applied to a homogeneous agricultural field. The current standard model scenarios for predicting pesticide aquatic exposure for these less complicated agricultural uses are not adequate for exposure predictions in urban residential environments. Therefore, in order to predict potential off-target exposure of pyrethroids in an urban residential setting, a new modeling approach capable of simulating pyrethroid applications and transport processes in this more complex setting is required.

The key requirements of the urban residential exposure modeling scenario that is described in this report included:

1. The runoff model should be watershed (technically a drain-shed since stormwater drainage systems are sometimes designed to operate independently from surface topography and natural watershed boundaries) scale and capable of simulating outdoor pyrethroid applications and runoff dynamics from heterogeneous pervious and impervious surfaces. Indoor pyrethroid applications and associated potential exposure sources are NOT considered.
2. The receiving water model should be able to simulate processes critical to the environmental fate of pyrethroids and ideally should allow comparison with agricultural exposure estimates.
3. The scenario should be representative of an urban residential environment with high potential pyrethroid use site intensity, and associated high vulnerability to pyrethroid exposure.
4. The scenario should be tested and validated against a robust dataset consisting of both hydrologic (flow) and chemical monitoring data.
5. The scenario should be designed such that alternative parameterizations representative of diverse regional climate and pyrethroid use patterns can be applied to the residential scenario so that comparisons of estimated aquatic concentrations can be readily made across geographic regions.

This study provides a description of the development of a new urban residential exposure scenario based upon a novel application of the Stormwater

Management Model (SWMM) and AGRO-2014 models to the high density, single family residential housing development in Aliso Viejo, California. The report begins with a discussion of model selection, and provides a justification for both the runoff model (SWMM) and receiving water model (AGRO-2014). The model selection discussion is followed by a section on the development of the urban scenario. This includes a description of the study site neighborhood chosen to represent the urban scenario, along with justification for its selection based on an analysis of its potential use site vulnerability. Details of the scenario conceptual model formulation, translation of the model into the SWMM structure, and parameterization of the model are also provided in this urban scenario development section. A special topic in the report is then devoted to the pyrethroid "washoff" component of the model, which utilized plot-scale monitoring data (*2*) to provide the foundation for the parameterization of pyrethroid washoff characteristics. The discussion then moves on to the calibration and testing of the new exposure model scenario and provides an evaluation of the model performance based on comparisons with monitoring data from the study site. The successful calibration of the scenario allowed for the next steps to be taken in developing the desired regional parameterizations, focusing on pyrethroid use and climate. For California, predicted pyrethroid aquatic concentrations are compared between pyrethroid use practices based on historical labels and use practices based on current labels that substantially reduce the allowable applications on impervious surfaces. The results of the application of the new urban residential scenario to seven different regional parameterizations and seven different pyrethroids are presented in the Results and Discussion section.

The urban residential aquatic exposure scenario described in this document was designed for a pyrethroid exposure assessment; however, it is flexible enough to be used in urban assessments for a broader range of pesticides, and for regions beyond those that were evaluated in the assessment presented here.

Model Selection

The development of a modeling approach to simulate pyrethroid exposure in aquatic urban environments required the selection of both a surface runoff model to predict the transport of pyrethroids from urban residential use sites and a receiving water body model to allow meaningful parallels to be drawn between residential and agricultural exposure assessments. The following sections provide a discussion of the selection of a runoff model followed by a discussion of the receiving water model selection.

Runoff Model

The use of pyrethroids in an urban residential environment is complex relative to their use in an agricultural environment. In an agricultural setting, pyrethroids are applied uniformly to a homogeneous field at set application rates and application intervals. In an urban setting, diverse pesticide use sites exist, (such as lawns, foundation perimeters, garage doors/walls) which receive applications at potentially different rates and frequencies, and also behave differently in terms of their chemical washoff response to hydrologic inputs. Furthermore, in an urban residential environment, the spatial relationship between pesticide use sites around homes can have an important impact on their potential for contributing chemical washoff loads to receiving stormwater systems and receiving waters. An example of this is when a concrete patio drains onto an adjacent lawn, versus a driveway which drains directly into a road and then into a storm drain. In order to simulate the runoff of pyrethroids from a complex urban residential environment, a model with the ability to represent multiple, heterogeneous residential landscape elements, as well as their hydrologic connectivity, is required.

The simulation of pesticide runoff from an urban residential setting requires a watershed scale model that can represent runoff dynamics and hydrologic routing from both pervious and impervious surfaces. In addition, due to the short time scale on which runoff generation and routing occurs from impervious surfaces, a model that is capable of simulating at a sub-hourly time-step is also important. The need for a modeling approach that can be applied to simulate residential pesticide runoff and exposure has been recognized for many years. In a review of candidate models for simulation of urban pesticide exposure, Cheplick et al. (*3*) reported that US EPA Stormwater Management Model (SWMM) (*4*) had the functionality and capabilities best suited for urban pesticide runoff simulation. The model simulates runoff and the buildup and washoff of pollutants from both pervious and impervious surfaces. SWMM does not explicitly model soil erosion and sediment transport processes, although sediment can be treated as a pollutant analogous to other chemicals and thus can be included with chemicals as a model output. The SWMM model has been a leading tool for hydrologic and water quality simulations in urban environments for more than 20 years (*5*, *6*). The use and calibration of the model for simulating urban runoff water quality and best management practices has appeared numerous times in peer-reviewed literature (*7–9*). The popularity of the model for use in urban runoff assessments continues, as new publications providing guidance on its use have been recently developed (*10*). SWMM is actively supported by the US EPA (http://www.epa.gov/athens/wwqtsc/html/swmm.html) and other third party software companies that have packaged more feature-rich user interfaces around the SWMM model (e.g., PCSWMM from CHI, http://www.chiwater.com/Software/PCSWMM/).

Since the time of Cheplick's report, demonstrations of the SWMM model for use in watershed scale simulations of urban pesticide runoff have been published (*11*) with results that indicate the model is capable of simulating observed pesticide concentrations. Since the work by Jackson and Winchell (*11*), several modifications to the SWMM model have been made that directly improve the model's ability to simulate pesticide applications and runoff transport. The first improvement was the addition of an option to define chemical build up as a time series (analogous to pesticide applications) instead of a continuous mathematical function; an improvement that was introduced in SWMM version 5.019 (released by US EPA on 7/30/2010 (*12*)). The second improvement was the incorporation of a new washoff algorithm specifically developed for use in predicting pesticide washoff from impervious surfaces. As part of this study, this new wash-off algorithm developed by the California Department of Pesticide Regulation (CDPR) (*13*) was incorporated into SWMM version 5.022 (released by US EPA on 4/21/11 (*14*)). These recent SWMM model improvements significantly elevated the model's suitability for simulation of pesticide runoff from urban residential environments, making it the clear choice for the runoff component of pyrethroid urban exposure assessment.

Receiving Water Model

SWMM simulates estimated end-of-pipe total water chemical concentration and flow rate, which are analogous to the edge-of-field Pesticide Root Zone Model (PRZM) pesticide and runoff fluxes. This output is used directly when calibrating the SWMM model using measured total water residues from stormwater outfall sampling. However, in order to develop comparisons with the typical ecological aquatic exposure concentrations used for pesticide risk assessment, it is necessary to simulate this storm drain output entering a receiving water body. As mentioned in the previous section, SWMM does not explicitly model erosion and sediment transport processes. Therefore, in order to provide a sediment load to a receiving water body, sediment load/concentration time series can be developed from other sources independent of SWMM.

One of the primary conclusions drawn in a recent report by Hendley (*15*) is the need for explicit modeling of sediment dynamics in a static water body in order to make accurate predictions of water column dissolved concentrations of pyrethroids. In the report, the AGRO-2014 model (*16*) is identified as a model version calibrated and parameterized in order to simulate the sediment dynamic processes required for pyrethroid environmental fate predictions. AGRO-2014 uses the underlying code of the AGRO model, developed at the Canadian Environmental Modelling Centre (CEMC), a well-established water quality mass-balance model used to predict the environmental fate of chemicals in a variety of water bodies (*17*). It combines the CEMC Quantitative Water, Air, Sediment Interaction (QWASI) fugacity model (*18*, *19*) with the Simon Fraser University Bioaccumulation food web model (*20*, *21*). The QWASI model, which defines AGRO's core water, air and sediment processes, has been used extensively to assess chemical dynamics in both lakes and rivers (*18*, *21*, *22*). The AGRO model was reviewed by the US EPA Science Advisory Panel in 2008 (*23*) and was recognized as having several features for improved handling of sediment dynamics.

The report by Padilla and Winchell (*16*) presents an in depth review of the AGRO model and its behavior compared to the Exposure Analysis Modeling System (EXAMS) model in simulating chemical fate in static water bodies after loading events from both direct surface deposition of spray drift and events associated with runoff and erosion. The report compares predictions of the two models to observed pyrethroid (lambda-cyhalothrin) dissipation reported by Leistra et al. (*24*). Based on this comparison, several modifications to the AGRO code and parameterization were proposed to improve AGRO's simulation of pesticide dissipation, particularly for highly hydrophobic compounds such as pyrethroids. The re-parameterized AGRO model was shown to better simulate pyrethroid dissipation than the EXAMS model with EPA's standard farm pond parameterization based on comparisons with the observed data in Leistra et al. (*24*). In addition, the AGRO model behavior of pyrethroid dissipation in the presence of additional eroded sediment was found to better fit the conceptual model of pyrethroid behavior than EXAMS. The enhanced version of AGRO presented by Padilla and Winchell (*16*) is now referred to as AGRO-2014. The AGRO-2014 model was chosen as the best model for representing pyrethroid behavior in static water bodies and was adopted for use with the SWMM runoff model in estimating pyrethroid concentrations in urban residential receiving water bodies.

Urban Scenario Development

The development of a new model scenario to simulate reasonable worst-case pyrethroid aquatic exposure in an urban residential environment occurred in several key steps. The first step was to identity a site with a sufficient amount of data to allow the testing and validation of the model scenario. The site selected was representative of a location with a relatively high vulnerability to pesticide runoff from outdoor residential pesticide applications, which was confirmed based on a national scale spatial analysis of residential housing density. A conceptual model of outdoor pyrethroid use sites and transport was then developed. An important requirement of the conceptual model was that it could be translated into a SWMM model structure. The conceptual model was then translated into a SWMM model structure and an initial model parameterization was performed. These steps are described in the sections that follow.

Site Selection

A study of residential pesticide runoff in Orange and Sacramento counties in California (*25*) reported the results of extensive monitoring of pyrethroids and other pesticides and water quality parameters spanning from October of 2007 through September of 2008. The monitoring reported in this study included four sites in southern California (Orange County) and four sites in northern California (Sacramento County). The monitoring for each location occurred at a stormwater outfall draining high density, generally more affluent residential neighborhoods. The monitoring data provided in the report included total water concentrations of several pesticides (fipronil, bifenthrin, cyfluthrin, deltamethrin, and others) and associated water quality parameters (including total suspended solids and total dissolved solids), as well as estimates of the total loading of these chemicals and parameters over both dry (non-storm event) and wet periods. The targeted monitoring conducted as part of this study was determined to be the best available data for which to evaluate an urban residential pyrethroid exposure modeling scenario.

One of the principal investigators of the residential pesticide runoff study in Orange and Sacramento Counties was contacted to inquire about the availability of additional supporting data from the study and for advice on an appropriate site on which to focus modeling efforts (*26*). Based on this communication, the "AV4" site from the study report (*25*) was selected to serve as the location for which to develop and test the urban residential model scenario. This site encompasses a 67.2 acre (27.2 ha) urban residential watershed in the city of Aliso Viejo in Orange County, California (Figure 1). The city of Aliso Viejo has a population of 47,823 (as of the 2010 census) and is situated along the east slopes of the San Joaquin Hills. The watershed/drainshed boundary delineation shown in Figure 1 was obtained through Dr. Haver (*26*) and was field verified during the monitoring study. The watershed includes 307 high density single family housing units with well-maintained lawns and landscaping, resulting in a housing density of 4.57 housing units/acre (11.29 units/ha). The flow measurements and chemical sampling for this urban residential watershed were taken at the outfall of the stormwater drainage system. Thus the samples represent concentration prior to entry into a receiving water body.

Figure 1. Aliso Viejo Watershed and Site Location. (see color insert)

Housing Density Assessment

Pyrethroids can be applied to pervious surfaces, such as lawns and landscape/ornamental areas, as well as impervious surfaces, such as driveways, patios, and walkways. A recent study, which focused on identifying the sources and pathways of off-site pyrethroid transport from urban residential applications (henceforth referred to as the "Pathway ID study") (*2*), has indicated that the pyrethroid use sites that are most vulnerable to off-target transport are the impervious surfaces with direct routes to roads and their associated storm water systems. This is most commonly associated with the portion of a foundation perimeter treatment at the top of a driveway and the vertical garage door and adjacent wall that is connected to the driveway (*2*). Therefore, the housing density and associated density of these high vulnerability driveway use sites can serve as a logical metric for evaluating the relative vulnerability of neighborhoods to potential off-site hydrologic transport of pyrethroids to surface waters. Based on this logic, a national-level spatial analysis of housing density was conducted to assess the relative pyrethroid transport vulnerability of the Aliso Viejo neighborhood compared to other urban residential settings throughout the United States.

Housing density was assessed across the entire United States at the US census block level. US census block spatial data and demographic tabular data from the 2010 census were obtained for each of the lower 48 states from the US Department of Commerce Census Bureau web site (*27*). Census blocks vary in size across different regions of the United States, but commonly represent neighborhoods or streets.

At the census block level, the attributes provided by the US Census Bureau include total housing units. The data do not distinguish between single family, multi-family units, or apartment buildings. We are most interested in assessing census blocks that are associated with single family housing (or multi-family with small numbers of units) because a high density of these types of housing units results in the greatest vulnerability in terms of pyrethroid use sites with high potential for off-site transport to surface waters, namely, driveways and garage doors. Other potentially higher density types of developments, such as condominiums and town houses, typically achieve their higher density through additional units on higher levels, which does not increase the pyrethroid potential use site footprint. Therefore, an analysis of land cover classification for all census blocks was conducted in order to identify the census blocks most likely associated with single family housing.

The National Land Cover Dataset (NLCD) (*28*) includes four developed land use classifications with the following descriptions:

1. Developed, Open Space (class 21): Areas with a mixture of some constructed materials, but mostly vegetation in the form of lawn grasses. Impervious surfaces account for less than 20% of total cover. These areas most commonly include large-lot single-family housing units, parks, golf courses, and vegetation planted in developed settings for recreation, erosion control, or aesthetic purposes.

2. Developed, Low Intensity (class 22): Areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 20% to 49% percent of total cover. These areas most commonly include single-family housing units.
3. Developed, Medium Intensity (class 23): Areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 50% to 79% of the total cover. These areas most commonly include single-family housing units.
4. Developed, High Intensity (class 24): Highly developed areas where people reside or work in high numbers. Examples include apartment complexes, row houses and commercial/industrial. Impervious surfaces account for 80% to 100% of the total cover.

The "Developed, Low Intensity" and "Developed, Medium Intensity" classes are most closely associated with single family housing. Therefore, those NLCD land use classifications were used to extract those census blocks consisting of single family housing. The land cover analysis of census blocks was conducted by overlaying the 2006 NLCD with all the census blocks nationwide and calculating the percentage of each land cover contained within each census block. The census blocks chosen for analysis were selected based on the following criteria:

1. It must contain some "Developed, Low Intensity" and/or "Developed, Medium Intensity" land cover.
2. The fraction of the census block classified as "Developed, High Intensity" must be less than 10% of the census block area.

The national analysis of census blocks calculated housing density and NLCD land cover fractions for all census blocks within the lower 48 states. A total of 6,279,464 census blocks containing low or medium intensity development and less than 10% high intensity development were identified. Table I below summarizes how the housing density of the Aliso Viejo neighborhood (at 11.29 units/ha) compares with California and several other regions of the lower 48 states. The additional examples of housing density reported in the table are for states or groups of states associated with other regions of the country where urban pyrethroid model parameterizations will be developed based on California's Aliso Viejo high vulnerability catchment characterization.

The data in Table I shows that across the contiguous US, 87.9% of census blocks associated with single family housing have housing unit densities less than Aliso Viejo (11.29 units/ha). In California where the occurrence of higher housing densities appears to be greater than the national average, 72.3% of census blocks have a lower density than Aliso Viejo. Housing densities in the other pyrethroid scenario regions are lower than in California, with the Mid-Atlantic regions being closest to California, with 77.9% of census blocks having lower density than Aliso Viejo. The South Central region (Texas) has the lowest housing density of the regions reported, with 91.9% of census blocks having housing densities of less than 11.29 units/ha.

Table I. Aliso Viejo Housing Density Compared to Other Regions

Geographic Region	*Single Family Residential Census Blocks*	*Census Bocks with Lower Density than Aliso Viejo (%)*
California	417,767	72.3
Northwest (WA, OR)	224,042	85.4
North Central (IL,WI, MO)	693,821	88.0
Northeast (VT, NH, MA, CT, RI)	208,756	89.1
Mid-Atlantic (NJ, DE, MD, DC)	222,414	77.9
Southeast (FL, GA)	512,269	87.7
South Central (TX)	504,509	91.9
Contiguous US	6,279,464	87.9

Urban Residential Neighborhood Conceptual Model

A conceptual model of how pyrethroids are applied and how off-site transport occurs in an urban residential environment is necessary prior to the development and application of an exposure modeling scenario. This section describes this conceptual model and its influence on the SWMM model structure development.

Pyrethroid Applications to Use Sites

Recent surveys of urban residential outdoor application practices have shown that applications to hard surfaces, such as driveways, patios, and walkways are common, in addition to application to pervious surfaces, such as lawns and landscape areas (*29*, *30*). A subsequent interpretation of these two independent surveys by Winchell (*31*) focused on quantifying the extent and frequency of applications to the primary pyrethroid use sites. These use sites included:

1. Building foundation perimeters: These use sites consist of the ground surface extending several feet out from a structure's foundation and several feet up the foundation wall (typically 1.52 feet out and 0.61 feet up (*2*)), with insecticide treatment intended to protect the home's perimeter from invading insects. During a foundation perimeter application, both pervious and impervious surfaces near the home are treated, including the driveway and patios/walkway areas within a several foot perimeter around the main house and garage. The treatment of these areas was specifically targeted for application reductions by more recent pyrethroid label changes (*32*, *33*).

2. Patios and walkways (away from the building): Applications made to patios and walkways away from the building are not explicitly associated with a foundation perimeter application, and tend to be targeted to portions of the surface showing evidence of insect activity.
3. Driveways (away from the garage door and wall): Similar to patios and walkways, applications made to driveways away from the building are not explicitly associated with a foundation perimeter application, and tend to be targeted to portions of the surface showing evidence of insect activity.
4. Lawns/landscape areas: Lawn applications include both localized applications (such as ant mounds) as well as broadcast applications intended to treat the entire lawn. The landscape component of this use site includes pervious landscaped areas that are not part of the turf portion of the lawn, with typically more localized applications than the lawn component.

A planimetric map delineating these surfaces for a single house lot is provided in Figure 2. It should be emphasized again that the surfaces treated in a foundation perimeter treatment will be variable (some pervious, some impervious) with different potential for off-site movement based on their hydrologic connectivity to receiving waters.

While understanding all use sites is valuable, accounting for the most important pyrethroid use sites (i.e., those with the greatest potential contributions to off-target aquatic exposure) is critical in the development of an urban residential model scenario. The Pathway ID study concluded that applications to hard surfaces were the dominant source of off-site movement (*2*, *34*). Specifically, the top of the driveway and the garage door and adjacent wall that is typically treated as part of a foundation perimeter application was responsible for nearly 100% of total pyrethroid off-site mass transport. The remaining use sites evaluated (the grass lawn, grass foundation perimeter, and house wall) generated less than 1% of the total off-site pyrethroid transport under historic application practices. Historic application practices allowed continuous band treatments to hard/impervious surfaces. For foundation perimeter applications, this typically included a 1.52 meter band out from the foundation and garage. In 2010, the US EPA began approving revised pyrethroid labels that restrict treatments of hard surfaces to crack and crevice applications. Product packages bearing these revised labels have gradually been making their way into the marketplace since then (*32*, *33*). It is therefore necessary that different types of impervious surfaces be represented in the urban residential model scenario. A model structure that differentiates between the various impervious surfaces will also allow for inclusion of the variability in application extent, frequency, and timing that was reported in the recent pyrethroid surveys (*29*, *30*) and the interpretation of these surveys (*31*).

Figure 2. Diagram of Outdoor Household Pyrethroid Use Sites. (see color insert)

Pathways for Pyrethroid Transport

Off-site transport of pyrethroids from urban residential use sites to stormwater conveyance systems and ultimately natural and manmade receiving waters is a result of rainfall and irrigation on both pervious and impervious use sites. As previously described, the Pathway ID study (*2*, *34*) demonstrated the dominance of transport from impervious surfaces, particularly under historic application practices. The Pathway ID study also showed that rainfall events, as opposed to irrigation events, were responsible for the majority of pyrethroid off-site mass transport. Neighborhood scale monitoring in California by Oki and Haver (*25*) showed that substantial amounts of pyrethroid transport occurs during "dry" periods (more than 50% of annual load for some pyrethroids), where irrigation is the primary source of flows into the stormwater system. Based on these two studies, it was determined that representing the potential off-site pyrethroid movement from both rainfall and irrigation events would be required, and in particular, off-target irrigation hitting impervious surfaces and causing washoff of previously applied insecticides.

Another important aspect of the urban model, both for simulation of flow volumes and pyrethroid transport, is the hydrologic connectivity of impervious surfaces. The hydrologic connectivity of pyrethroid use sites to the roadway gutter and stormwater conveyance system varies based on the position of the use site on the house lot. As was shown in the Pathway ID study (*2*, *34*), there is a direct hydrologic connection between impervious surfaces such as the driveway and the garage door and immediately adjacent house wall and the gutter/storm drain in the roadway immediately off the edge of the property. Other impervious surfaces, such as patios (typically located in the backyard) and walkways (often bordered by lawns and landscape areas) are often not directly connected to the roadway and stormwater system. These portions of the house lot will typically flow into adjacent pervious surfaces (lawns and landscape areas) and thus do not pose as much of a potential exposure risk as the driveway, which will almost always slope directly to the road. It is therefore a requirement that the urban model structure can differentiate between these impervious surfaces that are likely directly connected and those that are only partially connected.

Summary of Conceptual Model Requirements

Based on the conceptual model requirements just described, the watershed should be divided into the following landscape elements:

1. Roofs: receives only rainfall; no pyrethroid applications
2. Roads and sidewalks: receives only rainfall; no pyrethroid applications
3. Roads and sidewalks, irrigated: receives rainfall and off-target irrigation; no pyrethroid applications
4. Foundation perimeter, upper driveway: receives only rainfall; pyrethroid application as part of foundation perimeter application; directly connected to stormwater system
5. Foundation perimeter, upper driveway, irrigated: receives rainfall and off-target irrigation; pyrethroid application as part of perimeter application; directly connected to stormwater system
6. Foundation perimeter, garage wall: receives only rainfall; pyrethroid application as part of foundation perimeter application; vertical surface directly connected to stormwater system
7. Foundation perimeter, impervious: impervious surfaces within 1.52-meter foundation perimeter, other than the driveway and garage wall; receives only rainfall; pyrethroid application as part of foundation perimeter application; a fraction is directly connected to the stormwater system and the other fraction drains to adjacent lawn
8. Foundation perimeter, impervious, irrigated: impervious surfaces within 1.52-meter foundation perimeter, other than the driveway and garage wall; receives rainfall and off-target irrigation; pyrethroid application as part of foundation perimeter application; a fraction is directly connected to the stormwater system and the other fraction drains to adjacent lawn

9. Foundation perimeter, pervious, irrigated: pervious surfaces within 1.52-meter foundation perimeter; receives rainfall and off-target irrigation; pyrethroid application as part of foundation perimeter application
10. Driveway, lower: lower driveway section below foundation perimeter; receives only rainfall; pyrethroid application as part of driveway application; directly connected to stormwater system
11. Driveway, lower, irrigated: lower driveway section below foundation perimeter; receives rainfall and off-target irrigation; pyrethroid application as part of driveway application; directly connected to stormwater system
12. Patios/walkways: receives only rainfall; pyrethroid application as part of patio/walkway application; a fraction is directly connected to the stormwater system and the other fraction drains to adjacent lawn
13. Patios/walkways, irrigated: receives rainfall and off-target irrigation; pyrethroid application as part of patio/walkway application; a fraction is directly connected to the stormwater system and the other fraction drains to adjacent lawn
14. Lawn/landscape areas: house lot lawn and landscape areas; receives rainfall and irrigation; pyrethroid application as part of lawn application
15. Common landscape areas: landscaped and natural areas between house rows that are not associated with individual house lots; receives rainfall and irrigation
16. Pools/hot tubs: portions of the house lot that do not contribute runoff

The following are additional model structural requirements necessary to represent the conceptual model:

1. The neighborhood watershed will be divided into several notional "sub-watersheds" to allow variation in the scheduling of pyrethroid applications.
2. Each use site within each "sub-watershed" will be divided into "treated" and "untreated" portions. The "treated" fraction of each use site may be further sub-divided to allow for different treatment frequencies.

Translation of Conceptual Model into SWMM Model Structure

The Aliso Viejo neighborhood in Orange County, California was selected as the best available site to develop and validate an urban residential pyrethroid exposure model scenario. One of the principle characteristics of the conceptual model just described is the discretization of the urban residential environment into many landscape elements, allowing pyrethroid applications and hydrologic transport behavior of these elements to be controlled independently. This type of discretization is necessary because, unlike agricultural fields with a single crop, the pyrethroid labels for residential uses allow treatment of many different types of surfaces at different application rates. The delineation of these landscape elements will be described in this section, followed by a discussion of model parameterization in the section that follows.

The landscape elements of the urban residential conceptual model were listed in the previous section. In order to apply the SWMM model, the surface area associated with each of these elements must be quantified. This quantification was achieved through a manual, on-screen delineation of a sub-set of the types of landscape elements using satellite imagery (Esri, Imagery Basemap, June, 2012) within a Geographic Information System (GIS). The remaining landscape elements were delineated and their areas quantified through further additional spatial analysis within the GIS. The following steps describe the process for the spatial delineation of the Aliso Viejo neighborhood.

1. Roofs, driveways, patios/walkways, pools/hot tubs, roads/sidewalks, and common landscape areas were manually delineated
2. Lawn/landscape areas (house lot) represented the remaining neighborhood area and were spatially clipped out of the watershed
3. A 1.52-meter buffer around the roofs was created to represent the foundation perimeter
4. The 1.52-meter foundation perimeter was intersected with the driveway, and patios/walkways to create the following additional landscape elements:

    a. Foundation perimeter, upper driveway
    b. Foundation perimeter, impervious (intersection of the foundation perimeter and patios/walkways)
    c. Foundation perimeter, pervious (the remaining portion of the foundation perimeter)

5. A 0.46-meter buffer around all lawn/landscape areas (house lot) was created to represent the area of off-target irrigation.
6. The 0.46-meter "irrigation buffer" was intersected with the impervious surfaces to create the following additional landscape elements:

    a. Foundation perimeter, upper driveway, irrigated
    b. Foundation perimeter, impervious, irrigated
    c. Driveway, lower, irrigated
    d. Patios/walkways, irrigated
    e. Roads and sidewalks, irrigated

7. A 0.61-meter buffer around the driveways was created and then intersected with the roof landscape elements to represent a 0.61-meter vertical band along the garage door.

This spatial delineation is shown for a small section of the Aliso Viejo neighborhood in Figure 3. Each of the landscape elements included in the model is included in the legend using an abbreviation for its description. A description of each landscape element code is provided in Table II. After spatial delineation of the landscape elements, the watershed was split into five "sub-watersheds," which followed the primary roads within the neighborhood and were aligned with the stormwater drainage system.

Figure 3. Spatial Delineation of Aliso Viejo Neighborhood Landscape Elements. (see color insert)

Table II. Definition of SWMM Landscape Element Codes

SWMM Landscape Element Code	*Description*
Roof	Roof tops of all homes
RoadSW	Roads and sidewalks
RoadSW_IR	Roads and sidewalks, within 0.46 m buffer of lawns, receives off-target irrigation
FP_I_NI	Foundation perimeter (1.52 m out), impervious surface, no off-target irrigation

Continued on next page.

Table II. (Continued). Definition of SWMM Landscape Element Codes

SWMM Landscape Element Code	*Description*
FP_I_IR	Foundation perimeter (1.52 m out), impervious surface, within 0.46 m buffer of lawns, receives off-target irrigation
FP_PER	Foundation perimeter (1.52 m out), pervious surface
DW_FP	Foundation perimeter (1.52 m out), top of driveway, no off-target irrigation
DW_FP_IR	Foundation perimeter (1.52 m out), top of driveway, within 0.46 m buffer of lawns, receives off-target irrigation
DW_GW	Foundation perimeter, garage wall (0.61 m up)
DW_LW	Driveway, lower section below foundation perimeter, no off-target irrigation
DW_LW_IR	Driveway, lower section below foundation perimeter, within 0.46 m buffer of lawns, receives off-target irrigation
PW_NI	Patios/walkways, impervious surface, no off-target irrigation
PW_IR	Patios/walkways, impervious surface, within 0.46 m buffer of lawns, receives off-target irrigation
LL	Household lawn/landscape area
HOA_LS	Common area, landscape
Pool	Pools and hot tubs

General table notes: [a.)] The garage wall and top of driveway areas within the foundation perimeter are distinct landscape areas. [b.)] The garage wall in front of the driveway is the only vertical surface represented in the model (0.61 m up and includes the adjacent house wall). [c.)] 100% of the driveway and garage wall areas are directly connected to the stormwater system. [d.)] Impervious foundation perimeter and patio/walkway areas are divided into sections that directly connect to the stormwater system and those that flow into lawns/landscape areas.

Aliso Viejo SWMM Model Inputs and Parameterization

The SWMM model simulates the rapid rainfall/runoff response typical of urban environments. This requires precipitation input on an hourly timestep or shorter. For the Aliso Viejo model, a 30-year hourly time series of precipitation spanning from 1/1/1981 through 12/31/2010 was compiled based on weather stations located in Irvine and Long Beach California, approximately 15 km from the Aliso Viejo neighborhood. Automated lawn irrigation is a prevalent practice in the Aliso Viejo neighborhood (*35*). This is clearly supported by the monitoring data reported in Oki and Haver (*25*) and the hourly flow data collected during that study (*26*). Irrigation typically is scheduled for the early morning hours with a duration of around 15 minutes. A common irrigation amount during a 15 minute period is 8.89 mm, the same irrigation rate adopted for the Pathway ID study

(*36*). The number of times irrigation occurs per week varies with the time of year, with less frequent irrigation occurring in the winter and more frequent irrigation occurring during the summer. In the parameterization of the Aliso Viejo model, the frequency of irrigation (times per week) was calibrated based on the observed flow dataset.

The physical characteristics required by the SWMM model for each landscape element included total area, slope, roughness (Manning's N), and depression storage. These values were derived from topographic data, standard house lot building practices, and the SWMM manual. These values are summarized in Table III.

Table III. SWMM Landscape Element Characteristics

Landscape Element	*Area (ac)*	*Fraction Routed to Stormwater System*	*Slope (%)*	*Manning's N*	*Depression Storage (mm)*
Roof	6.147	1.0	20.0	0.024	1.27
RoadSW	4.957	1.0	1.4	0.024	1.27
RoadSW_IR	0.130	1.0	1.4	0.024	1.27
FP_I_NI	0.893	0.1	6.0	0.024	1.27
FP_I_IR	0.184	0.1	6.0	0.024	1.27
FP_PER	1.431	1.0	6.0	0.4	3.81
DW_FP	0.332	1.0	6.0	0.024	1.27
DW_FP_IR	0.038	1.0	6.0	0.024	1.27
DW_GW	0.156	1.0	6.0	0.024	1.27
DW_LW	1.445	1.0	6.0	0.024	1.27
DW_LW_IR	0.125	1.0	6.0	0.024	1.27
PW_NI	1.023	0.1	2.0	0.024	1.27
PW_IR	0.352	0.1	2.0	0.024	1.27
LL	3.521	1.0	6.0	0.4	3.81
HOA_LS	6.295	1.0	22.8	0.4	3.81
Pool	0.164	1.0	1.0	0.024	1.27

The pervious SWMM landscape elements (pervious foundation perimeter, house lot lawn/landscape area and common area landscape elements) require that infiltration parameters be established. The method chosen to simulate infiltration was the Green & Ampt method, which requires saturated hydraulic conductivity, soil suction head, and the initial soil moisture deficit. The Natural Resources Conservation Service (NRCS) Soil Survey Geography (SSURGO) data for the Aliso Viejo neighborhood shows a wide variety of soil conditions, ranging from extensive areas of rock outcrop complexes, to clay loams, to loamy sands. The map is clearly a pre-development map, representative of the natural soil conditions, not the post-development lawn and landscape area soils, and was determined to be of little value in the parameterization of infiltration parameters for Aliso Viejo. In place of using pre-development NRCS data, the representative soil for the Aliso Viejo development lawn and landscape areas was estimated to be a moderately drained sandy loam soil. Based on the SWMM manual, a sandy loam soil has a soil suction head parameter value of 110.0 (mm) and a saturated hydraulic conductivity of 10.9 (mm/hr).

The observed flow data for the Aliso Viejo stormwater outfall shows that a seasonal varying baseflow persists throughout the year (the model calibration shows examples of this). This constant flow is largely a result of subsurface drainage from the house lawns to the stormwater conveyance system (*26*). This was simulated in SWMM through the addition of aquifer objects and a subsurface flow component.

Stormwater system plans for the Aliso Viejo neighborhood were obtained from the City of Aliso Viejo. These plans showed the locations of catch basins and conduits, as well as their sizing. Based on these plans, a simplified representation of the stormwater system was developed for the SWMM model. The simplified plan maintained the locations of conduit lines, drainage areas, connectivity, and sizing. Because very limited information was known about catch basin characteristics within the urban drainage system, they were not explicitly included in the model. In addition, little is known about the environmental fate of pyrethroids in catch basins. Therefore, including catch basins and their effects on pyrethroid transport would have added greater uncertainty to the model than not including them. Because we are interested in daily loads of pyrethroid coming from the stormwater system, it is not expected that the absence of catch basins in the model will have an impact on the conclusions drawn from the modeling results.

Pyrethroid Washoff Model Development

Washoff from impervious concrete driveway surfaces is the dominant source of pyrethroid residue found in urban streams (*2*, *34*). Washoff is the hydrochemical process of pyrethroid transport during a runoff event. The options for washoff dynamics (i.e. the amount of applied pyrethroid transported via runoff after different periods of time post application) currently available in the SWMM model were found to be inadequate for modeling pyrethroid washoff from concrete surfaces. To better describe the physical washoff behavior of pyrethroids, an improved set of washoff equations, developed by Luo et al. (*13*), were implemented in SWMM.

Washoff Method

Pyrethroid washoff has been observed to be both insensitive to runoff rate and highly sensitive to the length of time between when an application is made and the first runoff event occurs (called “set time”) (*37*, *38*). As set time increases, the chemical available for washoff decreases due to degradation and effectively irreversible adsorption to concrete surfaces. During runoff events, the chemical available for washoff diffuses into the overland flow at a rate that decreases over the duration of the event. The current washoff options in SWMM include exponential, rating curve, and event mean concentration equations, all of which are dependent on the runoff rate and none of which keep track of the set time or the duration of the runoff event. Therefore, the current SWMM washoff equations are not capable of representing the physical washoff behavior of pyrethroids from hard surfaces.

A recent modeling approach, developed and calibrated to experimental data by Luo et al. (*13*) of California's Department of Pesticide Regulation, accounts for the effects of set time and runoff event duration on pyrethroid washoff. The Luo washoff method was incorporated into the SWMM model version 5.022 (*14*). The approximate analytic solutions to the conceptual model were implemented in the SWMM buildup and washoff code modules following Luo et al. (*13*) and recommendations from personal communications with Dr. Luo. The core buildup equation implemented is equation (3) from Luo et al. (*13*) supplementary material. The core washoff equations used are based on equations (12), (13), (16), and (18) from Luo et al. (*13*) supplementary material. Note that these equations are solved directly for the cumulative washoff over the duration of a runoff event, however the sequential time-stepping of the SWMM model requires values for incremental washoff. Incremental washoff was determined at each timestep by calculating the difference in current and previous cumulative washoff masses.

Washoff Calibration

A preliminary calibration of the Luo washoff model parameters to monitoring data from the very well characterized Pathway ID study (*2*, *34*) was performed in order to identify initial washoff parameters for the neighborhood scale model. By identifying a very good "starting point" for the neighborhood scale washoff parameterization, more appropriate adjustments to other aspects of the neighborhood model would be possible, leading to an overall stronger model calibration.

The washoff model parameters used in SWMM were calibrated to data from the Pathway Identification Study (*36*), a year-long, controlled experiment examining the major pathways for transport of pyrethroids from residential housing lots. Three of the Pathway ID replicate lots (numbers 1, 3, and 5) were modeled in SWMM to simulate washoff when using historic application practices. The modeled lots consisted of a driveway sub-catchment with a 1.52 m band across the upper driveway treated repeatedly with cypermethrin and a lawn sub-catchment treated once with deltamethrin. Measured simulated and natural rainfall, lawn irrigation, and applied chemical mass for each house lot were inputs into the model. All surfaces received uniform rainfall inputs. The lawn surfaces received uniform irrigation inputs, and a 0.41 m wide section along either side of the driveway along the lawn edge also received irrigation by the lawn sprinklers.

The main goal of the calibration was to match the distribution of daily washoff mass and the experiment-total washoff mass over the course of the year. The statistical performance of the model was emphasized rather than simulation-observation agreement for individual events because the washoff was sensitive to the set time and runoff event duration and there was some uncertainty associated with the timing of runoff events in the model. For example, some rainfall events in the Pathway ID study were observed to cause overflow of lawn runoff onto the driveway, however this contribution to driveway runoff was not quantifiable in the studies and thus could not be simulated in SWMM.

The goodness-of-fit parameters examined for the washoff cumulative distributions were the R^2, BR^2, and total bias. The R^2 calculation used to account for correlation between modeled and observed values was,

$$R^2 = \frac{\left[\sum_{i=1}^{n}(sim_i - \overline{sim}_i)(obs_i - \overline{obs}_i)\right]^2}{\sum_{i=1}^{n}(sim_i - \overline{sim}_i)^2 \sum_{i=1}^{n}(obs_i - \overline{obs}_i)^2}$$

where,

sim_i = simulated flow at time i
$\overline{sim}$ = mean of the simulated flow
obs_i= observed flow at time i
n = number of observations.

The BR^2 is the product of the R^2 and the slope of the best fit regression line, B, (or the inverse of the regression line slope if the slope is greater than one),

$$BR^2 = \begin{cases} BR^2, & B \leq 1 \\ B^{-1}R^2, & B > 1 \end{cases}$$

A BR^2 equal to one would indicate modeled and observed data that have one-to-one correlation or in other words, that simulation-observation correlation is maximized and the bias is minimized. The total bias calculation was used to compare the magnitudes of observed and simulated cumulative washoff mass through the end of the experiment period. Total bias was computed as,

$$total\ bias = \frac{\sum_{i=1}^{n} sim_i}{\sum_{i=1}^{n} obs_i}$$

The lawn and driveway washoff parameters were calibrated to achieve R^2, BR^2, and total bias close to one. Parameters and goodness-of-fit statistics are provided in Table IV.

Table IV. SWMM Washoff Parameter Calibration of Driveway (Cypermethrin) and Lawn (Deltamethrin), Pathway ID Study

	Washoff Parameters			*Goodness-of-fit Statistics*		
Surface	*$K_p(0)$*	*D*(0)*	*s*	*R^2*	*BR^2*	*Total Bias*
Driveway	2	1.30E-03	0.15	0.92	0.74	1.04
Lawn	20	1.50E-05	0.49	0.77	0.72	1.33

Notes: [a.)] Kp(0) = initial rate constant at beginning of dry period. [b.)] D*(0) = initial effective diffusivity. [c.)] s = slope factor.

Urban Scenario Calibration

The development of the urban residential modeling scenario has been discussed in the previous sections, including development and calibration of a new washoff method for SWMM. This section will discuss the application and calibration of this scenario to observed flow and pyrethroid data collected from the outfall of the Aliso Viejo stormwater system. The objectives of the calibration were to adjust a minimal number of model parameters in order to minimize the model bias in flow predictions (daily and hourly) and pyrethroid mass and concentrations. For the chemical calibration, bifenthrin was chosen as the pyrethroid to model because it was detected most frequently and at the highest levels of all the pyrethroids that were sampled at the monitoring site, giving it the most data with which to assess the calibration performance.

Pyrethroid Application Parameterization

In the context of the SWMM model, the bifenthrin application extent equates to the fraction of each landscape element that is treated with bifenthrin at each application interval. Because the time period being simulated for calibration of the Aliso Viejo neighborhood (2007- 2008) is prior to recent pyrethroid label language limiting the applications on impervious surfaces to "crack and crevice" applications (*32*, *33*), the application practices being simulated in the calibration scenario are representative of the historic bifenthrin label and deal solely with bifenthrin applications.

The data source used to define the bifenthrin application assumptions for the calibration scenario was the pyrethroid use analysis report by Winchell (*31*). The key pieces of data from Winchell (2013) that were used in the parameterization of bifenthrin application for the Aliso Viejo scenario were as follows:

1. The fraction of households using outdoor pest control products: For California, this value (75.9%) is derived from Table I of Winchell (*31*).
2. The estimated fractions of use sites treated with bifenthrin: For California, this is provided for each use site in Table VII of Winchell (*31*). This table also distinguishes between the fraction of use sites that are treated once every 6 weeks and those treated once every 12 weeks.

The bifenthrin use site fraction information has been extracted from this table and included in this report in Table V for convenience.

3. The percentage of a use site's surface area treated. While these data were not explicitly reported for California, the data for the other regions of the US (Tables XV – XVII from Winchell (*31*)) were used as guidance for these parameters in the Aliso Viejo scenario.

Table V. California, Estimated Frequency of Bifenthrin Applications by Use Site (from Table VII in Winchell (*31*)).

Use Site	*Estimated Total Percent Treated (%)*	*Estimated Percent Treated Every 6 Weeks (%)*	*Estimated Percent Treated Every 12 Weeks (%)*
Foundation Perimeter	25.7	13.1	12.6
Patios/Walkways	24.9	12.7	12.2
Driveways	24.1	10.6	13.5
Lawns	24.4	5.4	18.9

From Table V, we can make an example calculation of the fraction of foundation perimeters that receive a bifenthrin application every 6 weeks. Given:

1. 75.9% of households use outdoor pest control products
2. 13.1% of those receiving treatments apply bifenthrin once every 6 weeks to foundation perimeters
3. Total fraction of foundation perimeters receiving bifenthrin applications every 6 weeks = (0.759) × (0.131) = 0.099

The same calculation logic shown in the example above was applied for bifenthrin applications for all use sites and for both applications every 6 weeks and applications every 12 weeks. The one additional factor required when calculating the fraction of each SWMM landscape element treated with pyrethroids is the percent of the use site surface area treated. The Winchell (*31*) report provided these values for driveways, patios/walkways, and lawns for individual geographic regions and for six regions lumped together. The data showed a wide variety of application practices. For parameterizing the Aliso Viejo model, the following assumptions regarding the percent of surface area treated were made:

1. Foundation Perimeters, 100% surface area treated: Percent surface area treated data were not collected for foundation perimeter applications. Since these applications are typically a continuous band treatment, a value of 100% was assumed.
2. Patios/Walkways, 10%: The most common response (34% of responses) for all regions combined was that 10% or less of patio/walkways surface areas is treated. Therefore, 10% was assumed.

3. Driveways (away from foundation perimeters), 10%: The most common response (42% of responses) for all regions combined was that 10% or less of driveway surface areas is treated. Therefore, 10% was assumed.
4. Lawns, 100%: The most common response (62% of responses) for all regions combined was the entire area (100%) of lawn surface areas is treated. Therefore, 100% was assumed.

To determine the final fraction of each landscape element treated, the fraction of each use site treated at the different intervals is multiplied by the percent of the surface area treated.

The timing of pyrethroid applications in California was found to be evenly spaced throughout the year (Winchell (*31*), Tables XXVIII - XXXI). Therefore, the target dates for application in the 6-week and 12-week cycles were evenly spaced throughout the year. The target application dates (month/day) for the 6-week and 12-week application cycles are provided in Table VI.

Table VI. Bifenthrin Target Application Dates

Cycle	*App1*	*App2*	*App3*	*App4*	*App5*	*App6*	*App7*	*App8*
6-week	01/01	02/15	04/01	05/15	07/01	08/15	10/01	11/15
12-week	01/01	04/01	07/01	10/01				

An additional constraint imposed on the dates for pyrethroid application in the SWMM model was that an application had to be at least 48 hours before a rainfall event (this is a pyrethroid label requirement). To accommodate this requirement, the target application date was checked against the weather time series. If rainfall occurred within 48 hours after the target application date, then the date was progressed forward in time until a suitable date was found. Finally, in order to account for different households not being on the same application schedule, four different sets of application time series for each treatment cycle were generated. This was accomplished by creating new target application dates by staggering the dates in Table VI by 11 days.

The application rate assumed for bifenthrin applications to all use sites in the urban residential scenario was 0.224 kg/ha. This rate was identified as the maximum label rate for both residential foundation perimeter and broadcast lawn applications in a recent master label review (*1*).

Calibration Approach

Observed daily and hourly flow time series data for the Aliso Viejo neighborhood outfall from the period of 10/1/2007 – 9/30/2008 were obtained from Daren Haver of the University of California South Coast Research & Extension Center (*26*). The primary components of the SWMM model that were adjusted during calibration were:

1. Seasonal irrigation frequency
2. Subsurface flow response
3. Fraction of impervious surfaces (patios/walkways and foundation perimeters) draining to the lawns
4. Routing parameters (roughness and lengths) that affect runoff timing

The goodness-of-fit statistics used in assessing the daily and hourly flow calibration included the R^2, total flow volume bias, and the Nash-Sutcliffe Efficiency (NSE). The equations for calculating R^2 and total bias were provided previously. The NSE (*39*) is calculated as (a value of 1 indicates a perfect fit between the model and observations):

$$NSE = 1 - \left(\frac{\sum_{i=1}^{n}(obs_i - sim_i)^2}{\sum_{i=1}^{n}(obs_i - \overline{sim})^2}\right)$$

where,

sim_i = simulated flow at time i
$\overline{sim}$ = mean of the simulated flow
obs_i = observed flow at time i
n = number of observations.

The observed data for the bifenthrin calibration came directly from the report on the monitoring study by Oki and Haver (*25*). In that report, a table on page 125 provides bifenthrin **total water** concentrations taken from 31 samples between 10/3/2007 and 10/1/2008. The samples occurred approximately bi-weekly and included both storm and non-storm events. In addition, the report includes a table on page 140 of total weekly and annual loads of bifenthrin (combined soluble and sorbed) over the study period. These data served as the basis for the chemical calibration evaluation for the Aliso Viejo SWMM model. The primary components of the SWMM model that were adjusted during calibration that affected chemical simulation were:

1. Seasonal irrigation frequency
2. Fraction of impervious surfaces (patios/walkways and foundation perimeters) draining to the lawns
3. Washoff algorithm parameters

It should be noted that the SWMM model components that have been specified as being adjusted for both hydrology and chemical calibration (irrigation and impervious surface fraction draining to lawns) were calibrated to a single set of parameters appropriate for both hydrology and chemical simulations.

The goodness-of-fit statistics used in assessing the bifenthrin calibration included the total annual mass load bias, R^2 and BR^2 between the observed and simulated cumulative distributions of daily bifenthrin concentrations. In comparing the observed and simulated cumulative distributions, percentiles were calculated for the middle 95% of the distributions (2.5% - 97.5%) and the R^2 and

BR^2 statistics were calculated. The equations for calculating R^2, BR^2, and total bias are provided previously.

Calibration Parameter Adjustments

The irrigation parameterization was important for both accurate simulation of flow and chemical. The amount of daily irrigation was set at 8.89 mm, however the number of days of irrigation per month varied based on the time of year.

Subsurface flow parameters were also determined based on calibration to the daily observed flows. A subsurface flow component was necessary to simulate the constant baseflows that were observed in the Aliso Viejo monitoring dataset (*26*).

Conduit routing parameters were also adjusted (within reasonable limits) to achieve a slower hydrograph response. As will be shown in the results section that follows, the hydrograph timing is good, but still a bit too fast. Further adjustment of routing parameters would have brought some parameters to unrealistic levels. It is likely that the absence of catch basins in the model, which can serve to attenuate flows, is one reason why the simulated flows had a faster response than the observed flows.

The fraction of impervious surfaces (patios/walkways and foundation perimeter other than the driveway) draining to the stormwater system versus the adjacent lawn was adjusted from an initial estimation of 20% to stormwater system and 80% to lawns to values of 10% to stormwater system and 90% to lawns. This adjustment improved both the simulated flows and the simulated bifenthrin predictions.

The initial washoff algorithm parameters obtained from the Pathway ID driveway calibration were applied to all of the impervious surfaces. With these washoff parameters and the other adjustments already mentioned, the resulting simulated annual mass load was about 45% too high. This over-prediction was considered to be excessive. At this point, a small adjustment to the washoff algorithm parameters was determined to be the most reasonable adjustment to the model. An adjustment to one of the driveway washoff parameters, Kp(0) was adjusted from an initial value of 2.0 to a value of 2.8. The other washoff algorithm parameters were not changed from the original Pathway ID calibration. As will be shown in the chemical simulation calibration results, this change resulted in a better, yet still conservative, simulation.

Hydrology Calibration Results

A graph of the observed and simulated daily flow from the Aliso Viejo outfall is shown in Figure 4. The daily flow time series shows a good match in both high flows occurring during storm events, as well as the low flows that vary seasonally throughout the year. The low flow periods are driven by the irrigation returning to the stormwater system through surface runoff and subsurface drainage. The goodness-of-fit statistics for the daily and hourly flow calibrations are summarized in Table VII and confirm that the model simulation of flow is very close to the observed, particularly for the daily flows.

Table VII. Summary of Flow Calibration Statistics, 10/1/2007 – 9/30/2008

Flow Time Step	*Total Flow Bias*	*R^2*	*NSE*
Daily	0.98	0.85	0.83
Hourly	0.98	0.64	0.57

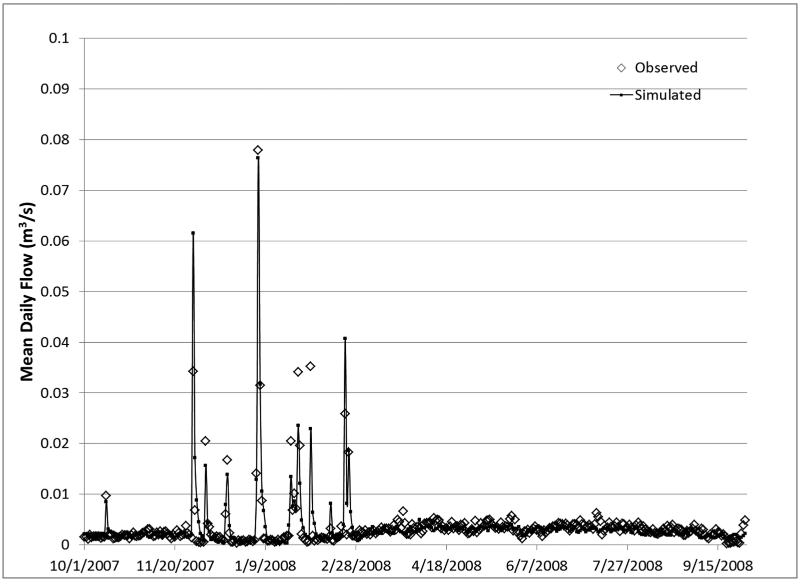

Figure 4. Observed and Simulated Daily Flow from Aliso Viejo Outfall.

Chemical Calibration Results

The objective of the bifenthrin calibration was to match the cumulative distribution of daily total water concentration and match the total annual mass load from the stormwater outfall. In addition, an effort was made to keep the calibration "conservative," in that a modest over-prediction of total mass load and high percentile concentrations was deemed desirable. Several graphs show the results of the calibration, looking at both bifenthrin concentration and mass. It should be noted that the SWMM predictions of chemical concentration and load represent total water (the sum of soluble and sorbed phases) chemical. SWMM does not have any mechanism for partitioning between chemical phases. Overall, the highest simulated concentrations are greater than the highest observed concentrations. Figure 5 compares the cumulative distributions of the observed and simulated concentrations. In Figure 5, the highest percentile concentration shown (97.5%) is greater for the simulated than the observed; however, all other percentiles are slightly lower for the simulated than the observed. Agreement between simulated and observed concentrations was targeted at the higher percentiles. A portion of the variability between the observed and simulated concentration percentiles can be attributed to comparison of a continuous time series of daily average simulated concentrations with a smaller sample of observed concentrations taken at a discrete time window during a sampling day. In Figure 6, the cumulative bifenthrin mass load as a function of time is plotted. The curves follow each other quite well, with the simulated cumulative mass load for the year ending about 10% higher than the observed.

The goodness-of-fit statistics for the bifenthrin calibration are provided in Table VIII. The statistics show that the total annual simulated mass bias is 10% above the observed. Also, the BR^2 value is very close to the R^2 value, indicating that the slope of the least squares linear regression line is very close to 1. The high value of BR^2 can be partly attributed to the close agreement between the observed and simulated concentrations at the 95th and 97.5th percentiles.

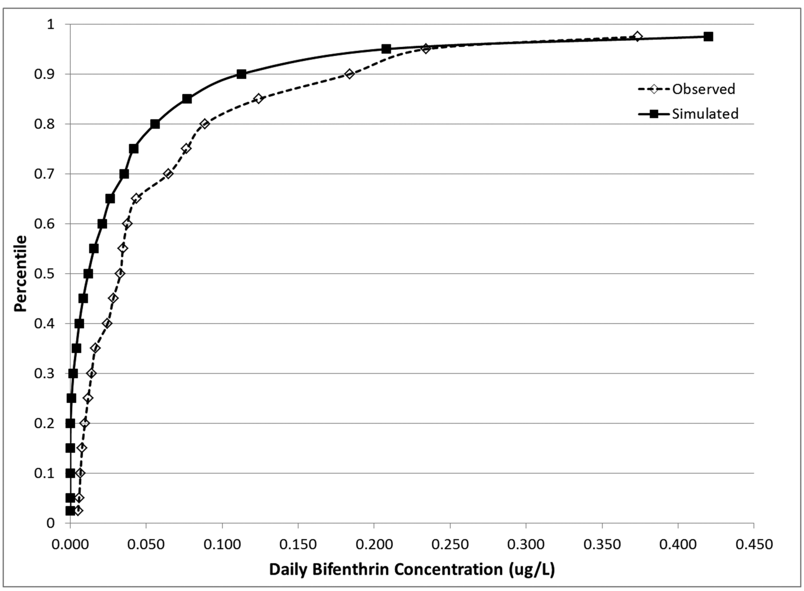

Figure 5. Observed and Simulated Cumulative Distribution of Bifenthrin Concentrations.

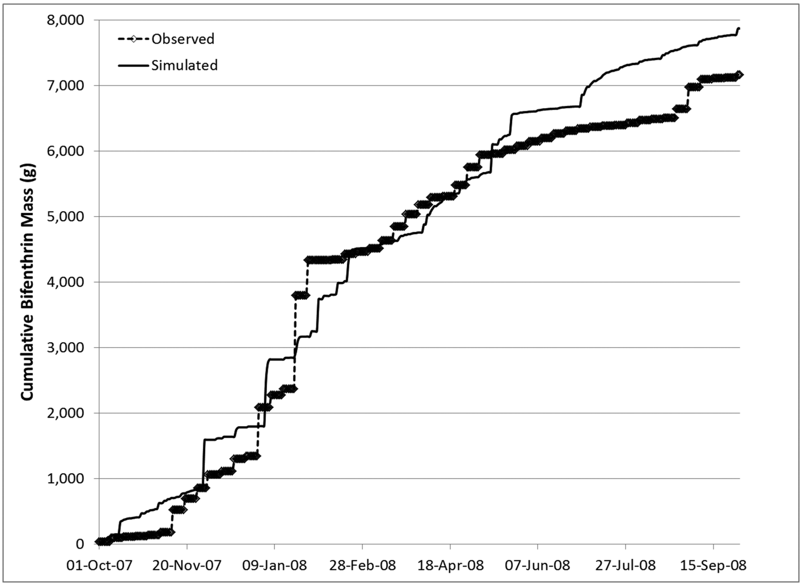

Figure 6. Observed and Simulated Cumulative Bifenthrin Mass Load, 10/1/2007 − 9/30/2008.

Table VIII. Bifenthrin Calibration Goodness-of-Fit Statistics

Bifenthrin Chemical Parameter	*Total Mass Bias*	R^2	BR^2
Total Cumulative Mass	1.10	N/A	N/A
Daily Concentration Distribution	N/A	0.95	0.94

Overall, the objective of achieving a modestly conservative calibration that matches both the total annual mass load and the concentration distribution was achieved. While the simulated bifenthrin concentrations for the lower end of the concentration distribution are under-predicted, we are ultimately interested in predicting pyrethroid concentrations in a receiving water body (pond). The longer duration (chronic) concentrations in a receiving water will be most heavily dependent upon the total pyrethroid load entering the pond. Therefore, the over-estimation of the total annual load should reduce the likelihood that chronic concentrations are under-predicted. Based on this bifenthrin calibration, the urban residential scenario developed for the Aliso Viejo neighborhood could now be applied to simulate additional, regionally specific parameterizations (i.e. combinations of pyrethroid use and weather parameters).

Model Application

The purpose in developing and calibrating an urban residential model scenario was so that it could be then modified to represent different pyrethroid use practice assumptions and different climate input regimes. The anthropogenic characteristics of the Aliso Viejo neighborhood, as quantified by the housing density analysis, indicated that the occurrence of potential pyrethroid use sites is very high in this neighborhood compared to others across the United States (88th percentile in terms of housing density). In this section, the coupling of the SWMM model with the AGRO-2014 receiving water model (*16*) will be introduced. In addition, the input data required to take the high vulnerability Aliso Viejo neighborhood and modify it to represent six additional regional pyrethroid use patterns and climate combinations will be presented. These new SWMM-AGRO model parameterizations will generate estimated environmental concentrations (EECs) in urban receiving waters to understand the relative vulnerabilities of California and six other regional locations for which pyrethroid use and associated climate data are available.

Linkage of SWMM with AGRO-2014

The runoff conceptual model development, implementation in SWMM, and calibration was the focus of the Model Development section. The SWMM model's strength is in the prediction of runoff and chemical loadings generated throughout heterogeneous urban watersheds over time. However, SWMM's representation of the persistence and fate of pesticides in aquatic environments is insufficient for prediction of pyrethroid behavior. For this reason, the AGRO-2014 model (*16*) was linked to the SWMM model to serve as the receiving water body. With this coupled model structure, EECs for chemical dissolved in the water column and benthic layer pore water, and adsorbed to benthic layer sediment of an urban water body can be predicted.

Urban Residential Regionalization Descriptions

The urban residential scenario developed for the purpose of SWMM model calibration was representative of California use of bifenthrin alone under historical application practices. Additional SWMM-AGRO model parameterizations were developed to represent an "all pyrethroid" historical application practices condition for California and current pyrethroid application practices for California, as well as use data and associated weather data inputs for six additional regions of the United States. The additional six geographic regions correspond to regions with recent survey results for pyrethroid use and application practices that have been interpreted for use in urban exposure model parameterizations (*30*, *31*). The historical practices and current practices model conditions are described in the following sections.

Historical Pyrethroid Application Practices

A historical application practice model parameterization was developed for California only. Many aspects of the California historical practices parameterization were adopted directly from the model calibration input set, including the practice of applying pyrethroids in a continuous, broad band to foundation perimeter, driveway, and garage wall areas without restricting the spray onto narrow bands along cracks and crevices, as required by the current label. This historic use practices parameterization results in a continuous 1.52 m band application around the entire foundation perimeter. It also includes a continuous 0.61 m band on the vertical garage door and adjacent house wall at the top of the driveway. Applications to impervious surfaces away from the house foundation (patios/walkways and driveway) are less restrictive, and result in 10% of the surface area being treated. The one notable difference between the calibration and the historic parameterization for the purpose of exposure prediction is that the extent of pyrethroid use is expanded in the exposure assessment. For example, in the calibration parameterization, bifenthrin accounted for 25.7% of the foundation perimeter treatments (see Table V), which is 44.5% of total pyrethroid use on foundation perimeters (see Table VI of Winchell (*31*),). In the California historical practices parameterization, bifenthrin use (and all other actives) will be assumed equivalent to all of the pyrethroids combined, resulting in bifenthrin (and all other actives) use on 57.8% of the foundation perimeters. The main purpose of the California historical practices parameterization is to establish a baseline for EECs. Because the assumptions here are based on pyrethroid labels that are no longer in practice, the predictions are not relevant to current estimations of exposure risk.

Current Pyrethroid Application Practices

Regional urban residential model parameterizations representative of current pyrethroid application practices were created for California and the Northwest, North Central, Northeast, Mid-Atlantic, Southeast, and South Central regions of the United States. The pyrethroid use characteristics for these seven regions are described in the report by Winchell (*31*). Outside of California, the data on pyrethroid use came from a survey that targeted specific metropolitan areas within each geographic region (*30*), (see Figure 7).

In 2010, the US EPA began approving revised pyrethroid labels (*32*, *33*) that restrict treatments of hard surfaces to crack and crevice applications. Product packages bearing these revised labels have gradually been making their way into the marketplace since then. The recent Pathway ID study (*2*, *34*) quantified the differences in pyrethroid applications (surface area and mass) and in runoff losses between the historical and current application practices. The study showed that for the use sites impacted by the change in practices (the driveway and garage wall), both the total runoff mass loss and the runoff mass loss as a fraction of mass applied were reduced. The reduction in the runoff loss as a fraction of applied indicates that the washoff process from crack and crevice areas differs to that from broader, smooth hard surfaces. Although a reduction in mass applied and a change in local washoff behavior appear to both act beneficially in reducing pyrethroid runoff losses under the current labels, only the reduction in mass applied will be addressed in the development of the current practices SWMM parameterization.

Figure 7. Metropolitan Areas Surveyed and Associated Geographic Regions. (from Winchell (31)).

In order to represent the reduction in applied pyrethroid mass under the current application practices in the calibrated Aliso Viejo scenario, reductions in the model parameters representing the fraction of the use site surface area being treated were made. The landscape elements in the SWMM model that required reductions in the treated surface area were the impervious foundation perimeter elements, the driveway elements, the garage door/wall, and the patio/walkway elements. The reduction factors in surface area treated were calculated for each of the landscape elements as follows:

1. Foundation perimeter, top of driveway: Under historical practices, a 1.52-m band at the top of the driveway was treated. Under current practices, only a 5-cm band along the expansion joint at the very top of the driveway is applied. This equates to a reduction factor of 2/60, or 0.033. This same 30x reduction of mass applied was reported in the Pathway ID study (*2*, *34*)
2. Garage door/wall: Under historical practices, a 0.61-m band along the entire garage door and adjacent wall was treated. Under current practices, application to the garage door itself is not permitted. Based on the Pathway ID study site, the 4.88 m garage door width plus 1 foot of the house wall on either side were treated under historical practices (5.49 m total). New practices would treat only a 0.3 m width on either

side of the garage door (0.61 m total). This equates to a reduction factor of 2/18, or 0.11.

3. Lower driveway, patio/walkway, other foundation perimeter impervious surfaces: These use sites were not explicitly evaluated in the Pathway ID study. Therefore, an estimation of the reduction in treated area for these SWMM landscape elements was made based on the following assumptions:

    a. Typical driveway is 5.49 m wide by 6.1 m long (33.46 m^2)
    b. Historical practices treat 10% of the lower driveway (area below perimeter treatment) equivalent to 2.51 m^2
    c. Assuming the area applied is the driveway edge, down to sidewalk, the total length is estimated as 6.7 m (3.35 m each edge); the equivalent spray width to equal the treated area estimate is 0.37 m.
    d. Assuming current practices will apply in a 50.8 mm (0.05 m) width (same as upper driveway), the ratio in sprayed widths is 0.14 (0.05 m / 0.37 ft)
    e. This equates to a treated area reduction factor of 0.14.

Model Regional Parameterization Inputs

This section will outline the development of specific inputs and parameters for the various SWMM-AGRO simulations. These inputs will include climate and irrigation, pyrethroid use and applications, and pyrethroid environmental fate.

Climate and Irrigation

The SWMM-AGRO simulations for each regional parameterization required climate inputs (precipitation, temperature, and evaporation) and irrigation inputs. A city within each geographic region was selected to represent the climate for the region. The cities chosen were ones included as the targeted metropolitan areas associated with each region. A 30-year time series of hourly precipitation and daily temperature was developed for each city for the period of 1/1/1981 – 12/31/2010. The sources for the hourly precipitation data and temperature data were the National Climatic Data Center (NCDC) Hourly Precipitation and Hourly Global datasets accessed from the NCDC online data mapping tool (*40*). In addition, monthly average evaporation data was needed for each regional parameterization. The collection of daily evaporation data at climate stations has become much less common in recent years. Therefore, historical data (1961 – 1990) from EPA's SAMSON weather dataset was used to calculate the average monthly evaporation. Because the evaporation values required by the SWMM model are free surface evaporation and not pan evaporation, the SAMSON evaporation values were multiplied by a pan factor. Pan factors for each region were estimated from Figure 5.9 in the PRZM 3.12.2 manual (*41*).

A seasonally varying irrigation schedule for the California scenario was developed during the initial model calibration. The irrigation frequency per month was in part calibrated to match the observed flow data. As was evident in the flow calibration discussion, over-irrigation in the Aliso Viejo neighborhood is the cause for sustained "dry weather" baseflows observed at the stormwater outfall. The adjustment of an irrigation schedule for the additional six regional parameterizations was conducted such that the difference in irrigation practices was only due to climate differences and not due to cultural differences. Therefore, the amount of excess irrigation (irrigation beyond the needs of the grass) applied in California was assumed to also be applied in the other six regions. A summary of the average annual precipitation, evapotranspiration, and irrigation is provided in Table IX.

Table IX. Regional Climate

Region	*City*	*Avg. Precip. (mm/yr)*	*Avg. ET (mm/yr)*	*Irrigation (mm/yr)*
California	Irvine	327.2	1258.1	1582.4
Southeast	Orlando	1265.7	1305.6	657.9
South Central	Houston	1235.7	1237.0	595.6
Northwest	Seattle	927.4	825.8	773.4
North Central	Chicago	882.9	984.8	462.3
Northeast	Boston	1081.8	1040.9	577.9
Mid-Atlantic	Philadelphia	1017.3	1063.0	604.5

Pyrethroid Application Extent and Frequency

The extent of pyrethroid use is an important differentiator between the regional parameterizations being developed. As has been referred to at several points in this report already, the analysis of regional pyrethroid use characteristics by Winchell (*31*) provided a comprehensive compilation of the critical pyrethroid use information necessary to parameterize urban residential exposure model simulations. The **Urban Scenario Development** section of this report provided an example of how the data reported in Winchell (*31*) was used to derive the parameters necessary for the SWMM model for the California bifenthrin-specific calibration scenario.

The same process was followed in the development of the additional regional pyrethroid use data sets, with the following differences:

1. The new historical and current practice parameterizations assumed a use extent for each active ingredient equivalent to that of all pyrethroids combined.
2. For the regions outside of California, each landscape element is split up into only two portions ("treated" and "untreated"), whereas the California parameterizations have the landscape elements split into "untreated", and treated on a "6-week" and "12-week" cycle.

The key data tables from Winchell (*31*) from which data were extracted to calculate the fraction of each landscape element treated were as follows:

1. Table I: California, fraction of households using outdoor pest control products
2. Table IV: All regions, other than California, fraction of households using outdoor non-plant insecticide and fraction using lawn/garden insecticides
3. Table VII: California, summary of the fraction of use sites treated at different frequencies
4. Tables VIII – XIII: All regions, other than California, summary of the fraction of use sites treated by region

The last piece of data required in the calculation of the fraction of each SWMM landscape element treated is the percent of the use site surface area that is treated. For historical application practices, the assumptions for these values were discussed in earlier section on **Urban Scenario Development**. For current application practices, the logic for the assumptions regarding the surface area treated reductions was provided in the section, **Current Pyrethroid Application Practices**. Table X provides a summary of the fraction of households receiving outdoor insecticide treatments for different types of use sites for the seven geographic regions. California has the highest fractions of households treated, followed by the Southeast and South Central regions.

For each region and use site, the number of applications per year and the fraction of use sites treated with pyrethroids (of the households fraction receiving outdoor insecticide treatments) is summarized in Table XI, XII, XIII, and XIV for foundation perimeters, driveways (away from garage door/wall), patios/walkways, and lawns/landscape areas. Note that California is separated into portions of households receiving treatments at 4 times per year and at 8 times per year. Overall, California has a higher fraction of use sites treated than the other regions. In addition, the fraction of foundation perimeters and lawn/landscape areas receiving pyrethroid treatments is higher than the driveway and patio/walkway use sites away from the garage door and foundation wall. The variability across geographic regions is believed to be largely attributable to differences in pest pressure. These data were used as inputs in the regional parameterizations of the SWMM model.

Table X. Fraction of Households Treated with Outdoor Insecticide

Region	*Fraction Households Treated (Foundation Perimeter, Driveways, Patios/Walkways)*	*Fraction Households Treated (Lawns/Landscape Areas)*
California	0.759	0.759
Southeast	0.584	0.633
South Central	0.584	0.633
Northwest	0.484	0.495
North Central	0.444	0.554
Northeast	0.472	0.543
Mid-Atlantic	0.472	0.543

Table XI. Foundation Perimeter Fraction of Use Sites Treated and Application Frequency

Region	*Applications per Year*	*Fraction of Use Sites Treated*
California	4	0.283
California	8	0.295
Southeast	5	0.536
South Central	5	0.548
Northwest	4	0.534
North Central	4	0.555
Northeast	4	0.561
Mid-Atlantic	4	0.46

Table XII. Driveway Fraction of Use Sites Treated and Application Frequency

Region	*Applications per Year*	*Fraction of Use Sites Treated*
California	4	0.274
California	8	0.286
Southeast	4	0.08
South Central	4	0.208
Northwest	3	0.11
North Central	4	0.118
Northeast	3	0.145
Mid-Atlantic	4	0.105

Table XIII. Driveway Fraction of Use Sites Treated and Application Frequency

Region	*Applications per Year*	*Fraction of Use Sites Treated*
California	4	0.274
California	8	0.286
Southeast	4	0.182
South Central	4	0.265
Northwest	4	0.22
North Central	4	0.177
Northeast	3	0.189
Mid-Atlantic	4	0.15

Table XIV. Driveway Fraction of Use Sites Treated and Application Frequency

Region	*Applications per Year*	*Fraction of Use Sites Treated*
California	4	0.426
California	8	0.122
Southeast	4	0.473
South Central	4	0.422
Northwest	3	0.253
North Central	3	0.407
Northeast	3	0.523
Mid-Atlantic	3	0.41

Pyrethroid Application Rate

Application rates for the seven pyrethroids simulated with urban residential uses were obtained from a Master Label compilation report completed by Collier (*1*). In cases where both "residential" and "non-residential" rates were reported for non-agricultural uses, the residential rates were chosen. The residential "broadcast, lawn" rates were assumed to occur for the house lot lawn/landscape use sites, and the residential "outdoor perimeter" rates were assumed to apply for the foundation perimeter, driveway, and patio/walkway applications. A summary of the application rates used for each of the pyrethroids simulated is provided in Table XV.

Table XV. Residential Application Rates Used in Urban Parameterizations

Active	*Use*	*Rate (kg/ha)*
Bifenthrin	Perimeter	0.224
Bifenthrin	Lawn/Broadcast	0.224
Cyfluthrin	Perimeter	0.430
Cyfluthrin	Lawn/Broadcast	0.216
Cypermethrin	Perimeter	1.008
Cypermethrin	Lawn/Broadcast	0.762
Cyhalothrin (lambda)	Perimeter	0.336
Cyhalothrin (lambda)	Lawn/Broadcast	0.134

Continued on next page.

Table XV. (Continued). Residential Application Rates Used in Urban Parameterizations

Active	*Use*	*Rate (kg/ha)*
Deltamethrin	Perimeter	0.235
Deltamethrin	Lawn/Broadcast	0.235
Esfenvalerate	Perimeter	0.213
Esfenvalerate	Lawn/Broadcast	0.213
Permethrin	Perimeter	1.949
Permethrin	Lawn/Broadcast	0.974

Pyrethroid Environmental Fate

The primary environmental fate parameters required by AGRO-2014 are summarized in Table XVI for each of the seven pyrethroids evaluated. The values reported in the table were obtained from the best available sources including EPA registration reviews, aquatic ecological and drinking water assessments and other documents (*42*). The Koc values determined by the Solid Phase Microextraction (SPME) method of analysis were selected as model inputs based on a Pyrethroid Working Group (PWG) evaluation of the most appropriate inputs for exposure modeling at the Tier II+ level of assessment (*15*).

Table XVI. AGRO Model Pyrethroid Environmental Fate Parameters

Pesticide	*Solubility (mg/L)*	*Sediment Koc (mL/g)*	*Aerobic Aquatic T½ (day)*	*Anaerobic Aquatic T½ (day)*
Bifenthrin	1.4E-05	3,487,917	189	528
Cyfluthrin	2.3E-03	2,955,775	21.9	40
Cypermethrin	4.0E-03	1,629,497	16.9	128
Deltamethrin	2.0E-04	2,564,467	46.1	96.7
Esfenvalerate	6.0E-03	3,581,361	54.4	77.9
Lambda Cyhalothrin	5.0E-03	2,941,300	56.2	100
Permethrin	5.5E-03	3,853,152	29.9	166

Notes: [a.] Soil organic carbon-water partition coefficient. [b.] Half-life.

Results and Discussion

The coupled SWMM-AGRO-2014 model was run for eight different regional parameterizations and seven different pyrethroids. The eight parameterizations included one that represented historical label specifications (California, historical) and seven that represented current label specifications (California, Southeast, South Central, Northwest, North Central, Northeast, and Mid-Atlantic). Each simulation used a 30-year weather time series and annual maximum EECs were compiled. The EECs for the different regions will be discussed, followed by a comparison of the different pyrethroids.

Comparison of Predicted Pyrethroid Concentrations for Different Regions

A comparison of the annual maximum 24-hour, 21-day, and annual bifenthrin EEC distributions for the seven regional current application practices simulations and the California historical application practices simulation are shown in Table XVII. The California current parameterization dissolved water column and sediment EECs are lower than those associated with the historic pyrethroid label parameterization by a factor of approximately 12 to 13, depending on the exposure duration. Of the current application practices simulations, the California parameterizations had the highest 1 in 10-year EECs for the dissolved water column, with the exception of the 24-hour duration where the Southeast parameterization had slightly higher EECs. The South Central parameterization EECs were third highest for the dissolved water column, followed by the Northwest and North Central (which were fairly close to one another) and then the Northeast and Mid-Atlantic. As an example, for bifenthrin current conditions, the 24-hour 1 in 10-year dissolved water column EECs ranged from a high of 0.00114 (µg/L) in the Southeast down to a low of 0.00046 (µg/L) in Mid-Atlantic.

The sediment EECs also show a similar pattern across all the seven pyrethroids to that observed for the dissolved water column EECs. The benthic EECs show less variability across the different parameterizations (generally within a factor of two) than do the dissolved water column EECs. The historic CA runs provide the highest sediment concentrations by a factor of approximately 12. For the current practice parameterizations, the California parameterization results in the highest EECs, followed by the Southeast and the South Central regions. The range in benthic sediment 1 in 10-year 21-day EECs for bifenthrin under the current conditions scenario ranged from a high of 8.09 (µg/kg) in California down to 4.29 (µg/kg) in the Mid-Atlantic.

The ranking of parameterizations by the dissolved water column EECs can be attributed to a combination of the extent and frequency of applications, and the climate. Pyrethroid use is highest and most frequent in California, which is the most significant driver of its higher vulnerability. Although use was less in the other regions, the substantially higher rainfall in regions like the Southeast and the South Central nearly compensated for this difference in use. The relatively low water column EECs for regions like the Northeast and the Mid-Atlantic can be attributed to both lower amounts of use and less rainfall than locations in the south.

Looking across the entire dissolved water column EEC distributions in Figure 8, the California EECs are around 25% higher than the region with the next highest EECs (Southeast) over the lower 90% of the distribution. The Mid-Atlantic EECs are the lowest, and are consistently around 50% less than the California EECs. The full distributions of benthic sediment 21-day EECs are shown in Figure 9, and the EEC distribution is again highest for California; however, in the benthic compartment, EECs for the North Central region are generally higher than the Southeast and South Central regions, with the Northeast nearly as high. The Northwest and Mid-Atlantic regions have the lowest benthic sediment concentration. The colder temperatures in the North Central and Northeast simulations can partly explain the reason for the higher concentrations observed for those regions compared to the Southern regions. With most of the pyrethroid material stored in the benthic layer, the slower degradation associated with colder temperatures becomes more important with slowly degrading pyrethroids like bifenthrin.

Table XVII. Bifenthrin, Dissolved Water Column, and Benthic Sediment 1 in 10-Year EECs

	1 in 10-Year Dissolved Water Column Concentrations (µg/L)		
Urban Scenario	***24-hour***	***21-day***	***Yearly***
California, Historical	0.01289	0.00697	0.00308
California, Current	0.00109	0.00058	0.00024
Southeast , Current	0.00114	0.0004	0.00012
South Central, Current	0.00088	0.00036	0.00012
Northwest, Current	0.00067	0.00028	0.00008
North Central, Current	0.00066	0.00029	0.0001
Northeast, Current	0.00059	0.00026	0.00008
Mid-Atlantic, Current	0.00046	0.00023	0.00009
	1 in 10-Year Benthic Sediment Concentrations (µg/kg)		
Urban Scenario	***24-hour***	***21-day***	***Yearly***
California, Historical	99.35	99.24	94.93
California, Current	8.11	8.09	7.63
Southeast , Current	4.89	4.87	4.57
South Central, Current	4.95	4.94	4.59
Northwest, Current	4.37	4.36	4.21

Continued on next page.

Table XVII. (Continued). Bifenthrin, Dissolved Water Column, and Benthic Sediment 1 in 10-Year EECs

	1 in 10-Year Benthic Sediment Concentrations (µg/kg)		
Urban Scenario	***24-hour***	***21-day***	***Yearly***
North Central, Current	5.47	5.45	5.22
Northeast, Current	4.81	4.79	4.67
Mid-Atlantic, Current	4.31	4.29	4.16

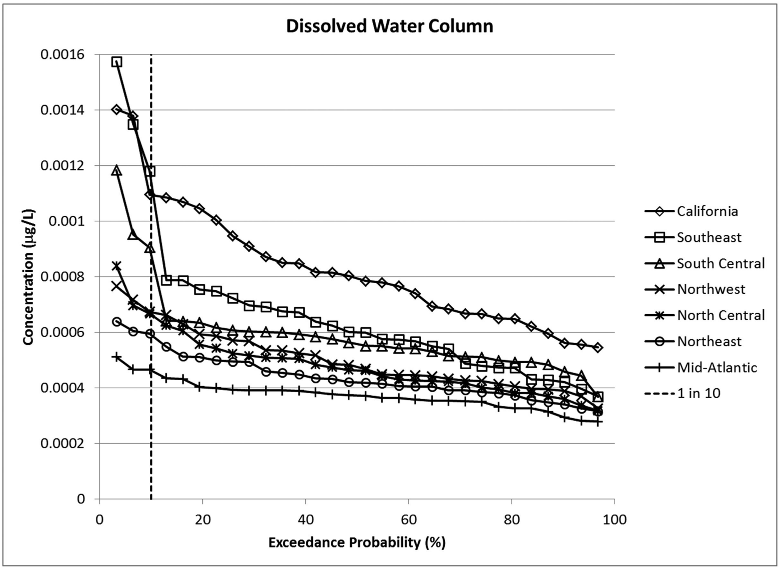

Figure 8. Annual Maximum 24-Hour Bifenthrin Dissolved Water Column EEC Distributions, Seven Regional Parameterizations Compared.

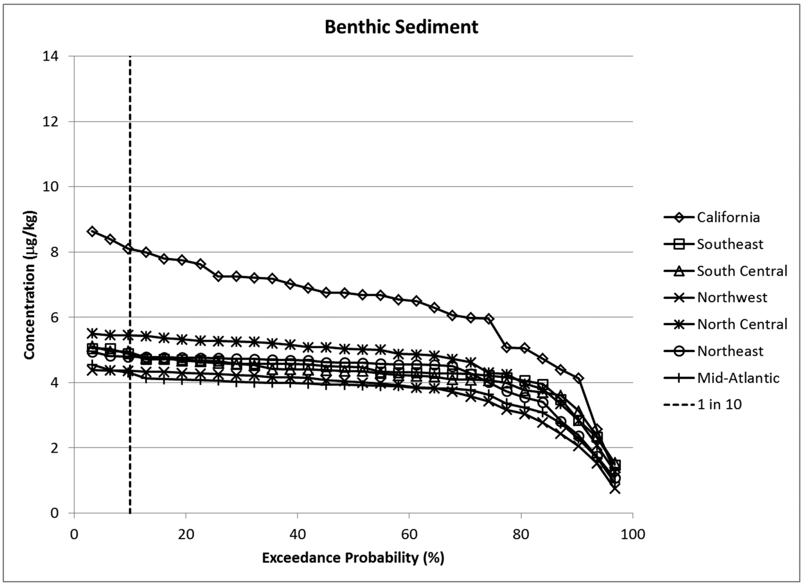

Figure 9. Annual Maximum 21-Day Bifenthrin Benthic Sediment EEC Distributions, Seven Regional Parameterizations Compared.

Comparison of Predicted Concentrations for Different Pyrethroids

The distribution of annual maximum EECs for the California current application practices scenario for all pyrethroid active ingredients is shown in Figure 10. Recall that the extent and frequency of applications was the same for all active ingredients, and was equal to the combined market share of all the pyrethroids. The differences in the magnitudes of the EECs are a function of the application rates and the environmental fate properties of the individual pyrethroids. As shown in Figure 10, permethrin and cypermethrin have the highest EECs, nearly an order of magnitude higher than esfenvalerate and bifenthrin. Another characteristic of the distributions shown for all of the active ingredients is that the largest change in annual maximum EECs occurs near the 1 in 10-year annual value. This is likely due to rare events that generate excessive runoff amounts, including significant contributions from pervious lawn areas.

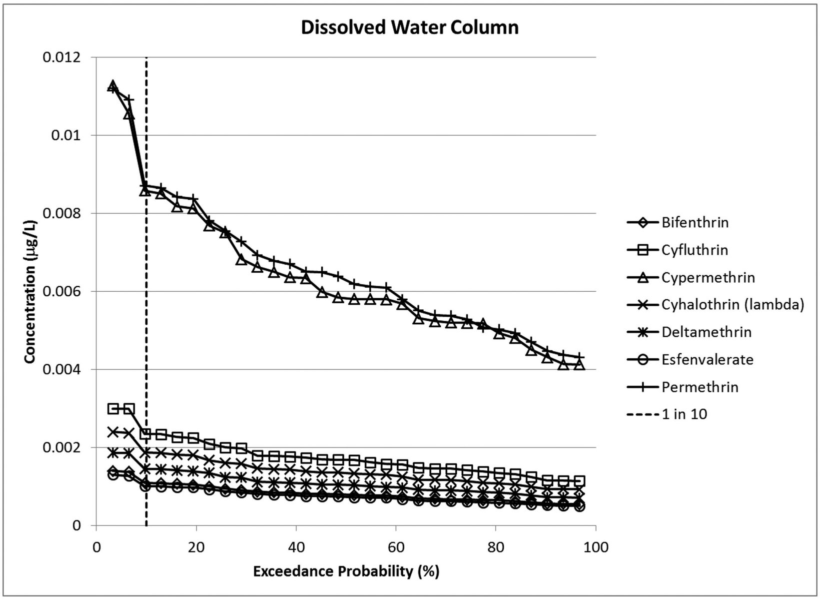

Figure 10. Annual Maximum 24-Hour Dissolved Water Column EEC Distributions, Seven Pyrethroid Active Ingredients Compared, California Current Conditions.

Interpretation of Current Application Conditions Simulations

The difference in EECs between the California historical practices parameterization and the California current practices parameterization provides another informative comparison. For all seven of the pyrethroids modeled, the reduction in the dissolved water EECs ranged from a factor of 11.8 to 12.9, with the higher reductions for the annual duration EECs. The parameterization of the current conditions was designed to simulate the reduction in the surface area of impervious use sites treated under the current practices, but did not address the change in washoff behavior of pyrethroids associated with a limitation to crack and crevice applications. In the Pathway ID study the total reduction in annual pyrethroid mass runoff from the driveway use site between the historic and current practices was a factor of 256 (*2*, *34*). While there was a factor of 30 reduction in the amount of pyrethroid applied under the current practices, there was an additional factor of 8.5 reduction as a result of where the pyrethroid was applied. This implies that pesticide washes off crack and crevice application locations less readily than flat surfaces of the same area.

Additional data comparing the mass loads from the California historic parameterization to the California current parameterization is provided in Table XVIII. The "Neighborhood Bifenthrin Runoff" represents the actual amount of chemical estimated to reach the stormwater outfall, which shows a 12.6x reduction in the total mass, very similar to the magnitude of the reduction of EECs that was noted for all the pyrethroids. The "Neighborhood Bifenthrin Washoff" is different from the "Runoff" in that it represents the amount of chemical that washes off the treated surface, but which does not necessarily reach the outlet of the watershed (due to run-on to pervious surfaces). In other words, under historic conditions, 1.48 kg of pyrethroid are moved from where it was applied but, of this only 0.67 kg (the neighborhood runoff value) enters the storm drain system. The neighborhood washoff is reduced by a factor of 8.4 under the current practices, which is proportional to the reduction in treated use site surface areas across the entire neighborhood. The reduction in driveway washoff was found to be a factor of 30.8, very nearly the same as the 30x reduction in treated surface area.

Table XVIII. Bifenthrin Mass Load Comparisons for California Historic and Current Parameterization

Parameterization	***Neighborhood Bifenthrin Runoff (kg)[a)]***	***Neighborhood Bifenthrin Washoff (kg)[b)]***	***Upper Driveway Bifenthrin Washoff (kg)***
Historic Label	0.67	1.48	0.27
Current Label	0.05	0.18	0.01
Reduction Factor	12.6	8.4	30.8

Notes: [a)] "Runoff" as measured at the outlet of the stormwater system. [b)] "Washoff" from treated surfaces … some of which infiltrates into adjacent pervious areas (lawns).

Several conclusions can be drawn from the data in Table XVIII that provide some context to the EEC predictions presented in this section. First, the overall mass washoff reduction of 8.4x led to EEC reductions of a factor of around 12x. The maximum reduction in washoff mass in the neighborhood model occurs for the upper driveway, where the 30x reduction in surface area treated leads to a 30x reduction in washoff. However, as mentioned above, the new label requirements not only reduce the mass applied/area treated, they ALSO position the chemical such that its propensity for runoff is reduced by around 8.5 fold. It is important to note that none of the current parameterizations incorporate the expected impact of this reduced washoff potential due to the new label requirements. This contributes to an over-estimation of likely EEC's in this urban scenario and associated parameterizations by around a factor of 8.

Conclusions

This report has presented the conceptualization, development, and application of a novel approach for simulating fate and transport of outdoor applied pesticides in a residential urban environment. One of the critical factors that facilitated the development of this urban modeling approach was the extensive monitoring of the high density, high pyrethroid use urban watersheds in California (*25*). The Aliso Viejo neighborhood that was selected from that study proved to be invaluable in both providing a better understanding of the off-target transport of residential applied pyrethroids, as well as serving as the basis for developing an urban residential model scenario and multiple associated regional parameterizations. Without the monitoring data at the Aliso Viejo site to calibrate and validate the SWMM-based pyrethroid runoff model component, the approach for development of new urban residential exposure model scenarios would have looked very different.

A conceptual model of pyrethroid applications and off-site transport in an urban residential environment was presented. The conceptual model was largely based on recent nationwide surveys of pyrethroid residential use practices (*29–31*). In addition, recent field studies that have sought to better understand the dominant pathways of pyrethroid transport from use sites to stormwater conveyance systems that discharge to urban receiving waters (*2*, *34*) have provided critical information. A significant realization during the conceptual model development was that the complexities of the multiple types of pyrethroid use sites in an urban residential environment and the temporal dynamics of the transport processes require that a watershed model capable of simulating hydrologic transport processes from heterogeneous interconnected surfaces must be implemented in order to meet the conceptual model requirements. The SWMM model currently in active use by US EPA, local governments, and industry for stormwater assessments (*4*) was determined to be the best available tool to meet these requirements.

The Aliso Viejo calibration scenario was designed to evaluate the model performance against observed flow and chemical concentration and load data, and to adjust model inputs and assumptions if necessary. Bifenthrin was chosen as the pyrethroid used in calibration because of its frequent detections in the monitoring dataset. The calibration process helped to better define the contributions of irrigation to flow and chemical washoff in the neighborhood, and to better understand the hydrologic connectivity of impervious surfaces to the stormwater system. Overall, a strong agreement between observed and simulated flow and chemical mass and concentrations was achieved by the calibration.

Pyrethroid use data for seven different regions (California, the Southeast, South Central, Northwest, North Central, Northeast, and Mid-Atlantic) were developed based on a recent analysis of regional pyrethroid application extent and practices (*31*). For California, model parameterizations were developed for historical application practices, as well as for the current application practices required by recent label changes that limit treatment of many hard surface areas to crack and crevice applications. The parameterization of the current practices drew heavily upon the Pathway ID study (*2*, *34*) to derive appropriate reductions in the treated areas of each potential use site. The current application practices parameterizations were designed with the intention of being conservative, as they only accounted for a reduction in treated area and do not take into account reductions in mass transport due to changes in the washoff dynamics that were observed in the Pathway ID study.

The parameterizations for historical application practices for California and the current practices parameterizations for California and the six additional regions were simulated in SWMM and linked with the AGRO-2014 model to predict aquatic EECs for use in a pyrethroid environmental risk assessment. Simulations for seven pyrethroids (bifenthrin, cyfluthrin, cypermethrin, cyhalothrin (lambda), deltamethrin, esfenvalerate, and permethrin) were run for each regional use and climate parameterization. A highly conservative assumption was made regarding the extent of pyrethroid use since the inputs simulated that each individual pyrethroid had 100% of the current total pyrethroid market share. In other words, the EEC's reported here for each active ingredient assume that every pyrethroid application made in the entire residential area was made with that particular active ingredient. This means that the variability observed in EECs is dictated only by the differences in application rates and environmental fate parameters of each pyrethroid. The results of the simulations showed that, given current application practices, for the water column, the highest 96-hour EECs always occurred in the California parameterization, with the Southeast having slightly higher EECs for a portion of the 24-hour annual maximum exposure distribution. The Northeast and Mid-Atlantic parameterizations generated the lowest water column EECs. In the benthic layer, the highest EECs occurred for all exposure duration based on the California parameterization, with the Northwest and Mid-Atlantic parameterizations having the lowest EECs. Considering both the water column and benthic EECs, the California parameterization represented the worst case exposure scenario of the seven that were evaluated. The patterns seen in EECs across the different regional scenarios were consistent for all seven pyrethroids modeled.

A comparison between the California historic application and the California current application practices parameterizations demonstrated that the model inputs and assumptions that went into the current practices urban scenario were very conservative, and that the predictions of pyrethroid washoff and annual maximum EECs may be as much as a factor of 8 higher than what would be observed. Further extensive examples of conservatism in the model scenario parameterization were identified, leading to confidence that the simulated EECs over-estimate the potential for pyrethroid aquatic exposure.

The approach for simulating the fate and transport of pyrethroids in an urban residential environment presented in this report is the only approach to date (that the authors are aware of) that is capable of representing the complexities of application characteristics and transport processes that occur in an urban environment, coupled with a receiving water model capable of simulating pyrethroid behavior in a water body in the presence of suspended sediment. It reflects the best-available approach for assessing pyrethroid urban aquatic exposures and comparing the effects of recent label changes. We believe it also offers potential for more general application for aquatic exposure assessments for urban residential use of other classes of pesticides.

Acknowledgments

This work was sponsored by the Pyrethroid Working Group, composed of AMVAC Chemical Corporation, BASF Corporation, Bayer CropScience LP, Cheminova A/S, DuPont Crop Protection, FMC Corporation, Syngenta Crop Protection, Inc., and Valent U.S.A. Corporation. The authors would also like to acknowledge Dr. Russell Jones of Bayer CropScience and Dr. Paul Hendley of Phasera Ltd., who provided valuable ideas and expertise throughout this project. In addition, Dr. Darren Haver of the University of California South Coast Research & Extension Center was extremely helpful in providing Aliso Viejo flow data and insight. Finally, Dr. Yuzhou Luo of the California Department of Pesticide Regulation provided invaluable guidance in the implementation of his washoff algorithm into the SWMM model.

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Chapter 6

A Summary of Case Studies Designed To Determine the Influence of Multiple Stressors on Benthic Communities in Urban California Streams

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Bioassessment multiple stressor case studies using benthic macroinvertebrates were conducted concurrently with measurements of habitat metrics, metals and pyrethroids in order to determine which stressors were most important in influencing the condition of benthic communities in four urban wadeable California streams. These bioassessment multiple stressor annual studies were conducted in the following urban California waterbodies: Pleasant Grove Creek from 2006 to 2008; Kirker Creek in 2006 and 2007; Arcade Creek from 2009-2011; and Salinas streams from 2009 to 2011. Summary results showed the following: (1) analysis of the 3 year data sets for Pleasant Grove Creek showed significant relationships ($\alpha < 0.01$) with benthic metrics and both habitat metrics and metals but not pyrethroids; (2) analysis of the 2 year data sets for Kirker Creek showed that habitat and metals have stronger statistical relationships ($\alpha <0.01$) with benthic metrics than pyrethroids; (3) analysis of the 3 year data sets for Arcade Creek showed more significant relationships ($\alpha <0.01$) with benthic metrics and habitat metrics than with metals or pyrethroids; and (4) analysis of the 3 year data sets for Salinas streams showed that habitat and not metals or pyrethroids was the only stressor to show a significant relationship ($\alpha <0.01$) with benthic metrics. In summary, physical habitat metrics were the most important factors influencing benthic community condition in four urban California streams while metal concentrations were the second most important factors influencing benthic community conditions in these streams. Pyrethroids were the least important factors influencing benthic community conditions in these urban streams and for two of these streams (Pleasant Grove Creek and Salinas streams) pyrethroids were not a significant stressor to benthic communities when considered in a multiple stressor analysis.

Introduction

Urbanization has been reported to result in a major negative impact on aquatic ecosystems. Large areas of impervious surfaces and high levels of hydraulic connection of impervious surfaces to streams, through stormwater pipes or drains, can lead to major negative impacts on urban/residential stream biological communities (*1*). The above two two characteristics of urban streams cause decreased levels of evapotranspiration and infiltration and rapid delivery of water to these lotic waterbodies. Other investigators have reported that human activities in the urban environment can degrade aquatic ecosystems by altering one or more of the following principal groups of attributes: water or sediment quality; habitat structure; flow regime; energy source (food); or biotic interactions (*2*). Rhodes (*3*) reported that urbanization specifically leads to fundamental changes in the hydrologic, hydraulic, erosional, and depositional characteristics of fluvial systems causing increased channel instability. Urbanization in the western United States was reported to produce lower Index of Biotic Integrity (IBI) scores than activities such as logging and larger cities were reported to have lower IBI scores than smaller cities (*4–6*). States such as California, that have experienced expanded population growth in many urban and residential areas, provide an example of multiple stressors in aquatic environments that can contribute to degradation. Therefore, studies designed to evaluate the potential impact of multiple stressors in these aquatic environments are needed.

Common approaches used to assess impairments in waterbodies are chemical monitoring, toxicity testing, and biological assessments (bioassessment). Bioassessments are particularly useful in providing an observed response to environmental stressors because the status and condition of resident biological communities are used to evaluate the quality of an aquatic system. Bioassessment, formally defined as a quantitative survey of physical habitats and biological communities of a water body, is a well established approach for determining the ecological condition of stream and river systems (*2*, *7–10*). Assessments of benthic invertebrate assemblages and physical habitat (bioassessments) have been conducted in wadeable streams in California's Central Valley for a number of years (*11–14*). Most of the bioassessments conducted in California have occurred in rural areas with minimal data available for urban streams (*15–17*).

Bioassessments provide a useful approach for integrating effects from physical, chemical, and biological stressors on aquatic organisms. The underpinnings of bioassessments are that the structure and function of an aquatic biological community can provide critical information about the quality of the surface water. Bioassessments are valuable for determining the status of aquatic biological communities across large spatial scales and land use types (agricultural and urban). Information on the status of resident biological communities is particularly useful for determining impaired water bodies, developing Total Maximum Daily Loads (TMDLs), and measuring success of voluntary or regulatory actions. Bioassessments serve monitoring needs through three primary functions: (1) screening or initial assessment of conditions; (2) characterization of impairment and diagnosis; and (3) trend monitoring to evaluate improvements from mitigation practices or further degradation. Bioassessments also provide a direct means of measuring compliance with the goal of biotic integrity stipulated under the Clean Water Act because assemblages of aquatic organisms (i.e., macroinvertebrates) are comprised of taxa that are differentially responsive to different environmental stressors.

In recent years, pyrethroid insecticides - replacements for the organophosphates used for structural pest control, landscape maintenance and residential home and garden use - were reported at potentially toxic concentrations in the following California streams: Pleasant Grove Creek in Roseville; Kirker Creek in Pittsburg; Arcade Creek in Sacramento; and three small urban streams in Salinas (Gabilan Creek, Natividid Creek, and Alisal Creek – Salinas streams) (*18–21*). The toxicity assessment of pyrethroids in these stream areas was based on sediment toxicity test results with a single species, the amphipod *Hyalella azteca*, which is highly sensitive to pyrethroids in laboratory based clean water toxicity tests (*22*). Uncertainty exists when using only one species - particularly a highly sensitive one - as a benthic barometer for suggesting impairment of general ecosystem health. By contrast, bioassessments that include assessing the status of the entire benthic assemblage in concert with physical habitat assessments, as described above, are a preferred approach for determining the ecological status of these streams. In addition, the assumption that pyrethroids are the only stressor in urban waterbodies is questionable as other investigators have reported that chemical stressors such as metals (*23*, *24*) and polycyclic aromatic hydrocarbons (PAHs) (*25*) may also be present at concentrations that are potentially toxic to aquatic life.

The goal of this study was to summarize the results from four bioassessment multiple stressor annual case studies conducted in Pleasant Grove Creek from 2006 to 2008 (*13*, *17*, *26*); Kirker Creek in 2006 and 2007 (*26*), Arcade Creek from 2009 to 2011 (*27*); and Salinas streams from 2009 to 2011 (*27*). Basic water quality parameters, eight specific pyrethroids, Total Organic Carbon (TOC), grain size, and bulk metals {including simultaneously extracted metals (SEM) and acid volatile sulfides (AVS)} were evaluated in sediment in each stream area in concert with the bioassessments. The relationship between various benthic community metrics (i.e., taxa richness, abundance) and physical habitat metrics, pyrethroids, and metals were evaluated. Benthic community data were interpreted in the context of biological expectations for these urban streams.

Materials and Methods

Site Selection

Complete descriptions of the sampling sites for the Pleasant Grove Creek (21 sites), Kirker Creek (14 sites), Arcade Creek (11 sites) and Salinas stream sites (13 sites) are available in other publications (*13*, *17*, *27*). The locations of all four streams are presented in Figure 1. Annual spring sampling frequency for all parameters described below was as follows: Pleasant Grove Creek in 2006, 2007 and 2008; Kirker Creek 2006 and 2007; Arcade Creek in 2009, 2010, and 2011; and Salinas streams in 2009, 2010, and 2011.

Physical Habitat Assessments

Physical habitat was evaluated at each site concurrently with benthic collections, water quality evaluations, sediment parameters, pyrethroids, and metals. The physical habitat evaluation methods followed protocols described in Harrington and Born (*28*). The physical habitat metrics used for this study were based on nationally standardized protocols described in Barbour *et al.* (*8*). A total of 10 continuous metrics scored on a 0-20 scale were evaluated. Other non-continuous metrics such as percent canopy, percent gradient, and substrate composition were also measured as described in Harrington and Born (*28*).

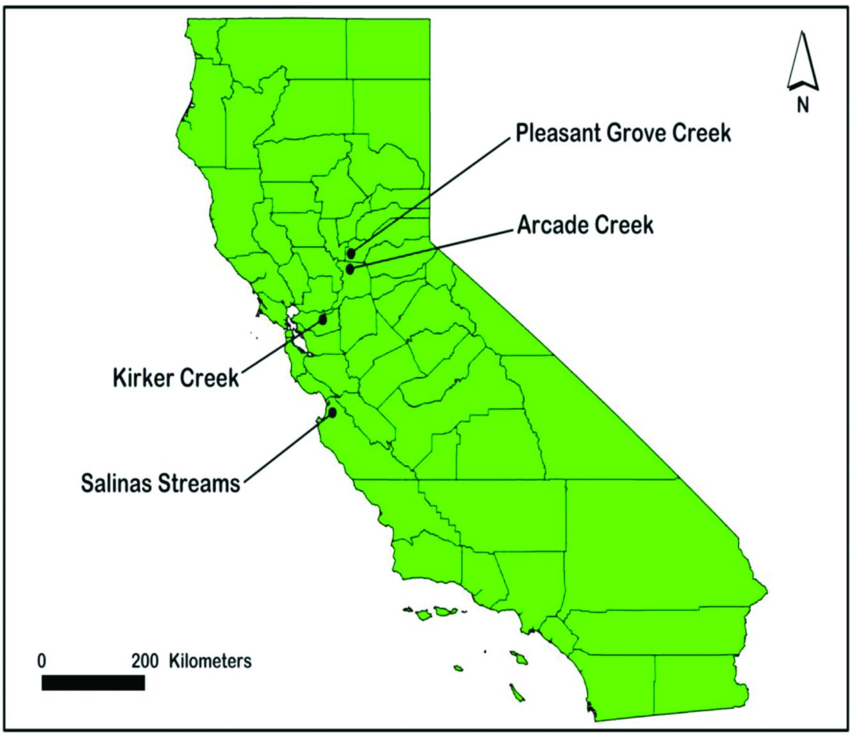

Figure 1. Locations of four California streams.

Benthic Macroinvertebrate Sampling

Benthic macroinvertebrates were collected in the spring (April – May) from three replicate samples at all sites in the four streams by year as described above. The sampling procedures were conducted in accordance with methods described in Harrington and Born (*28*). Within each of these sample reaches, a riffle was located (if possible) for the collection of benthic macroinvertebrates. A tape measure was placed along the riffle and potential sampling transects were located at each meter interval of the tape. Using a random numbers table, three transects were randomly selected for sampling from among those available within the riffle. Benthic samples were taken using a standard D-net with 0.5 mm mesh starting with the most downstream portion of the riffle. A 1x2 foot section of the riffle immediately upstream of the net was disturbed to a depth of 4-6 inches to dislodge benthic macroinvertebrates for collection. Large rocks and woody debris were scrubbed and leaves were examined to dislodge organisms clinging to these substrates. Within each of the randomly chosen transects, three replicate samples were collected to reflect the structure and complexity (ex., gravel, vegetation, woody debris) of the habitat within the transect. If habitat complexity was lacking, samples were taken near the side margins and thalweg (deepest path) of the transect and the procedures described above were followed. All samples were preserved in 95% ethanol.

Due to the physical nature of these urban streams, it was often difficult to locate a substantial number of riffles to sample. Therefore, the alternative sampling methods for non-riffle areas was used as outlined in Harrington and Born (*28*). This involved sampling the best available 1x2 foot sections of habitat throughout the reach using the same riffle procedures described above. Nine 1x2 foot sections were randomly selected for sampling (i.e, stratified random sampling). Groups of three 1x2 foot sections were composited for each replicate for a total of three replicates per site.

Taxonomy of Benthic Macroinvertebrates

Benthic samples were identified to the species level if possible. For taxa such as oligochaetes and chironomids, family and genus level, respectively, were often the lowest level of identification possible. Benthic macroinvertebrate subsampling (resulting in a maximum of 300 individuals) and identifications were conducted by California's Department of Fish and Game (CDFG). The benthic macroinvertebrate samples were subsampled and sorted by personnel at the CDFG Laboratory located at Chico State University. Species level identifications followed protocols outlined in Harrington and Born (*28*). Slide preparations and mounting for species such as midges and oligochaetes followed protocols from the United States Geological Survey National Quality Control Laboratory (*29*).

Water Quality and Sediment Measurements

Temperature, pH, salinity, specific conductivity, dissolved oxygen, and turbidity were measured at each site following procedures described in Kazyak (*30*).

Grain size (*31*) and TOC (*32*) were measured on sediment samples collected from each site. Depositional areas - fine grain areas most likely to contain hydrophobic pesticides such as pyrethroids - were specifically sampled at each site and three to five sediment samples from depositional areas were composited for the final sample. A stainless steel spoon (similar to a scoop) was used to collect the top 2-3 cm of sediment from each site. Approximately one liter of sediment was collected from each site for grain size and TOC determinations as well as pyrethroids and metals concentrations. All sampling equipment was cleaned between sites using ACS grade nitric acid, CDA 19 ethanol and distilled water. Sediment samples were stored in a cooler on ice in the field and later transferred to a refrigerator before shipment to Alpha Analytical Laboratory in Mansfield, Massachusetts for grain size and TOC analysis.

Pyrethroid Analysis

The pyrethroids bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin and permethrin residues were extracted from sediment by shaking with methanol/water mixture and hexane for one hour. The sample was centrifuged and an aliquot of the upper hexane layer evaporated to dryness and re-dissolved in a small volume of hexane. The hexane sample was then subjected to a silica solid phase extraction (SPE) procedure prior to residue determination by gas chromatography with mass selective detection using negative ion chemical ionisation (GC-MS/NICI). The limit of quantitation (LOQ) of the method was 0.12 – 0.32 ng/g dry weight for bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin and 1.2 – 3.2 ng/g dry weight for permethrin (*33*). Morse Laboratories in Sacramento, California conducted the pyrethroid analysis.

Bulk Metals and SEM/AVS Analysis

The following bulk metals with existing Threshold Effects Levels (TELs), conservative protective benchmarks, as described by Buchman (*34*), were measured on composited sediment samples for each site as previously described using EPA method 6020m: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn). The method detection limit (MDL) for these seven metals ranged from 0.02 to 0.90 µg/g dry weight. Mercury (Hg) was also measured on all sediment samples using EPA method 245.7m. The MDL for mercury was 0.02 µg/g dry weight.

Simultaneously extracted metals (SEM) analysis was conducted for Ni, Cu, Zn, Cd, and Pb using EPA method 200.8m. The MDLs (µmol/dry g) for these SEMs were as follows: Ni (0.02), Cu (0.009), Zn (0.02), Cd (0.0005), and Pb (0.006). Acid volatile sulfides (AVS) were evaluated on sediment samples from each site using procedures described by Plumb (*35*). SEM/AVS ratios were then developed for each site to provide insight on the bioavailability of these metals in sediment. The principle of SEM/AVS is based on the observation that there are some components in sediment that bind certain metals such that they are no longer available and therefore not toxic to benthic organisms (*36*, *37*). Sulfides in sediments have the ability to bind with divalent metals such as cadmium, copper, lead, mercury, nickel and zinc and may render these metals unavailable to the extent sulfides are available. Sediments from the study sites were therefore analyzed for the amount of SEM and for the amount of freely available divalent metals as (SEM). Assuming that sulfides would bind with metals on a 1:1 molar basis, dividing SEM by the amount of AVS would suggest that these metals are available when the ratio is greater than 1.

Statistical Analysis

The statistical approach used is described in detail in previous publications (*13*, *17*, *27*). Data for the 14 key benthic metrics were averaged across the three transects sampled for each site in the four streams. These data were merged with data sets of habitat metrics, sediment concentrations of metals, concentrations of simultaneously extracted metals (SEM) to AVS ratios, and sediment pyrethoid concentrations for each site. The sediment concentration data for each pyrethroid were converted to toxicity units (TUs) by standardizing them to 1% TOC and dividing by LC_{50} values that were also standardized to 1% TOC. Metals in sediment concentrations were also standardized to their relative toxicities by dividing the dry weight concentrations of each metal by their respective Threshold Effects Levels (TEL) values. The potential associations between the benthic metrics and the toxicity units for pyrethroids and metals were explored by a series of regression techniques. Prior to this analysis, all data were unit deviate standardized to place all dependent and independent variables on the same relative scales, as well as to produce normal distributions. The various steps used in the statistical approach are described as follows:

I. Univariate general linear model regressions (*38*) were conducted for each study area to determine whether there were indications of significant relationships (α=0.01) between benthic metrics and specific pyrethroids (expressed as TUs) and specific metals (both metal concentrations to TELs ratios and SEM to AVS ratios for each metal).

II. A series of stepwise multiple regressions were conducted to determine potential relationships between the benthic metrics and pyrethroids (in TUs), metals (metals to TEL ratios), and habitat metrics (*38*). Stepwise regressions were conducted separately for each of these three groups of independent variables, as well as with all variables combined into the same model.

III a. A second series of stepwise regressions were conducted for the benthic metrics versus principal components of the environmental data (pyrethroids, metals, and habitat metrics) that were produced by a principal components analysis (PCA) with an orthogonal rotation (*Proc*

Factor, principal components method with a "varimax" rotation) (*38*). The analyses of Set III were used to confirm the results of the Set II, due to concerns over multicollinearity between the independent variables, a common characteristic of environmental data sets.

III b. A pair of complementary multivariate models involving the principal components was also employed: Model 1 was designed to take the effects of the toxicants (pyrethroids TUs or metals to TELs) on the benthic metrics into account before the effects of the habitat metrics were assessed; and Model 2 was designed to take the effects of the habitat metrics on the benthic metrics into account before the effects of potential toxicants were assessed.

1. In Model 1, the principal components (PCs) from the PCA on environmental data that were most highly "loaded" by the toxicants (i.e. those PCs identified principally by salient factor loadings of pyrethroids and/or metals) were forced into multiple regression models (*38*) to remove their potential effects, and the residuals were re-analyzed by the two stepwise regression series: the benthic metrics versus the habitat metrics; and the benthic metrics versus the habitat Principal Components (i.e., PCs associated with the habitat metrics).
2. In the Model 2 analyses, the effects of the PCs that were most highly loaded by the habitat metrics were removed in a similar manner prior to re-assessing the effects of the toxicants by the two regression series: the benthic metrics versus the pyrethroids and metals metrics; and the benthic metrics versus the PCs associated with pyrethroids and/or metals.

In each case, if the significant relationships between the benthic and the environmental variables (habitat and toxicants) were observed to persist from the results of the original stepwise regression series to the results from Models 1 or 2, they were considered to be less confounded by the effects of other environmental variables and, therefore, more compelling.

Results and Discussion

A detailed analysis of results and discussion for the each stream is available in the following documents by stream: Pleasant Grove Creek (*13*, *17*); Kirker Creek (*17*); Arcade Creek (*27*) and Salinas Streams (*27*). The sections below highlight the key results and discussion from stepwise multiple linear regression models for the multiple year studies by stream. All significant variables in Tables I-IV were statistically significant at $\alpha < 0.01$.

Pleasant Grove Creek

The results from stepwise regressions of the three-year data set for Pleasant Grove Creek did not display significant relationships between benthic metrics and pyrethroids (Table I). Rather, the significant relationships tended to be those between the benthic metrics and the habitat metrics, particularly velocity depth regimes. A few benthic metrics displayed significant relationships with metals: Taxonomic richness was directly related to lead to TEL combined with an inverse relationship with cadmium to TEL; % Dominant taxon displayed significant relationships to the same metals, but the direction of the relationships were reversed (i.e., inverse relationship with lead to TEL and direct relationship with cadmium to TEL); % Tolerant taxa was directly related to cadmium to TEL and arsenic to TEL; % Grazers was directly related to arsenic to TEL. However, all of these relationships between benthic metrics and toxicity-standardized metals were quite weak ($R^2 \leq 0.12$) and did not persist in the Model 2 confirmation analyses. Conversely, stronger relationships ($R^2 \geq 0.27$) were observed between a number of benthic metrics and the habitat metric velocity depth regimes.

Ephemeroptera taxa, EPT taxa, EPT index, and % collectors/filterers displayed direct relationships to velocity depth regimes; while tolerance value, % tolerant taxa, and % collectors/gatherers were all inversely related to this habitat metric. All of these relationships persisted in the Model 1 confirmation analyses. There were other significant, but somewhat weaker relationships between benthic metrics and habitat metrics: Taxonomic richness was directly related to % gravel; Ephemeroptera taxa was directly related to riparian buffer zone, while % Tolerant taxa was inversely related to riparian buffer zone. Shannon Diversity was inversely related to vegetative protection; and % predators was inversely related to channel alteration. Despite the weaker relationships (lower R^2 values), all of these relationships, except the one between Ephemeroptera taxa and riparian buffer zone, persisted in the Model 1 confirmation analyses.

Table I. Results of stepwise multiple linear regression models of benthic metrics versus toxic units (TUs) for pyrethroids, habitat metrics, and metal to Threshold Effect Levels (TELs) ratios for Pleasant Grove Creek for 2006, 2007 and 2008, including r^2 values. The (+) symbol designates a direct relationship with a benthic metric while (-) indicates an inverse relationship.

Benthic Metrics	*Significant Variables (r^2)*
taxonomic richness	+ % gravel (.17), + Pb to TEL (.11), -Cd to TEL (.08)
% dominant taxa	-Pb to TEL (.11), +Cd to TEL (.07)
Ephemeroptera taxa	+velocity/depth (.37), + rparian buffer (.06)
EPT taxa	+velocity/depth (.42)
EPT index (%)	+velocity/depth (.42)
Shannon Diversity	-vegetative protection (.10)
tolerance value	-velocity/depth (.45)
% tolerant taxa	-velocity/depth (.51), +Cd to TEL (.11), -riparian buffer (.09), +As to TEL (.03)

Continued on next page.

Table I. (Continued). Results of stepwise multiple linear regression models of benthic metrics versus toxic units (TUs) for pyrethroids, habitat metrics, and metal to Threshold Effect Levels (TELs) ratios for Pleasant Grove Creek for 2006, 2007 and 2008, including r^2 values. The (+) symbol designates a direct relationship with a benthic metric while (-) indicates an inverse relationship.

Benthic Metrics	*Significant Variables (r^2)*
% collectors/filterers	+velocity/depth (.27)
% collectors/gatherers	-velocity/depth (.14)
% grazers	+As to TEL (.12)
% predators	-channel alteration (.13)

Kirker Creek

For the Kirker Creek two year data set, the stepwise regression models that included pyrethroids, metals to TELs and habitat metrics are displayed in Table II. It that showed that taxonomic richness was directly related to frequency of riffles/bends (R^2=0.26) and inversely related to vegetative protection (R^2=0.14). In addition, % tolerant taxa was inversely related to frequency of riffles/bends (R^2=0.46). The persistence of the frequency of riffles/bends habitat metric in the multiple regression models tends to re-enforce that it is directly related to benthic community health and inversely related to the dominance of pollution tolerant taxa.

Ephemeroptera taxa and % predators were both directly correlated to chromium (R^2=0.25 and 0.29, respectively). However only minimal significant should be attributed to these relationships because both of the benthic metrics had about 25% of the data represented by non-zero values. The tolerance value metric was directly related to cypermethrin TUs (R^2=0.37), although this was only one of six highly correlated pyrethroids (including Total TUs) that could have been selected by the stepwise procedure, if their R^2 values had been only slightly higher (e.g., the R^2 values for Total TUs and bifenthrin were both 0.34, while the R^2 for cypermethrin was 0.37) (*17*). In addition, examination of the data suggests that only a few samples appeared to be responsible for the significant regression relationship (i.e. they displayed both above average tolerance values and above average cypermethrin TU values for one of the two years). Morever, the cypermethrin concentrations did not exceed 70% of a toxicity unit in any of the samples. Conversely, some of the other highly correlated pyrethroids did display TUs that exceeded 1 in a number of samples. Thus, only limited ecological significance should be attributed to this specific relationship with cypermethrin.

There were a few other relationships displayed by stepwise regression analyses that included all of the potential independent variables from Kirker Creek (Table II): % collector/filterers were inversely related to % fines (R^2=0.35), % shredders were inversely related to sediment deposition and nickel to TEL ratios (R^2=0.17 for both), and abundance was inversely related to lead to TEL and % canopy cover (R^2=0.17 for both). While only accounting for approximately a third of the variance in the benthic metrics (R^2~0.34), the relationships tended to make ecological sense.

Table II. Results of stepwise multiple linear regression models of benthic metrics versus toxic units (TUs) for pyrethroids, habitat metrics, and metal to Threshold Effect Levels (TELs) ratios for Kirker Creek in 2006 and 2007, including r^2 values. The (+) symbol designates a direct relationship with a benthic metric while (-) indicates an inverse relationship.

Benthic Metrics	*Significant Variables (r^2)*
taxonomic richness	+frequency riffles/bends (.26), -vegetative protection (.14)
Ephemeroptera taxa	+Cr to TEL (.25)
tolerance value	+cypermethrin (.37)
% tolerant taxa	-frequency riffles/bends (.46)
% collectors/filterers	-% fines (.35)
% predators	+Cr to TEL (.29)
% shredders	-sediment deposition (.17), -Ni to TEL (.17)
abundance (#/sample)	-Pb to TEL (.17), - % canopy cover (.17)

Arcade Creek

The results of the stepwise multiple regression analyses of the 2009, 2010, and 2011 data sets from Arcade Creek are shown in Table III. The benthic metric taxonomic richness displayed an inverse relationship to total pyrethroid TUs, while % dominant taxon was directly related. Both of these relationships were confirmed by the Model 2 analyses. Taxonomic richness, which tends to decrease with environmental impairment, displayed an inverse relationship with PC1, the principal component that was heavily loaded by all pyrethroids, mercury, and zinc. The % dominant taxon, a metric which tends to increase with stress, was directly related to PC1 (*27*). Both of these relationships were confirmed by the Model 2 analyses. The % dominant taxon metric was also directly related to deltamethrin and vegetative protection and inversely related to lamda-cyhalothrin, but these relationships were not confirmed by the Model 1 or 2 analyses, respectively, and are not shown in Table III.

Shannon Diversity, another diversity-related benthic metric, displayed an inverse relationship with zinc to TEL and PC1, the principal component that was positively loaded by toxicants, including pyrethroids, mercury and zinc. The Model 2 analyses confirmed both of these relationships. However, causality cannot be inferred by the inverse relationship with zinc, since this metal is very highly correlated ($p \leq 0.0001$) to all of the pyrethroids and all of the metals except arsenic and nickel. Shannon Diversity was also shown to be directly related to %

fines, but this relationship was not confirmed by the Model 1 analysis and is not presented in Table III.

The Ephemeroptera taxa metric was directly related to frequency of riffles/bends, and EPT taxa and EPT index were both directly related to the habitat metric embeddedness. All of these relationships were confirmed by the Model 1 analyses. These benthic metrics, which tend to decrease with environmental impairment, also displayed direct relationships with PC2, the principal component that was positively associated with habitat metrics such as total score, embeddedness, frequency of riffles/bends, sediment deposition, velocity depth regimes and coarser sediments (*27*). These relationships were confirmed by the Model 1 analyses on the principal components.

Table III. Results of stepwise multiple linear regression models of benthic metrics versus toxic units (TUs) for pyrethroids, habitat metrics, and metal to Threshold Effect Levels (TELs) ratios for Arcade Creek for 2009, 2010 and 2011, including r^2 values. The (+) symbol designates a direct relationship with a benthic metric while (-) indicates an inverse relationship.

Benthic Metrics	*Significant Variables (r^2)*
taxonomic richness	-total pyrethroid TUs (.25)
% dominant taxa	+total pyrethroid TUs (.31)
Ephemeroptera taxa	+frequency riffles/bends (.32)
EPT taxa	+embeddedness (.30)
EPT index (%)	+embeddedness (.16)
Shannon Diversity	-Zn to TEL (.21)
tolerance value	+Hg to TEL (.39)
% tolerant taxa	+Hg to TEL (.53)
% collectors/gatherers	-embeddedness (.30)
% grazers	+total pyrethroid TUs (.68), -riparian vegetative zone (.11)
% predators	+Pb to TEL (.29)

The EPT index metric was also inversely related to permethrin and directly related to cypermethrin, but neither of these relationships was confirmed by the Model 2 analyses.

The benthic metrics tolerance value and % tolerant taxa were both directly correlated to mercury to TEL, and the relationships were confirmed confirmed by the Model 2 analysis. As was the case of the inverse relationship between Shannon Diversity and zinc, causality cannot be inferred by these apparent direct relationships, since mercury is very highly correlated ($p \leq 0.0001$) to all of the pyrethroids and all of the metals except arsenic and nickel. Both the tolerance value and the % tolerant taxa metrics were inversely related to PC2, while the latter metric was also directly related to PC1 and PC6 (*27*). These relationships were confirmed by the Model 1 and 2 analyses. Thus, these benthic metrics, which tend to increase with environmental impairment, appeared to have an inverse relationship with the principal component for habitat metrics indicative of environmental quality (PC2) and, at least with % tolerant taxa, a direct relationship with the principal component that was positively loaded by toxicants (PC1).

The benthic metric % collectors/filterers was inversely related to embeddedness and inversely related to velocity depth regimes. Neither of these relationships were confirmed by the Model 1 analyses. There were no significant relationships detected in the analyses of principal components with these metrics.

The metric % collectors/gatherers was inversely related to embeddedness and to PC2, the principal component that was positively loaded by total score, embeddedness, sediment deposition, frequency of riffles/bends and velocity depth regimes and negatively loaded by % fines (*27*). Both of these relationships were confirmed by Model 1 analyses. Thus, this benthic metric that increased with impairment appears to be inversely related to habitat metrics that reflect relative habitat quality.

The metric % grazers was directly related to total pyrethroids and inversely related to riparian vegetative zone. The direct relationship with total pyrethroids was confirmed by the Model 2 analysis, while the relationship with riparian vegetative zone was confirmed by the Model 1 analysis. This benthic metric was shown to be directly related to PC1, the principal component that was positively loaded by toxicants (all pyrethroids and certain metals) and to PC5, the principal component that was negatively loaded by riparian vegetative zone and channel alteration, and positively loaded by epifaunal substrate/available cover, % boulder, and % cobble (*27*). These relationships were confirmed by the Model 1 and 2 analyses, respectively. Thus, this benthic metric appeared to have a direct relationship to habitats associated with toxicants and to have an inverse/negative relationship to vegetative buffer zones.

The benthic metric % predators was directly related to lead to TEL. This relationship was confirmed by the Model 2 analysis. No significant relationships were observed between this benthic metric and the environmental principal components as discussed in detail in a previous publication (*27*).

Salinas Streams

The results of the stepwise multiple regression analyses of the 2009, 2010, and 2011 data sets from the three Salinas stream are presented in Table IV. The benthic metric taxonomic richness was inversely related to bifenthrin and directly related to % canopy cover. This benthic metric was inversely related to the PC6, the principal component that was positively loaded by deltamethrin and bifenthrin (*27*). None of these relationships were confirmed by the Model 1 or 2 analyses and are therefore not presented in Table IV.

Shannon Diversity was inversely related to esfenvalerate, as it was to PC5, the principal component that was positively loaded by this pyrethroid (*27*). Neither of these relationships was confirmed by the Model 2 analyses. Percent tolerant taxa and % collectors/filterers, two benthic metrics expected to increase with impairment, were shown to be directly related to esfenvalerate. The latter benthic metric was also shown to be directly related to PC5, the principal component that was positively loaded by esfenvalerate (*27*). However, none of these relationships were confirmed by the Model 2 analysis.

Tolerance value, another benthic metric that would be expected to increase with environmental impairment, was inversely related to % canopy cover. This relationship was not confirmed by the Model 1 analysis.

Table IV. Results of stepwise multiple linear regression models of benthic metrics versus toxic units (TUs) for pyrethroids, habitat metrics, and metal to Threshold Effect Levels (TELs) ratios for Salinas streams for 2009, 2010 and 2011, including r^2 values. The (+) symbol designates a direct relationship with a benthic metric while (-) indicates an inverse relationship.

Benthic Metrics	*Significant Variables (r^2)*
% collectors/gatherers	-sediment deposition (.15)
% grazers	+sediment deposition (.27)

The metric % collectors/gatherers was inversely related to sediment deposition, while the metric % grazers was directly related to this habitat metric. Both of these relationships were confirmed by the Model 1 analyses. These were the only two significant relationships reported for benthic metrics and environmental variables for the three year Salinas stream data sets (Table IV). The % grazers metric was also shown to be inversely related to zinc to TEL and directly related to lead to TEL. However, neither of these relationships was confirmed in the Model 2 analysis.

The benthic metric % predators was directly related to velocity depth regime and cypermethrin and inversely related to arsenic to TEL. However, these relationships were not confirmed by the Model 1 and Model 2 analysis. None of the other analysis between benthic metrics and principal components for environmental variables were significant for the three year Salinas stream data set (*27*).

Summary of the Four Streams

The majority of ecotoxicological studies and regulatory risk assessments of chemicals in aquatic environments focus mainly on the toxicity of single compounds in controlled conditions (*39*). However, in the natural environment aquatic assemblages, such as benthic communities, are exposed to multiple stressors such as complex mixtures of chemicals and other potential stressors such as impaired physical habitat. The focus of the bioassessment multiple stressor case studies presented in this chapter was to determine the most significant stressors to resident benthic communities in selected urban water bodies in California. A summary of the bioassessment multiple stressor case studies in Table V displayed the number of significant ($\alpha < 0.01$) habitat, metals and pyrethroid relationships with benthic metrics for the four California streams. Table V showed: (1) significant relationships with benthic metrics and both habitat metrics and metals but not pyrethroids in Pleasant Grove Creek; (2) habitat and metals have stronger statistical relationships with benthic metrics than pyrethroids in Kirker Creek; (3) more significant relationships with benthic metrics and habitat metrics than with metals or pyrethroids in Arcade Creek; and (4) habitat and not metals or pyrethroids was the only stressor to show a significant relationship with benthic metrics in Salinas streams.

Table V. Summary of bioassessment multiple stressor case studies showing number of significant ($\alpha < 0.01$) habitat, metals and pyrethroid relationships to benthic community metrics for four California streams.

Stream	*Yrs and # samples*	*Habitat*	*Metals*	*Pyrethroids*
Pleasant Gr. Cr.	2006-2008 (n=63)	12	7	0
Kirker Cr.	2006-2007 (n=28)	6	4	1
Arcade Cr.	2009-2011 (n=33)	5	4	3
Salinas streams	2009-2011 (n=39)	2	0	0
All streams	2006-2011 (n=163)	25	15	4

The summary results from these four case studies showed that physical habitat metrics were the most important factors influencing benthic community condition in four urban California streams while metal concentrations were the second most important factors influencing benthic community conditions in these urban streams. Pyrethroids, which are listed as impairing constituents in all these streams, were the least important factors influencing benthic community conditions in these urban streams. For two of these streams (Pleasant Grove Creek and Salinas streams) pyrethroids were not a significant stressor to benthic communities when considered in a multiple stressor analysis. The results from the bioassessment multiple stressor field studies (including pyrethroids) demonstrated that ecological risk to resident benthic communities from pyrethroid exposure in sediment is generally low when evaluated concurrently with other stressors.

Acknowledgments

We would like to thank the Pyrethroid Working Group for sponsoring this study. California Department of Fish and Game are acknowledged for identification of benthic species and development of metrics. Morse Laboratories is acknowledged for pyrethroid analysis. Alpha Analytical Laboratory is acknowledged for TOC, grain size and metals analysis.

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Chapter 7

Influence of Landcover, Rainfall, and River Flow on the Concentration of Pyrethroids in the Lower American River, Sacramento, California, United States

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A multi-site, spatio-temporal transect study on the Lower American River was conducted to systematically investigate the influence of agricultural and urban landcover, river flows and rainfall events on the concentration of pyrethroids. The majority of the flow in this section of the river throughout the year is controlled discharge from Folsom Dam. Local storm drains, small ephemeral channels and an extensive network of organized storm drain collection and pump stations discharge excess rainfall from surrounding urban and suburban environments into the Lower American River channel. Rainfall event-driven sampling was carried out during the 2011-2012 and 2012-2013 rainy seasons for eight pyrethroids. Results indicate that rainfall-runoff events are the driving perturbations behind the infrequent and highly variable pyrethroid movement into the Lower American River. A variety of factors contribute to environmental complexity. However, rainfall is the only true driver, while other land cover complexities, stormwater detention systems, and hard surfaces contribute to the variability in local rainfall-runoff contribution to river flows.

Introduction

Pyrethroids are a class of insecticides used to control a wide range of pests in both agricultural and urban settings. Pyrethroid use in urban areas has increased since the registration of organophosphate insecticides for urban uses has been withdrawn. California is an area where pyrethroids are used extensively and have been detected in the sediments of urban creek (*1–3*).

The Pyrethroid Working Group (PWG) is completing a larger program of studies to better understand the critical factors governing the fate and transport of pyrethroids in urban areas. This study is part of that larger program, and is designed to build upon the findings of recent studies which examined pyrethroid residues in grab samples collected from along the bank of the American River (*3*).

Whereas the aforementioned studies prescribed subjective point sampling of the American River, there was a need to develop a larger scale, more comprehensive sampling approach for the river for a thorough examination of factors which may influence pyrethroid concentrations. The larger scale monitoring program would allow for the investigation of pyrethroid concentrations in the context of a greater distribution of rain events and river flow conditions – both major potential driving forces in the movement of pyrethroids. The larger scale program would also include improved sampling techniques that can be used to answer basic questions about variability in pyrethroid concentrations within river flows and in different portions of the river.

Developing a sound sampling strategy is a crucial step in understanding the occurrence of pyrethroids in the American River; and elucidating the relationship between pyrethroid detections with rainfall and river flow.

Sampling and Analysis Techniques

The following sections describe the study area, identify the analysis techniques used to select and sample transects of the river, and describe how river samples at various river conditions were obtained.

Study Area

The American River is a large river system with a watershed that stretches from a portion of the Sierra Nevada mountains near Lake Tahoe down into the Central Valley eventually draining into the Sacramento River at Sacramento, California. The upper watershed drains primarily undisturbed forest land east of Folsom Lake. As the river flows west, the watershed land area drastically shifts into an agriculturally dominated land cover that transitions to highly urbanized near the outlet of the lower American River and into the Sacramento River. Based on previous monitoring (*3*), the waters in the upper reaches of the river system have been shown to be typically free of pyrethroids. However, Weston and Lydy (*3*) reported that the lower river reach at times contained pyrethroid residue concentrations in water samples at levels potentially harmful to the aquatic toxicity indicator species, *Hyallela azteca* (Range of detections: 1.2 – 5.6 ng/L Bifenthrin, 5.0 ng/L Permethrin). The detections of pyrethroid are likely the result of suburban and urban uses and higher human population density within the lower watershed (Figure 1).

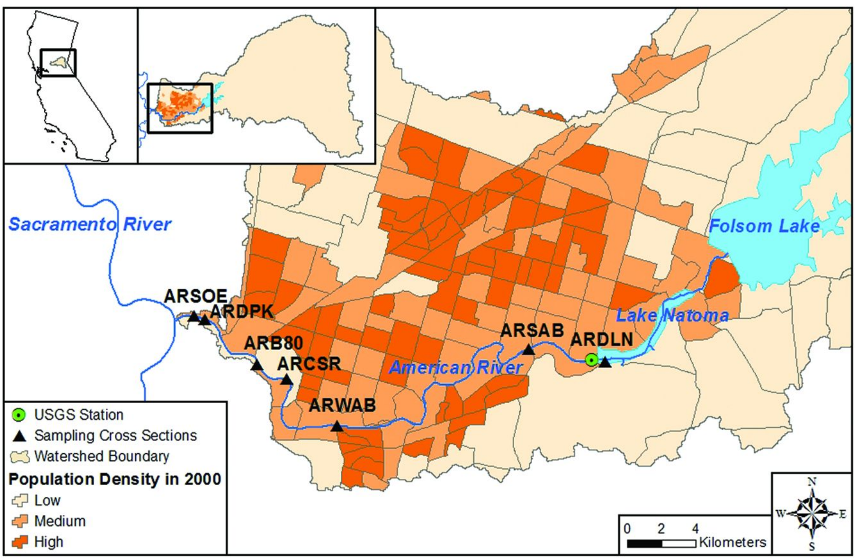

Figure 1. Population density distribution throughout the lower American River Watershed. (see color insert)

Seven locations were selected to conduct transect sampling under a variety of conditions. A list of the transect descriptions and geographic locations corresponding to Figure 1 can be found in Table I.

Table I. Transect Descriptions and Locations

Site Name	*Description*	*Latitude*	*Longitude*
ARDLN	Downstream of Lake Natoma	38.636542	-121.218436
ARSAB	Sunrise Avenue Bridge	38.632275	-121.270653
ARWAB	Watt Avenue Bridge	38.566867	-121.382994
ARCSR	Downstream of the Chicken Ranch / Strong Ranch Slough storm drain discharge point	38.583633	-121.424472
ARB80	Upstream of Business 80 Bridge	38.587156	-121.446647
ARDPK	Discovery Park upstream of Sacramento River	38.602300	-121.489444
ARSOE	Downstream of Sump 11 storm drain discharge point	38.602636	-121.496686

Table II summarizes the developed land fraction for each transect-based subcatchment in the watershed, as defined by the USDA Cropping Data Layer (CDL) which also accounts for non agricultural land uses.

Table II. Developed Land Fraction for Subcatchments Associated with Each Transect Location in Order from Farthest Upstream to Farthest Downstream

Transect	*Developed Land Fraction*
ARSAB	42%
ARWAB	64%
ARCSR	75%
ARB80	75%
ARDPK	69%
ARSOE	69%

In Table II, all transects except ARSAB contain relatively high (>50%) developed land fractions. The city of Sacramento falls within this part of the watershed with heavy development near the confluence with the Sacramento River. A further illustration of the watershed area that contributes to the river transect locations can be seen in Figure 2. The developed land fraction percentage for each transect moving downstream represents not only the additional area shown for each transect, but also the sum of the watershed area upstream of it, excluding the watershed area upstream of Lake Natoma. This watershed area was excluded to highlight the portion of developed area in the lower watershed that provides runoff directly to the river and is not buffered by the upstream reservoirs/lakes.

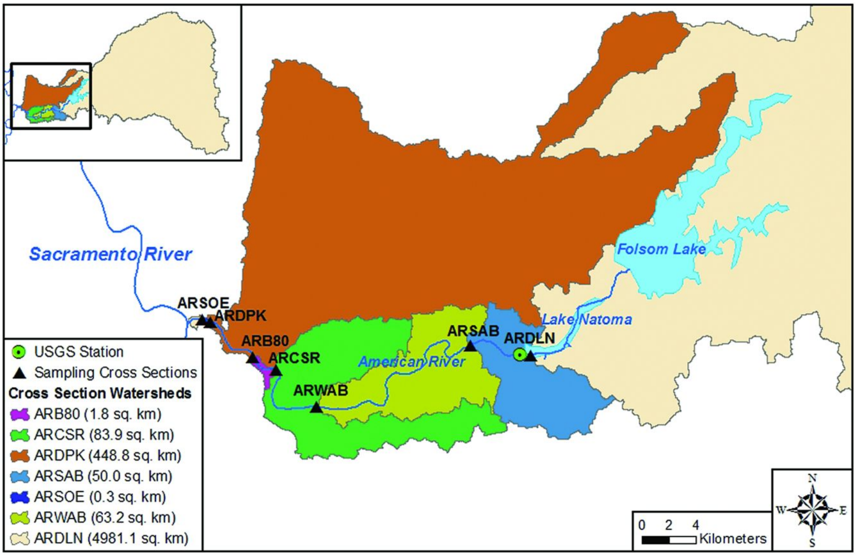

Figure 2. Individual cross-section delineations. (see color insert)

Watershed Hyrdrology

The lower American River is a highly managed river system controlled by a series of dams and prescribed discharges to meet various river flow criteria. Folsom Lake is a significant impoundment covering approximately 46 sq-km followed closely downstream by the relativley narrow Lake Natoma covering 2 sq-km but stretching more than 22 km in length. The lower American River begins at the outfall from Lake Natoma. Seasonally flows vary as dam discharges upstream vary, but they typically do so to meet seasonal prescribed discharge ranges that are not nessesarily linked to recent (last few days) rainfall trends. Instead, variations in flow of the lower American River during rainfall events are more a function of the suburban and urban free-flowing side channels and pumped discharges of stormwater. Although these urban discharges do account for variation, the range of baseflows delivered by the upstream dam releases account for the majority of river flow even on days of significant rainfall in the lower American River watershed (*4*).

Overall Study Design

In this multi-year study, the first year sampling covered rainfall events, event flows, and dry condition flows using discrete samples laterally and vertically within the river, at a number of cross-sections scattered through the lower American River. Second year sampling focused on rainfall event sampling only and depth integrated samping at more locations laterally in each identified cross-section. Changes in the second year were based on the nature and residue detection distribution of sampling results in year one.

2011-2012 Monitoring Design

Year one (2011-2012) monitoring consisted of an approach designed to examine residues in the water column and bed sediment for determination of overall pyrethroid presence. "Wet" (rainfall driven) and "Dry" (non-rainfall driven) events were sampled. "Wet" event monitoring was conducted the first full day following a precipitation exceedence threshold of 7.6 mm occurring in a period of 24 hours throughout the majority of the lower American River watershed. "Dry" events were declared as monitoring occurring at least one week after the last precipitation. "Dry" event monitoring was conducted on three separate occasions, once at the beginning of the rainy season (late October – early November), once mid-rainy season (mid January), and once at the end of the rainy season (late May – early June).

Water Samples

A representative transect sample consisted of several discrete stations each consisting of several disctete depth samples. The wetted width of the channel at the sampling location was estimated and divided into five approximately equal segments, representing the distance between each sampling station along a transect perpendicular to the flow of the river. The first sample location was located at one half of one segment width from the right bank (1/10th of the distance across the channel). The subsequent sampling locations were positioned at 30%, 50%, 70%, and 90% of the distance across the channel from the right bank.

Samples were collected from three discreet depths at each sampling station: 1' below the water surface, mid channel depth, and 1' above the bottom of the channel. However, depending on the water depth at each sampling location, not all of the samples may have been collected based on the following practical sample collection guidance:

a) dry – no water means no water sample
b) <2' depth – only collect one sample at mid-depth
c) >2' and <5' depth – collect a sample 1' from the bottom and 1' from the surface
d) ≥5' depth – collect a sample 1' from the bottom, a sample from mid-depth, and 1' from the surface

A Van Dorn sampler (WildCo, Yulee, Florida) was utilized for each of those water samples for both "Dry" and "Wet" event sampling. Prior to use, the Polyvinyl Chloride (PVC) sample containment chamber on the sampler was replaced with a stainless steel chamber with identical specifications. A Van Dorn sampler is designed for collecting a sample of water at a known depth. The device is lowered into a body of water in the open position, and when it reaches the desired depth it is triggered to close capturing and sealing a discrete aliquot.

Upon the arrival at each sampling station and prior to deploying the Van Dorn sampler, the interior and exterior of the sampler was thoroughly decontaminated using Alconox, followed with a thorough rinse of Type I water (*5*). The sampler was then given a solvent rinse with methanol, followed by another Type I water rinse.

Samples analyzed for pyrethroids were collected in pre-cleaned amber glass bottles preserved with formic acid. Total Organic Carbon (TOC) samples were collected and placed in 40 ml pre-cleaned amber vials and preserved with hydrochloric acid. Total Suspended Solids (TSS) samples were collected and stored in polyethylene bottles with no chemical preservative.

After sampling, the sample containers were stored on ice (<6°C) and the sample collection process was repeated to collect samples from the remaining depths at the sampling location.

In addition to sample collection, temperature and electrical conductivity (E.C.) were also collected using a YSI 556 MPS (Multiprobe System) water quality meter (YSI, Yellow Springs, Ohio). The meters were calibrated prior to sampling each day, following the manufacturer's protocol. The measurements were collected discretely at each discrete water sampling depth at each lateral sampling station.

Bed Sediment Sampling

Bed sediment sampling was conducted during the "Dry" pre and post rainy season sampling events. A petite ponar dredge (WildCo, Yulee, Florida) sampling device was used to collect the bed sediment samples. A petite ponar dredge is a heavyweight sediment sampling device with weighted jaws that are lever or spring activated. It is used to collect consolidated fine to coarse textured sediment. Sediment grab samples were collected from each station along each transect during the first sampling event.

Samples that were comprised of fines/sand were retained for laboratory analyses; samples that were comprised of gravel and cobble were not retained. For the samples that consisted of fines or sand, the top 5 cm of the sediment in the petite ponar were removed using a stainless spoon or spatula and transferred to a stainless steel mixing bowl, thoroughly homogenized, and then distributed to sample containers and placed on ice for pyrethroids, grain size, and TOC analysis.

2012-2013 Monitoring Design

Monitoring continued for a second year (2012-2013), and focused on "Wet" or rainfall driven monitoring events based on lessons learned from year one (2011-2012). However, the decision was made to target larger storm events (greater than 0.5 inches in a 24 hour period) and focus on the collection of water samples only. In addition, it was determined that the ARDLN (Downstream end of Lake Natoma) transect should no longer be monitored due to the lack of residue detections during the 2011-2012 sampling season. Along with this decision also came an expanded monitoring design to examine not only pyrethroid residue presence, but also residue persistence. As in year one, spatial and temporal variation was also a focus. An emphasis was also placed on the collection of contextual information to aid in the general understanding of stream conditions (i.e., in stream velocities, discharge variation at different locations, sediment suspension) as they related to the transport of pyrethroid residues.

The straightforward monitoring design implemented in year one was continued into year two, but with slight methodology adjustments. Based on the variation observed in residue concentrations in general being more prominent longitudinally as opposed to vertically, the decision was made to alter the sampling methodology from collecting vertical point samples to collecting vertically depth integrated composite samples. This included collecting a greater number of samples across a stream transect for a greater resolution in the longitudinal direction.

An Acoustic Doppler Current Profiler (ADCP) was deployed and used to collect stream flow data during a majority of the sampling events. Included in the information collected were stream discharge, instantaneous and average stream velocity, stream depth/bed profile, and acoustic backscatter. These data offered contextual information regarding general stream conditions during the various flow events, inflow contribution from various stream inputs, and accurate stream discharge.

Water Samples

The wetted width of the channel at the sampling location was measured and divided into approximately nine equal segments, representing the distance that would occur between each sampling location along a transect perpendicular to the flow of the current. The first sample location was placed at one half of one segment width from the right bank (1/18th of the distance across the channel). The sampling locations were positioned at 5%, 16%, 28%, 39%, 50%, 61%, 72%, 83%, and 95% of the distance across the channel from the right bank.

Upon the arrival at each sampling station and prior to deploying the DH-76 sampler, the interior and exterior of the sampler was thoroughly decontaminated as previously described for the Van Dorn sampler.

A DH-76 integrated depth sampler was utilized for water sample collection for the continuation of "Phase I" sampling in 2012-2013 following Edwards and Glysson (*6*). The DH-76 depth-integrated sampler is designed to isokinetically and continuously accumulate a representative sample from a stream vertical while transiting the vertical at a uniform rate. The depth-integrated sampler collects and accumulates a velocity or discharge-weighted sample as it is lowered to the bottom of the stream and raised back to the surface. The DH-76 is hand-held and is thus best suited for water depths not exceeding 15 feet.

The 1-L amber bottle containing the sample was then split into appropriate sample containers and stored on ice for pesticide analysis, TOC, and TSS.

In addition to sample collection, temperature and E.C. were also collected using a YSI 556 MPS water quality meter. The meters were calibrated prior to sampling each day, following the manufacturer's protocol. The measurements were collected discretely at mid-depth at each sampling station.

2012-2013 Expanded Monitoring

An expanded monitoring approach was implemented during the 2012-2013 sampling season. Three additional sampling regimes were included.

Drift/Lagrangian Sampling

As part of the expanded approach, a "drift" or Lagrangian style sampling event was conducted. This monitoring event was designed to examine how a "pulse" of water might behave as it moved downstream between two cross-sections known to have higher pyrethroid residue detection rates. This "drift" study was designed to follow a pulse of stormwater downstream of the ARCSR site, a major stormwater discharge. The speed of the drift was determined by deploying approximately one dozen oranges (oranges are neutrally buoyant, and travel at approximately mean river velocity) into the main current at the time of the initiation of the drift and ensuring that the boat was in alignment with the main group of oranges each time a sample was collected while zig-zaging downriver. The sampling vessel travelled in a zig-zag pattern down river, while samples were collected from the left bank, center channel, and right bank. The first sample of this study began above the ARCSR outfall and the sampling vessel followed a zig-zag course while drifting downriver until just upstream of the I-80 bridge (ARB80).

The samples were collected using a pole sampling apparatus, designed and constructed by Waterborne, onto which sample bottles were attached to adjustable mounts. Depending on the depth of the water at the time a sampling, samples were collected at mid depth, for water <3' deep, or 1/3 and 2/3 depth for locations where the water was >3' deep. Upon the retrieval of each of the grab samples, the sample bottle was removed from the pole sampler and split into appropriately labeled and preserved sample containers, which were then stored on ice.

Additional Methods

Two additional monitoring methods used the same sampling approach as that used for the continued "Phase I" sampling (DH-76 sampler). All samples collected during these events were analyzed for pyrethroids, TOC, and TSS via the same analytical methods.

A single transect (ARB80) revisit sampling study was conducted as part of the expanded sampling approach for 2012-2013. This sampling design was developed to mimic the potential exposure of an in-stream organism attached to the stream bed over a short duration of time (i.e., approximately 2 hour duration).

A multi-day sampling event was also targeted for the 2012-2013 sampling year, with the goal of this monitoring being to determine pyrethroid residue presence and persistence over a period of days. This monitoring began by sampling a day prior to a foreseeable storm (for background levels), the day (or days) of storm duration, and the day following the storm. In addition to this, multiple transect visits were to be made to a select transect on the day or days of rainfall, with the intent to transect specific residue concentrations over varying periods of time.

Analytical Methodology

Once collected, the samples, equipment blanks, and matrix spikes were stored on wet/blue ice at Pacific EcoRisk until they were transported to Caltest Analytical Laboratory and stored refrigerated between 0–6 °C until analysis. TOC was determined using 20th Edition of Standard Methods (SM) 5310B, TSS by method SM 2540D (*7*), and pyrethroids by method Gas Chromatography Mass Spectrometry – Negative Chemical Ion – Selective Ion Monitoring (GCMS-NCI-SIM) (*8*). Pyrethroid target analytes consisted of bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, deltamethrin:tralomethrin, esfenvalerate:fenvalerate, fenpropathrin, and permethrin. The Limit of Quantification (LOQ) for each analyte is listed in Table III.

Table III. Analytes To Be Determined and Respective Analytical Limits

Analytes	*Method Detection Limit (MDL)*[1]	*Reporting Limit (RL)*[1]
Water Samples (ng/L)		
Bifenthrin	0.1	1.5
Cyfluthrin	0.2	1.5
Lambda-Cyhalothrin	0.2	1.5
Cypermethrin	0.2	1.5
Deltamethrin	0.2	3
Esfenvalerate:Fenvalerate	0.2	3
Fenpropathrin	0.2	1.5
Permethrin	2	15
Total Organic Carbon (TOC)	0.3	0.5
Total Suspended Solids (TSS)	1	3
Bed Sediment Samples (µg/kg)		
Bifenthrin	0.1	0.3
Cyfluthrin	0.1	0.3
Lambda-Cyhalothrin	0.1	0.3
Cypermethrin	0.1	0.3
Deltamethrin	0.1	0.3
Esfenvalerate:Fenvalerate	0.1	0.3

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Table III. (Continued). Analytes To Be Determined and Respective Analytical Limits

Analytes	*Method Detection Limit (MDL)[1]*	*Reporting Limit (RL)[1]*
Fenpropathrin	0.1	0.3
Permethrin	0.1	0.3
Total Organic Carbon (TOC)	100	200

[1] MDL and RL values are subject to small variation due to varying sample volume between sample analysis batches.

Pyrethroid Method Validation

Every method was initially validated by establishing appropriate calibration ranges spanning the expected detection levels of interest. Additionally, an initial demonstration of competency precision study of at least 4 lab-matrix samples, spiked at mid-calibration range levels achieving a RSD ≤20%, for water matrices. Also, each method reporting levels were established as a multiple of the initial method detection limits, which were determined for each analyte based on precision study of at least seven low-level spiked replicates, computed from the 99% confidence level student-t factor.

Ongoing accuracy (bias) and precision were evaluated for each prepared batch of samples, which contains positive and negative controls. Initial instrument calibration curves were verified using a second source standard, traceable to a national standard when it was commercially available. Continuing calibration verifications (CCV) were performed on a daily basis for each analytical run. Inorganics & physical analyses required CCVs on a frequency of at least every 10 samples in a run, with an opening and closing CCV. Pyrethroid analyses involved internal standards for quantitation and surrogates, analytes with chemical properties and behaviors similar to the analytes of interest, were added to assess method performance in individual samples.

Routine Analysis

Samples were prepared in batches containing no more than 20 samples. Each preparation batch contained a negative control (laboratory blank) and a positive control (fortified recovery sample). When sufficient sample was provided, at least one sample per batch was analyzed in duplicate or fortified in duplicate. Fortification levels ranged from at least five times the LOQ to a level that encompassed concentrations found in the sample. Samples were prepared and analyzed within prescribed holding times as listed in Table IV.

Table IV. Sample Holding Times

Action Required by Lab	*Holding Time (Days)*
Pyrethroid Extraction	3
Pyrethroid Extraction (if preserved)	7
Pyrethroid Analysis (from extraction date)	40
TOC Analysis (from collection date)	28
TSS Analysis (from collection date)	7

Sample Preparation Procedure for Substrates

For pyrethroids, the volume of sample collected, usually between 500 and 1000 mL, were pH adjusted to a range ≤6 and serially extracted with methylene chloride. The resultant extract was concentrated and exchanged into a solvent compatible for cleanup (if necessary) or determinative method used.

For TOC, samples were collected in 40 mL VOA vials, were pH checked, and loaded onto the instrument with appropriate batch quality control.

For TSS, an aliquot of the well-mixed sample was measured and filtered through a pre-weighed glass fiber filter. The residue retained on the filter was dried to a constant weight.

Bias Control

Bias, or accuracy, was determined as percent recovery via positive controls, as Laboratory Control Spikes or Fortified Blanks (LCS) and fortified sample matrix. Precision was determined as Relative Percent Difference (RPD) of LCS and/or matrix duplicates, which included fortified sample duplicates.

Individual pyrethroid recoveries for fortified samples were in the range of 30%–180%, while the percent difference between duplicates were <50%. Fortified sample recoveries for total organic carbon were in the range of 80%–120%, while the percent difference between duplicates were <20%. The percent difference for total suspended solids were <20% (Table V).

Method blanks were used as negative controls, to identify background contamination if detected at or above the Reporting Limit.

Control charts were generated at least annually to determine or confirm positive controls levels on the basis of at least 20 QC samples. Upper and lower controls were determined as ± 3 sigma of mean.

Table V. Project Specific Control Limits for Samples Collected in November 2011

Analyte	*MS Control Limits*[1]	*MS Control Limits*[2]	*MS Control Limits (n=)*	*Mean %RPD*	*MS RPD (n=)*
Bifenthrin	60-130	33-155	19	8.89	8
Cyfluthrin	65-150	31-177	20	10.8	9
Lambda-Cyhalothrin	60-130	43-149	19	11.8	9
Cypermethrin	65-140	45-147	19	12.8	9
Deltamethrin	60-125	44-137	20	10.6	9
Esfenvalerate: Fenvalerate	60-140	34-158	20	10.9	9
Fenpropathrin	65-135	30-176	19	11.2	8
Permethrin	65-145	30-168	19	10.5	8

[1] Based on Warning Limits. [2] Based on Control Limits.

Results and Discussion

Ten monitoring events were completed during the two year (2011-2013) study. Figure 3 and Table VI offer a snapshot of each event, including those performed by Weston and Lydy (2010), in the context of observed and historical flow conditions. This study's monitoring events covered a variety of flow conditions, including several outside of normal (25^{th}–75^{th} percentile) historical flow conditions, whereas a significant portion of the events sampled by Weston and Lydy (*3*) were below the 25^{th} percentile of normal flow.

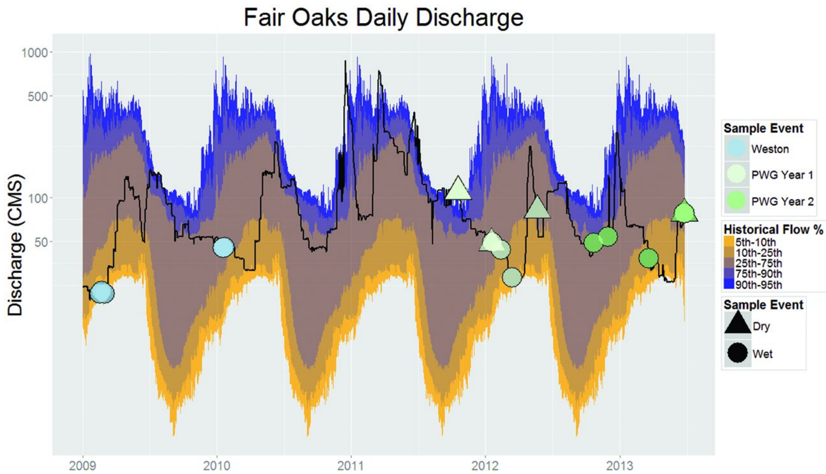

Figure 3. Sampling events in the context of observed and historical flow according to the Fair Oaks USGS gaging station. (see color insert)

Table VI. Rainfall and Discharge for All Study Sampling Events

Sampling Date	*2-Day Precipitation (mm)*	*Discharge (CMS)*
2/18/2009[1]	30.0	21.7
2/23/2009[1]	33.0	22.6
3/3/2009[1]	39.9	21.6
1/18/2010[1]	21.1	44.7
1/19/2010[1]	34.0	44.7
1/22/2010[1]	20.1	45.3
10/18/2011	0.0	109.5
10/19/2011	0.0	110.1
1/18/2012	0.0	48.4
1/20/2012	25.9	48.7
2/13/2012	11.9	43.3
3/14/2012	5.1	28.0
5/21/2012	0.0	81.5
10/22/2012	1.0	48.4
11/29/2012	13.0	53.5
3/20/2013	6.1	37.9
6/24/2013	0.0	77.3

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Table VI. (Continued). Rainfall and Discharge for All Study Sampling Events

Sampling Date	*2-Day Precipitation (mm)*	*Discharge (CMS)*
6/25/2013	4.8	77.0
6/26/2013	8.4	77.3

[1] Events sampled by Weston and Lydy, 2009-2010.

"Dry" Events

Three "Dry" events were monitored on October 18-19, 2011 and on January 18 and May 21 in 2012. The first event was split into two days due to only one boat crew available to sample. All other events were monitored within one day. Six trace detections were found in the samples collected on these dates; all were below the reporting limit of 1.5 ng/L. A summary of the samples is listed in Table VII. No discernable pattern was determined to be evident based on the results of the three "Dry" sampling events. Due to the lack of reportable concentrations over the monitoring of these dates, "Dry" events were not shown to be a driver for the presence of pyrethroid concentrations in water samples and were not monitored during the second year of the study period.

Table VII. Pyrethroid Detection for "Dry" Sampling Events

Analyte	*% of Samples > MDL*	*% of Samples > RL*	*Maximum (ng/L)*	*Cross Sections with Detected Pyrethroids*
Bifenthrin	0.4	0.0	0.30	ARSOE
Cyfluthrin	1.2	0.0	1.10	ARSAB, ARWAB, ARSOE
Cypermethrin	0.4	0.0	1.10	ARCSR
Deltamethrin: Tralomethrin	0.0	0.0	---	---
Efenvalerate: Fenvalerate	0.4	0.0	0.20	ARSOE
Fenpropathrin	0.0	0.0	---	---
Lambda-Cyhalothrin	0.0	0.0	---	---
Permethrin	0.0	0.0	---	---

[1] Percentages out of 241 total samples collected.

“Wet” Events

“Wet,” or rainfall driven events were monitored on January 20, February 13, March 14, October 22 and November 29 in 2012 and March 20, and June 24–26, 2013. The results from the “Wet” events tended to indicate spatial variation in pyrethroid concentrations both among transects (i.e., from one transect to another) and within transects (i.e., from one sampling point within a transect to another sampling point within a single transect). Temporal variation was also evident (i.e., residues that were detected were not consistent from sampling event to sampling event). The summary of the results can be seen in Table VIII.

Table VIII. Pyrethroid Detection for “Wet” Sampling Events

Analyte	*% of Samples > MDL*[1]	*% of Samples > RL*[1]	*Range > RL (ng/L)*	*Cross Sections with Detected Pyrethroids*
Bifenthrin	55.9	19.2	1.5–7.8	ARB80, ARCSR, ARDLN, ARDPK, ARSAB, ARSOE, ARWAB
Cyfluthrin	10.9	2.7	1.6–3.2	ARB80, ARCSR, ARDLN, ARDPK, ARSAB, ARSOE, ARWAB
Cypermethrin	7.2	0.0	---	ARB80, ARCSR, ARDLN, ARDPK, ARSAB, ARSOE, ARWAB
Deltamethrin: Tralomethrin	1.2	0.2	3.1–3.1	ARB80, ARCSR, ARDLN, ARDPK
Efenvalerate: Fenvalerate	1.6	0.0	---	ARB80, ARCSR, ARDLN, ARDPK, ARWAB
Fenpropathrin	0.4	0.0	---	ARB80, ARDLN
Lambda-Cyhalothrin	8.4	0.2	1.9–1.9	ARB80, ARCSR, ARDLN, ARDPK, ARSOE, ARWAB
Permethrin	0.0	0.0	---	---

[1] Percentages out of 515 total samples collected.

The results of the “Wet” events show that, while not exclusively, rainfall events generally are the driving factor causing movement of pyrethroids into the river system. There was a high degree of variability across events due to differences in timing of rainfall, storm duration, total rainfall amount, and base river discharge.

As can be noted from the table, bifenthrin was the most commonly detected analyte, being detected in just over 19% of all samples at levels above the reporting limit. Cyfluthrin was the second most commonly found analyte, however, it was detected at a much lower frequency, being present in only 2.7% of samples collected. All other analytes were only detected over their respective reporting limits at a frequency of 0 and 0.2% of all samples collected.

Bed Sediment

Bed sediment samples were collected during the October 18–19, 2011 and May 21, 2012, pre– and post–“rainy” season sampling events. Bed sediment samping was somewhat limited by the type of bed substrate. Only portions of the stream bed that contained primarily sand and small gravel were sampled. In general, bifenthrin was the most prominent analyte detected above the reporting limit, at a frequency of 27.4% of all samples collected. The sampling results are presented in Tables IX and X.

As the focus of this study was directed at examining pyrethroid residues in the water column, no further bed sediment sampling events were conducted throughout the remainder of the study.

Table IX. -yrethroid Detection for the Pre-“Rainy” Season Bed Sediment Sampling Event on October 18–19, 2011

Analyte	*% of Samples > MDL[1]*	*% of Samples > RL[1]*	*Range > RL (ug/L)*	*Cross Sections with Detected Pyrethroids*
Bifenthrin	60.0	33.3	0.34–5.3	ARDLN, ARWAB, ARCSR, ARDPK, ARSOE,
Cyfluthrin	20.0	6.7	0.55–0.55	ARCSR, ARDPK, ARSOE
Cypermethrin	20.0	0.0	---	ARCSR, ARB80, ARDPK
Deltamethrin: Tralomethrin	6.7	6.7	1.3–1.3	ARDPK
Efenvalerate: Fenvalerate	0.0	0.0	---	---
Fenpropathrin	0.0	0.0	---	---
Lambda-Cyhalothrin	13.3	6.7	0.79–0.79	ARB80, ARDPK
Permethrin	20.0	20.0	1.9–4.3	ARDLN, ARCSR, ARDPK

[1] Percentages out of 15 total samples collected.

Table X. Pyrethroid Detection for the Post-"Rainy" Season Bed Sediment Sampling Event on May 21, 2012

Analyte	*% of Samples > MDL*[1]	*% of Samples > RL*[1]	*Range > RL (ug/L)*	*Cross Sections with Detected Pyrethroids*
Bifenthrin	64.3	21.4	1.5–1.7	ARDLN, ARDPK, ARSOE
Cyfluthrin	14.3	7.1	0.82−0.82	ARDPK, ARSOE
Cypermethrin	7.1	0.0	---	ARDPK
Deltamethrin: Tralomethrin	0.0	0.0	---	---
Efenvalerate: Fenvalerate	0.0	0.0	---	---
Fenpropathrin	0.0	0.0	---	---
Lambda-Cyhalothrin	14.3	0.0	---	ARDPK, ARSOE
Permethrin	14.3	7.1	4.7–4.7	ARDPK

[1] Percentages out of 14 total samples collected.

Other Events

As the results of the first year of monitoring suggested the presence of pyrethroid residues in the river sysem as a result of storm events, additional monitoring studies were proposed during the second year of the study. Three alternative types of monitoring studies were targeted to address questions regarding pyrethroid residue persistence as a result of storm events.

Two of the additional studies were employed during the sampling event that took place on March 20, 2013. The first study during this span was the Lagrangian/Drift style sampling method used to sample between the ARCSR and ARB80 cross-sections. This river reach was chosen based on a history of more frequent detections due to the ARCSR cross-section proximity to the Chicken Ranch/Strong Ranch slough discharge into the river. The results of this sampling study are highlighted in Table XI.

Table XI. Intertransect Drift Study Detection Summary for March 20, 2013

Analyte	*% of Samples > MDL*[1]	*% of Samples > RL*[1]	*Range > RL (ng/L)*
Bifenthrin	97.9	2.1	1.5–1.5
Cyfluthrin	0.0	0.0	---
Cypermethrin	0.0	0.0	---
Deltamethrin:Tralomethrin	2.1	0.0	---
Efenvalerate:Fenvalerate	0.0	0.0	---
Fenpropathrin	0.0	0.0	---
Lambda-Cyhalothrin	0.0	0.0	---
Permethrin	0.0	0.0	---

[1] Percentages out of 47 total samples collected.

The results of this monitoring event only yielded one sample with a concentration above the reporting limits, which was for bifenthrin detected at a level of 1.5 ng/L. However, bifenthrin was detected at levels between the method detection limit (MDL) and reporting limit (RL) in nearly 98% of samples collected. A spatial view of these data is provided in Figure 4.

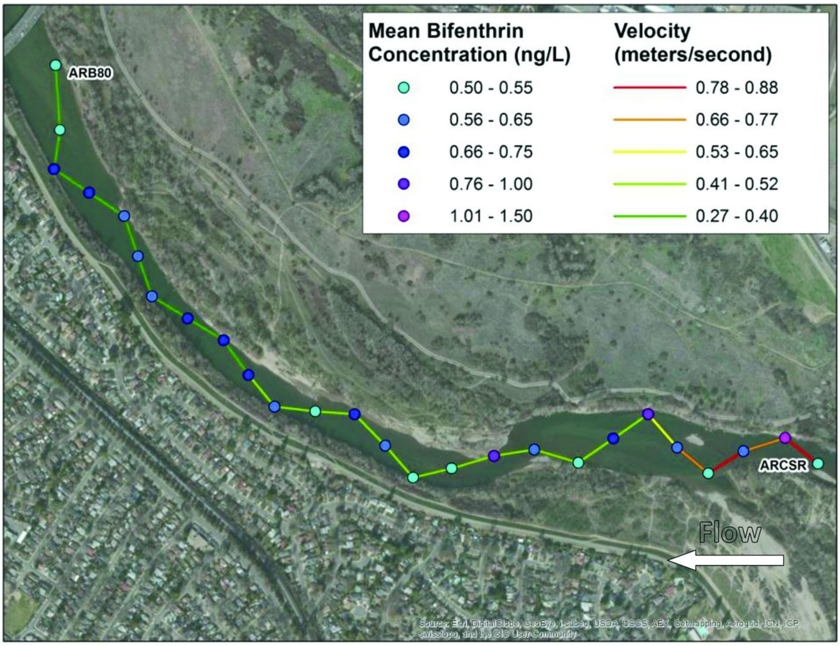

Figure 4. Concentration values and velocity during the inter-transect study on March 20, 2013. (see color insert)

The second study conducted on March 20, 2013, was the revisiting of a single transect to address persistence of pyrethroid residues at a single transect. Two bank to bank samplings of the transect were conducted similar to other "Wet" sampling events. The overall summary of the detections found during this study are provided in Table XII.

This sampling study also yielded a high frequency of bifenthrin detections; however, all detections were between the MDL and RL. Single detections of all other analytes except permethrin were also found, but again at concentrations below the RL. In general, concentrations between the first and second traverse of the sampling transect were fairly consistant, however, all either remained the same, or declined between the first and second sampling pass; the greatest difference in any single concentration a sampling location being only 0.4 ng/L. This result was somewhat expected, however, because of the relatively short time period that elapsed between the first and second pass across the transect (approximately 1 hour). Even so, relatively little data exists regarding duration of residue persistence.

Table XII. Transect Revisit Sampling at ARB80 on March 20, 2013

Analyte	*% of Samples > MDL*[1]	*% of Samples > RL*[1]	*Range > RL (ng/L)*
Bifenthrin	100.0	0.0	---
Cyfluthrin	5.6	0.0	---
Cypermethrin	5.6	0.0	---
Deltamethrin:Tralomethrin	5.6	0.0	---
Efenvalerate:Fenvalerate	5.6	0.0	---
Fenpropathrin	5.6	0.0	---
Lambda-Cyhalothrin	5.6	0.0	---
Permethrin	0.0	0.0	---

[1] Percentages out of 18 total samples collected.

The third alternative sampling study consisted of multiple transect revisits over a three day period between June 24–26, 2013 during a "Wet" event. These events were monitored in the same way as the "Wet" events and the transect revisit sampling at the ARB80 transect; however, monitoring was only conducted at a subset of transects. This event consisted of sampling the ARCSR and ARB80 transects on all three days of monitoring, and the ARCSR cross-section twice on the second day. Additionally, ARDPK and ARSOE transects were sampled on the second day as well. The summary of detections can be seen in Table XIII.

Table XIII. Detections During Multi-Day Monitoring Event June 24–26, 2013

Analyte	*% of Samples > MDL*[1]	*% of Samples > RL*[1]	*Range > RL (ng/L)*	*Cross Sections with Detected Pyrethroids*
Bifenthrin	6.2	1.2	4.8–4.8	ARB80, ARCSR, ARDPK
Cyfluthrin	1.2	1.2	2.5–2.5	ARDPK
Cypermethrin	0.0	0.0	---	---
Deltamethrin:Tralomethrin	0.0	0.0	---	---
Efenvalerate:Fenvalerate	0.0	0.0	---	---
Fenpropathrin	0.0	0.0	---	---
Lambda-Cyhalothrin	0.0	0.0	---	---
Permethrin	0.0	0.0	---	---

[1] Percentages out of 81 total samples collected.

Very few detections were found during this monitoring event and no detections were observed on either day one or three of the event. Only 5 samples collected over the three day period yielded detectable concentrations. All 5 samples contained detectable concentrations of bifenthrin, however, only one was over the reporting limit. This same sample also contained cyfluthrin above the reportable limit.

Conclusions

The data collected and analysis conducted during this multi-year study identified rainfall-runoff events are the driving perturbations behind the infrequent and highly variable pyrethroid movement into the lower American River. A variety of factors contribute to environmental complexity. However, rainfall is the only true driver, while other land cover complexities, stormwater detention systems, and hard surfaces contribute to the variability in local rainfall-runoff contribution to river flows. Additionally these local rainfall-runoff flows are small relative to the much larger controlled dam releases upstream from larger lake storage. Among these complexities, it is clear that river base flow and rainfall event timing both play critical roles in determining the presence, persistence, and magnitude of pyrethroid residues. Due to these factors, and in addition to receiving water characteristics, assessments of this waterway cannot be based on selective point sampling near a river bank. As the results of this study suggest, heterogeneity among river cross-sections and reaches require a more robust sampling regime, such as the one implemented during this study. Through such study design, the dynamics of pyrethroid concentrations in this waterway can be investigated and results to date demonstrate that pyrethroid residues have generally been low and infrequent.

The range across the combination of river base flow, dry periods, and significant rainfall-runoff conditions monitored during this study are extensive, but not exhaustive. The range monitored, however, does represent a significant portion of the conditions typically experienced in this watershed. In an attempt to target a larger range of river and rainfall conditions to provide a more comprehensive data set, this study has continued into the 2013–2014 rainy season.

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Chapter 8

Pyrethroid Pesticides in Municipal Wastewater: A Baseline Survey of Publicly Owned Treatment Works Facilities in California in 2013

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Publicly Owned Treatment Works (POTWs), also known as wastewater or sewage treatment plants, are typically owned by local city and county agencies. Approximately 564 California POTWs collectively treat approximately 3.47 billion gallons per day. This study was a survey of a diverse group of 32 California POTWs that together treat more than 40% of California's wastewater and was designed to show which of eight Group III pyrethroids (bifenthrin cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, and permethrin) might potentially be found in the influent, effluent and biosolids of California's POTWs. Consistent with the intent of this study as a survey, the samples were grab samples (influent, effluent and biosolids) taken at a single point in time.

Introduction

Synthetic pyrethroid insecticides are potential contaminants of wastewater. As a class, these insecticides are widely used in both urban and rural environments. In the urban environment, pyrethroids are used for lawn and garden care, pet care (shampoos, spot-on products and collars to prevent fleas), controlling insects around and inside buildings (flies, ants and spiders), head lice and scabies treatments, mosquito abatement, sewer manhole treatments, termite control and some clothing treatment. A number of researchers (*1–3*) have detected these products in aquatic surface waters and sediment samples at levels potentially harmful to aquatic invertebrates. In addition, Rogers (*4*) , Gomez (*5*) and Turner (*6*) have identified pyrethroids in influent, effluent and sludge from sewage treatment plants in Europe and the USA. Weston and Lydy (*7*) have shown that pyrethroids are present in secondary-treated municipal wastewater in California at concentration levels above the LC_{50} for the test system organism, *Hyalella azteca*.

In August 2006, the California Department of Pesticide Regulation initiated a data reevaluation of pesticides containing pyrethroid active ingredients. The data requirements included "monitoring in areas appropriate to the use" and applied to products likely to enter wastewater treatment plants. Shortly thereafter, the Pyrethroid Working Group (PWG), an industry-based group that was formed in 1990 to collectively address questions raised by the United States Environmental Protection Agency on aquatic ecotoxicity of cotton-use pyrethroids, committed to work with the California Department of Pesticide Regulation (DPR) to develop a program that will meet the requirements of the pyrethroid re-evaluation for monitoring in effluents of Publicly Owned Treatment Works. The member companies of the PWG are: Amvac Corporation, Bayer CropScience, BASF Corporation, DuPont Crop Protection, FMC Corporation, Pytech/Cheminova, Syngenta Crop Protection, and Valent USA Corporation.

In order to meet the requirements of the study, the PWG joined in a partnership with Tri-TAC. Tri-TAC's name reflects its membership and role: "Tri" from its three sponsoring organizations (the League of California Cities, the California Association of Sanitation Agencies, and the California Water Environment Association); and "TAC" from its role as a Technical Advisory Committee. Tri-TAC works with State and Federal Regulatory Agencies and interest groups on matters related to Publicly Owned Treatment Works (POTWs), with the goal of improving the overall effectiveness and accountability of environmental projects that impact POTWs in California. The PWG would be responsible for conducting the study, while Tri-TAC would be a key advisor in the development of the study protocol, obtain volunteers for the study, review of the analytical data and peer review the final report.

Materials and Methods

Study Design

This project was designed to meet the requirements from the Department of Pesticide Regulation as well as being comparable to California's Surface Water

Ambient Monitoring Program (SWAMP) guidelines. These requirements called for eight (Group III) pyrethroids in at least 20 POTWs to be monitored in effluent, influent, and biosolids matrices. The eight pyrethroids to be monitored were bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, and permethrin. Analyses for total organic carbon, total suspended solids, and total solids were added. Prior to the initiation of the study, a Quality Assurance Project Plan (QAPP) was prepared by the Study Director and the study design was reviewed by the SWAMP Quality Assurance Help Desk and found to be SWAMP-comparable.

A total of 32 POTW facilities volunteered for this program. A total of 31 sites collected effluent (one of the sites served as a dechlorination facility for other POTWs), 31 sites collected influent and 24 sites collected biosolids (not all of the sites either collect or treat the biosolids at their facility). Facilities varied in volume of wastewater treated, location, treatment processes used (primary, secondary, tertiary), customer base (industrial, commercial and residential) and population served. The facilities participating in this study are regulated by seven of the nine California Regional Water Quality Boards and represent more than 40% of the total wastewater treatment volume in California (see Tables 1 and 2). Each of the sites was pre-assigned a letter code (A through GG). The only individuals who knew the identity of the sites were the Study Director, the Quality Assurance Manager, the Engineering Consultant and the individual responsible for shipping and receiving at the distribution laboratory.

Table 1. All California POTWs and POTW Survey Volunteers by Flow (Totals may not add up due to rounding.). Source: EPA 2008 Needs Survey data (*8*) and Tri-TAC survey of volunteers.

All California POTWs			*POTW Study Volunteers*		
Flow (MGD)	*#POTWs*	*Total Discharge Flow (MGD)*	*Flow (MGD)*	*#POTWs*	*Total Discharge Flow (MGD)*
<1	337	81	<1	3	1
1-9.9	174	617	1-9.9	11	58.3
10-19.9	30	400	10-19.9	7	102.6
20-100	22	944	20-100	6	249.5
>100	6	1,427	>100	5	1,079.4
Total	**569**	**3,469**	**Total**	**32**	**1,490.8**

Total Discharge Flow is the sum of the daily average flow for every POTW in the size category. Note: None of the study volunteers had "combined" systems (i.e., they do not deliberately collect and treat urban runoff).

Each of the POTWs was asked to collect consecutive grab samples of influent, effluent and, where available, biosolids. In addition, samples of influent and effluent were collected for total suspended solids (TSS) and total organic carbon (TOC). The facilities were asked to deliver the samples to the analytical laboratory no later than the afternoon following sampling using either a courier or overnight shipment service to ensure analytical hold times for influent and effluent (72 hours) were met. A total of 724 samples were collected for the study.

Table 2. California POTWs with Discharge Permits and POTW Pyrethroid Survey Volunteers by Region (Totals may not add up due to rounding.). Source: EPA 2008 Needs Survey data (*8*)and Tri-TAC survey of volunteers.

All California POTWs			*POTW Pyrethroid Study Volunteers*		
Water Board Region	***#POTWs with NPDES Permits***	***Total Discharge Flow (MGD)***	***Water Board Region***	***#POTWs with NPDES Permits***	***Total Discharge Flow (MGD)***
1-North Coast	232	20	1-North Coast	2	18.4
2-SF Bay	43	674	2-SF Bay	7	178.9
3-Central Coast	22	81	3-Central Coast	4	13.5
4-Los Angeles	27	1.152	4-Los Angeles	7	645.1
5-Central Valley	60	388	5-Central Valley	3*	97.5
6-Lahontan	4	4	6-Lahontan	0	0
7-Colorado River	12	18	7-Colorado River	0	0
8-Santa Ana	19	389	8-Santa Ana	2	332
9-San Diego	12	286	9-San Diego	7	205.4
Total	**222**	**3,011**	**Total**	**32**	**1,490.8**

Total Dischage Flow is the sum of the daily average flow for every POTW in the region. Note: Two volunteers are not dischargers so table does not represent total volume treated.

Two laboratories, Caltest Analytical Laboratory located in Napa, California and Morse Laboratories, Incorporated (a wholly-owned subsidiary of Analytical Bio-Chemistry Laboratories, Inc.) located in Sacramento, California were selected for the analytical work. The laboratories were chosen based on their ability to work at trace (parts per trillion) levels, the availability of proven pyrethroid analytical methods and the ability to confirm pyrethroids using secondary ion mass spectrometry. Both laboratories were asked to prepare and analyze the samples using their routine methods, instrumentation, and quality control samples. The Study Director provided each laboratory with a set of eight stable isotope-enriched (d6) standards of each of the eight pyrethroids in the study to be used as internal standards and surrogates as well as a standardized reporting format.

Caltest was selected as the Study Distribution Laboratory. This laboratory was responsible for securing the sample containers, sending the containers to the 32 POTWs, receiving the samples from the POTWs and preparing and distributing the test materials to Morse Laboratories. In addition, Caltest was responsible for pyrethroid analysis of influent, effluent and biosolids, the analysis of total suspended solids (TSS) and total organic content (TOC) on influent and effluent and total solids (TS) on the biosolids.

Laboratory Analysis

The analytical methods and detectors used for the project are listed in Table 3.

Pyrethroids Analysis in Influent and Effluent Samples by GC-MSD/NCI (Morse)

The method described herein is capable of determining bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin and permethrin in influent and effluent wastewater. Esfenvalerate-d6 and fenpropathrin-d6 are used as surrogate standards in this method. The surrogates are added to the sample prior to the initial extraction step to demonstrate extraction efficiency. Pyrethoid residues are extracted from wastewater by first adding methanol and sodium chloride to the aqueous sample, then partitioning the mixture two times with hexane. The upper hexane layer is passed through sodium sulfate, evaporated to dryness and re-dissolved in a small volume of hexane. The hexane extract is then subjected to a Bond Elut® LRC Silica solid phase extraction (SPE) procedure prior to residue determination. analysis is performed using an Agilent GC-MS (A6890/5973N) in negative chemical ionization (NCI) mode, using selective ion monitoring mode of detection and quantification. The instrument is initially calibrated using a minimum of five standards (of increasing concentrations) that meets a RSD or Grand Mean of < 15%. Quantitation for all samples is performed using mid-calibration level standards, bracketing every four samples. The limit of quantitation of the method for effluent wastewater and water is 0.50 ng/L for esfenvalerate, fenpropathrin, lambda-cyhalothrin, bifenthrin, cypermethrin and cyfluthrin, 1.0 ng/L for deltamethrin and 5.0 ng/L for permethrin. The limit of quantitation of the method for influent wastewater is 5.0 ng/L for esfenvalerate, fenpropathrin, lambda-cyhalothrin, bifenthrin, cypermethrin and cyfluthrin, 10 ng/L for deltamethrin and 50 ng/L for permethrin.

The method provides for an optional Bond Elut® Florisil SPE cleanup for the influent wastewater if further extract cleanup is deemed necessary (as determined by unacceptable chromatography resulting from co-elution of interfering compounds or analyte GC response enhancement/suppression). For samples where additional cleanup is necessary, the fortified (spike) samples were treated the same way and re-analyzed to verify recovery. The limit of quantitation (LOQ) remains as stated.

Table 3. List of Analytical Methods and Detectors

Analyte or Group	*Matrix*	*Method*	*Detector Type*	*Prep/ Extraction/ Digestion*	*Lab*
TOC	Influent/ Effluent	SM 5310B	NDIR	SM 5310B	Caltest
TSS	Influent/ Effluent	SM 2540D	Analytical Balance (0.0001g)	None	Caltest
TS	Biosolids	SM 2540G	Analytical Balance (0.0001g)	None	Caltest
Pyrethroids	Influent/ Effluent	8270(M)	GCMS-NCI	SW846 3510C	Caltest
Pyrethroids	Biosolids	8270(M)	GCMS-NCI	SW846 3540C	Caltest
Pyrethroids	Influent/ Effluent	Morse Method 201, Rev. 1	GCMS-NCI	Ref. (*12*)	Morse
Pyrethroids	Biosolids	Morse Method 213 original	GCMS-NCI	Ref. (*12*)	Morse

Pyrethroids Analysis in Biosolids by GC-MSD/NCI (Morse)

The method described herein is capable of determining bifenthrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin and permethrin in wastewater treatment dewatered cake. Esfenvalerate-d6 and fenpropathrin-d6 are used as surrogate standards in this method. The surrogates are added to the sample prior to the initial extraction to demonstrate extraction efficiency. Pyrethroid residues are extracted from wastewater dewatered cake by first homogenizing with methanol, followed by multiple extractions with methanol:methylene chloride (50:50, v/v) using a platform shaker (2 extractions). Following extraction, the crude extract (supernatant) from each shaking is decanted through sodium sulfate into the same 250-mL mixing cylinder and the combined extract is brought to a known volume. An aliquot of the combined sample extract is evaporated to dryness, reconstituted in hexane, then purified by subjecting to a Bond Elut® LRC Silica solid phase extraction (SPE) followed by a Bond Elut® Florisil SPE procedure. The purified extract is evaporated to dryness, re-dissolved in 1.0 mL of internal standard solution with ultrasonication and submitted for residue determination. The analysis is performed using an Agilent GC-MS (A6890/5973N) in negative chemical ionization (NCI) mode, using selective ion monitoring mode of detection and quantification. The instrument is initially calibrated using a minimum of five standards (of increasing concentrations) that meets a RSD or Grand Mean of < 15%. Quantitation for all samples is performed using mid-calibration level standards, bracketing every four samples. The limit of quantitation of the method is 2.5 ng/g for bifenthrin, cypermethrin, cyfluthrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, 5.0 ng/g for deltamethrin, and 25 ng/g for permethrin.

Pyrethroids Analysis in Influent, Effluent, and Biosolids by GC-MS/NCI SIM (Caltest)

Sample preparation for influent and effluent employs EPA SW846 (*9*) -3510C (*10*) extraction method, which calls for 500 ml of influent, or 1,000 ml of effluent to be extracted. A surrogate (Esfenvalerate-d6) is added to the sample prior to the addition of extraction solvents to demonstrate extraction efficiency and the original container is solvent rinsed with dichloromethane (DCM) to start the liquid-liquid extraction process, using 60 mL of DCM followed by vigorous shaking, settled & drained (repeated twice more). Biosolids are extracted by SW846 (*9*)-3540C (*11*) method employing the soxhlet extraction process with 1200 mL of DCM. The sample extract (influent, effluent or biosolids) is solvent exchanged into hexane then passed through a three-phase clean-up step (GCB-graphitized carbon; PSA-Primary & Secondary Amine; alumina), then is concentrated and brought to final volume of 1 mL. The sample analysis for all matrices (influent, effluent and biosolids) is performed using SW846-8270, as modified in the Pyrethroid Working Group method for sediments (*12*). The analysis is performed using an Agilent GC-MS (A7890/5975) in negative chemical ionization (NCI) mode, using selective ion monitoring mode of detection and quantification. The instrument is initially calibrated using a minimum of five standards (of increasing concentrations) that meets a RSD or Grand Mean of < 15%, which then is confirmed by a second-source calibration verification standard to +/- 30%. Quantitation for all samples is performed using mid-calibration level standards, bracketing every four samples.

Total Suspended Solids (TSS) by Gravimetric Analysis (Caltest)

This analysis is performed using Standard Methods 2540 D where a well-mixed sample is filtered through a weighed glass fiber filter and the residue retained on the filter is dried to a constant weight at 103-105 °C. The filter is weighed repeatedly (maximum 5 weightings) until a constant, dried weight is achieved, and the final weight is factored to the sample volume used to determine value of the residue as mg/L. The practical range of the determination is 3 mg/L to 20,000 mg/L.

Total Organic Carbon (TOC) Analysis by NDIR (Caltest)

This analysis is performed using Standard Methods 5310 B for the determination of total organic carbon in waters which contain carbonaceous matter that is soluble. The applicable range for the instrument is 0.5 mg/L to 200 mg/L. A preserved sample (pH <2) contained in a 40 mL VOA vial is placed into the auto-sampler of the TOC analyzer, a Shimadzu TOC CSH. The sample is sparged in acid and injected onto a furnace containing a platinum catalyst. The sample is combusted in an oxygen rich environment to form carbon dioxide which is carried to the non-dispersive infra-red, (NDIR), detector.

Total Solids as Percentage Solids by Gravimetric Analysis (Caltest)

This analysis is performed using Standard Methods 2540 G / EPA 160.4 for the determination of total solids as a percentage of sample weight. Place 25-50 grams of a well-mixed aliquot of the sample in a pre-weighed evaporating dish and evaporated to constant dryness at 103-105 °C. The vessel containing the dried sample is weighted repeatedly (maximum 5 weightings) until a constant, dried weight is achieved. The final weight is divided by the initial weight of the sample aliquot, multiplied by 100, to calculate the solids-only portion of the sample expressed as percentage of the original, semi-solids sample weight.

Results and Discussion

This study was a survey designed to show which of the Group III pyrethroids might be found in influent, effluent and biosolids of California POTWs and to gain an understanding of the range and magnitude of these residues. Consistent with the intent of the study as a survey, the samples were grab samples taken at a single point in time. The samples were not flow or time weighted nor was there an attempt to account for the hydrologic travel time from influent to effluent or an investigation of the pyrethroid concentrations that might occur at different times of the year. For these reasons, care must be taken to avoid over-interpreting the data.

The project developed a comprehensive QA Project Plan with detailed quality control criteria including holding times. All sites were sampled in duplicate and each site's samples were analyzed by two, distinct laboratories. A full suite of QC samples (MS, MSD, LCS) were analyzed with each batch of samples. Analytical data was third-party validated by a team including analytical chemists, QA personnel, and project management. All data was required to meet control limits and quality objectives outline in the QA project plan.

Figure 1 is a graph of the residue profile for effluent (31 sites). To construct this graph the pyrethroid residues from each of the samples were plotted on the x-axis. The graph shows that, typically, the major residue in terms of concentration is permethrin (approximately 85% of the total pyrethroid residue). Cypermethrin is next at approximately 10% of the total residue followed by cyfluthrin, bifenthrin and lambda-cyhalothrin, Esfenvalerate, deltamethrin and fenpropathrin were minor constituents in the profile. Similar profiles were observed in influent and biosolids.

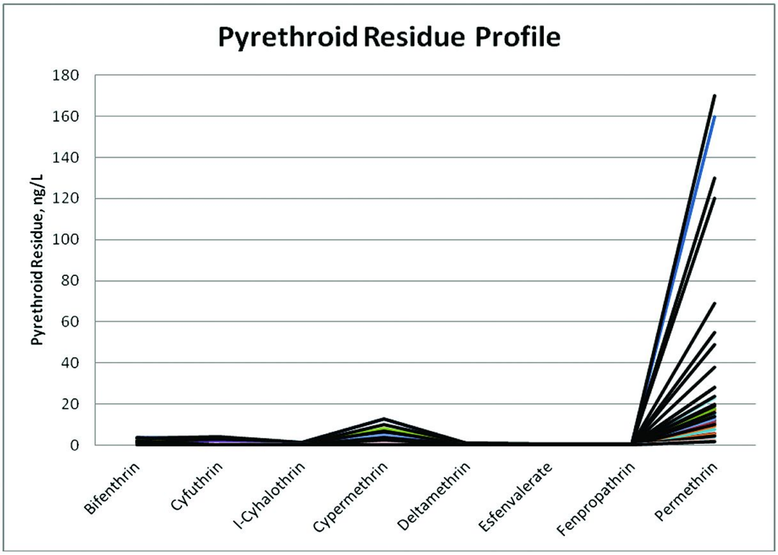


Figure 1. Pyrethroid Residue Profile (ng/L) in Effluent-All Sites.

For effluent, a total of 62 samples were analyzed for pyrethroid residues (Analysis of samples from 31 sites by both laboratories). Total pyrethroid residues ranged from non-detectable to a maximum residue of 190 ng/L. The most frequently detected pyrethroids in effluent were bifenthrin (82%), followed by cypermethrin (81%) and then permethrin (65%). Fenpropathrin has the lowest frequency of detection (3.3%). The range of residues and the median residues for each of the 8 pyrethroids can be found in Table 4. Three sites contained no detectable residues of the 8 monitored pyrethroids. Six sites contain trace residues at or near the level of detection.

For influent, a total of 67 samples (62 samples plus 5 repeats) were analyzed for pyrethroid residues. Total pyrethroid residues ranged from 42 ng/L to a maximum of 3800 ng/L. Permethrin was the predominant pyrethroid found both in terms of frequency of detection (100%) and maximum residue (3800 ng/L) found. Bifenthrin (96%), cyfluthrin (88%), lambda-cyhalothrin, (81%) and cypermethrin (81%) were also detected in most samples. Fenpropathrin was rarely detected (4.5%) although at one site it was the predominant residue found. Fenpropathrin was found in the effluent and biosolids sample from this site and was confirmed by both labs as the dominant pyrethroid. In a query of the State of California's Surface Water Ambient Monitoring Program's database, fenpropathrin was rarely detected, but had been found in sediment samples from agricultural areas. The range of residues and the median residues found for each of the 8 pyrethroids can be found in Table 5.

Table 4. Comparison of Pyrethroid Residues in Effluent from 31 California POTWs

	Bifenthrin ng/L	*Cyfluthrin ng/L*	*Lambda-Cyhalothrin ng/L*	*Cypermethrin ng/L*	*Deltamethrin ng/L*	*Esfenvalerate ng/L*	*Fenpropathrin ng/L*	*Permethrin ng/L*	*Total Pyrethroid[1] ng/L*
# of Samples	62	62	62	62	62	62	62	62	62
# of Detects	51	37	30	50	10	20	2	40	56
% Detected	82	60	48	81	16	32	3.2	65	90
Maximum	3.9	4	1.6	13	1.2	0.6	0.8	170	190
Minimum	ND[2]	ND	ND	ND	ND	ND	ND	ND	ND
Average[3]	0.89	0.60	0.30	2.11	0.31	0.25	0.22	20	25
Median[3]	0.6	0.3	0.2	1.3	0.3	0.2	0.2	9.4	13

[1] Total pyrethroids=sum of the Group III pyrethroids. [2] ND=Non-detected (<LOD or MDL). [3] For average and median calculations, ND values are assumed to be at the LOD or MDL value.

Table 5. Comparison of Pyrethroid Residues in Influent from 31 California POTWs

	Bifenthrin ng/L	*Cyfluthrin ng/L*	*Lambda-Cyhalothrin ng/L*	*Cypermethrin ng/L*	*Deltamethrin ng/L*	*Esfenvalerate ng/L*	*Fenpropathrin ng/L*	*Permethrin ng/L*	*Total Pyrethroid[1] ng/L*
# of Samples	67	62	67	67	67	67	67	67	67
# of Detects	64	59	54	54	29	31	3	67	67
% Detected	96	88	81	81	43	46	4.5	100	100
Maximum	74	55	72	200	210	360	130	3800	3800
Minimum	ND[2]	ND	ND	ND	ND	ND	ND	30	42
Average[3]	15	11	5.6	35	8.0	8.1	4.6	330	420
Median[3]	9.7	7.4	2.8	21	3.3	1.7	1.7	230	300

1 Total pyrethroids=sum of the Group III pyrethroids 2 ND=Non-detected (<LOD or MDL) 3 For average and median calculations, ND values are assumed to be at the LOD or MDL value.

For biosolids, a total of 52 samples (48 samples plus 4 repeats) from 24 sites were analyzed for pyrethroid residues. Total pyrethroid residues ranged from a low of 130 ng/g to a maximum of 13000 ng/g on a dry weight basis. Bifenthrin was in 96% of the samples. Permethrin (92%), followed by cypermethrin (90%), cyfluthrin (87%) and lambda-cyhalothrin (52%) were the next most frequently detected. Median residues for total pyrethroid in biosolids were 1500 ng/g on a dry weight basis. The range of residues and the median residues for each of the 8 pyrethroids can be found in Table 6.

Box and whisker plots were used to compare the range of residues found in influent and effluent from all sites. Figure 2 shows distribution of pyrethroid residues found in influent and effluent for bifenthrin, cypermethrin and cyfluthrin. For all pyrethroids, the average effluent concentration is less than 10% of the influent concentration.. Similar profiles are obseved for the other pyrethroids.

To examine differences in treatment type (primary, secondary and tertiary), scatter plots of the effluent concentrations for each of the pyrethroids were prepared. The sites were separated by treatment type and then the residues plotted against each site. Figure 3 shows the plots for permethrin and Figure 4 shows the plots for cypermethrin. All of the pyrethroids show a similar profile. Clearly there is a pattern of a reduction in residues as the wastewater receives further treatment, but this correlation is imperfect. There are secondary treatment sites that have lower residues than some of the tertiary sites and there are tertiary sites that have higher residues than the median secondary treatment sites.

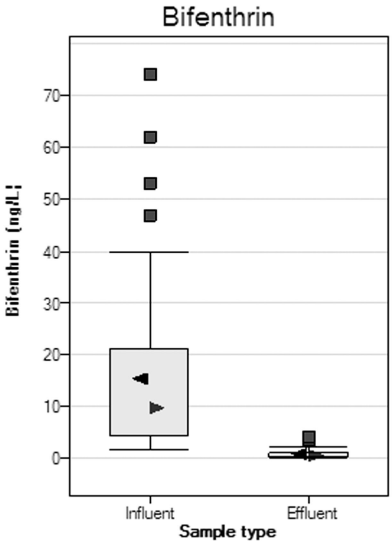
Hydrophobic compounds, such as pyrethroid pesticides, tend to sorb to solids (biosolids) and organic matter. Plots of the pyrethroid residues in effluent versus total suspended solids (TSS) were made for each of the individual pyrethroids. In all instances, there is a trend toward higher residues with increasing TSS, however, the pattern is not definitive and the correlation is strongly influenced by the data from the primary treatment site. Plots of the correlation using the cypermethrin data are shown both with the primary site included (Figure 5) and taking this data out (Figure 6). Including the primary site data, the correlation is poor (r^2=31.4%) and several data points fall just outside of the 95% confidence limits. Excluding the primary site, there is no correlation between the pyrethroid concentration and TSS (r^2=6.8%).

Similarly, plots of pyrethroid residues in effluent versus total organic content (TOC) were made to examine potential relationships. Again, there is a trend toward higher pyrethroid residues with increasing TOC in effluent, but the pattern is not definitive.

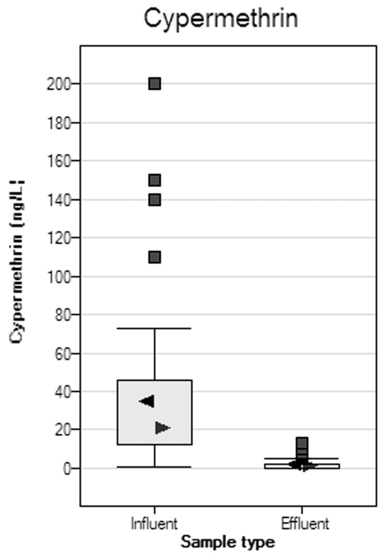
Table 6. Comparison of Pyrethroid Residues in Biosolids from 24 California POTWs

	Bifenthrin ng/L	*Cyfluthrin ng/L*	*Lambda-Cyhalothrin ng/L*	*Cypermethrin ng/L*	*Deltamethrin ng/L*	*Esfenvalerate ng/L*	*Fenpropathrin ng/L*	*Permethrin ng/L*	*Total Pyrethroid[1] ng/L*
# of Samples	52	52	52	52	52	52	52	52	52
# of Detects	50	45	27	47	16	16	3	48	52
% Detected	96	87	52	90	31	31	5.8	92	100
Maximum	1100	190	200	1000	78	42	71	11000	13000
Minimum	ND[2]	ND	ND	ND	ND	ND	ND	ND	130
Average[3]	150	34	29	110	28	15	12	1500	1900
Median[3]	120	29	28	79	24	14	6.8	1200	1500

[1] Total pyrethroids=sum of the Group III pyrethroids. [2] ND=Non-detected (<LOD or MDL). [3] For average and median calculations, ND values are assumed to be at the LOD or MDL value.



Left Arrow-Average Concentration
Right arrow-Median Concentration



Left Arrow-Average Concentration
Right arrow-Median Concentration

Figure 2. Distribution of Bifenthrin and Cypermethrin in Influent and Effluent.

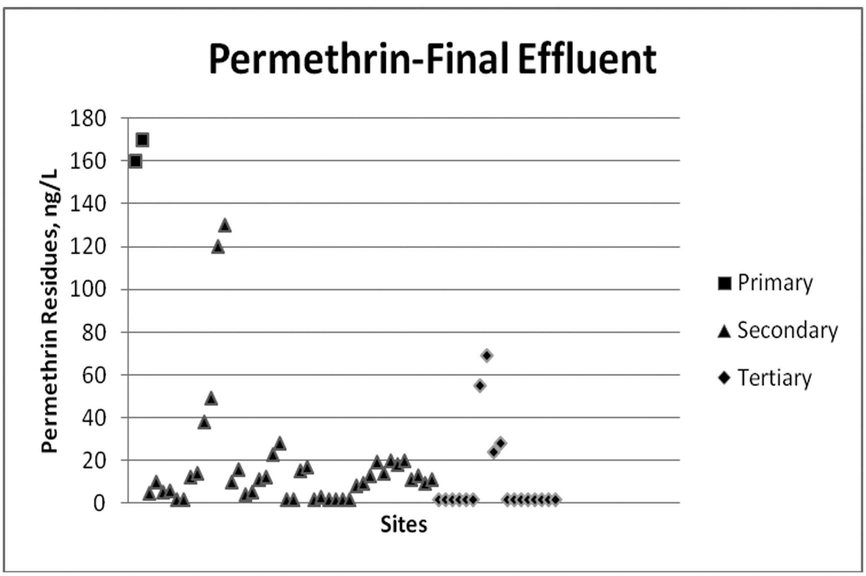


Figure 3. Comparison of Treatment Effects-Permethrin Concentrations in Final Effluent.

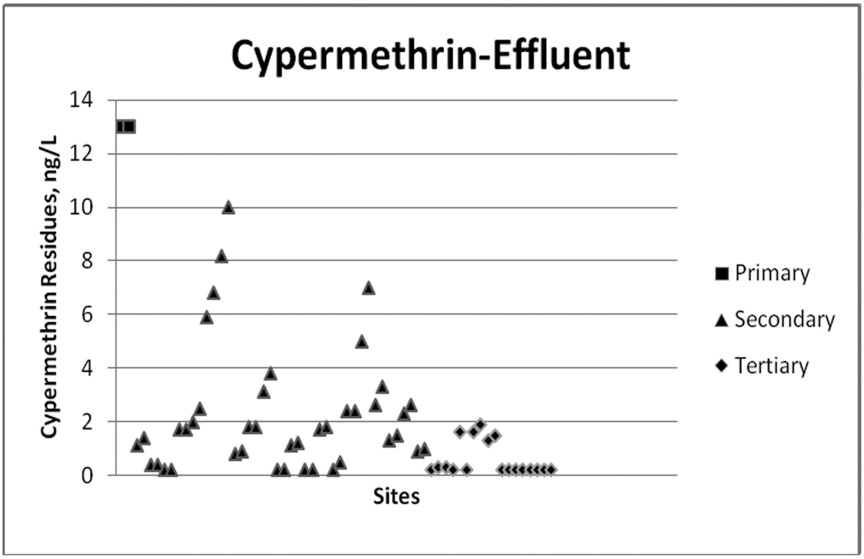


Figure 4. Comparison of Treatment Effects-Cypermethrin Concentrations in Final Effluent

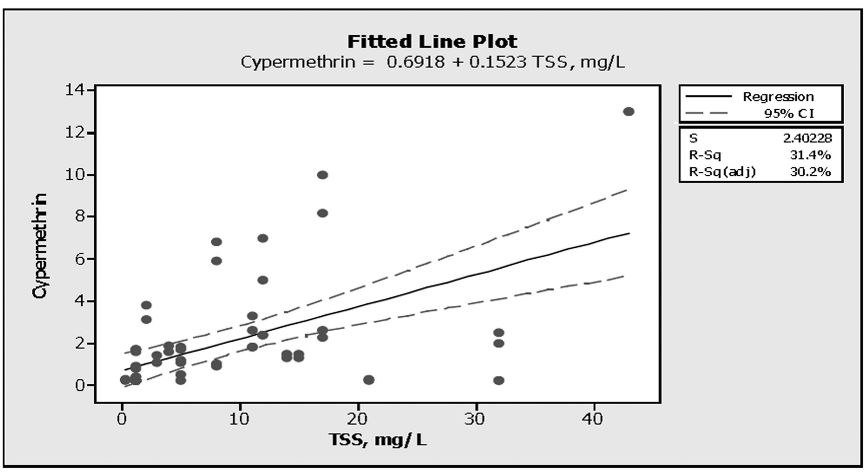


Figure 5. Cypermethrin(ng/L) vs. Total Suspended Solids (TSS, mg/L) in Effluent-With Primary Site.

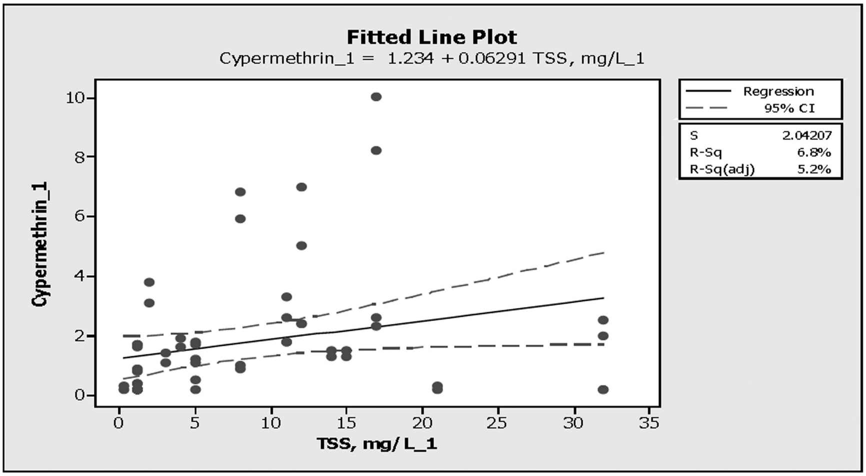


Figure 6. Cypermethrin(ng/L) vs. Total Suspended Solids (TSS, mg/L) in Effluent-Without Primary Site

Conclusions

This project was established to achieve a baseline understanding of the range and frequency of detections of eight Group III pyrethroid insecticides in California publicly-owned treatment works. Only one grab sample was collected for each matrix at a given site. The samples were not timed between influent, effluent, and biosolids collection. This was a targeted study design and was not intended to support a statistically nor comprehensive approach to site characterization or to characterize the type of facilities. However, with these caveats, the following observations can be made.

- In effluent, pyrethroids were detected in 28 of the 31 sites examined. Bifenthrin (82%) was the most frequently detected pyrethroid in effluent followed by cypermethrin (81%) and permethrin (65%).Total pyrethroid residues in effluent ranged from non-detectable to a maximum of 190 ng/L. The median residue was 13 ng/L.
- In influent, permethrin was the predominant residue both in terms of the frequency of detection (100%) and the maximum residues found (3800 ng/L). Bifenthrin (96%), cyfluthrin (88%), l-cyhalothrin (81%) and cypermethrin (81%) were also frequently detected. Total residues of pyrethroid in influent ranged from 42 ng/L to a maximum of 3800 ng/L. The median residue was 300 ng/L.
- As expected for hydrophobic compounds, the highest residue concentrations were found in the biosolids. Bifenthrin was the most frequently detected (96%) in the 24 facilities examined followed by permethrin (92%) and cyfluthrin (87%). Total pyrethroids found ranged from 130 ng/g to 13,000 ng/g on a dry weight basis. Median residue was 1500 ng/g dry weight.

- Pyrethroid residues suggest a trend towards greater reduction as treatment increases from primary to tertiary. The percentage of tertiary plants with pyrethroids near the reporting limit is greater than for secondary plants. However, the trend is not definitive.
- For secondary and tertiary plants with measurable residues, effluent residues are less than 10 % of influent residues with four exceptions-3 secondary and 1 tertiary.
- The correlation between total suspended solids and pyrethroid residues is suggestive, but not compelling. Regression analysis does not show statistically significant correlation.

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Chapter 9

Analysis of Pyrethroid Insecticides in Complex Environmental Samples, Using Stable Isotope-Labeled Standards as Surrogates

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Several synthetic pyrethroids have indoor, as well as lawn, garden, and external structural barrier uses. This broad range of use patterns may result in the presence of multiple pyrethroids in influent/effluent waters and biosolids from publicly owned treatment works (POTWs). This book chapter will describe an analytical approach to analyzing these complex matrices for eight representative pyrethroids, using the previously reported NCI-GC-MS instrumental analysis with D_6 stable isotope analogues as internal standards. Due to significant variability in the composition of biosolids from different POTWs, adding known amounts of surrogate compounds to each sample prior to extraction and then measuring recoveries in order to demonstrate acceptable method performance is highly desirable. The presentation will further describe the use of two selected D_6 analogues as surrogates that closely match the method behavior of the eight target analytes. Details of a recently-validated biosolids method now in routine use are reported herein, along with associated method performance and surrogate stable isotope analogue recovery data.

Introduction

Synthetic pyrethroids exhibit low acute mammalian activity and currently have multiple uses for insect control. These include indoor, as well as lawn, garden, and external structural barrier uses in the urban environment. Pyrethroids are employed for pet care (shampoos, collars, etc. for flea control); control of mosquitos, termites, and other insects; treatment for head lice and scabies; and on clothing as a repellent. These multiple use patterns can result in the presence of a range of pyrethroids in influent and effluent waters and biosolids from publicly owned treatment works (POTWs). The Pyrethroid Working Group (PWG) required robust and highly sensitive multianalyte methods for eight pyrethroids in these substrates. The critically important use of d_6 isotopically labeled analogues of two selected pyrethroids as surrogates (with d_6 analogues of the other six target pyrethroids employed as instrumental analysis internal standards) is highlighted herein. This new inclusion of surrogates was incorporated into previously developed wastewater (influent and effluent) method, as well as a modified version of the previously develop biosolids method. Performance data, along with the surrogate stable isotope analogue recovery data for these methods, are reported and evaluated.

Analytical Method Approach

The multi-analyte method reported here for analysis of influent and effluent waters and biosolids quantifies the following eight pyrethroid insecticides and their isomer variants:

- Bifenthrin
- Cyfluthrin
- Cypermethrin
- Deltamethrin
- Esfenvalerate
- Fenpropathrin
- Lambda-cyhalothrin
- Permethrin

Stable isotope (d_6) analogues were synthesized for each of the eight targeted method analytes and have been successfully used as internal standards (IS) for normalization of NCI-GC-MS instrumental response for aqueous (*1*, *2*) and biosolids (*3*) extracts. A mixed d_6 standard solution is used for reconstitution of the sample extracts, and the response ratios of each pyrethroid and corresponding d_6 IS are compared to the ratios of standards of known native analyte concentration, with the same IS concentration as the sample extracts. This approach, due to the near-identical chemical behavior of the d_6 compounds, provides the most accurate available correction of fluctuations or drift in the instrumental system response.

Analytical Challenges

Pyrethroid analysis in wastewaters and biosolids is challenging due to multiple factors. Co-extractives that survive the method cleanup steps can over time affect the instrumental (NCI-GC-MS) response. Water analysis typically involves a large (i.e., 500X) concentration factor in order to reach LOQs as low as 0.5 parts per trillion (for effluent water). Biosolids by their nature are complex mixtures, which can result in dirty extracts. The considerable variability of the substrate material between sample sources (especially for biosolids) adds complexity to the application of the method. Due to extensive historical use of pyrethroids it can be difficult to obtain control samples that are totally free of trace pyrethroids, thus there are practical limitations on the lowest fortification levels when determining method recoveries by fortifying with those particular compounds.

In practice, the analysis of unknown samples is accompanied by the analysis of fortified (or overspiked) samples so that analyte recovery through the method can be measured and the method performance evaluated. However, variability in composition between the sample chosen for fortification analysis and the other monitoring samples could in theory result in undetected method failure (i.e., poor recovery of analytes) for specific samples.

Method Refinements

The biosolids method employed previously by Morse Laboratories for primary sludge (*4*) was updated for use in a 2013 study examining the potential for occurrence of pyrethroid residues in POTW effluent and dewatered cake biosolids, and also the extent of pyrethroid removal from influents by the POTW processes (*5*). In addition to the incorporation of the d_6 internal standards (to allow normalization of variability in the instrumental response), a change in the extraction procedure was implemented. The former method, developed for liquid sludge, employed shaking once with methanol/water mixture and hexane. When this technique was applied to dewatered cake samples, however, the (presumed) presence of flocculating agents produced aggregations of particulates in the water-methanol solvent mixture that were difficult to disperse in order to allow for efficient extraction. It was determined that two extractions (by shaking) with 50:50 methanol:methylene chloride avoided the aggregation. As reported (*5*), this technique generated sample analysis results that were comparable to an 18-hour methylene chloride reflux extraction that was performed in parallel at another laboratory (on split samples). Also, in order to employ a more robust method, with a lesser propensity for contamination of the instrumental components (e.g., inlet, analytical column, and detector) and premature detector filament burnout, a second solid phase extraction (SPE) cleanup has been incorporated, with Florisil cleanup being used following (and in addition to) the previously-developed Silica SPE cleanup. The Florisil SPE elution parameters were developed based upon historical parameters for pesticide residue cleanup procedures.

Details of the updated method are presented in the following flowchart (Figure 1).

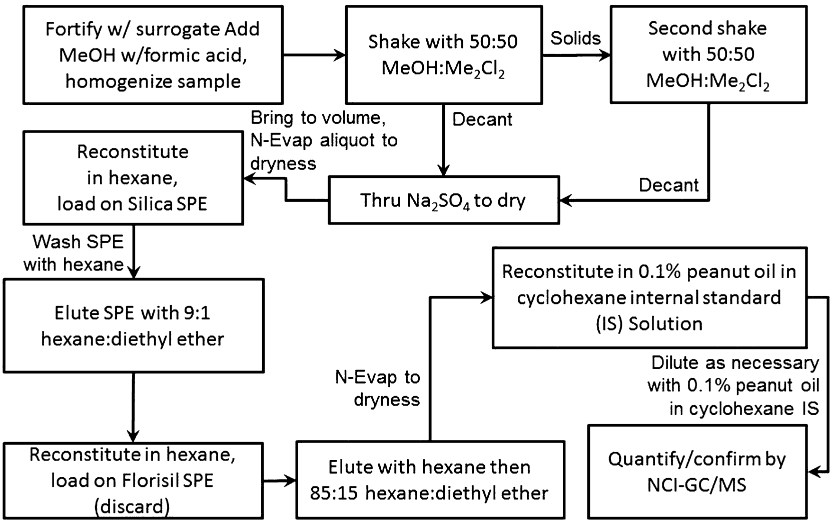

Figure 1. Biosolids Method Flow Chart Use of Surrogates in Environmental Monitoring Methods.

As defined in US EPA Method 507, a surrogate is "A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample (*6*)."

Surrogates may be chosen based upon the expectation that they will behave similarly to the target analyte(s) in the extraction and cleanup steps of the method, and will respond acceptably to the instrumentation used for the determinative step. For example, the method cited above specifies the use of 1,3-dimethyl-2 nitrobenzene as a surrogate in the analysis for nitrogen- and phosphorus-containing pesticides in water by gas chromatography with nitrogen-phosphorus detection (GC-NPD).

When available, surrogates can include stable isotope analogues of one or more representative target analytes (for methods which use mass spectrometry for the instrumental determinative step). For example, US EPA Method 8260B, for volatile organics by GC/MS, toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane are listed as surrogates (*7*).

Use of d_6 Stable Isotope Standards as Surrogates for Pyrethroids

Stable isotope (d_6) analogues of the eight pyrethroids included in the method were custom-synthesized by Kalexsyn, Inc. (Kalamazoo, MI). The molecular weight differential of +6 was important in particular for pyrethroids with two chlorine atoms in the molecule (cypermethrin, for example), as the isotopic distribution of ^{35}Cl and ^{37}Cl in the native compound results in a significant response at +2 and +4 of the target ion being monitored for quantification (207 m/z for cypermethrin). It was observed experimentally that none of the eight analytes exhibited any measurable response at +6 of the primary quantification ions. (This was also true for the qualifier, or confirmatory, ions.)

Esfenvalerate-d_6 and fenpropathrin-d_6 were chosen from the eight available d_6 stable isotope analogues for use as surrogates for the wastewater and biosolids (POTW) analyses. Any of the d_6 analogues are extremely unlikely to be found in urban wastewater or biosolids samples. Under the instrumental conditions of the NCI-GC-MS systems used (*1*), the observed retention time window for the eight targeted pyrethroids was 18.0 – 25.4 min. Esfenvalerate-d_6 elutes near the end, at 24.5 and 24.7 min for the two measurable peaks (just before deltamethrin). Fenpropathrin-d_6 elutes near the beginning of this range, at 18.4 min (just after bifenthrin).

One drawback to the use of esfenvalerate-d_6 and fenpropathrin-d_6 as surrogates to measure method recovery in every sample is that these two materials could no longer be used as instrumental internal standards to normalize variability in instrumental response (and thus more accurately and precisely quantify native esfenvalerate and fenpropathrin, respectively).

Experimentation indicated that and deltamethrin-d_6 and bifenthrin-d_6 served adequately as "replacement" internal standards for the quantification of native esfenvalerate and fenpropathrin, respectively. The deltamethrin-d_6 and bifenthrin-d_6 were also used as the internal standards for the quantification of the esfenvalerate-d_6 and fenpropathrin-d_6 surrogate recoveries, respectively.

Examination of native analyte recoveries for the eight pyrethroids supports the use of esfenvalerate-d_6 and fenpropathrin-d_6 as surrogates. As indicated in Tables I-III, the overall recovery data indicate that the surrogate recoveries are representative of the entire targeted group for this multi-analyte method, and not just of native esfenvalerate and fenpropathrin.

Influent Water

As part of a 2013 baseline survey of publicly owned treatment works facilities in California in 2013 (*5*), influent water samples were analyzed for the target list of eight pyrethroids. The methodology used was as cited previously (*1*, *2*). Quality control measures included the fortification of selected influent water samples (n=10) at concentrations of 40 ng/L for bifenthrin, cyfluthrin, cypermethrin, fenpropathrin, and lambda-cyhalothrin; 80 ng/L for deltamethrin and esfenvalerate; and 200 ng/L for permethrin. These 10 fortified samples were also fortified with the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates at 40 ng/L, as were all of the unfortified influent water samples that were analyzed (n= 37). A summary of recovery results is provided in Table I.

As can be seen, the recoveries of 76% and 86%, respectively, for the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates in the 10 fortified samples fit well in the overall average recovery range of range of 71% to 86% for the eight native analyte fortifications. Similarly, the standard deviations of 7.7% and 15.2%, respectively, for the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates in the 10 fortified samples bracket the range of standard deviations, permethrin excepted, of 9.5% to 14.4%. Permethrin recoveries exhibited a standard deviation of 34.1%. This large SD is consistent with the fact that the background response in the unfortified analysis of the selected samples that were used for QC fortifications ranged from 128 – 250 ng/L, levels that are unquestionably significant in proportion to the fortification level of 200 ng/L. After including the surrogate data for the 27 unknown samples (for a total of n=37), the esfenvalerate-d_6 and fenpropathrin-d_6 average recoveries were unchanged, but the SDs decreased to 7.0% and 10.7%, respectively.

The results of the recoveries in the laboratory-fortified samples are presented graphically in Figure 2, with the bar graphs arranged in order of increasing average recoveries.

Table I. Influent water concurrent fortification recoveries and surrogate results from 2013 POTW monitoring program

Compound Name	*Fortification Level (ng/L)*	*N*	*Average Recovery (%)*	*Std. Dev.*
Bifenthrin	40	10	82	14.3
Cyfluthrin	40	10	81	13.2
Cypermethrin	40	10	83	14.4
Deltamethrin	80	10	71	12.5
Esfenvalerate	80	10	73	9.5
Fenpropathrin	40	10	85	10.8
Lambda-Cyhalothrin	40	10	81	11.4
Permethrin	200	10	86	34.1
Surr-Esfenvalerate-d_6 [a]	40	10	76	7.7
Surr-Fenpropathrin-d_6 [a]	40	10	86	15.2
Surr-Esfenvalerate-d_6 [b]	*40*	*37*	*78*	*7.0*
Surr-Fenpropathrin-d_6 [b]	*40*	*37*	*86*	*10.7*

[a] Surrogate recoveries from the laboratory-fortified samples. [b] Surrogate recoveries from laboratory fortifications and all monitoring samples.

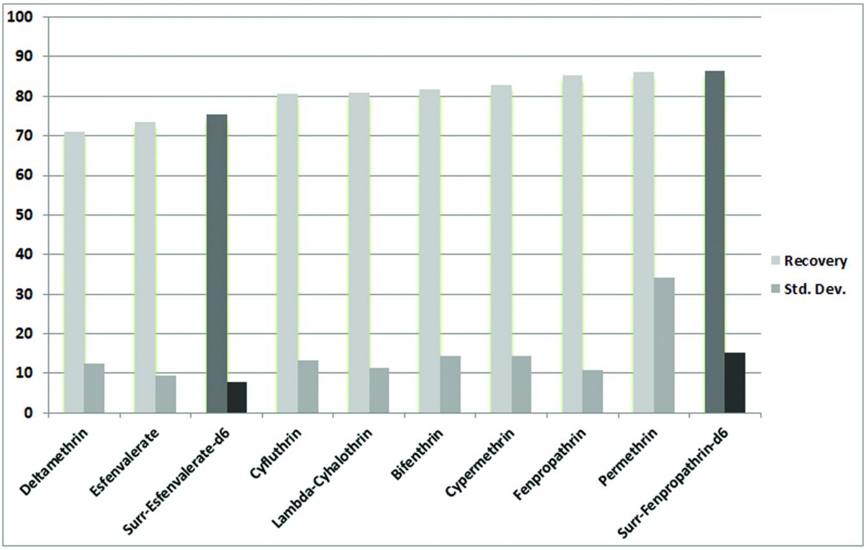

Figure 2. Influent Water Surrogate Results from POTW Monitoring, 2013.

Effluent Water

The 2013 California POTW baseline survey also encompassed the analysis of effluent samples, for the eight pyrethroids. The methodology used was as cited previously (*1*, *2*). The effluent water concentrations tended to be significantly lower than the influent samples taken at any given treatment facility. The quality control fortifications of selected influent water samples (n=10) were at concentrations of 20 ng/L for bifenthrin, cyfluthrin, cypermethrin, fenpropathrin, and lambda-cyhalothrin; 40 ng/L for deltamethrin and esfenvalerate; and 100 ng/L for permethrin. These 10 fortified samples were also fortified with the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates at 10 ng/L, as were all of the unfortified influent water samples that were analyzed (n= 33). A summary of recovery results is provided in Table II.

As can be seen, the recoveries of 86% and 90%, respectively, for the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates in the 10 fortified samples fit in very well with the overall average recovery range of range of 86% to 91% for the eight native analyte fortifications. Similarly, the standard deviations of 9.5% and 14.2%, respectively, for the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates in the 10 fortified samples bracket the range of native analyte SDs 9.5% to 13.9%. After including the surrogate data for the 23 unknown samples (for a total of n=33), the esfenvalerate-d_6 and fenpropathrin-d_6 recoveries changed only slightly to 87% and 89%, respectively, and the SDs decreased to 9.3% and 12.6%, respectively.

The results of the recoveries in the laboratory-fortified samples are presented graphically in Figure 3, with the bar graphs arranged in order of increasing average recoveries.

Table II. Effluent water concurrent fortification recoveries and surrogate results from 2013 POTW monitoring program

Compound Name	*Fortification Level (ng/L)*	*N*	*Average Recovery (%)*	*Std. Dev.*
Bifenthrin	20	6	87	13.3
Cyfluthrin	20	6	90	11.0
Cypermethrin	20	6	89	9.9
Deltamethrin	40	6	88	13.9
Esfenvalerate	40	6	86	9.5
Fenpropathrin	20	6	91	11.5
Lambda-Cyhalothrin	20	6	89	11.6
Permethrin	100	6	90	12.8
Surr-Esfenvalerate-d_6 [a]	10	6	86	9.5
Surr-Fenpropathrin-d_6 [a]	10	6	90	14.2
Surr-Esfenvalerate-d_6 [b]	*10*	*33*	*87*	*9.3*
Surr-Fenpropathrin-d_6 [b]	*10*	*33*	*89*	*12.6*

[a] Surrogate recoveries from the laboratory-fortified samples. [b] Surrogate recoveries from laboratory fortifications and all monitoring samples.

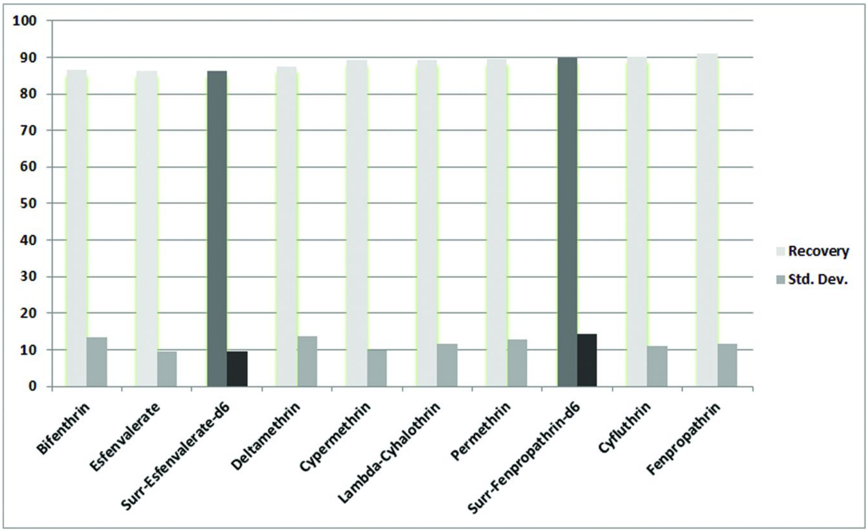

Figure 3. Effluent Water Surrogate Results from POTW Monitoring, 2013.

Biosolids

The biosolids collected in the 2013 California POTW baseline survey were dewatered cake samples, which were also analyzed for the eight pyrethroids. The methodology used was as cited previously (*3*). The quality control fortifications of selected influent water samples (n=6) were at concentrations of 200 ng/g for bifenthrin, cyfluthrin, cypermethrin, fenpropathrin, and lambda-cyhalothrin; 400 ng/g for deltamethrin, either 200 or 400 ng/g for esfenvalerate; and 1,000 ng/g for permethrin. These 6 fortified samples were also fortified with the esfenvalerate-d_6 and fenpropathrin-d^6 surrogates at 25 ng/L, as were all of the unfortified influent water samples that were analyzed (n= 27). A summary of recovery results is provided in Table III.

Table III. Biosolids concurrent fortification recoveries and surrogate results from 2013 POTW monitoring program

Compound Name	*Fortification Level (ng/L)*	*n*	*Average Recovery (%)*	*Std. Dev.*
Bifenthrin	200	6	88	12.4
Cyfluthrin	200	6	87	11.4
Cypermethrin	200	6	88	11.7
Deltamethrin	400	6	83	13.5
Esfenvalerate	200/400	6	88	9.0
Fenpropathrin	200	6	88	13.1
Lambda-Cyhalothrin	200	6	88	12.6
Permethrin	1000	6	89	12.4
Surr-Esfenvalerate-d_6 [a]	25	6	85	11.3
Surr-Fenpropathrin-d_6 [a]	25	6	85	15.5
Surr-Esfenvalerate-d_6 [b]	*25*	*27*	*80*	*9.2*
Surr-Fenpropathrin-d_6 [b]	*25*	*27*	*86*	*12.4*

[a] Surrogate recoveries from the laboratory-fortified samples. [b] Surrogate recoveries from laboratory fortifications and all monitoring samples.

Although the fortification level (25 ng/g) for the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates in the 6 fortified samples were much lower than the native analyte fortification levels, the recovery value of 85% for both analytes were still similar to the observed average recovery range of 83% to 89% for the eight native analyte fortifications. Similarly, the standard deviations of 11.3% and 15.5%, respectively, for the esfenvalerate-d_6 and fenpropathrin-d_6 surrogates in the 6 fortified samples were not far off from the range of native analyte

SDs of 9.0% to 13.5%. After including the surrogate data for the 21 unknown samples (for a total of n=27), the esfenvalerate-d_6 and fenpropathrin-d_6 recoveries were 80% and 86%, respectively, and the SDs decreased to 9.2% and 12.4%, respectively.

The results of the recoveries in the laboratory-fortified samples are presented graphically in Figure 4, with the bar graphs arranged in order of increasing average recoveries.

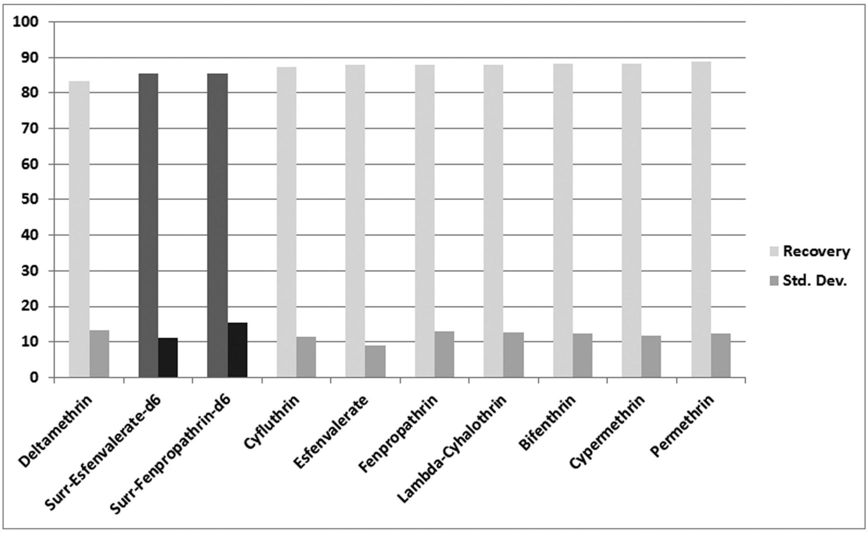

Figure 4. Biosolids Surrogate Results from POTW Monitoring, 2013.

Use of d_6 Stable Isotope Standards To Address Other Analytical Challenges

Method Validation

When validating analytical methods, it is typical to attempt to obtain control matrix samples which are free of any incurred target analyte residues. For these particular matrices, it has proven difficult to obtain materials which have the same (or at least similar) composition as the type of samples to be analyzed by the method but are yet free of any background incurred residues. The trace background residues, when present in samples used for the method validation fortifications, can prevent the accurate quantification of analyte recoveries, particularly when the fortification levels are near (or in some cases, even lower than) the background contribution.

The use of the d_6 stable isotope analogues for method validation allows for an alternate (and accurate) evaluation of method recovery at comparatively low levels, as both logic and empirical data concur in the expectation of non-detectable background responses for the d_6 materials.

As was the case when using the d_6 standards as surrogates, an alternative approach for internal standard correction was required for instrumental variability normalization. It was experimentally determined that the following "replacement" internal standard assignments yielded acceptable (*8*) method validation results.

For calculation of the IS ratios, fenpropathrin d_6 can serve as the IS for bifenthrin- d_6 and lambda-cyhalothrin- d_6; permethrin- d_6 can serve as the IS for cyfluthrin-d_6 and cypermethrin- d_6; and esfenvalerate- d_6 can be used as the IS for deltamethrin-d_6.

For calculation of the IS ratios, bifenthrin-d_6 can serve as the IS for fenpropathrin-d_6; cypermethrin-d_6 can serve as the IS for permethrin-d_6; and deltamethrin-d_6 will be used as the IS for esfenvalerate-d_6.

Conclusions

The PWG has invested in the development of rugged, reproducible, multi-analyte methods for POTW samples. These include Influent water, effluent water, and biosolids (primary sludge and dewatered cake). These multi-analyte methods are based upon extraction, clean-up, and sensitive/selective instrumental analysis by NCI-GC/MS, with d_6 stable isotope analogues used to normalize instrumental response.

The availability of the d_6 stable isotope analogue standards has been exploited to develop surrogate methodology which allows for more accurate assessment of method performance, as compared to surrogate compounds which less closely mimic analyte behavior and recoverability. The surrogate recovery results overall support the conclusion that the POTW analysis methods are well under control, and able to generate valid results from samples of variable compositions (with variability being of particular concern with biosolids). Beyond the surrogate data, it was noteworthy that overall, all of the average recoveries for all analytes in all three matrices fell within the recovery range considered acceptable by the US EPA for pesticide environmental chemistry methods, 70% – 120% (*8*).

Acknowledgments

The financial support of the PWG (AMVAC Chemical Corporation, BASF Corporation, Bayer CropScience, Cheminova , DuPont Crop Protection, FMC Corporation, Syngenta Crop Protection, and Valent U.S.A.) and the collaborative assistance of many PWG-related individuals toward the development and evaluation of these methods were fundamental to the success that was achieved. The assistance and responsiveness of Kalexsyn, Inc. in supplying the stable isotope internal standards and surrogates are gratefully acknowledged.

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Chapter 10

Conducting Ecological Risk Assessments of Urban Pesticide Uses

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Recent studies have reported pesticides in toxicologically significant concentrations in surface water, sediments, stormwater, and publicly owned treatment works (POTW) influent/effluent wastewater from residential uses at locations across the United States. The USEPA faces many challenges in assessing the ecological risks from indoor and outdoor residential pesticide uses, many of which stem from limitations in quantifying exposure from the wide array of application scenarios available for residential pesticide use. Data on the timing, frequency and location of residential pesticide application at a national scale has been collected and submitted to the USEPA. These data will be useful for constructing representative residential exposure scenarios. In the absence of these data and tools, the USEPA has relied on urban monitoring data for conducting the ecological risk assessments. The use of certain chemicals as mosquito adulticides has resulted in exposure and risk to non-target aquatic organisms. Various methods and approaches to assess exposure are presented to conduct ecological risk assessments of these insecticides. Pesticides released to domestic wastewater from indoor residential uses are being assessed with the Exposure and Fate Assessment Screening Tool (E-FAST). Bench-scale treatability studies and POTW monitoring data will be used to refine exposure estimates of pesticides in wastewater, surface water and biosolids resulting from indoor uses.

Introduction

Urban uses of pesticides are widespread and their use patterns present many challenges in conducting a national scale ecological risk assessment (ERA). Pesticides are used outdoor and indoor in residential, public, commercial, industrial and military areas. In California alone, nearly ten million pounds of pesticides active ingredients were used in the year 2009 (California Department of Pesticide Regulations Pesticides Use Reporting or CDPR PUR database (*1*)). Use in urban areas includes nearly thirty PUR categories with the top five being structural pest control, rights-of-ways, public health, landscaping, and indoor homeowner use.

Ecological risks associated with urban uses of pesticides is a critical emerging issue. As highlighted by the 2007 USGS report "*The Quality of our Nation's Waters* (*2*)," urban streams have the highest frequency of U.S. stream sites with pesticide concentrations that exceed aquatic life benchmarks (83%). Agriculturally dominated streams had the next highest frequency of aquatic life benchmark exceedance (57%), followed by mixed use streams (42%) and undeveloped sites (13%). This chapter describes major risk assessment challenges and approaches being considered by USEPA for assessing ecological risks from urban/residential pesticide uses. Specifically, three residential/urban assessment scenarios are described: (1) stormwater discharges resulting from outdoor uses; (2) exposure from adulticide uses; and (3) releases to POTWs (waste water discharges) from indoor uses. Within each of these assessment scenarios, the available methods and data being considered for modeling pesticide exposure and risk are summarized. In addition, the results from selected model-based assessments are compared to available information from targeted pesticide monitoring studies.

Assessing Stormwater Discharges from Outdoor Urban Uses

Outdoor urban uses of pesticides can result in significant exposure to water bodies through drift and runoff. These uses include structural pest control, rights of ways, and landscaping. Many pesticides are labeled for outdoor uses to control insect pests such as ants, cockroaches, fleas, occasional invaders, spiders, and wasps, in addition to others used for lawn care. Control is accomplished by professional pest control operators (PCOs) and homeowners through different pesticide formulations, application methods, and timing.

Many types of documentation, information and data are used by USEPA in conducting the ecological risk assessment for all pesticides including those used outdoors in urban settings. In a regulatory setting, labels are considered first in determining pesticide exposure in various compartments of the environment, as the label is the legal document governing the permitted pesticide use patterns. Labels specify pesticide contents of active(s)/inert material(s), formulation type, target pests/areas, and detailed use instructions (application rate, number of applications permitted, frequency, timing and type of applications. In addition to label use information, pesticide usage data are also important as it indicates quantity, seasonality, historical and geographic usage extent of currently registered pesticides. Monitoring data are also important and could be the only reliable exposure data available for use in a risk assessment due to limitations associated with the current modeling approaches. Important aspects of exposure modeling uncertainties for outdoors uses include establishing a conceptual model for varied types of outdoor uses along with percent/type of areas treated, percent of pesticide available for washoff, and other possible sources of pesticide contamination (*i.e.*, drift, contaminated airborne particles and others). As discussed in more detail later, recent studies have concentrated in obtaining such important modeling parameters in addition to many other data such as frequency/seasonality of applications, and most frequently used application rate, frequency, equipment and formulations. This data could be used as inputs for the exposure models to characterize and refine the exposure estimates.

Use Characterization

Early CDPR Surveys (2001-2005)

The California Department of Pesticide Regulation (CDPR) funded a number of use and usage surveys between 2001 and 2005 to get a better understanding of the pesticide use pattern in urban environments. The 2001 survey (*3*), involved the San Diego Creek and East Costa Mesa/Newport Beach watershed areas of Orange County, CA. A majority of the surveyed people that apply pesticide products (58.3%) reported applications one to three times, or four to six times per year. Another survey was conducted in 2002, of residents of the Chollas Creek area of San Diego County and the Delhi Channel area in Orange County (*4*). Ants and other insects were the primary target pests. The most frequent use pattern of pesticide application was once every few months (43.1%). Of the responses, 47.2% indicated that they had purchased or used a weed control product, 77.1% indicated that they purchased or used an insecticide, and 32.5% indicated they had purchased or used a product to control plant diseases. The 2003 survey covered the areas of the Arcade Creek watershed in Sacramento, Five Mile Slough watershed in Stockton and San Francisco Bay (*5*). From 20-41% indicated they did not apply pesticides in their homes and 37-65% of respondents identified insects as their primary pest of concern. Other pests included snails/slugs (24.4-29.2%) and vertebrates (15-27%). The majority (58-64%) indicated they applied pesticides on hard surfaces such as perimeters of buildings, driveways, sidewalks, or walls; further 44-47% responded that they applied pesticides 1-3 times per year.

The previous surveys examined residential users of pesticides; in contrast, a 2005 survey (*6*) evaluated pesticide use by pesticide managers and applicators in three urban watersheds: Arcade Creek (Sacramento County), Chollas Creek (San Diego County), and Upper Newport Bay/San Diego Creek (Orange County), CA. The CDPR PUR Report database indicated that in 2003 structural PCO use comprised 40% of the total reported non-agricultural use, rights-of-ways (32%), landscape maintenance (15%), public health (12%), and regulatory pest control (1%) in Sacramento, Orange and San Diego Counties. Structural pest control comprised 93-98% of the total insecticide usage. An analysis of usage indicated that organophosphates had been declining and pyrethroids increasing. Rights-of-ways accounted for 47-60% of the total herbicide use. The top herbicides used were glyphosate and diuron. Landscape maintenance reported 38-53% of the total herbicide use. The most commonly applied herbicide was glyphosate. San Diego County was the major urban pesticide user (48%), followed by Orange County and Sacramento County.

Pyrethroid Working Group Use Surveys (2009-2013)

In response to concerns over increasing pyrethroid use and detections in California, a survey was conducted by Pyrethroid Working Group (PWG) for CDPR in 2009 (MRID 48762913 (*7*)), which assessed pesticide usage by professional pest management companies. Outdoor usage represented 83% of the total pounds of pesticides applied in urban environment, with indoor usage constituting the balance. Application frequency was monthly or every other month for residential customers (80% of responses) and monthly for commercial customers (83% of responses) (Table 1). For outdoor use, the dominant type of formulations used were liquid sprays (liquids 95% and wettable powder 2%); granules represented 3%, with very small amounts of baits. The most common equipment used in applying liquid sprays included power sprayers, followed by handheld or back pack sprayers. Granular products were most often used in broadcast application. Treatment types included home or fence perimeter treatments (1-2 feet up and 1-5 feet out with 1x1 ft being the most common) and/or spot treatment while treatment of the entire yard was less common. Hard surfaces such as patios, outdoor congregation areas and driveways were almost always treated. Less commonly treated areas include vertical walls and uncovered storage. Pest management professionals were asked to name the "Top 5" pesticide products they used, based on volume. The product most commonly named was Termidor (fipronil, named by 73% of respondents). The named products were related to their corresponding active ingredients, which included bifenthrin, fipronil, and deltamethrin (named among the "Top 5" by 60-75% of the pest management professionals surveyed); followed by indoxacarb, *beta*-cyfluthrin, permethrin, cyfluthrin, cypermethrin, *lambda*-cyhalothrin and chlorfenapyr (named among the "Top 5" used by 22-33% of the pest management professionals surveyed); and thiamethoxam, abamectin, and pyriproxyfen (named among the "Top 5" by 2-10% of the pest operators surveyed). Timing of application for most compounds was found to be throughout the year although few compounds were applied more often either in spring and winter or in the summer.

Another survey of PCOs and LCOs was sponsored by PWG (Winchell and Cyr, MRID 49292101 (*8*)). The survey covered six national regions, excluding California and included both pest control operators (PCOs) and lawn care operators (LCOs). Pyrethroids were associated with 58% of the outdoor insecticide applications overall for all regions. Overall, for all regions the percentage uses were bifenthrin (40%), cyfluthrin/*beta*-cyfluthrin (17%), *lambda*-cyhalothrin (12%), deltamethrin (11%), permethrin (9%), cypermethrin (8%), and other pyrethroids (2%). The percent of LCOs and PCOs that applied each pyrethroid active ingredient, by use site, is depicted in Figure 1. Seven types of surfaces were investigated of which only a selection is presented in the figure.

Table 1. Service Interval for Residential and Commercial Pesticide Accounts

Service Interval	*Residential (%)*	*Commercial (%)*
Weekly	4	6
Monthly	39	83
Every other month	41	7
Quarterly	12	0
Other	0	4

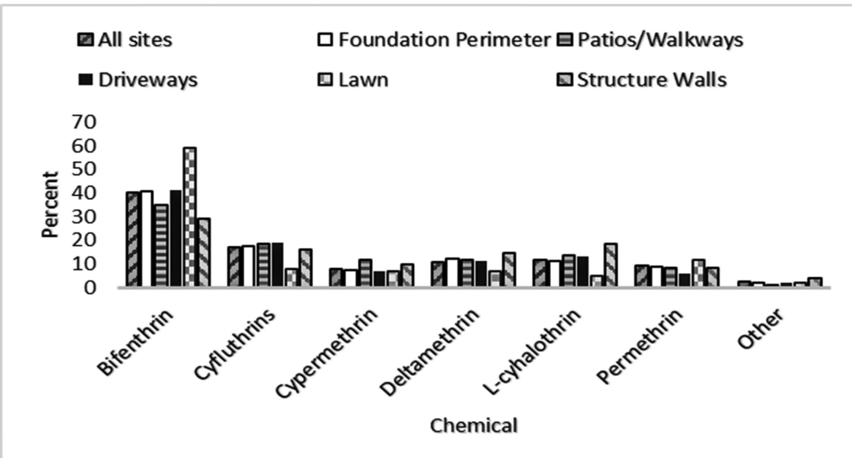

Figure 1. Percent of Respondents' Pyrethroid Active Ingredient Use in Outdoor Applications by Selected Use Sites, Excluding California.

The percent applying pyrethroids to different types of surfaces in an urban environment, including California, is depicted in Figure 2. By far, the foundation perimeter treatments are the most commonly applied by PCOs. Note that all regions but California receive approximately the same number of building foundation perimeter treatments. Meanwhile, lawn treatments are lower. The methodology to estimate California use was different since the questions asked to PCOs and LCOs were different. The foundation perimeters treatment represented an estimated value since this specific question was not asked in California.

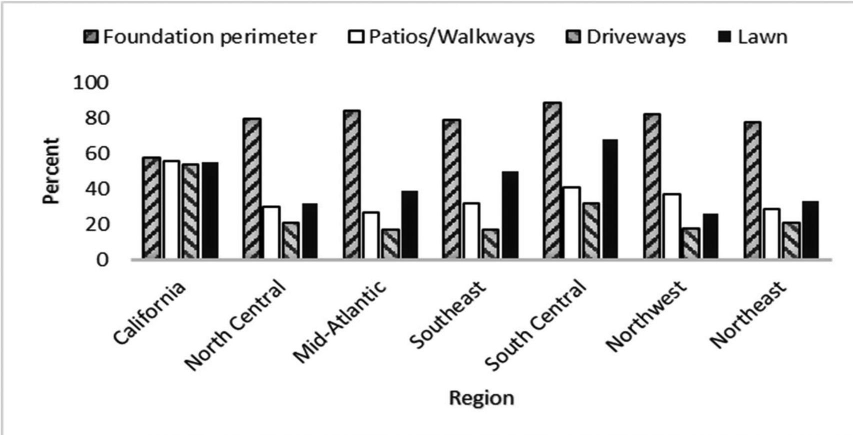

Figure 2. Percent of PCOs and LCOs Applying Pyrethroids to Selected Sites by Region.

The number of applications per year, average area treated, and the active ingredient most commonly used on each of the use sites for all regions, except CA, is summarized in Table 2. Each use site receives on average close to 4 applications per year although the foundation perimeters are treated more often than other use sites, and the fraction of the use site ranges from 36% (driveways away from the garage door or wall) to 77% for lawns. The active ingredient most commonly applied is bifenthrin, irrespective of the use site.

Figure 3 summarized for each active ingredient, the frequency by which PCOs and LCOs responded that they used each active ingredient for each region. This figure confirms that bifenthrin is the active ingredient most commonly used. Note the high use of cypermethrin in the south central region, compared to the other regions. Approximately a two-fold increase of cypermethrin applied as compared to other regions, is unexplained at this time.

These surveys were supplemented by work by Fugate and Hall (*9*), which includes frequency of consumer use of specific insecticides, in and around homes, outdoor non-plant, and lawn and garden in 2011. (This report was not provided to the USEPA. Rather, certain data were extracted and provided in MRIDs 49292101 (*8*) and 49292102 (*10*)). Nationally, the likelihood of consumer use of LCO services to apply fertilizer and chemicals is 14% and consumer use of PCO services is 26%. The likelihood of a consumer to purchase lawn and garden insecticides is 31% and outdoor non-plant insecticides is 15%. The likelihood of a consumer applying lawn and garden insecticide is 47% and outdoor non-plant insecticides is 28%. Bifenthrin is the insecticide most likely to be purchased, followed by *lambda*-cyhalothrin.

Table 2. Averages of Treatments per Year, Fraction of Use Site Surface Area Treated and Pyrethroid Active Ingredient Most Commonly Used by Use Site in Six National Regions, Excluding California

Use Site Type of Surface	*Average Number of Treatments Per Year*	*Fraction of Use Site Surface Area Treated*	*Most Commonly Used Active Ingredient*
Building foundation perimeters	4.25	2.4 ft up; 2.9 ft out	Bifenthrin
Patios and walkways away from building	3.73	44%	Bifenthrin
Driveways away from the garage door and wall	3.66	36%	Bifenthrin
Lawn	3.62	77%	Bifenthrin
Landscape and ornamental areas	3.82	63%	Bifenthrin
Structure walls	3.71	42%	Bifenthrin
Eaves	3.38	44%	Bifenthrin

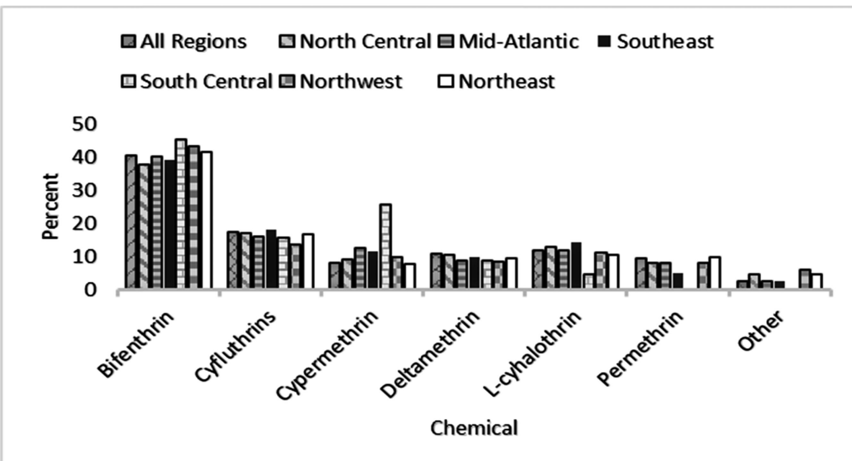

Figure 3. Percent of Respondents' Pyrethroid Active Ingredient Use in Outdoor Applications by Region, Excluding California.

Winchell (*10*) (MRID 49292102 (*10*)) provided an interpretation of the following studies: MRIDs 48762913 (*7*), 49292101 (*8*), Wilen (*3*), and the work by Fugate and Hall (*9*). Winchell used certain data manipulations to derive suitable variables, with the potential to be useful in modeling for aquatic exposure in an urban environment. These manipulations were different for CA and other regions of the U.S. due to differences in survey design. These variables for aquatic modeling include 1) the fraction of the use site treated with each active ingredient; 2) the seasonal application frequency made to each use site; and, 3) the percentage of the use site's surface area that is treated. The work by

Fugate and Hall (*9*) helped to establish the extent of pyrethroid use in different geographical regions of the U.S. (compared to other insecticides), and the fraction of the households receiving pyrethroid applications outdoors (including LCOs, PCOs, and resident's applications), and to compare against the 2010 and 2013 results. Regarding the frequency of applications, it was estimated that in CA, it ranged from 4-8 per year, while in other regions of the U.S., it ranged from 4-5 per year. The percentage of the use site surface area, treated with pyrethroids was not asked in the CA surveys and data for other regions of the U.S. would be used to cover CA.

Value of Surveys

These reports include data on the frequency of homeowners using lawn care or pest control services, the frequency of consumers using outdoor non-plant and lawn & garden insecticides, and data on the frequency of a consumer using specific insecticide active ingredients. The datasets provided the starting point to determine the overall likelihood of an individual homeowner using an applicator service, and then from the survey responses, determine the likelihood by region and use site of the top six pyrethroids being used by both professional applicators and/or homeowners themselves.

Of all the above surveys, it is apparent that the most recent ones, conducted in 2009 and 2013 (MRIDs 48762913 (*7*), 49292101 (*8*), and 49292102 (*10*)), with supplemental data from Wilen (*3*), and Fugate and Hall (*9*), may be used to estimate the needed usage and the amount of pesticide applied on each use site per region. The studies have the potential to establish the conceptual model for outdoor pesticide exposure for a variety of outdoor use sites, along with percent/type of areas treated, and, with the help of the washoff studies, the percent of pesticide available for wash-off, and other possible sources of pesticide contamination (*i.e.*, drift, contaminated airborne particles and others). But more than that, they could be used in characterizing and refining exposure and in finding mitigation measures to reduce exposure, such as frequency/seasonality of applications, and most frequently used application rate, frequency, equipment, and formulations (typical application pattern), percent area treated by each use site, *etc*. Winchell (*10*) (MRID 49292102 (*10*)) synthetizes previous useful studies in tables that are suitable to do the above tasks for the pyrethroid insecticides.

Modeling Approach for Stormwater Discharges

The Environmental Fate and Effects Division (EFED) currently obtains estimated exposure concentrations (EECs) by modeling the residential and impervious scenarios in the Pesticide Root Zone Model coupled with the Exposure Analysis Modeling System (PRZM/EXAMS). Two PRZM/EXAMS runs are executed for each application type/weather combination. The application types are dependent on the label and may include three types of applications: (1) application to pervious areas alone with drift to adjacent impervious surfaces such as application to a lawn and/or garden adjacent to impervious driveway and/or porch; (2) application to impervious surfaces alone with drift to adjacent pervious surfaces such as application to driveway and/or porch adjacent to a lawn and/or garden; or (3) a combined application to pervious and impervious surfaces such as application to both impervious driveway and/or porch and to the lawn and/or garden).

At the present time, the CA impervious PRZM scenario is considered as the most suitable available modeling approach for impervious runoff. The PRZM CA impervious scenario may be used in the Tier 2 coupled aquatic models PRZM/EXAMS along with the CA residential or other appropriate scenario such as CA rights-of-ways (ROW) to obtain EECs. The "residential" and various other "urban" use patterns require the PRZM CA residential and CA impervious scenarios for modeling. Both scenarios are run separately. This approach assumes that no watershed is completely covered by either the ¼ acre lot (the basis for the residential scenario) or undeveloped land (the basis for the ROW scenario), for residential and ROW use patterns, respectively. By modeling a separate scenario for impervious surfaces, it is also possible to estimate the amount of exposure that could occur when the pesticide is over-sprayed onto this surface. Using two scenarios in tandem requires post-processing of the modeled output in order to derive a weighted EEC that represents the contribution of both the pervious (*i.e.*, residential and ROW scenarios) and the impervious surfaces. Exposure from both scenarios can also be weighted and aggregated. The second critical assumption is that 50% of a ¼ acre lot will be pervious and 50% impervious. In addition to the footprint of the typical house, it is assumed that a typical house would have a driveway of approximately 25 by 30 feet or 750 square feet and roughly 250 square feet of sidewalk. A typical suburban home could also be assumed to have roughly 300 square feet of deck space and 900 square feet of garage. Finally, it is assumed that a substantial portion of the typical home would be planted in landscaping (*e.g.*, residential lawn and/or ornamentals) with an estimate of 2,000 square feet. The sum of all these areas is 5,200 square feet. Taking a total ¼-acre lot size of 10,890 square feet and subtracting the house square footage yields a total remaining area of 5,690, or roughly 50% of the total lot untreated area. The residential and impervious scenarios are parameterized to represent a California urban site. For modeling uses in other metropolitan regions (not located in California), the residential and impervious scenarios can be run with meteorological files from other locations of the U.S.

Pathway Identification Study

The main objective of this study (Davidson *et al.*, MRID 49137401 (*11*); and Davidson *et al.* (*12*)) was to identify the major transport mechanisms of pyrethroids from a range of outdoor residential applications and determine the effects of mitigation measures put in place by the USEPA to control off-site transport. The study was conducted at a test facility which represented typical California residential developments. It consisted of six replicate house lots which included front lawns, stucco walls, garage doors, driveways and residential lawns. The off-site movement of different pyrethroids applied to these surfaces (representing pervious and impervious surfaces) was assessed using irrigation and simulated artificial rainfall to complement the natural rainfall events. The results showed that natural and simulated rainfall events contributed to the majority of mass loss compared to the mass loss due to lawn irrigation. Runoff losses expressed as a percentage of chemical applied were highest for the driveway and garage door surfaces compared to grass lawn, grass perimeter and house wall surfaces. Also, a comparison of historic applications with revised application due to label changes showed that the amount of losses from garage and driveway were dramatically reduced (40 times lower) using the revised application practices.

Washoff/Runoff Study from Impervious Surfaces

The main objective of the study was to examine the potential for simulated rain to washoff of a pyrethroid (cypermethrin) that had been applied to different external building materials using two different representative formulations (Trask *et al.* (*13*); MRID 48072902 (*14*)). The building materials selected were those typically used for construction of residential/urban structures in California that may receive applications of pyrethroids. These included: clean painted/unpainted concrete, clean painted/unpainted stucco, clean painted/unpainted wood with a dusty surface, clean vinyl/aluminum siding and clean asphalt. Washoff quantified as percent of applied mass of cypermethrin ranged from <0.01/0.07 to 16.8/11.3% for the two representative formulations. Clean vinyl siding had the highest percent of applied cypermethrin in runoff whereas clean unpainted stucco had the least amount of cypermethrin in washoff. All building materials had similar runoff volumes except for the clean asphalt which was lower in comparison.

Runoff Losses from Treated Turfgrass

In a study conducted in 2008, the authors examined the potential of pyrethroid insecticides uses on turf to contribute to residue detections in Sacramento, CA urban sediments, particularly due to over irrigation (*i.e.*, irrigation producing excess runoff) (Hanzas *et al.* (*15*); and MRID 47647801 (*16*)). Model pyrethroids included bifenthrin and *beta*-cyfluthrin in both granular and liquid formulations. Four treated turf plots were prepared, using normal irrigation or three over irrigation events. Runoff flow was measured during the irrigation events and runoff samples taken and analyzed for bifenthrin and *beta*-cyfluthrin. For the bifenthrin over irrigated plots, during the first irrigation event, 0.052-0.081% of the applied chemical was found in runoff, while no reported bifenthrin was found in the non-over irrigated plots. Meanwhile, for *beta*-cyfluthrin, 0.23-0.58% of the applied was found in runoff of the first over irrigation, with no runoff in the non-over irrigated plots. During the normal simulated rainfall event, simulating a winter storm, the amount of chemical present in runoff was much smaller (≤0.011% of the applied for all chemicals and formulations). It was noted that for *beta*-cyfluthrin, the majority of the chemical loss occurred during the first over irrigation event while for bifenthrin the loss was more evenly distributed across three over irrigation events, particularly for the granular formulation.

Monitoring of Urban Waters

Two recent extensive reviews are available on monitoring of urban pesticides in receiving water bodies in the United States, especially in California. The first review was submitted to US EPA by the PWG covering available data for synthetic pyrethroid in surface water and sediment in the United States (Giddings, *et al.*, MRID 49314703 (*17*)). The second review was conducted for the California Stormwater Quality Association (CASQA) and the County of Sacramento covering monitoring data from California urban watersheds on pyrethroids and fipronil toxicity (Ruby, MRID 49354001 (*18*)). This section deals with only few examples of targeted surface water/sediment monitoring data for pesticides used outdoors. Therefore, selected chemistry data are included herein with emphasis on pesticides used in urban areas and reaching surface waters mainly by urban runoff into surface waters (urban creeks and lakes and rivers passing through urban areas). Urban runoff water, contaminated with urban pesticides, is usually pumped, drained and/or naturally flow into these water bodies. Many factors will affect detected concentrations in these water bodies such as the pesticide physical/chemical and fate properties; labeled use patterns; pattern of timing of the application; application procedure; usage intensity (depends mainly on pest pressure which is associated with many factors such as climate); hydrological setting, urban drainage (sources/quantities); and characteristics of urban areas/receiving waters, climatic conditions. Effects of these factors, will be included when reported.

Monitoring of Stormwater Discharges and Affected Water Bodies

Urban areas stormwater discharges and affected water bodies were extensively monitored in California. Targeted monitoring data in these studies were for stormwater discharges and affected water bodies (water and underlying sediment). In the first study, monitoring data were for eight pyrethroids and the organophosphate insecticide chlorpyrifos (*19*). In the second study, monitoring data were for 63 insecticides/herbicides/degradates in the water column plus nine pyrethroids and chlorpyrifos in water and underlying sediment (*20*). For northern California, the first study included the city of Vacaville and urban areas along the American River, Sacramento River and San Joaquin River (the cities of Folsom, Cordova, Sacramento and Stockton) while the second study included the cities of Roseville, Martinez/Pleasant Hill, Stockton and Dublin. For southern California, the second study included urban areas of Laguna Nigel, AlisoViejo, San Diego, and Lakeside (Figure 4). Sampling events took place during or shortly after rain events (Rain) and during the dry season (Dry). Sources of pesticides contamination were verified to be stormwater run-off from treated residential areas during the rainy season and landscape water run-off from treated landscaped areas during the dry season.

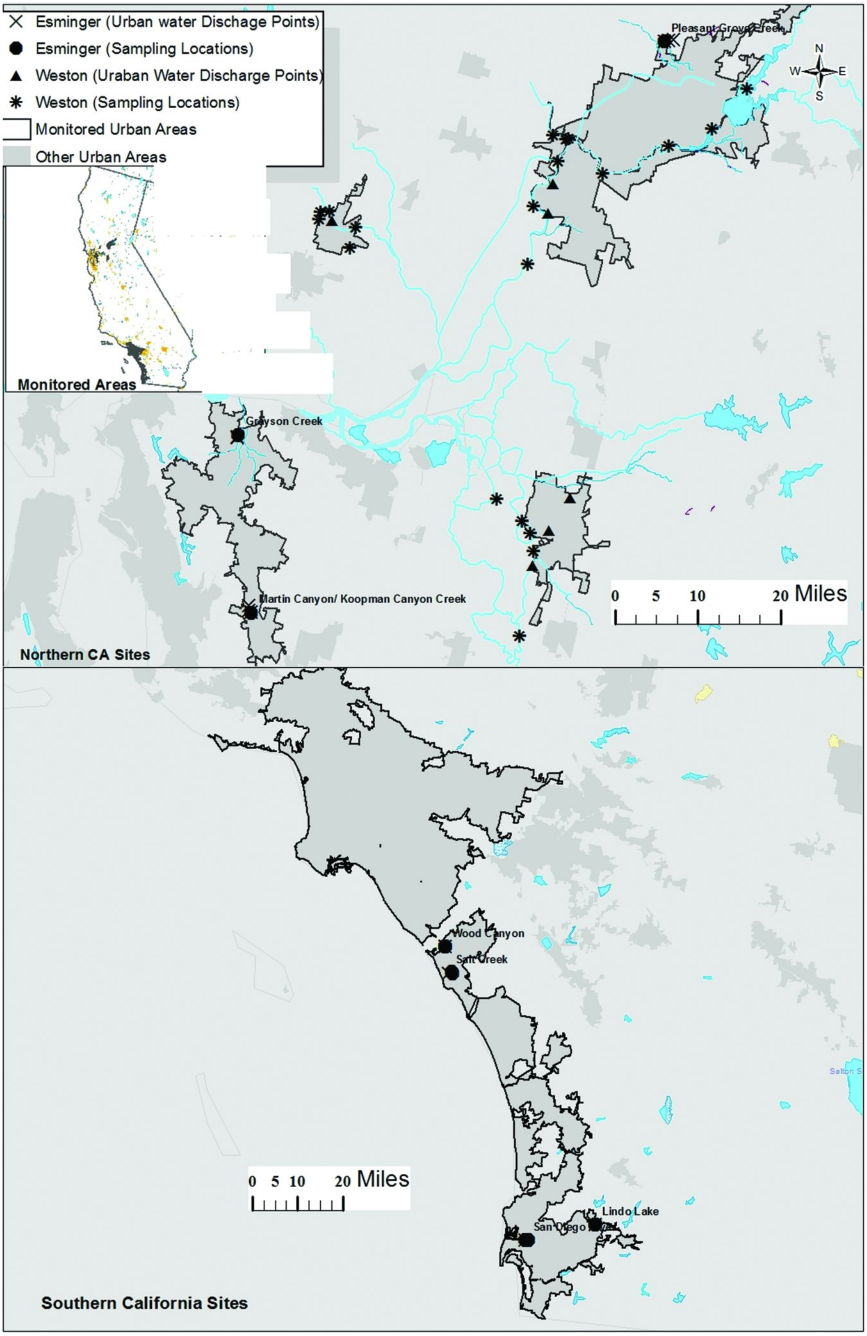

Figure 4. Monitored urban areas in Northern and Southern California (Weston and Lydy (19); and Ensminger and Kelley (20)).

In the Weston and Lydy study (*19*), concentrations detected in sump waters were high enough to be of toxic concern and were found to be related to either the pyrethroids or chlorpyrifos based on the toxicity identification evaluation (TIE) data. This was also confirmed by chemical analyses and comparison to known toxicity thresholds. Chemical analyses of 33 sump water samples show that the overall percentage of samples containing concentrations exceeding 1 ng/L ranged from 3 to 79% for eight pyrethroids and chlorpyrifos. The majority of the samples contained bifenthrin (79%) and chlorpyrifos (77%) with lesser percentages containing: permethrin (61%), cyfluthrin (55%), λ-cyhalothrin (*lambda*-cyhalothrin, 45%), cypermethrin (33%), deltamethrin (12%), esfenvalerate (6%) and fenpropathrin (3%). As expected, pesticides in sump waters that were discharged (by pumping) into receiving creeks and rivers were diluted to lower levels. Varied levels of pesticides and toxicity were found in receiving creeks and rivers as it passed through the urban areas of Sacramento (the Sacramento River), Stockton (the American River) and Vacaville (two urban creeks). Water column toxicity, related to the pyrethroid bifenthrin, was not observed in the Sacramento River but was evident along the urban creeks, the American river, and at only one site in the San Joaquin River. For example, no evidence of contamination with pyrethroids and toxicity was observed upstream in the water as the creeks enter the city of Vacaville while a high level of toxicity was observed in waters leaving the city downstream. In these water samples, pyrethroid concentrations were 4-10 times the toxicity with, bifenthrin and cyfluthrin providing most of the toxic units (TU). The level of pesticide contamination in receiving waters appeared to be related to the intensity of rain events. For example, no toxicity was observed in water samples taken from the San Joaquin River near Stockton just after the first rain event, but toxicity was evident, in one location at the edge of the city, following a more intense second rain event. Again, water toxicity was established to be related to pyrethroids as it contained 0.7 TU of bifenthrin and 0.3 TU of permethrin.

Monitoring data from the Ensminger and Kelley (*20*) study may be considered as an example of concentrations and detection frequencies (DFs) for registered and extensively used pesticides in urban areas. Therefore, data from this study are summarized herein for reported DFs and concentrations of insecticides, herbicides and pyrethroids detected in urban drain waters (DRNs) and receiving water bodies (RWBs) during dry (Dry) and rainy (Rain) seasons. Table 3 contains reported sampling information and abbreviations used in this summary and associated graphs. In the summary, statewide data reported for all locations in the study are used to obtain maximum and minimum concentrations and DFs for each pesticide. DFs are calculated for each pesticide as percent (%) from the number of samples containing that pesticide over the detection limit (number of detects) divided by the total number of samples (number of detects plus non-detects; trace detections were considered, in this summary, as non-detects). The summary includes data on pesticides that were most frequently detected in the samples of DRNs and RWBs during Dry and Rain events. The number of samples for each urban area are included in the summary table as it is an important indicator for intensity of sampling (Table 3).

Table 3. Reported Sampling Information and Abbreviations Used in the Summary of Ensminger and Kelley (*20*) Statewide Monitoring Data

Urban Area	*City (Source Of Urban Runoff Water "Drn")*	*Receiving Water Body "Rwb"*	*Sampling Season*	*Number Of Samples (N)* [1]					
				Insect[2]		*Herb*[3]		*Pyreth*[4]	
				Drn	***Rwb***	***Drn***	***Rwb***	***Drn***	***Rwb***
Sacramento **"Sac"**	Roseville	Pleasant Grove Creek	Dry	14	5	12	4	8	3
			Rain	12	4	12	4	9	3
San Francisco Bay **"Sfb"**	Martinez/Pleasant Hill; And Dublin	Grayson Creek; And Martin Canyon/Koopman Canyon Creek	Dry	20	8	20	8	10	4
			Rain	17	7	17	7	12	5
Greater Los Angeles (Orange County) **"Orn"**	Laguna Nigel; And Aliso Viejo	Salt Creek; And Wood Canyon Creek	Dry	23	9	24	10	9	3
			Rain	4	2	4	2	None	None
San Diego **"Snd"**	San Diego; And Lakeside	San Diego River; And Lindo Lake	Dry	14	10	14	10	None	None
			Rain	5	2	5	2	None	None
		Statewide	Dry/Rain	8	8	8	8	5	5

[1] ***Number of Samples (n)*** **=** The total number of samples for each sampling event. For example, in the Sacramento area (SAC), insecticides were monitored in 14 drain water samples (DRN) during the dry season (Dry) and in 12 drain water samples (DRN) during the rainy season (Rain). Additionally, insecticides were also monitored in 5 receiving water samples (RWB) during the dry season (Dry) and in 4 receiving water samples (RWB) during the rainy season (Rain). [2] ***Insect***= Monitored Insecticides: carbaryl (carb), chlorpyrifos (Chl) diazinon (Diaz), fipronil (Fip), fipronil degradates (FipD= desulfinyl fipronil, desulfinyfepronil amide, fipronil amide, fipronil sulfide, and fipronil sulfone), malathion (Mal), and oxamyl (oxa). [3] ***Herb***= Monitored Herbicides: 2,4-D (2,4-D), ACET, bromacil (Brom), dicamba (Dicam), diuron (Diur), MCPA, oryzalin (Oryzal), oxyfluorfen (Oxyfl), pendimethalin (Pendi), prodiamine (Prodi), prometon (Promet), simazine (Simaz), triclopyr (triclo) and trifluralin (Trifl). [4] ***Pyreth***= Monitored Pyrethroids: bifenthrin (bif), cyfluthrin (Cyf), λ-cyhalothrin (λ-cyh), cypermethrin (cyp), fenvalerateesfenvalerate (FenEsV) and permethrin (Per= *cis* and *trans*).

In this summary, concentrations and DFs for each pesticide are examined in DRNs vs. RWBs, Dry vs. Rain, and in varied geographical locations. The objectives are to summarize reported data as DFs and concentrations for pesticides detected in urban surface waters and examine the effects of dry flow vs. rainstorm flow and geographic location on these parameters. Summaries are established for the top five insecticides, five herbicides and all of the monitored pyrethroids.

Insecticides Detection Frequencies/Concentrations

The top five insecticides that were frequently detected in source and receiving waters include carbaryl, fipronil, fipronil degradates (total of desulfinyl fipronil, desulfinyfipronil amide, fipronil amide, fipronil sulfide, and fipronil sulfone), malathion, and diazinon (Figure 5). The insecticides chlorpyrifos and oxamyl were not in the top 5 because they were both less frequently detected in DRNs (DF = 8-24% "N = 2" and 4% "N = 1", respectively) and oxamyl was not detected in RWBs although chlorpyrifos was at a DF of 29% (N=1).

A summary is calculated from reported monitoring data for each insecticide as follows:

(1) For each geographic location (SAC, SFB, ORN and SND), the Max/Min DFs and concentrations are calculated separately for DRN waters (Dry and Rain) and RWBs (Dry and Rain) from the Dry and Rain data;
(2) A statewide Max/Min DFs and concentrations are calculated for DRN waters and RWBs separately from the combined SAC, SFB, ORN and SND values arrived at from step 1;
(3) Each set of statewide values, such as Carb-DRN or Carb-RWB, was calculated from eight data entries (N = 8 = 2 x 4; two each for SAC, SFB, ORN and SND) and in case of no detection the value of N will be <8 and no detection at all the value of N will be zero.

Data in Figure 5 show that the most frequently detected insecticides in source and receiving waters were carbaryl, fipronil and fipronil degradates (75-100%; N= 4-6). The organophosphate insecticides malathion, and especially diazinon, were detected at lower range of frequencies (24-100%; N= 2-5). Data show no apparent differences in DFs between source waters (DRN) and receiving waters (RWB) possibly due to proximity of sampling in location and timing. Except for fipronil, the maximum detected concentrations for the top 5 insecticides ranged from 0.1 to 0.8 µg/L. For fipronil, the maximum was 2.1 µg/L observed in DRN waters from Orange County. As expected, maximum chemical concentrations in drain waters were higher than those detected in receiving water bodies (2 to 5x) reflecting the effect of dilution. It is also noted that both chlorpyrifos and diazinon are still being detected despite drastic reduction in urban use resulting from EPA's regulatory actions. As pointed out by the most recent USGS report on trends in pesticides in the US rivers and streams, concentrations of diazinon declined, by nearly two orders of magnitude, in urban streams across the country from the year 2003 to 2008 due to phasing out of its use (*21*). However, the report pointed out that use of new or alternative pesticides, such as fipronil, caused a widespread increase in fipronil concentrations in urban streams. An observed, trend in fipronil concentrations in 12 locations throughout the U.S. shows concentration increase in 10 locations with a decrease in only one location in NC and no change in one other location in TX.

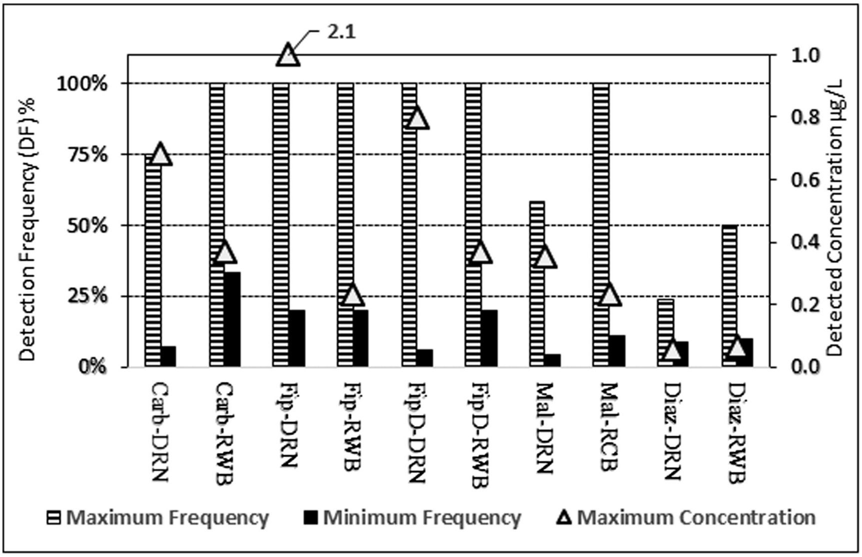

Figure 5. A summary graph for the top five insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in four of the major urban areas of California.

Herbicides Occurrence Frequencies/Concentrations

The top five herbicides that were frequently detected in source and receiving waters were 2,4-D, triclopyr, dicamba, diuron and MCPA (Figure 6). Other herbicides were detected at lower DFs and concentrations.

Data in Figure 6 show that the most frequently detected herbicides in receiving waters were 2,4-D, triclopyr, and diuron (75-100%; N= 6-8). Slightly lower DF were observed for dicamba and MCPA (67-100%; N=3-6). Except of dicamba, the maximum detected concentrations for the top 5 herbicides ranged from 6.7 to 27.6 µg/L. For dicamba, the maximum was 3.1 µg/L observed in DRN waters from the Sacramento area. In drain waters, the maximum concentrations of four of the top five herbicides (MCPA, dicamba, diuron and 2,4-D), in drain waters, were higher than those detected in receiving water bodies (1.1 to 51x) reflecting variable effect of dilution. In contrast, the maximum concentrations of triclopyr in DRN waters were much lower (0.2x). Results obtained for triclopyr may be explained by the possibility that receiving waters at these locations may have been contaminated with this herbicide before the point of DRN discharge. Although the DFs for herbicides are higher than insecticides, both data show no apparent differences in DFs between source waters (DRN) and receiving waters (RWB).

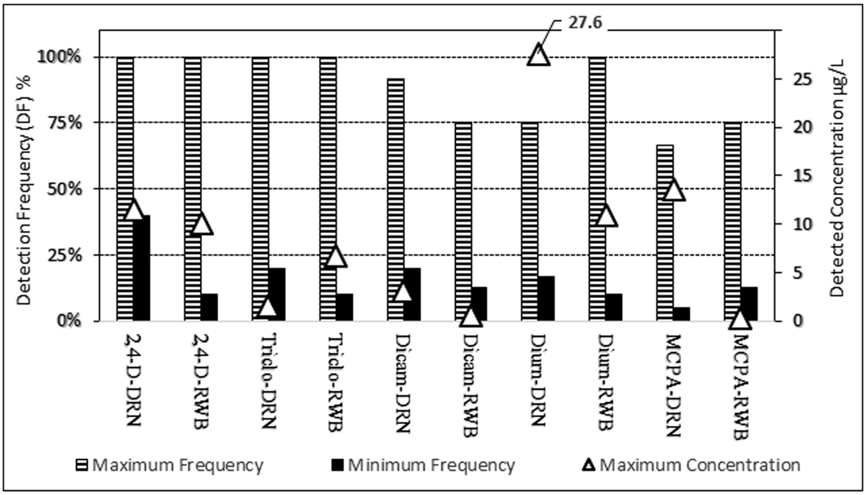

Figure 6. A summary graph for the top five insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in four of the major urban areas of California.

Pyrethroids Occurrence Frequencies/Concentrations

Pyrethroid insecticides that were frequently detected in source and receiving waters included bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, fenvalerate/ esfenvalerate and permethrin (Figure 7). The pyrethroid bifenthrin was detected in all source and receiving water samples with DFs ranging from 56-100% (N= 3-4) followed by permethrin with a range of 20-33% (N= 1-3). DFs for the other pyrethroids were much lower than bifenthrin and permethrin as they were in the range of 0-22% (N= 0-1).

Detected concentrations of pyrethroids in source and receiving waters ranged from 0-203 ng/L. In all of the monitoring events, higher pyrethroid concentrations were observed in source waters (DRNs) as compared to receiving water bodies (RWBs). Source water concentrations were 1.6-7.3 times higher than receiving waters in 4 out of 6 monitoring events and no pyrethroid was detected in the receiving waters of two out of the six events. This is probably a result of partitioning of the pyrethroids to the organic carbon in suspended/underlying sediments of receiving water bodies.

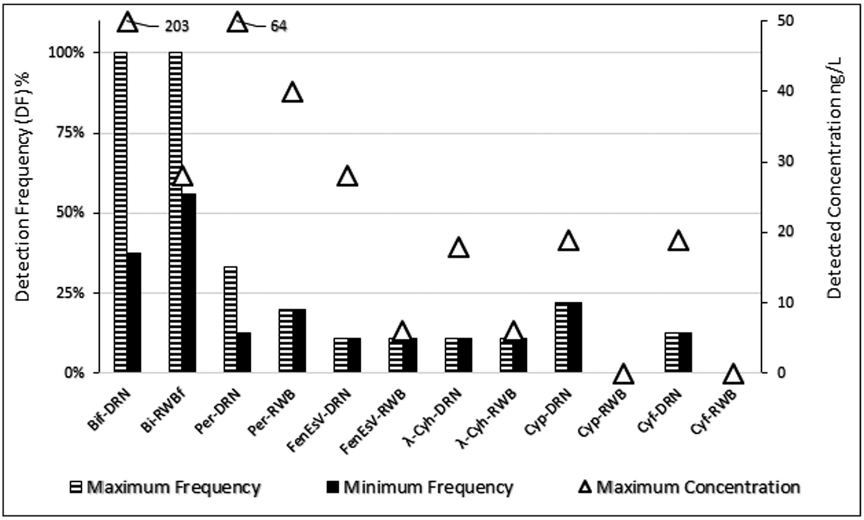

Figure 7. A summary graph for pyrethroid insecticides frequently detected in source drain water (DRN) and receiving water bodies (RWB) in three of the major urban areas in California.

Variations Associated with Geographical Locations

Variations in both concentrations and DFs are summarized in two ways based on the reported monitoring data for the four major urban areas of California. The first is by comparing maximum DFs of the insecticide in all monitoring events (DRN/Dry, DRN/Rain, RCB/Dry and RWB/Rain; referred to as the DFs comparison). The second is by comparing maximum/minimum DFs and maximum concentrations detected in the major source of contamination; that is the storm water drains in the two monitoring events (DRN/Dry and DRN/Rain; referred to as the DRN DF/Concentration comparison). The two types of comparisons are conducted herein for insecticides, herbicides and pyrethroids.

For insecticides, Figure 8 shows differences in the maximum DFs of monitored insecticides between various urban locations in the state of California.

The DFs comparison show that all of the top five insecticides were detected, in varied maximum DFs, in three of the major urban areas of California (SFB, ORN and SND). Diazinon was the only insecticide that was not detected in SAC area. It is also apparent that urban areas of southern California (ORN and SND) show higher maximum DFs, for these five insecticides, compared to the northern urban areas of the State (SAC and SFB). Observed differences could be a reflection of expected higher insecticides usage in the hot climate of the south as compared to the northern part of the State.

Figure 9 shows differences in DFs and concentrations detected in storm waters reflecting the contribution of this important source of insecticides reaching surface waters.

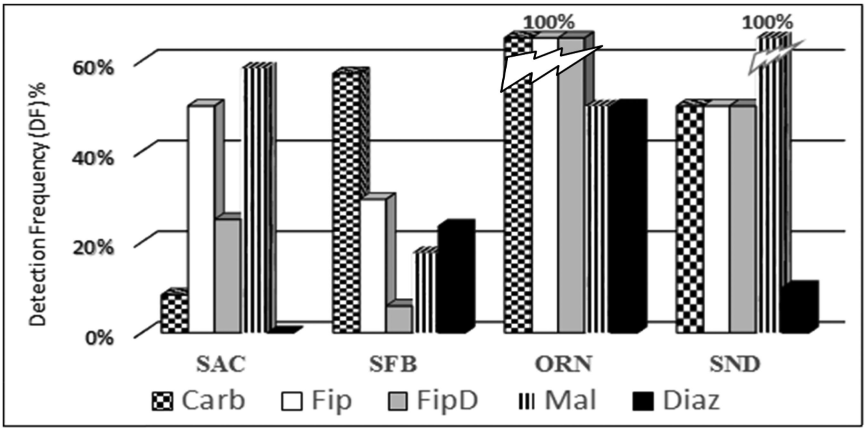

Figure 8. Maximum detection frequencies (DFs) for the top five insecticides detected in source/receiving waters of four of the major urban areas of California (SAC= Sacramento, SFB= San Francisco Bay, ORN= Orange County and SND= San Diego).

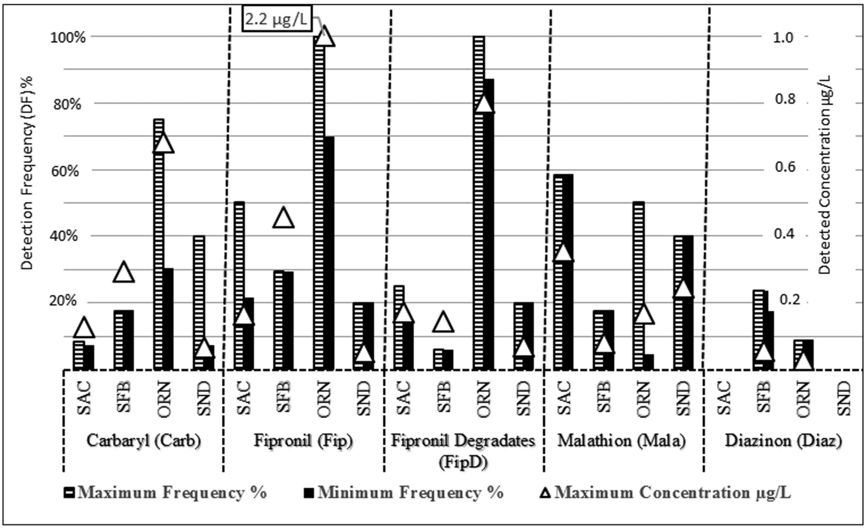

Figure 9. Max/min Detection Frequencies (DFs) and maximum concentrations of major insecticides detected in source drain waters (DRNs) in Sacramento (SAC), San Francisco Bay (SFB), Orange County (ORN) and San Diego (SND) urban areas of California.

The DRN DF/concentration comparison show variations in the insecticide load of the storm water. ORN County appears to have the highest detections for three out of the four insecticides (Carb, Fip, and FipD) and the second highest for the other two insecticides (Mal and Diaz). Data also show that maximum DFs appear to be associated with higher concentrations detected in the storm water in all of the four urban areas.

For herbicides, similar analyses was conducted (not shown) and results show that all of the top five herbicides were detected, in varied maximum DFs, in all of the major urban areas of California. Herbicides were detected at higher DFs than 40%, except for MCPA which was detected at a DF of 13% in ORN, 20% in SND. ORN showed the highest DFs of three herbicides (2,4-D, Triclo, and Diurn) followed by SAC with the lowest being the SND area. The herbicide 2,4-D was the most frequently detected in all of the four area followed by triclopyr in SFB and ORN. MCPA had the least DFs ranging from 13 to 75% with the least DFs in ORN followed by SND, SFB and SAC (highest).

DRN DF/concentration comparison show that ORN county with the highest detections for three out of the four herbicides (2,4,-D, Triclo and Diur) and the 3rd and 4th highest for the other herbicides (Dicam and MCPA). Data also show that maximum DFs do not always coincide with higher concentrations detected in the storm water. For example, SAC had the lowest DF of diuron compared to the other three areas of California but had the second highest observed concentrations and SFB had the 3rd DFs associated with the highest concentrations. Additionally, data on the maximum concentrations observed in source and receiving waters are summarized in Figure 10.

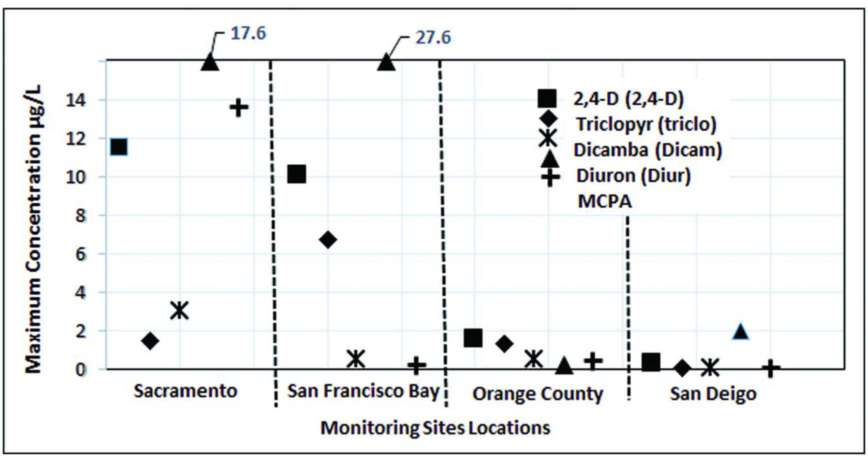

Figure 10. Maximum concentrations of herbicides detected in urban monitoring data from Northern and Southern California.

The summary shows that higher concentrations of the top 5 herbicides (>6.8 to 27.6 µg/L) were observed in source and receiving waters of Northern California urban areas (SAC and SFB) compared to ORN and SND of southern California (<2 µg/L). In Northern California, observed maximum diuron concentrations were the highest (17.6 to 27.6 µg/L) followed by 2, 4-D with maximum concentrations ranging from 10.1 to 11.5 µg/L. The MCPA maximum concentration was highest in SAC area (13.6 µg/L) while triclopyr was highest in SFB area (6.75 µg/L).

Similar analyses was performed on the pyrethroids data which includes only three urban areas SAC, SFB and ORN; SND was not monitored. Results of the DRN DF/concentration comparison show that bifenthrin was detected in DRN waters in the three monitored areas with maximum DFs/concentrations of 56%/26 ng/L), 93%/33 ng/L) and 100%/203 ng/L). The other four pyrethroids were only detected in SAC (cyfluthrin with DF/concentration of 13%/18.9 ng/L and cypermethrin with DF/concentration of 22%/18.9 ng/L), ORN (λ-cyhalothrin with DF/concentration of 11%/18.0 ng/L and fenvalerate/esfenvalerate with DF/concentration of 11%/28.0 ng/L). Additionally, data on the maximum DFs/concentrations observed in source and receiving water are summarized in Figure 11.

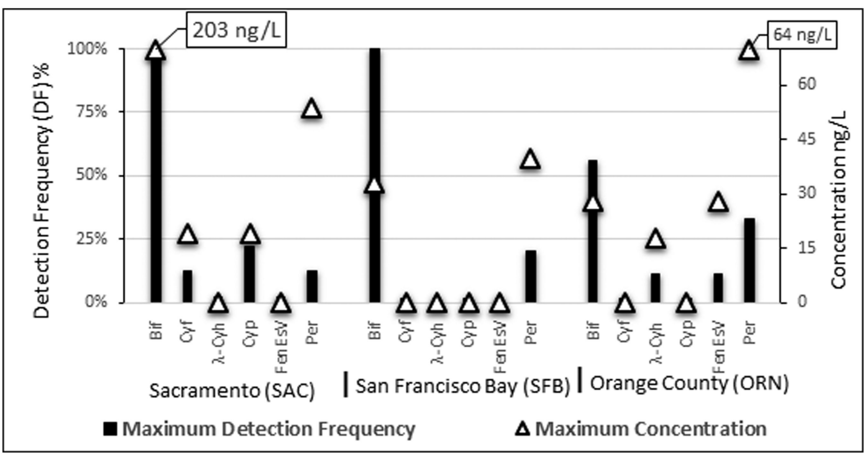

Figure 11. Observed maximum detection frequencies (DFs)/concentrations for pyrethroids detected in source/receiving waters of three major urban areas of California (San Diego (SND) not monitored).

Summary data indicate that the maximum DFs for bifenthrin were 100% in SAC/SFB areas and 56% in ORN County area. In the SAC area, the maximum observed concentrations of bifenthrin, permethrin, cypermethrin and cyfluthrin were 203, 53.9, 18.9 and 18.9 ng/L, respectively. In SFB area, only permethrin and bifenthrin were detected at maximum concentrations of 40 and 33 ng/L. Finally, in ORN County the maximum observed concentrations were 64 ng/L for permethrin, 28 ng/L for bifenthrin, 28 ng/L for fenvalerate/esfenvalerate and 18 ng/L for λ-cyhalothrin.

Variations Associated with Wet/Dry Conditions

Urban pesticides are mainly transported from application sites into surface waters by urban runoff waters resulting from rain storms and/or irrigation. It is thus expected that DFs and concentrations in drain and receiving waters to be related to pesticide properties (persistence and solubility), water availability (rain and irrigation), and timing of application. Additionally, application rate and frequency of application are expected to play a role in determining expected pesticide concentrations in surface waters as these factors are important in determining the pesticide load in quantity and timing. The latter factors can be deduced from usage data.

The results of the monitoring study indicated that most pesticides were detected during wet than dry conditions. One exception was fipronil and its degradates which were detected at higher frequency during dry flow in ORN County. Other reported results included the following: (1) First rainstorm gave the highest DFs in all of monitored site except in ORN county; (2) Detection of fipronil and its degradates with the first storm was similar to dry flow conditions and correlated with usage in Northern California; (3) Pesticides used in urban areas may show continuous load, similar to fipronil, independent of rain; (4) Bifenthrin had high detections associated with rain events although it is mostly applied during the dry season; and (5) Herbicides had more frequency of detections during the rainy season which coincides with timing of its application. Furthermore, the authors used the difference between DFs during wet flow and DFs during dry flow as an indicator for the influence of rain on pesticide detections. The results indicate that most of the pesticides are influenced by rain giving higher detection with the exception of fipronil degradates. Rain appeared to cause the highest detections for bifenthrin followed by diuron, MCPA, 2,4-D, malathion, dicamba, triclopyr, pendimethalin, carbaryl and fipronil (lowest).

The influence of dry and rain conditions on DFs and concentrations was examined based on monitoring data from stormwater ouflows (DRN) using bubble graphs and an example of these graphs is shown in Figure 12 for the top five frequently detected insecticides. DRN data were used because it reflect pesticide load carried out by run-off. In general, Figure 12 shows, that larger number/size and higher positions are for detections following rain compared to small number/size and lower positions for detections associated with dry flow. This is true for almost all of the examined insecticides, except of carbaryl, fipronil and fipronil degradates observed in ORN County.

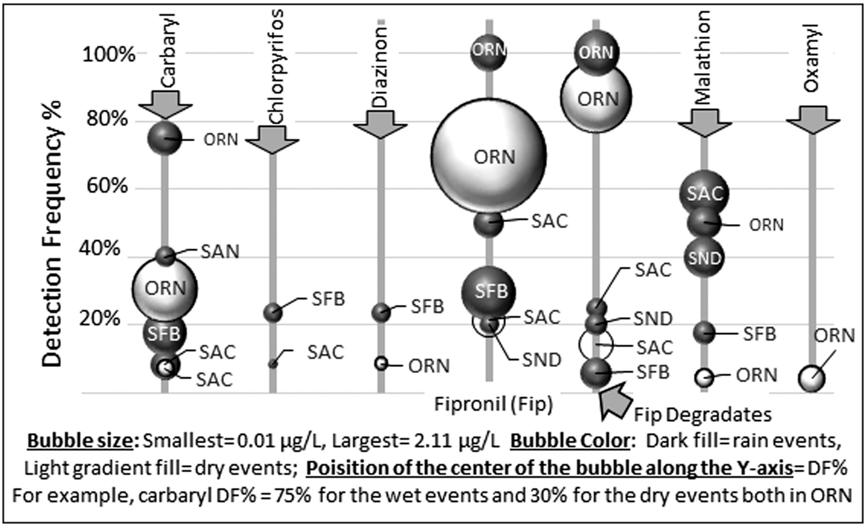

Figure 12. Influence of dry and rain flow conditions on DFs and concentrations of insecticides in the urban areas of Sacramento (SAC), San Francisco Bay (SFB), Orange County (ORN) and San Diego (SND).

Sediment Monitoring

Stream bed sediment samples were collected, during dry flow conditions, in creeks, a river, and a lake receiving waters from identified storm drains of five urban areas in Northern and Southern California (CA-N and CA-S) (*20*). The CA-N site was from Grayson creek receiving stormwater from the mixed residential/commercial urban area of Martinez/Pleasant Hill in the San Francisco Bay area. The CA-S sites were from Salt Creek, Wood Canyon Creek, San Diego River, and Lindo Lake receiving storm waters from the mostly residential or mixed residential/commercial urban areas of Laguna Nigel (Orange Co.), Aliso Viejo (Orange Co.), San Diego and Lakeside cities, respectively (Figure 13). In this California study, sediment samples were analyzed for 9 pyrethroids and chlorpyrifos and only 8 pyrethroids were identified. The pyrethroid fenpropathrin and the insecticide chlorpyrifos were not detected.

In another study, occurances and potential sources of pyrethroids in stream bed sediments from seven U.S. metropolitan areas were assessed. Sediment samples were collected in 2007 from 98 urban streams within the metropolitan areas of Atlanta, GA (ATL); Boston, MA, NH (BOS); Dallas−Fort Worth, TX (DAL); Denver, CO (CO); Milwaukee−Green Bay, WI (MGB); Seattle−Tacoma, WA (SEA); and Salt Lake City, UT (SLC) (*22*) (Figure 13). In this national scale study, sediment samples were analyzed for 14 pyrethroids and reported data were for five pyrethroids.

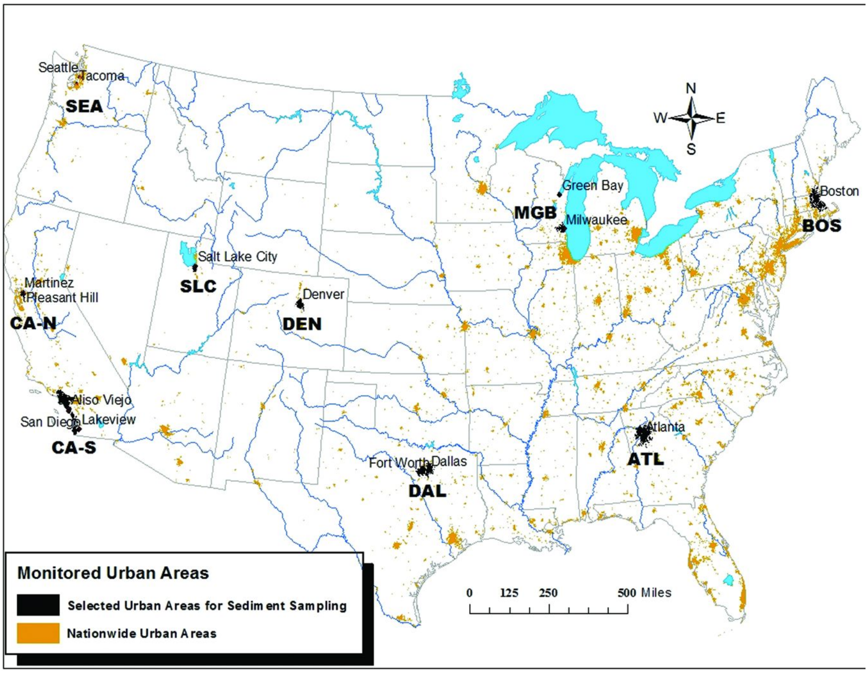

Figure 13. Stream bed sediment sampling sites for the statewide California study by Ensminger and Kelley (20) and the nationwide study by Kuivila et al. (22).

The pyrethroids bifenthrin, λ-cyhalothrin, cypermethrin, permethrin and resmethrin were monitored in both studies. Data from Ensminger and Kelley (*20*) included monitoring data for sediments underlying storm drains in addition to receiving water bodies. The data show relatively high DFs for bifenthrin, cyfluthrin, permethrin deltamethrin, λ-cyhalothrin and cypermethrin (41-97%) with maximum concentrations ranging from 32 to 680 µg/kg dry sediment. Fenvalerate/esfenvalerate maximum DF/concentration was reported to be relatively lower (14% and 24 µg/kg). However, of interest in this section is the pyrethroid chemicals data for sediments underlying receiving water bodies as it can be compared with data obtained for the nationwide bed stream sediments study conducted by Kuivila, *et al.* (*22*) This will permit comparison between bed sediments obtained nationwide from urban areas varied in hydrology, weather, pesticide use, timing of application and land characteristics/use. Figure 14 summarizes the concentration and DF data obtained from both studies for bifenthrin, λ-cyhalothrin, cypermethrin, permethrin.

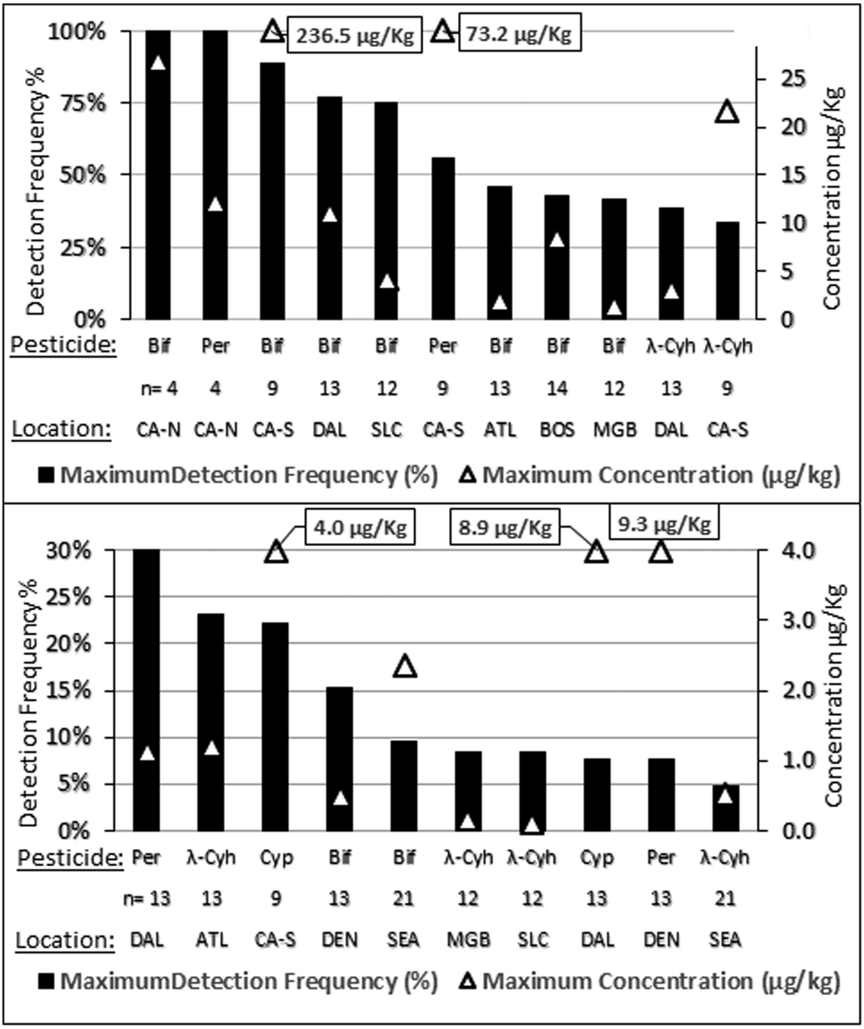

Figure 14. A summary of the sediment concentration/DF data obtained for bifenthrin (bif), λ-cyhalothrin (λ-Cyh), cypermethrin (Cyp) and permethrin (Per) (n = number of samples; for sampling location abbreviation refer to map in Figure 13).

Data show variable occurrence frequencies and concentrations of pyrethroids detected in bed sediment streams across the country. Reported data may be categorized by the frequencies of occurrence into three categories as shown in Table 4.

Table 4. Categories for the Frequencies of Pyrethroid Occurances in Bed Sediments

Detection Frequencies	*Maximum Concentrations*	*Bed Sediment Location*	*Pyrethroid Detected*	*Exception*	*Reference*
56 - 100%	**11.2 – 237** µg/kg	**CA-S, CA-N, DAL**	Bif	SLC= **4.2** µg/kg	Figure 14 Top Graph
		CA-N	Per	None	
33 - 46%	**1.4 - 8.4** µg/kg	**BOS, ATL, MGB**	Bif		
		DAL	λ-Cyh	CA-S= **22** µg/kg	
5 - 31%	**2.4 - 9.2** µg/kg	**DEN**	Per	None	Figure 14 Bottom Graph
		DAL, CA-S	Cyp		
		SEA	Bif		
	0.1 - 1.2 µg/kg	**ATL, SEA, MGB, SLC**	λ-Cyh		
		DEN	Bif		

Monitoring vs. Modeling

Targeted monitoring data, similar to those discussed earlier, are important resource for regulators of urban pesticides. These type of data are available for pesticides that have been in use for many years. Quality monitoring data can be used as a ground truth for verifying modeled estimated environmental concentrations (EECs) that determine aquatic exposure. EECs are used in ecological and drinking water assessments. In the case of pesticides used in urban setting, monitoring data are much more important due to the usually high uncertainties associated with modeling surface water exposure in the urban environment. In some cases, it was necessary to use EECs from monitoring data instead of modeling due to lack of scenarios that would represent application of a given pesticide and associated processes. For example, application rate/acre, number of applications and timing are required to perform PRZM/EXAMS modeling. Label information is not enough and assumptions had to be made to estimate these key parameters. For example, in the case of house perimeter treatment the label usually gives application rate in lbs a.i/1000 sq. ft and possibly a recommended treatment of 2 ft around the house. A residential area factor is usually estimated in order to arrive at a reasonable application rate for modeling which needs estimates of housing density/acre and area that would be treated (need to assume house dimensions). The assumptions should be reasonably conservative and represent the area where the pesticide is to be applied. The task of arriving at reasonable estimates becomes much more difficult when the pesticide is to be used on a national scale. Many scenarios would be needed to represent housing densities across the U.S. Additionally, other needed parameters, such as timing of application, is assumed conservatively to happen at one time for all houses within a 10-hectare area. PRZM calculates daily load of pesticide transported by water run-off and erosion into 20,000 m^3 pond 2 m deep with no outlet to further simulate degradation. In contrast, urban runoff waters transports pesticides, through urban drainage/pumping systems (in some cases through POTWs), into surface water bodies such as urban creeks, lakes, and rivers. Pesticides arriving to these water bodies may then be transported via running water rather being held into a pond with no outlet. Although EECs estimated in pond, by EXAMS, are expected to be conservative but much higher conservatism may result in unrealistic estimates especially with highly persistent pesticides that accumulates in the pond yielding high EECs.

Monitoring data and examples of previous modeling for surface water EECs are compared for two of the most frequently detected pesticides; Fipronil and bifenthrin (Table 5).

Table 5. Modeled vs. Monitored EECs for CA

Chemical	*Treatment Type*	***Label Rate*** *(lbs ai/A)*	***Modeled rate (No. of Applications)***[1]	***Modeled EECs (ng/L)***			***Observed EECs in CA Monitoring (ng/L)***[2]
				Peak	***21-day***	***60-day***	
Fipronil	House perimeter treatment	2 ft. @ 0.357	0.012 lbs ai/A (1)	41.2	26.7	15.2	Maximum= 232 and 90^{th}%= 83
	Broadcast fire ant treatment	Not Stated	0.014 lbs ai/A (1)	6.3	4.1	2.3	
Fipronil total degradates	House perimeter treatment	Three degradates modeled individually similar to parent using the fate properties of the degradates and the max daily conversion observed in environmental fate studies corrected for differences in molecular weights		19.5	15.5	14.1	Maximum= 372 and 90^{th}%= 125
	Broadcast fire ant treatment			3.2	2.6	2.4	
Bifenthrin	Many residential uses	Varied label rates with calculate range of application rate of 0.001 to 2.2 lbs ai/A and from one application to twelve applications @ 7-180 days intervals		Capped by the solubility limit of 14 ng/L			Maximum= 27.2 and 90^{th}%= 24.2

[1] Modeled rate = Could be different from label rate because it is an adjusted rate based on treated area of the acre. [2] Maximum and 90^{th} percentile values detected in Receiving water bodies (RWB).

Monitored maximum and 90th percentile EECs for both fipronil and bifenthrin are higher than modeled EECs suggesting possible improper parameterization of the model. In the case of fipronil, lower EECs might be related to the application rate calculated for modeling and possibly a reflection of the scenario used. In case of bifenthrin, modeled EECs were capped to the limit of solubility of the chemical which is 14 ng/L. Modeled EECs are higher than the 14 ng/L concentration expected for this insoluble chemical. In fact, bifenthrin was detected to occur at concentration as high as 27.2 ng/L which is almost two times its laboratory determined solubility. The observed relatively high occurrence for bifenthrin in run-off and surface waters may be attributed to factors such as water chemistry, such as presence of dissolved organic carbon or colloids, and possible effects of the formulation that makes bifenthrin more soluble in surface waters than in pure laboratory water.

The above example of comparison between monitored and modeled data is at best an approximation due to many factors such as (1) Modeled EECs were not a result of proper parameterization of the model to represent monitored areas, (2) The summary concentrated on the maximum observed concentrations in order to identify sites having the highest EECs indicating their vulnerability noting that these values may have been influenced by contamination from other sources such as spills and transported pesticides from areas upstream or with airborne particles and/or drift (3) Ideally, only targeted monitoring data, for an identified vulnerable site, may be compared to modeling data using parameters representing the same site. This is not the case for the comparison above, monitoring data were for four different urban areas of the State of California, consisted of 47 values for fipronil and degradates and only 14 values for bifenthrin and the maximum number of values for each site ranged from 1 to 8 (dry + wet events) and only from 1 to 5 for dry event and 1 to 4 for wet events, Monitoring data needed for comparison should represent only one area and should be extensive (daily or weekly). The monitoring data used were with intervals ranging from 24 to 167 days 7 to 118 days. for bifenthrin, (4) It is important to point out that the ultimate maximum exposure EECs in receiving water bodies is dependent on the mass of pesticide transferred into the water body. Winter stormwater high flow with low concentration is expected to contribute more pesticide mass to receiving waters than summer low flow with high concentration, (5) In flowing waters, such as rivers and streams, observed concentrations are expected to be influenced by the flow status of the rivers and streams because higher dilution will occur at high flow compared to low flow, and (3) EECs are also influenced by the pesticide fate and transport properties as well as the receiving water characteristic such as type of suspended matter (content of dissolved/suspended organic carbon and other colloidal materials). Such contents may additionally influence the bioavailability of the pesticide and its toxic effects.

Potential Refinement for Modelling EECs

Currently, the USEPA considers the modeling approaches described above and resultant EECs as crude estimates and provide only a screening-level information. This is due to uncertainties regarding: variability in site characteristics that govern runoff, effect of different formulations, types of impervious surfaces, application methods and timing and national representation of regions with varied landscape, housing density and hydrological features. Therefore, refinement of residential and impervious surface exposure scenarios is needed. This can be done by incorporating recent findings that could be used to accurately parameterize the residential and impervious scenarios used in modeling. This information helps in refinement by providing data necessary to establish national representative scenarios for vulnerable sites. The conceptual model for establishing these standard scenarios involves the following steps: (1) identify vulnerable urban watersheds based on available monitoring data and different climatic conditions, pesticide pressure, and hydrology; (2) understand the hydrology of the chosen watersheds especially the drainage system inputs and outputs; (3) classify each of the chosen watersheds according to land use (commercial, industrial, mixed and others), determine fractions of pervious, impervious surfaces and drainage systems for urban runoff waters; (4) choose 10-hectare vulnerable areas of the watershed that represent typical residential, commercial, industrial and mixed developments (that is the catchment area for PRZM); (5) specify the types of surface areas, in the chosen catchments, that would be treated for various label use patterns (i.e., home perimeters patios, driveways, etc.) and the fraction of that area that would be treated (i.e., fraction treated for home perimeters patios, driveways, etc.); (6) determine the application rates for the residential and impervious surface exposure scenarios; (7) adjust the rate for varied impervious surfaces based on available washoff studies (this adjustment would be dependent on the modeled chemicals); (8) establish a pattern for timing of application within the chosen watershed; and (9) run PRZM simulations with outputs processed through mixing cells into varied receiving water bodies (urban streams, lakes and rivers) to arrive at exposure EEC averages needed for risk assessment.

Assessing Adulticide Uses

Mosquito control remains as an important issue in urban environments in the United States due to the need to limit mosquito-borne diseases, such as West Nile virus (affecting human health) (*23*), or dog heartworm (affecting pets) (*24*). Wide area adult mosquito control is accomplished through a different pesticide method of application. In lieu of conventional ground or aerial applications using fine, medium or course droplets (according to American Society of Agricultural and Biological Engineers (ASABE) Standard S-572.1), mosquito adulticides are applied as ground or aerial mists, using extremely fine droplets, known as Ultra-Low Volume (ULV) droplets. Adulticide application rates are usually a very small fraction of the rate of coarser droplet applications used to control other insects (*e.g.*, in the ounces of product per acre range). Conventional pesticide applications are typically intended to hit the crop (*i.e.*, for foliar applications), while the ULV droplets are intended to remain airborne to hit mosquitoes in flight. A critical review of ULV technology, including efficacy, variables that affect space ULV applications, and some information on non-target impact, has been published (*25*).

Examples of pesticides applied through ULV spray products are permethrin, prallethrin, *d*-phenothrin (commonly known as Sumithrin®), pyrethrins, etofenprox, malathion and naled. These chemicals are often times co-formulated with the synergist piperonyl butoxide (PBO) to enhance their activity. Given that many of these pesticides are considered very toxic to aquatic organisms, an approach to calculate aquatic estimated environmental exposure concentrations (EECs) is required. In this section of the chapter, a brief description of how the USEPA assesses ecological exposure from adulticides is presented, using modeling and open literature data for aerial and ground applications, respectively. The section will provide a synopsis of the use information and modeling, which includes discussions of aquatic and terrestrial exposure. For aerial applications, the AGricultural DISPpersal drift model (AGDISP v.8.26) is used for this purpose. For ground applications, a review of literature information and other lines-of-evidence provided an upper bound deposition level. A short example of an adulticide ecological risk assessment's results will be provided, and compared against monitoring data.

Use of Adulticides

In 2005, a Pesticide Registration (PR) Notice, titled "Labeling Statements on Products Used for Adult Mosquito Control", was issued (PR Notice 2005-1 (*26*)). The PR Notice 2005-1 (*26*) provided recommendations for label language for pesticides products for wide area ground or aerial adult mosquito control products, applied only through ULV spray or fog.

The PR Notice 2005-1 (*26*) included seven major recommendations (*27*). Among the recommendations, adult mosquito control applications should be limited to trained personnel and users should consult their State and Tribal agency to determine if permits or regulatory requirements exist. Additionally, adulticide applications should be clearly distinguished from conventional applications of insecticides in the label directions. The "Environmental Hazards" section of the labels should be clear and direct applications over bodies of water should be allowed under certain circumstances. Bee precautionary language should allow adulticide applications in order to respond to threats to public health that might be identified. As of October 15, 2005, registrants were expected to submit label amendments reflecting recommended label language; however, some labels were changed after this date. This language also provided more consistent instructions across different products relative to the quality of spray droplet, application rate, seasonal or annual rate, *etc*. Adulticide application parameters are also highly dependent on actual weather conditions, such as wind speed and direction. PR Notice 2005-1 (*26*) addresses such issues as well. The labels for mosquito adulticides now include restrictions surrounding the size of the droplets from the applications. According to the recommendation, two droplet dimensions should be specified: one is the Dv0.5 (the volume median diameter: half of the volume of spray contains droplets which are smaller than the stated value), and the other is the Dv0.9 (90% of the spray is contained in droplets smaller than this value), both expressed in microns (*e.g.*, Dv0.5 <60 μm and Dv0.9 <115 μm, for aerial applications). Furthermore, labels now indicate the frequency and timing of applications, and the maximum annual application rate. This information is very useful and allows the assessor to determine which conditions should be assessed for risk of aquatic (and terrestrial) exposure. Moreover, the altitude of aerial applications is oftentimes also specified (*e.g.*, ≥75 ft).

Modeling Approach for Adulticide Assessment

As indicated earlier, the modeling approach for the aerial adulticide use includes calculations of spray drift using the exposure model AGDISP. This computer program estimates the deposition of the pesticide to the treated area, which is the application efficiency. Further, by means of its toolbox "Deposition Assessment," the deposition to adjacent bodies of water (*i.e.* the standard pond), the value of spray drift can be obtained. AGDISP provides a prediction of spray drift under circumstances where a mosquito adulticide is used. Besides the Dv0.5, Dv0.9, and boom height, other parameters of importance in modeling in AGDISP include the spray volume (usually expressed in gallons per acre), wind speed range (miles per hour), wind direction, spray material (*e.g.*, oil or water based), and specific gravity. The spray volume, material, and specific gravity, are specified or can be estimated from the label or the material safety data sheet (MSDS) for the product, or from product chemistry submissions. To model aerial applications, the lowest boom height allowed in the label is selected, which is expected to result in the highest deposition and drift. The model output of AGDISP includes the spray drift fraction (obtained from the "Deposition Assessment" tool of the model's Toolbox), and application efficiency (fraction of the material that deposits in the target area under the aircraft, which is expected to be much lower than the default values for typical agricultural applications). In order to obtain aquatic EECs, these values are utilized as input parameters in the aquatic models PRZM/EXAMS. To obtain terrestrial EECs, the application efficiency can be used to correct the application rate in T-REX (Terrestrial Residue Exposure, v.1.5.2). The "adjusted application rate", based on application efficiency estimated by AGDISP, is the rate that is entered into T-REX for estimating exposure and risk to non-target terrestrial animals. The model can also be used to estimate exposure to wildlife off the field, by means of the terrestrial point estimate of the "Deposition Assessment" tool.

The AGDISP model has been used for aerial applications; however, it has not been approved for wide use in EFED for ground applications. Recently, in response to a request to amend certain labels, and a petition by the Health Effects Division (HED), EFED evaluated aerial ULV applications using the model AGDISP (*28*). The model chemical was etofenprox. Given the same application parameters (*i.e.*, drop size distribution, application material, application height), model results indicated that the deposition value is sensitive to wind speed as an input parameter. For etofenprox the wind speed range allowed by the label is 1-10 mph. Based on AGDISP modeling of aerial applications, at wind speeds of 1 mph the application efficiency (percent of the chemical that deposits on the crop) was estimated to be ~33%. Additionally, the application efficiency decreases with increasing wind speeds.

For ground applications, eight open literature studies (Table 6) and a dissertation focused on the mechanistic aspects of drift from ground-based adulticide applications (Schleier III (*29*), Schleier III *et al.* (*30*)). EFED evaluated these articles and detected that peak deposition rates, measured in a variety of dosimeters, and at different wind speeds and distances from the application sites were similar to aerially based ULV applications. Consensus of the studies indicated that ground ULV pesticide deposition is similar to that from aerial ULV pesticides. For ground applications, the deposition is expected to range from 0 to 33% of the applied (Table 6).

Table 6. Summary of Peak Deposition Rates Reported in Literature Studies [1]

Reference	***Material***	***Peak deposition (ng/cm²)***	***Peak deposition (% applied)[2]***	***Distance from application source to peak deposition (m)***	***Wind speed (mph)[2]***
Tucker *et al.* (*31*)	Fenthion	2.92	2	8	NR
	Malathion	85.8	15	8	NR
	Naled	57.3	20	8	NR
Moore *et al.* (*32*)	Malathion	84.1	14	30.4	0.9–3.4
Tietze *et al.* (*33*)	Malathion	50	9	5	2.1–4.0
Knepper *et al.* (*34*)	Malathion	9,222	NA	7.6	1
	Permethrin	14,389	NA	7.6	1
Tietze *et al.* (*35*)	Malathion	473	NA	Unknown	0–2.5
Schleier & Peterson (*36*)	Naled	74	33	50	1.5
	Permethrin	4.6	5.9	25	4.3
Pierce *et al.* (*37*)	Permethrin	5.1	10	Unknown	6−12
Preftakes *et al.* (*38*)	Permethrin	8	10	25−50 m	4.8

[1] Source: USEPA (*28*). [2] NA – insufficient information to assess; NR – not reported.

The review concluded, based on EFED's analysis and guidance provided in the label, that a deposition rate of 33% for sprays reaching agricultural crops is a conservative estimate for both ground (based on submitted literature data) and aerial (based on AGDISP modeling) ULV applications for etofenprox.

Adulticide Insecticides Monitoring Data

Monitoring data for adulticides is scarce. Given that they are applied at extremely low rates, and some of these pesticides have other uses, monitoring results can be confounded with other uses. For example, permethrin can be used as an adulticide; however, it can be used on agricultural crops, in residential settings, and industrial sites, and it has uses that may lead to residues in wastewater discharges, and consequently in treatment plant effluents.

In 2000, Milam *et al.* (*39*) published a report of monitoring for toxicity of ground and aerial permethrin adulticidal applications (product Biomist®) in Arkansas. Toxicity was performed *in situ* in 10 replicate test chambers plus controls. Test organisms included *Daphnia pulex*, *Ceriodaphnia dubia*, and *Pimephales promelas*. Five test organisms were placed in each chamber. Once permethrin was allowed to settle, the chambers were transferred to the laboratory for the remainder of the exposure period (24 or 48 hours). *P. promelas* did not appear to be susceptible to aerial or ground ULV permethrin applications, showing 100% survival in all instances. Both *D. pulex* and *C. dubia* appeared to be more susceptible to aerial than to ground applications and showed variable survival rates from ground applications of permethrin.

Weston *et al.* (*40*) reported their results from monitoring of aerial applications of pyrethrins and PBO in August 2005, using the product Evergreen Crop Protection EC 60-6 (containing 6% pyrethrins and 60% PBO), on ~50,000 hectares over the densely populated area of Sacramento, CA. (across the American River). Treated areas were primarily commercial and residential. Water and sediments from six creeks draining the treatment area were sampled and tested for toxicity (water *C. dubia* test (~6-8-day tests); sediment *Hyalella azteca* (10-day test) and chemistry (pyrethrins, chlorpyrifos, diazinon and PBO in water; pyrethroids, pyrethrins, PBO and chlorpyrifos in sediment). Additionally, two separate experiments were performed to determine the effect of PBO on sediment sorbed pyrethroids: one was conducted with a sediment that showed near total lethality to *H. azteca*, and another with a sediment spiked with bifenthrin. The sediment's LC_{50}s were determined, with PBO present in the overlaying water at 0, 4, and 25 μg/L. Water analysis indicated that the sum of pyrethrins I and II, were not detected above the reporting limit of 0.01 μg/L, which was attributed to degradation via photolysis and adsorption by bed sediments; however, PBO was undetected prior to application and reached a maximum level of 3.92 μg/L after application. Sediment sample analyses revealed that pyrethrins I were present at a concentration of up to 403 μg/kg dry weight after application and PBO concentrations were up to 61.4 μg/kg dry weight. There was no evidence of aquatic toxicity due to the application of pyrethrins and PBO alone. The additional testing indicated that PBO concentrations of 2-4 μg/L in the overlaying water were sufficient to enhance previously present sediment pyrethroid toxicity to *H. azteca* by a factor of up to two. Even though there is uncertainty about the PBO actual exposure duration in the environment, at the treatment site PBO was applied on three consecutive nights. This could cause prolonged PBO concentrations in the environment. Water sampling occurred at 10 and 34 hours after application and the difference in PBO concentration between samplings was not appreciable. This article was the first to show that the synergist PBO could pose additional risk to aquatic animals, compared to risk posed by individual insecticide active ingredients, at an environmentally realistic PBO concentration.

The Sacramento-Yolo Mosquito and Vector Control District provided a water quality monitoring effort for the same applications by Weston *et al.* (*40*) (Ziegler (*41*)). No sediment samples were taken for analysis. Water samples were analyzed for pyrethrins and PBO, with respective reporting limits of 0.2 and 1.0 μg/L. Since applications were made in the evening (usually after 8:00 pm), for each application event water samples were taken three times, which represented before application (baseline), in the morning on the day after application (representing immediate post-application), and in the afternoon on the day after application (next day post-application, taken approximately 15 hours after the immediate post-application samples). For the first application event, immediate post-application samples were not taken. Results indicated that the pre-application (baseline) samples were non-detects at the reporting limit for both pyrethrins and PBO. For the immediate post-application samples, 35% and 56% of the water samples were reported as detects for pyrethrins and PBO, respectively. For the next day post-application samples, pyrethrins were not detected in any samples and PBO was detected in 35% of the samples. The maximum pyrethrins concentration reported was 3.77 μg/L and PBO was at a maximum concentration of 20 μg/L.

Schleier and Peterson (*42*) derived LC_{50}s for permethrin, permethrin synergized with PBO, permethrin in the product Permenone®, Permanone® plus PBO, technical naled, and naled in the product Trumpet®, towards the representative medium–to-large ground-dwelling non-target insect, the house cricket (*Acheta domesticus* (L.)). Using ground ULV applications, there were no significant differences in mortalities of caged house crickets exposed to Permanone® or naled, compared to controls. The authors calculated EECs using the Industrial Source Complex Short-Term (ISCST3) dispersion model, which resulted in exceedance of the levels of concern (LOCs) for the house cricket in all cases, except for technical grade permethrin. However, using actual environmental concentrations, only the risk quotient (RQ) for technical grade naled exceeded the LOC. RQs were 10- to 100-fold lower using the measured environmental concentrations than using modeling.

In another monitoring effort, Kuivila *et al.* (*22*) reported sampling for several synthetic pyrethroids in 7 metropolitan areas across the U.S., which excluded California. Among the pyrethroids analyzed, resmethrin was included, which has been used primarily for mosquito abatement. The study reported a frequency of detection of resmethrin in sediment samples of 4% and a highest concentration of 38.3 μg/kg dry weight, a median 5.3 μg/kg, with a method detection limit of 0.5 μg/kg dry weight. According to the article, given that resmethrin is used primarily as an adulticide, the source of the chemical for the site that showed the maximum resmethrin concentration at a site within Estes Park, Colorado (an undeveloped watershed), is aerial applications of resmethrin for mosquito control. According to this article, a previous study had reported a maximum resmethrin concentration in suspended sediment of a San Joaquin Valley, California watershed of 19 μg/kg (*43*).

Phillips *et al.* (*44*) incorporated toxicity testing to monitoring relative to mosquito adulticide applications. As a requirement of a National Pollutant Discharge Elimination System (NPDES) General Permit to comprise discharges to waters from mosquito control applications in California in 2011, the California State Water Resources Control Board and the Mosquito Vector Control Association of California conducted chemical and toxicity analyses in the water column and sediment pre- and post-applications of malathion, naled (and its degradate dichlorvos), permethrin, *d*-phenothrin, pyrethrins, etofenprox, and PBO (plus a suite of other pyrethroids), during 15 mosquitocide applications in 2011 and 2012. Settings included and were labeled as urban, agricultural and wetland environments. Pre-application water and sediment samples were collected in the evening of each application day. Post-application water samples were collected in the early morning hours (12-hr post-application) and evenings of the day after each application (24-hr post-application). The post-application sediment samples were taken 4-7 days post-applications, to allow time for partitioning with the sediments. The toxicity of malathion and naled was assessed using *Ceriodaphnia dubia*, while the toxicity of pyrethroids and pyrethrins was assessed using *Hyalella azteca*.

Only four post-application sediment samples were more toxic than their corresponding pre-application samples; however, the toxicity could not be attributed to the spray events and there was a limited number of chemicals tested (Table 7).

Toxicity of nine out of 16 toxic water samples was related to applications of naled and attributed to it's degradate dichlorvos. Given the limited number of adulticide chemicals available in the market, and that naled is only one of two organophosphate pesticides used for this purpose, the authors recommended best management practices to prevent toxicity due to naled applications. They indicated that some practices are already being implemented (Table 7).

Table 7. Summary of Sampling Results from Monitoring Mosquitocide Applications. (Source: Phillips *et al.* (*44*))

Chemical	***Toxicity***	***Concentrations and Other Notes***
	Sediment	
Pre-App Samples	Out of 17 samples, only one exhibited significant toxicity (*H. azteca*), taken before a *d*-phenothrin application.	The corresponding post-application sample exhibited the same mean survival (74%), and it was not found to be significant.
Permethrin	Only one urban site was sampled for permethrin, which exhibited significant toxicity pre-application (*H. azteca*). See above.	The permethrin concentration was below the toxicity threshold.
Pyrethrins	Two of the urban sites exhibited toxicity post-application (*H. azteca*).	There were no detections of pyrethrins and no sample exceeded the PBO toxicity threshold.
d-phenothrin	Five wetland and five agricultural sites were sampled for *d*-phenothrin, all of which did not exhibit significant toxicity pre- and post-application (*H. azteca*).	No sample had concentrations of *d*-phenothrin or PBO exceeding their toxicity thresholds.
	Water Column	
Pre-App Samples	Out of 53 samples, only one exhibited significant toxicity (*H. azteca*), taken before a *d*-phenothrin application.	The corresponding post-application sample was not significantly toxic at the same site.
Malathion	Two sites were tested, which did not exhibit significant toxicity (*C. dubia*).	The concentrations of malathion were below the organism threshold.
Naled	Six urban, two wetland and one agricultural sites were tested. Significant toxicity was observed in both wetland and all six urban sites (*C. dubia*).	Naled was not detected in any of the sites but its degradate, dichlorvos, was observed at concentrations exceeding the organism threshold in both wetland and four of the urban sites. Trichlorfon, another precursor of dichlorvos, was noted at levels exceeding thresholds in one of the wetland sites.

Continued on next page.

Table 7. (Continued). Summary of Sampling Results from Monitoring Mosquitocide Applications

Chemical	***Toxicity***	***Concentrations and Other Notes***
Etofenprox	The 24-hr post-application sample exhibited significant toxicity (*H. azteca*).	The chemical's concentration was below the reporting limit.
Permethrin	Six agricultural, one wetland and five urban sites were sampled. Three permethrin post-application sites exhibited significant toxicity (one agricultural and two urban) (*H. azteca*).	Permethrin, bifenthrin and PBO concentrations were all below toxicity thresholds in these samples (*H. azteca*) with the exception of one bifenthrin concentration exceeding the threshold in one of the urban sites that exhibited toxicity (12- and 24-hours post-application).
Pyrethrins	Six urban and six wetland sites were monitored, of which only one urban site exhibited toxicity (*H. azteca*).	Even though the concentration of pyrethrins and PBO were below their toxicity thresholds, it turned out that the concentrations of PBO were the highest reported for the samples that exhibited toxicity. The authors speculated that the PBO may have synergized the toxicity of other pyrethroids present in the samples.
d-phenothrin	None of the six agricultural, six wetland and six urban sites monitored exhibited significant toxicity post-application (*H. azteca*).	The concentrations of *d*-phenothrin and PBO were below their toxicity thresholds.

Example Ecological Risk Assessment

In 2008, EFED issued an analysis of the ecological risk assessment for permethrin for the following endangered or threatened species in California (*45*): California red-legged frog *(Rana aurora draytonii*), California clapper rail (*Rallus longirostris obsoletus*), Salt marsh harvest mouse (*Reithrodontomys raviventris*), San Francisco garter snake (*Thamnophis sirtalis tetrataenia*), and Bay checkerspot butterfly (*Euphydryas editha bayensis*). One of the assessed uses of permethrin was for vector control through ULV applications. In the assessment, aquatic and terrestrial species were evaluated. At the time of the review, some labels did not comply with PR Notice 2005-1 (*26*), and therefore, analyses were performed using both pre- and post-PR Notice 2005-1 labels. Table 8 provides the urban aquatic EECs. Compared to a peak water EEC of 0.221 µg/L (post-CFR 2005-1), the single monitoring study that provided water column concentrations of permethrin (*44*) presented a maximum concentration of 0.03 µg/L. The ecological risk assessment did not provide sediment concentrations for comparison; however, they can be estimated based upon the value of organic/carbon partition coefficient (K_{OC} = 76800 L/kg). An estimated conversion factor of 3073 from pore water concentration to sediment concentration is calculated using a spreadsheet and the constants that define the EXAMS ecological pond. The peak pore water concentration was 0.0515 µg/L. The estimated peak sediment concentration is 158 µg/kg, which is above 2-fold higher than the monitored concentration of 65.9 µg/kg.

Table 8. Water Column EECs (µg/L) for Permethrin Uses in California

Scenario	*App Rate (lb a.i./A)*	*Peak (µg/L)*
Recreational areas (Pre-CFR 2005-1)	0.007x7	0.496
Recreational areas (Post-CFR 2005-1)	0.007x7	0.221

In the past, EFED has based its adulticide evaluations on existing turf Pesticide Root Zone Model (PRZM) scenarios for modeling aquatic exposure (*e.g.*, FL, PA or CA turf). These scenarios are used as surrogates for areas such as, but not limited to parks, campsites, woodlands, athletic fields, golf courses, garden playgrounds, and recreational areas; however, for uses in other urban sites, such as residential, the combination of the residential and impervious scenario, run in tandem may be utilized in upcoming assessments. It is expected that the development of new scenarios depicting residential sites and/or impervious surfaces may be further used in the future.

Assessing Pesticide Releases to POTWs

In the context of ecological risk assessment of conventional pesticides at USEPA, the issue of household wastewater releases of pesticides was first raised by public stakeholders from California during the Re-registration Eligibility

Decision (RED) process of the pyrethroid insecticide permethrin (*46*). Concerns were raised that clothes pretreated with permethrin may cause adverse water quality impacts due to releases to POTWs when washed and result in subsequent discharges to receiving waters by POTWs. It is noteworthy that potential releases of antimicrobial pesticides to POTWs have routinely been considered in OPP environmental risk assessments due to their widespread use in consumer care products that result in substantive 'down the drain' releases (*e.g.,* antibacterial ingredients in hand soaps). In contrast, this issue is relatively new for conventional pesticides where exposure from outdoor uses has traditionally been assumed to dominate environmental risk concerns. Monitoring data described later in this section indicates that for some pesticides, releases to (and from) POTWs may be significant to the extent that this exposure pathway requires consideration in USEPA environmental risk assessments. More recently as part of OPP's pesticide Registration Review process, the aforementioned concerns were echoed and additional concerns were identified regarding the potential for environmental exposure to pesticides resulting from their sorption onto biosolids and subsequent biosolid application to land (*47*).

In this section, we summarize the currently available information regarding conventional pesticide releases to POTWs in the U.S. and approaches being considered for evaluating these exposure pathways in OPP's forthcoming ecological risk assessments. We first discuss sources and pesticide uses associated with releases to POTWs. Following this, we describe approaches and data that are being used to model the fate of these releases in POTWs. Finally, we summarize available monitoring data which have been generated specifically to characterize potential pesticide exposure to and from POTWs.

Pesticide Sources to POTWs

In response to the concerns raised by the public regarding the potential release of conventional pesticides to POTWs, OPP reviewed indoor uses of conventional pesticides and identified those that present a high potential for "down the drain" (DtD) releases (Table 9). Generally, these include pesticidal treatments of fabric, clothing and carpets, pet shampoos, and drains with hydrologic connections to sewer systems. Selected uses in greenhouses have been evaluated previously in the context of pesticide releases to both POTWs (assuming connectivity with sewer systems) and surface waters (assuming direct discharge to bodies of water). These uses are therefore being considered as exposure pathways of potential concern in current and forthcoming environmental risk assessments by OPP.

A number of indoor pesticide uses are considered to have lower potential for substantive releases to POTWs based on labeled uses. These include labeled applications of indoor foggers, baits, crack and crevice treatment, and bed and mattress treatments where a hydrological connection to sewer systems is considered highly unlikely or at most, rare. Considerable discussion arose around the use of 'spot on' treatments for pets (*e.g.,* flea and tick control) as well as insecticide-impregnated collars. With spot on treatments, it is expected (and advised on some pesticide labels) that shampooing soon after application of spot on treatments would reduce the efficacy of such treatments, and those would not be cost effective and discouraged. Regarding pet collars, the potential substantive releases to POTWs are considered low based on their expected slow release rate of pesticides from the collars.

Table 9. Indoor Uses of Conventional Pesticides and Their Potential for 'Down the Drain' Release to POTWs

Uses With High Potential for Substantive Release to POTWs
• Pet lotions or shampoos (*e.g.*, treatment for fleas and ticks)
• Products for the treatment of shoes/clothing/textiles (*e.g.*, miticides, sanitizers, deodorizers)
• Pre-treated clothes/textiles, bed sheets, linens, etc.
• Drain treatments that convey water to sanitary sewer systems (root herbicides)
• Storm drain/storm system treatments connected to sewer systems (*e.g.*, root herbicides and filtration media for storm water filtration systems)
• Sewage system treatments (*e.g.*, filtration media for municipal wastewater filtration)
• Carpet treatments (except materials preservatives) removed from carpets during shampooing then subsequently disposed with wash water down-the-drain
• Lice shampoos, skin lotion treatments (*e.g.*, for mites)[1]
• Selected greenhouse uses with drains connected to sewer systems
• Pool treatment[2]
Uses With Lower Potential for Substantive Release to POTWs
• Pesticide-containing pet collars and spot-on treatments
• Bed and mattress treatments (except products to treat bed sheets)
• Storm water system treatments not connected to sewer systems
• Crack and crevice treatment
• Indoor foggers
• Indoor baits

[1] Although this is considered a pharmaceutical use, EPA in agreement with FDA is assessing exposure from down the drain releases. [2] Even though pools are typically considered outdoor use patterns, generally localities require discharging their water to sanitary sewers.

It is important to note that the pesticide uses identified in Table 9 do not represent *all* potential sources of pesticide input to POTWs. Rather, they represent those uses that are currently being assessed as part of DtD modeling in OPP environmental risk assessments. For example, pesticides may potentially be released by industrial discharges to POTWs from pesticide manufacturers. However, such releases are subject to regulation under other environmental statutes and regulatory programs (*e.g.,* state and federal pretreatment programs under the authority of the Clean Water Act), and not under FIFRA. It is recognized that certain outdoor residential uses of pesticides may contribute to pesticide loadings to storm water systems which are connected to POTWs. Modeling of outdoor residential use of pesticides in OPP environmental assessments is presently focused on direct loadings to surface water. Information from the open literature suggests that some POTWs may experience greater flow during wet weather events even when direct connections to storm water inputs are not apparent (*19*). Presumably, such inputs represent groundwater intrusion and/or fugitive inputs from storm water runoff. For these and other sources of pesticides to POTWs unaccounted for in Table 9, OPP is relying on targeted monitoring data to ascertain inputs to and discharges from POTWs.

Modeling Approach for POTW Assessment

In order to address the issue of releases to domestic wastewater, OPP has relied on the consumer exposure model, *Exposure and Fate Assessment Screening Tool* (E-FAST, v.2.0) that was developed for assessing industrial chemicals in EPA's Office of Pollution Prevention and Toxics (*48*). The 'Down-the-Drain' module (DtD) of E-FAST v.2.0 is specifically designed to address sources of a chemical that could potentially be disposed into domestic wastewater from a DtD application. The DtD module can be used to represent residential, domestic and certain commercial facilities (*e.g.*, supermarkets, storage facilities and warehouse uses likely to end up in drains). This model provides screening-level estimates of chemical residues in surface water that may result from household uses and the disposal of consumer products into wastewater.

Conceptually, the E-FAST's DtD module assumes that in a given year the entire production volume of a chemical (*i.e.*, the amount of pesticide) is parceled out on a daily basis to the entire U.S. population and converted to a mass release per capita, and subsequently, a daily per capita release to a wastewater treatment facility (*i.e.,* g/person/day). This mass is then diluted into the average daily volume of wastewater released per person to arrive at an estimated concentration of the chemical in wastewater prior to entering a treatment facility. The underlying equations used by the DtD module are shown below. The daily per capita release is defined as follows.

$$H_R = \frac{PV}{Pop} \times \frac{1000\ g}{1\ kg} \times \frac{1\ year}{365\ days}$$

where,

i. H_R is the daily per capita release of the chemical (g/person/day);
ii. P_V is the production volume of the chemical being evaluated that is produced annually in the USA that is discharged into domestic wastewaters (kg/year); and
iii. *Pop* is the 2003 U.S. resident population (2.908×10^8 persons) (U.S. Bureau of the Census, 2004-2005).

The chemical's concentration in untreated wastewater is then reduced by the fraction removed during wastewater treatment processes. The remaining chemical is discharged into surface water (*e.g.,* a river or stream), where it is assumed that it is instantaneously diluted, with no further removal. The surface water concentration is calculated using the following general equation.

$$SWC = \frac{H_R \times \frac{1}{Q_H} \times \left(1 - \frac{WWT}{100}\right) \times \frac{10^6\ \mu g}{g}}{SDF}$$

where,

i. *SWC* is the surface water concentration (µg/L);
ii. Q_H is the household wastewater volume released daily (it is estimated to be 388 L per person per day), it includes only domestic and residential POTWs;
iii. *WWT* is the wastewater treatment removal (percent removed prior to discharging into a body of water, %); and
iv. *SDF* is the stream dilution factor.

The Stream Dilution Factor (SDF) is the volume of the receiving stream flow divided by the volume of the wastewater released from the POTW or effluent flow (SDF = SF/EF). There are four types of stream flows that the developers of the model have deemed adequate for the protection of aquatic life and human health (acute and chronic). Additionally, flows have been characterized to represent mid-sized receiving bodies of water and smaller streams. It should be noted that the DtD module of E-FAST is a screening-level model and the results should be treated as such. It does not take into account processes such as degradation prior to treatment at the facility, or partitioning (*i.e.,* sorption by sediment or particulate matter).

Model Inputs

There are two main input values in the E-FAST's DtD module: the production volume (PV), and the percent removal from wastewater treatment (WWT). (The BCF is an input parameter, which the model uses for calculations that are not relevant to EFED's purpose to calculate aquatic EECs.) The PV can be obtained from the registrant(s) sources or can be supplied by the Biological and Economic Analysis Division (BEAD). Model results are sensitive to the WWT, which in turn is dependent on the physicochemical properties of the active ingredient of concern and the extent of wastewater treatment (*e.g.,* primary, secondary, tertiary, or ultrafiltration). An estimate of WWT is available from the Sewage Treatment Plant Fugacity Model (STPWIN™) of EPI Suite v.4.11 (*49*). This model provides estimates of the fate of organic chemicals in conventional wastewater treatment plant that uses activated sludge secondary treatment. According to the STPWIN™ Help manual, EPI Suite's STP program was conservative predicting removal percent (WWT) 88% of the time using its default half-lives of 10,000 hours for 29 of 33 chemicals evaluated, for primary clarifier, aeration vessel and settling tank; however, the evaluation was based on a set chemicals which are not pesticides. A more suitable and reliable alternative, is data derived from a bench scale study (described further below) that may be required either during the registration process of the chemical or during registration review, to further refine this input parameter. Finally, for a few chemicals, WWT can be obtained from actual monitoring studies of influent and effluent from POTWs. This has been used in the past to refine estimates of permethrin.

Table 10 provides a summary of removals by various mechanisms for eight pyrethroid insecticides predicted by STPWIN™. As shown in the table, the module predicts that for these chemicals, the main removal mechanism is sludge adsorption. The total biodegradation is low while the release to air is minimal.

Model Outputs

In the past, EFED has conducted preliminary DtD screens of a pesticide to determine the need for a bench scale POTW treatability study. In some cases the modeling results indicated that the study is not needed (*e.g.*, pyrethrins, spinosad). The modeling is possible if the production volume or its estimate, is available to the assessor. The assessor models the chemical with the aid of the EPI Suite v.4.11 model and gets an estimate of the level of removal (*i.e.*, WWT) from the module 'Sewage Treatment Plant Fugacity Model (STP)' using the default half-lives of 10,000 hours (~417 d) in the primary tank, the aeration tank, and the settling tank. This may be considered a conservative value (alternatively EPI Suite provides the second option to enter half-lives derived from monitoring experiments, or the third option to use model-estimated half-lives for the above mentioned processes). Suitable flows and the 10th percentile concentrations are used to derive RQs. The RQs derived from this process are compared against the LOCs. If they are well below the LOCs, it may be determined whether a treatability study is required using best professional judgment and considering the conservativeness of the preliminary risk assessment.

The most recent assessment for which the E-FAST's DtD module was used was an ecological risk assessment for deltamethrin. Uses assessed included sewage systems treatments (*50*). It was assumed that the upper bound value of the production volume is 50 kg a.i./year. After running the chemical using the DtD module, the acute concentration was found to be 0.000425 ppb and the chronic concentration was 0.000425 ppb (the same value). For freshwater and estuarine/marine fish and vascular and non-vascular plants there were no exceedances of LOCs. A summary of the findings on invertebrates is shown in Table 11.

Table 10. Removal Percent of Eight Pyrethroids in Wastewater Treatment Plants Obtained from EPISUITE v.4.11 and Its STPWIN Module[1]

Process	*Bifent.*	*Fenprop.*	*Cyhalot.*	*Permet.*	*Cyflut.*	*Cypermet*	*Esfenval.*	*Deltamet.*
Sludge Adsorption	93.2	91.4	93.1	92.7	91.2	93.0	92.1	92.1
Total Biodegradation	0.78	0.77	0.78	0.78	0.77	0.78	0.77	0.77
Total to Air	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Total Removal	94.0	92.2	93.8	93.4	91.9	93.8	92.9	92.8

[1] All results were rounded to two decimal places or three significant figures.

Table 11. Summary of Acute and Chronic RQs for Aquatic Freshwater and Estuarine/Marine Invertebrates Exposed to Deltamethrin

Use	*App Rate*	*Peak EEC (µg/L)*	*21-day EEC (µg/L)*	*Acute RQ*	*Chronic RQ*
Freshwater Invertebrates[2]	50 kg/yr	0.000425	0.000425	0.11[1]	>16.3[1]
Estuarine/Marine Invertebrates[3]	50 kg/yr	0.000425	0.000425	0.11[1]	0.58

[1] RQs that exceed the EPA's levels of concern. [2] Acute RQ = use-specific peak EEC/0.004 ppb [for the amphipod *G. fossarum*]. Chronic RQ = use-specific 21-day EEC/10-d NOAEC of <2.6×10^{-5} ug a.i./L [for the amphipod, *H. azteca*]. Chronic RQ values are expressed as ">" values because the NOAEC is non-definitive ("<") [3] Acute RQ = use-specific peak EEC/0.0037 ppb [for mysid shrimp, *Americamysis bahia*]. Chronic RQ = use-specific 21-day EEC/0.00073 ppb [from data for *A. bahia*].

Refinement of E-FAST (Bench Scale Study)

Based on experience with DtD modeling with pyrethroids, OPP requested additional data from registrants to improve modeling of the fate and removal efficiency of pyrethroids in POTWs. In response, registrants conducted a bench scale study simulating four processes that occur in POTWs: primary settling, aerobic biological treatment, anaerobic digestion, and ultra-filtration (Cleary and McGrath, MRID 48762906 (*51*)). Pyrethroids studied in these processes included: permethrin, deltamethrin, bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin, esfenvalerate, and fenpropathrin. Although in treatment plants, they occur simultaneously, these processes were evaluated separately from each other (*i.e.*, they were treated as modules). First, primary settling, anaerobic digestion, and ultrafiltration were measured in batch mode (*i.e.*, a set amount of sample was submitted to the process and evaluated after a period of time, *e.g.*, two hours for primary settling, up to 35 days for anaerobic digestion). Meanwhile, the aerobic biological treatment was evaluated in a continuous process (*i.e.*, process was continuously circulated and sample was evaluated throughout the procedure for 50 days, with a target solids retention time (SRT) of 10 days). Table 12 provides a results synopsis of the study. Note that the estimated removals are for specific modules and not overall removals. The percentages are not additive.

Wastewater from a treatment plant in Ridgewood, New Jersey, was spiked with known levels of the eight pyrethroids, well above background levels (5 µg/L of each pyrethroid, with the exception of permethrin at 50 µg/L), in order to characterize each process. This study was not conducted in compliance with Good Laboratory Practice Standards set forth in Title 40, Part 160 of the Code of Federal Regulations.

Table 12. Results Synopsis: Removal Percent of Eight Pyrethroids in Certain Treatment Processes Simulated in a Bench Scale Wastewater Treatability Study[1]

Process	*Bifent.*	*Fenprop.*	*l-Cyhal.*	*Permet.*	*Cyflut.*	*Cyperme.*	*Esfenval.*	*Deltamet.*
Primary Settling	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]	LR[2]
Aerobic Chamber	51.9	80.1	48.6	86.6	73.2	76.3	56.1	59.1
Anaerobic Digestion	32.1	45.5	57.0	43.5	81.2	78.1	79.2	77.1
Ultrafiltration	91.7	95.7	93.1	96.9	95.7	95.4	93.6	92.6

[1] The percent shown is for each of the individual modules (refer to text). [2] LR means limited removal was achieved in this process.

Primary Settling

The primary settling experiment was conducted in batch mode. In primary settling, incoming wastewater (primary influent), was kept in a quiescent state for a specific period of time (in this study it was 2 hours), to allow heavy particles to settle. The result of the process was primary effluent (the supernatant) and primary sludge. Pyrethroids were measured in the primary influent wastewater and in the primary effluent and sludge. The primary effluent had concentrations of pyrethroids that were very similar to the concentrations in the primary influent. Primary settling did not appear to be effective to remove substantial amounts of pyrethroids from the primary influent.

Aerobic Biological Treatment

The primary effluent was added to the aerobic biological treatment system to reduce its organic content. The aerobic system was kept at *ca.* 20°C and it consisted of two submodules: the aeration system in which dissolved oxygen promotes aerobic biological degradation, and secondary settling. This part of the experiment was run for 50 days, where secondary sludge and primary effluent were fed to the aerobic chamber, in a continuous flow system. The target SRT was 10 days, which was reported to represent a likely best case scenario. Pyrethroids were removed moderately from the secondary influent (or primary effluent from the primary settling module), in the aerobic chamber. Removals ranged from 52 to 87 percent, for bifenthrin and permethrin, respectively.

Anaerobic Digestion

A specific amount of primary sludge (*i.e.*, sludge from primary settling) was submitted to digestion and run in batch mode for 35 days at *ca.* 35°C under anaerobic conditions. Pyrethroids were also removed moderately from primary sludge under these testing conditions in the anaerobic chamber. Among eight pyrethroids tested, removals ranged from 32 to 81 percent, for bifenthrin and cyfluthrin, respectively, attributed to anaerobic biological digestion.

Ultrafiltration

In ultrafiltration, the supernatants from the secondary settling were filtered and remaining solids were removed, reducing further the suspended particles, and thus the organic matter associated with those particles, and its associated pyrethroids. This process was run in batch mode, using an apparatus and method similar to the one used to measure total suspended solids. Removal represents the amount remaining in the effluent minus the amount applied of each pyrethroid in the influent. Ultrafiltration appeared to be the process that removed the highest percentage of pyrethroids from the secondary effluent, with over 90 percent of pyrethroid removed from the final effluent. It is noted, however, that ultrafiltration is not a process employed by all WWTPs nationwide. Results presented in Table 12 are the means of two values, using a 0.1 μm filter.

Utility of the Bench Scale Study

The bench scale treatability study is useful in understanding the relative contributions of the different processes that occur at a treatment facility. Removal processes include primary settling, which shows very limited removal, and aerobic and anaerobic digestion, which show moderate levels of removal. Only ultrafiltration appeared to remove over 90% of the material in the bench scale study. Results from modeling (using EPISUITE giving total removal) and monitoring data (as discussed below) indicate levels of removal of above 90%. However, direct comparison of the bench scale study results to modeling and monitoring data is confounded by the fact that the bench scale study design does not enable determination of an overall removal efficiency based on the sum of the simulated treatment processes. Therefore, the utility of the bench scale study mostly relates to how separate processes affect pyrethroid removal and not for an estimate of the overall removal efficiency of pyrethroids from POTWs.

POTW Monitoring Data

The available information on the occurrence of pesticides in U.S. POTW influent, effluent and biosolids was reviewed and is summarized here with a focus on the following questions:

1. Which pesticides are most commonly detected in POTWs and how does this relate to their intended uses?
2. What is the removal efficiency of pesticides by wastewater treatment processes and how does this compare to estimates based on modeling and bench scale treatability studies?

Although a number of country-wide surveys of pesticides and other micropollutants in POTW wastewater have been conducted in Europe (*e.g.,* Loos *et al.* (*52*); Luo *et al.* (*53*)), an analogous U.S. wide survey was not identified in this review. Instead, several state-wide and POTW-specific surveys were identified and are summarized below.

Pesticides in POTW Influent and Effluent

Oregon POTWs

In one of the most comprehensive surveys of chemical contaminants in POTW effluent in the U.S., Hope *et al.* (*54*) analyzed effluents from 52 POTWs throughout Oregon once during the summer and during the fall of

2010. Of the 406 chemicals included in the survey, 149 were categorized as pesticides or pesticide-related chemicals (pesticide precursors, degradation products). The most frequently detected pesticide-related compounds include: 2,6-dichlorophenol (93%), arsenic (86%), DEET (78%), 2,4,6-trichlorophenol (72%), 2,4-dichlorophenol (62%), diuron (46%) 2,4,5-trichlorophenol (16%) and 2,3,4,5-tetrachlorophenol (13%) (Table 13). However, the presence of many of these compounds cannot be unambiguously traced to pesticide use. Specifically, the chlorinated phenols may be used as chemical intermediaries, are no longer registered as pesticides, and/or may be produced as a byproduct of effluent chlorination. Arsenic has some remaining commercial and industrial uses (*e.g.,* as a component of the chromated copper arsenate wood preservative) but also occurs naturally in the environment and may be released to POTWs via other commercial or industrial processes.

On the contrary, the presence of the insect repellant DEET most likely results from its widespread application to skin and subsequent washoff into household drains. DEET, the third most frequently detected pesticide, has the second greatest median concentration (232 ng/L and the greatest maximum concentration detected (13,600 ng/L). Diuron, the 6th most frequently detected pesticide, is a pre- and post-emergent herbicide with numerous agricultural and residential use sites, including application to water bodies for aquatic weed control. Particularly relevant to its occurrence in POTW effluent is its use as a mildewcide in certain paints and stains. This use could conceivably lead to down-the-drain releases to POTWs through washing of brushes and other painting equipment. Diuron and DEET were also among the most commonly detected pesticides in POTW effluent across Europe (*52*).

Triclopyr (detected in 11% of the samples), is used for broadleaf control in a variety of agricultural and residential settings. With no registered indoor uses in the U.S., direct release of triclopyr to POTWs via household drains is not expected. However, its use for weed control in residential settings could result in releases into stormwater runoff and subsequently to POTWs with hydrologically-connected stormwater conveyances. Interestingly, the herbicide 2,4-DB has no registered indoor or residential uses. Potential reasons for occurrence in 10% of the Oregon POTW effluent samples are not clear. Imidacloprid (10%) and imazapyr (9%), both have widespread residential uses for insect and weed control, respectively. Imidacloprid is also commonly used for flea control on pets via pet collars and spot-on treatments. It seems possible that its presence in POTWs could relate to pet washing or inappropriate disposal down the drain.

Hope *et al.* (*54*) report that detection of the fungicide propiconazole, used to prevent mold on wood, may have been related to discharge from a wood processing facility that discharged to a POTW. Propiconazole is also an ingredient in paints and stains which may also lead to releases to POTWs, possibly through washing of painting equipment and/or runoff into storm water connected to POTWs. The authors also note that fluridone, imazapyr and terbutylazine are applied directly to surface water for algae and macrophyte control and speculate that surface water intrusion into POTW conveyance systems may be occurring.

Table 13. Pesticides and Related Compounds Detected in a Survey of 52 Oregon POTWs. Source: Hope *et al.* (*54*)

Chemical	*CAS*	*LOQ (ng/L)*	*% Detect. (n=102)*	*Min. (ng/L)*	*Median (ng/L)*	*Max. (ng/L)*	*Category*
2,6-Dichlorophenol	87-65-0	7.7	93	10.3	82.4	864	other [1]
Arsenic (TR)	7440-38-2	250	86	260	620	4320	other [2]
DEET (*N,N*-diethyl-*m*-toluamide)	134-62-3	5	78	53	232	13600	other (insect repellant)
2,4,6-Trichlorophenol	88-06-2	19	72	25	55.6	339	wood preservative [3]
2,4-Dichlorophenol	120-83-2	19	62	19.8	68.5	470	other [1]
Diuron	330-54-1	4	46	38	89	775	herbicide
2,4,5-Trichlorophenol	95-95-4	19	16	21.4	42.4	300	other [3]
2,3,4,5-Tetrachlorophenol	4901-51-3	19	13	43.6	48.3	200	other [1]
Triclopyr	55335-06-3	300	11	310	620	3900	herbicide
2,4-DB	94-82-6	610	10	660	127	7440	herbicide
Imidacloprid	138261-41-3	20	10	202	237	387	insecticide
Imazapyr	81334-34-1	40	9	534	1670	17200	herbicide
Azobenzene	103-33-3	19	7	55	108	178	other [3]
Carbaryl	63-25-2	5	7	66	137	663	insecticide
2,4-D	94-75-7	100	3	1600	1630	1890	herbicide
Chlorpropham (CIPC)	101-21-3	7.7	3	17	46.1	72.4	herbicide

Continued on next page.

Table 13. (Continued). Pesticides and Related Compounds Detected in a Survey of 52 Oregon POTWs

Chemical	*CAS*	*LOQ (ng/L)*	*% Detect. (n=102)*	*Min. (ng/L)*	*Median (ng/L)*	*Max. (ng/L)*	*Category*
Dicamba	1918-00-9	300	3	380	700	760	herbicide
Prometon	1610-18-0	4	3	55	63	64	herbicide
Propiconazole	60207-90-1	20	3	387	7210	9020	fungicide
Pentachlorophenol	87-86-5	100	2	220	260	300	fungicide
Baygon	127779-20-8	4	1	42	42	42	insecticide
Dichloroprop (2,4-DP)	120-36-5	300	1	370	370	370	herbicide
Fluridone	59756-60-4	7.7	1	27	27	27	herbicide
Pentachlorobenzene	1825-21-4	380	1	416	416	416	other (PCP degradate)
Pentachlorophenol	87-86-5	380	1	700	700	700	fungicide
Simazine	122-34-9	4	1	56	56	56	herbicide
Terbutylazine	5915-49-3	4	1	61	61	61	herbicide

[1] Pesticide precursor or other chemical intermediary. [2] Organo arsenate and residential CCA uses no longer registered in the U.S. [3] Pesticide is no longer registered in the U.S.

California POTWs

In another comprehensive state-wide survey, Markle *et al.* (*55*) sampled 31 POTWs in California for the presence of eight pyrethroids in influent, effluent, and/or biosolids. This effort was conducted by the Pyrethroid Working Group (PWG), a consortium of registrants representing eight pyrethroids, in response to pyrethroid re-evaluation activities by both the California Department of Pesticide Regulation and the USEPA. The POTWs the surveyed represent approximately 40% of the treated municipal wastewater in California and include primary, secondary and tertiary treatment as terminal wastewater treatment processes. Samples were taken from January through March, 2013 during dry weather period. Consecutive grab samples were taken from influent, effluent and biosolids (when available) and did not account for hydrologic retention time between entry to the POTW and discharge. Extensive quality control measures were instituted including separate analytical measurement by two laboratories.

Results indicate high detection frequencies (*e.g.*, 43% to 100%) for 7 of the 8 pyrethroids sampled in POTW influent (Table 14). Frequencies of detection exceeded 80% for bifenthrin, cyfluthrin, *lambda*-cyhalothrin, cypermethrin and permethrin. Fenpropathrin was the least detected pyrethroid in effluent at 4.5% and is the only pyrethroid sampled that is not registered for residential uses in California. This suggests residential uses of these products are contributing to their loadings to California POTWs. By far the highest maximum and median influent concentrations reported are for permethrin (3,800 and 230 ng/L, respectively), which may be related to its topical use to treat lice infestations.

In POTW effluent, the greatest detection frequencies are observed for bifenthrin (82%), followed by cypermethrin (81%), permethrin (65%), cyfluthrin (60%), *lambda*-cyhalothrin (48%) and esfenvalerate (32%; Table 15). Comparatively, the rates of detection for deltamethrin and fenpropathrin are much lower (16% and 3% respectively) in effluent than influent. Consistent with the influent sampling results, the greatest maximum and median concentrations in POTW effluent are observed for permethrin (170 and 9.4 ng/L, respectively). Cypermethrin showed the next highest effluent concentrations with maximum and median values of 13 and 1.3 ng/L, respectively. Maximum and median concentrations for the other six pyrethroid are 2 orders of magnitude below that for permethrin.

It is instructive to compare the results of POTW monitoring to that predicted by down-the-drain modeling (DtD) using E-FAST described earlier, as a way of evaluating model predictions. Previous DtD assessments were conducted with permethrin and deltamethrin (USEPA (*45*) and USEPA (*50*), respectively) and are shown in Table 16 along with the monitored concentrations in effluent summarized in Table 15. With permethrin, the predicted concentrations in POTW effluent is 0.09 ppb, which is an order of magnitude above the median concentration measured in California POTWs by Markle *et al.* (*55*) However, it is about 2X below the maximum concentration detected in California POTW effluent (0.17 ppb). With deltamethrin, the predicted concentration (0.0004 ppb) is comparable to the median and maximum measured concentrations (0.0003 and 0.001 ppb, respectively).

Table 14. Summary of Pyrethroid Measurements in Influent from 31 California POTWs. (Source: Markle *et al.* (55))

Chemical	*# of Detects*	*% Detected*	*LOQ (ng/L)*	*Max. (ng/L)*	*Min. (ng/L)*	*Average[1] (ng/L)*	*Median[1] (ng/L)*
Bifenthrin	64	96%	5	74	ND	15	9.7
Cyfluthrin	59	88%	5	55	ND	11	7.4
Lambda-Cyhalothrin	54	81%	5	72	ND	5.6	2.8
Cypermethrin	54	81%	5	200	ND	35	21
Deltamethrin	29	43%	10	210	ND	8	3.3
Esfenvalerate	31	46%	5	360	ND	8.1	1.7
Fenpropathrin	3	4.5%	5	130	ND	4.6	1.7
Permethrin	67	100%	50	3800	30	330	230

ND = Not detected. A total of 67 influent samples were collected (62 samples + 5 repeats). [1] Median and average values were calculated assuming the limit of quantitation for non-detects.

Table 15. Summary of Pyrethroid Measurements in Effluent from 31 California POTWs. (Source: Markle *et al.* (*55*))

Chemical	*# of Detects*	*% Detected*	*LOQ (ng/L)*	*Max. (ng/L)*	*Min. (ng/L)*	*Average[1] (ng/L)*	*Median[1] (ng/L)*
Bifenthrin	51	82%	0.5	3.9	ND	0.89	0.6
Cyfluthrin	37	60%	0.5	4	ND	0.6	0.3
Lambda-Cyhalothrin	30	48%	0.5	1.6	ND	0.3	0.2
Cypermethrin	50	81%	0.5	13	ND	2.11	1.3
Deltamethrin	10	16%	1.0	1.2	ND	0.31	0.3
Esfenvalerate	20	32%	0.5	0.6	ND	0.25	0.2
Fenpropathrin	2	3.2%	0.5	0.8	ND	0.22	0.2
Permethrin	40	65%	5.0	170	ND	20	9.4

ND = Not detected. A total of 67 effluent samples were collected. [1] Median and average values were calculated assuming the limit of quantitation for non-detects.

Table 16. Estimated Environmental Exposure Concentrations of Permethrin and Deltamethrin, from POTW Discharges

Chemical	*Production Volume (kg)*	*WWT (%)*[1]	*Predicted Conc. (ppb)*	*Measured Conc. (ppb) (min, med, max)*
Permethrin	60,900	93.4	0.09	ND, 0.009, 0.17
Deltamethrin	50	65	0.0004	ND, 0.0003, 0.001

[1] WWT = percent removal from wastewater treatment.

It is also of interest to evaluate the removal of pyrethroids by POTW treatment, since this information can help inform modeling approaches for estimating pyrethroid loadings from POTWs. Influent and effluent data from Markle *et al.* (*55*) were used to calculate percent removal of pyrethroids using the following equation:

$$\%\ \text{Removal} = \left(1 - \frac{\text{Effluent Concentration}}{\text{Influent Concentration}}\right) \times (100\%)$$

When the effluent concentration was reported below limits of quantitation (LOQ), the concentration was equated to the LOQ. When the influent was reported to be below the LOQ, no calculation was made. On average, pyrethroid concentrations measured in POTW effluent are approximately 10% those measured in influent, representing a reduction of approximately 90% (Figure 15). The higher mean % removal indicated for esfenvalerate (97%) and fenpropathrin (99%) are based on very few samples and are therefore considered highly uncertain.

In terms of POTW-specific factors affecting pyrethroid concentrations, there was typically a large reduction in pyrethroid concentrations in effluent from primary to secondary treatment, although only one plant sampled had primary treatment as its terminal treatment process. The relationship between secondary and tertiary treatment was less clear, whereby some POTWs containing secondary treatment had higher concentrations in effluent compared to those with tertiary treatment and vice versa.

It is noted that the study by Markle *et al.* (*55*) was not specifically designed to estimate % removal efficiency of pyrethroids because samples were taken concurrently from influent and effluent without regard to the retention time of treated water in the POTW. Therefore, differences between concentrations of pyrethroid in influent and effluent may reflect, not only partitioning and degradation processes associated with wastewater treatment, but also variation in pesticide loadings over time. Nonetheless, average % removal efficiencies based on the monitoring data (90-99%) are quite similar to those calculated using the STPWIN™ model summarized in Table 10 (91-93%).

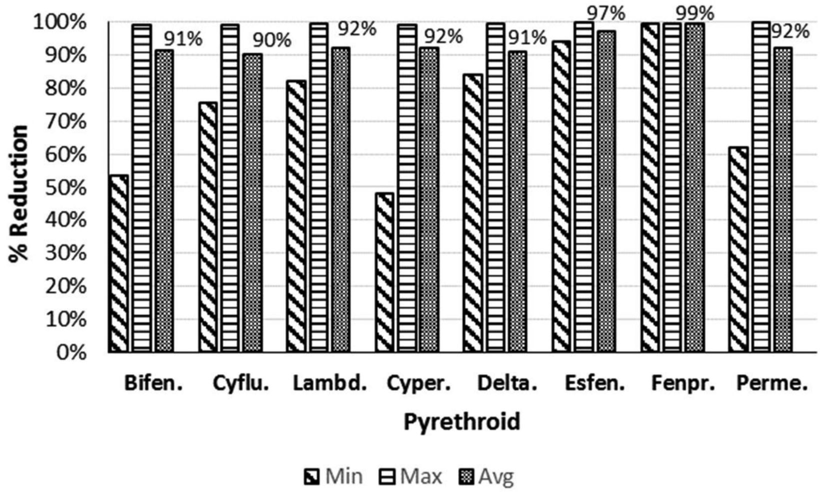

Figure 15. Percent reduction in pyrethroid concentrations in POTW effluent relative to influent. (Source: Markle et al. (55))

Sacramento POTW

In contrast to the previous two studies which conducted limited sampling of POTW wastewater across many facilities, Weston *et al.* (*56*) focused their efforts on a single facility, the Sacramento Regional County Sanitation District Treatment Plant. Concentrations of eight pyrethroids in influent and effluent were sampled over multiple time periods from November 2010 to January 2012. Twelve, 24-h composite samples were taken monthly from influent and seven 24-h, flow-weighted composite samples were taken from effluent (4 during rain events and 3 during dry events). Importantly, the timing of effluent samples was adjusted to account for the retention time of the wastewater in the plant. This facilitates more accurate estimation of % removal efficiency compared to the previous study by Markle *et al.* (*55*) Weston *et al.* (*56*) also sampled three POTW wastewater interceptors during the course of this study, one of which (City interceptor) received both municipal sewage and storm water runoff while the other two (Folsom and Laguna interceptors) received only municipal sewage.

Results from this study indicate that four pyrethroids were detected in all (100%) of the 12 monthly POTW influent samples (permethrin, bifenthrin cypermethrin, and *lambda*-cyhalothrin). Among these, permethrin was the dominant pyrethroid detected in terms of overall concentration and typically ranged between 200 and 400 ng/L. Cypermethrin and bifenthrin were generally found between 20 and 40 ng/L in influent while cyhalothrins were found up to 30 ng/L. Cyfluthrin was detected once in influent during the study, while deltamethrin, fenpropathrin and esfenvalerate were not detected in any of the 12 influent samples. Attempts to correlate temporal peaks in influent concentrations with known use pattern or sales data were not successful. Analysis of pyrethroids in the wastewater interceptor upstream of the treatment plant suggest that storm water runoff was not the dominant source of pyrethroids to the plant. Concentrations of permethrin in the City interceptor (receiving stormwater) were slightly lower than those which did not receive stormwater. Furthermore, all the interceptors sampled contained substantially lower concentrations of permethrin than what was found in the POTW influent, suggesting that other sources of permethrin to the plant are likely. The other pyrethroids were found in similar concentrations in the three interceptors compared to POTW influent. The authors speculate that indoor uses of pyrethroids, container washing and possibly improper disposal of unwanted pesticide may be leading to the loadings to the Sacramento POTW.

In terms of effluent quality, permethrin was again the dominant pyrethroid detected in all but one of the seven effluent samples, ranging from 12-45 ng/L. Bifenthrin and cyhalothrins ranged from 1-5 ng/L in effluent and were detected 43% and 29% of the time, respectively. Concentrations of permethrin, bifenthrin and cyhalothrin were up to 2 times the respective 96-h EC_{50} values reported for the freshwater amphipod, *Hyalella azteca*. However, attempts to correlate observed toxicity to *H. azteca* in effluent samples with toxic units or TIE procedure were not definitive in terms of the cause of toxicity. Removal efficiencies of the pyrethroids from the POTW influent generally ranged from 90-95%, which is similar to the findings reported by Markle *et al.* (*55*) in their California-wide POTW survey.

Weston and Lydy (19)

In this study, Weston and Lydy sampled three California POTWs (Sacramento, Stockton, and Vacaville) for the presence of 8 pyrethroids and chlorpyrifos during three dry and three wet seasons in 2008 and 2009. The authors indicate that except for a small portion of the Sacramento POTW influent, all plants contained sanitary sewer systems that were separate from stormwater systems. They further note that the Stockton POTW included tertiary treatment via routing secondary treated wastewater through 240 ha of treatment ponds which yielded a retention time of about 30 days. Results above 1 ng/L are considered by the authors to be reliable. A total of 18 POTW samples were taken. Other samples of agricultural drains and urban runoff were also analyzed but are not discussed here.

Weston and Lydy (*19*) report that of all the samples, quantifiable concentrations of one or more pyrethroids were found in 67% of the samples taken. Across all three facilities, chlorpyrifos (40%), bifenthrin (39%) and permethrin (33%) were most commonly detected (Table 17). Generally, the highest concentrations of pyrethroids and chlorpyrifos are seen with the Sacramento POTW. In terms of toxicological relevance, 22% of the effluent samples containing bifenthrin, 17% containing *lambda*-cyhalothrin, and 6% of the samples containing cypermethrin exceeded the respective EC_{50} or LC_{50} values for *H. azteca*. The authors note that the presence of pyrethroids is surprising especially given the low levels of suspended solids in the effluent (< 8 mg/L). They suggest that sewer disposal of household pesticides, use of pet and lice control shampoos and laundering of permethrin-treated clothing may be potential sources of pyrethroids to the POTWs. Despite 25-50% greater flows in wet weather, Weston and Lydy (*19*) report similar concentrations in effluent during dry and wet weather flows, which indicates that pesticide loadings from urban/residential runoff may be contributing to loadings to POTWs.

Pesticides in POTW Biosolids

Section 405(d) of the Clean Water Act (CWA) requires the U.S. Environmental Protection Agency (EPA) to identify and regulate toxic pollutants that may be present in biosolids (sewage sludge) at levels of concern for public health and the environment. Historically, the focus of identification and regulatory efforts has been on industrial chemicals, pharmaceuticals, metals, and selected antimicrobial chemicals. (*57*). However, recent studies have raised attention on the occurrence of conventional pesticides in biosolids, which often are treated and applied to land. Potential consequences of land-applied biosolids that contain appreciable amounts of pesticides include alteration of soil and terrestrial biota, runoff to surface waters and contamination of ground water.

In addition to quantifying pyrethroid concentrations in POTW influent and effluent, the previously summarized study conducted Markle *et al.* (*55*) also measured pyrethroids in biosolids from 24 of the POTWs included in the survey (Table 18). In terms of overall detection frequency, results mirror those described previously for influent and effluent, with the highest detection frequencies reported for bifenthrin (96%), permethrin (92%), cypermethrin (90%), and cyfluthrin (87%). The maximum concentration of permethrin (11,000 ng/g d.w.) is 10X that of the pyrethroids with the next highest maxima concentrations (bifenthrin, cypermethrin). Median concentrations are greatest for permethrin (1,200 ng/g d.w.), bifenthrin (120 ng/g d.w.) and cypermethrin (79 ng/g d.w.). Permethrin was also reported in sewage sludge from the U.K. (*58*) and Switzerland (*59*).

As a consequence of these and other reports of conventional pesticides in POTW biosolids, OPP has undertaken efforts along with counterparts in the Office of Water to develop approaches to screen uses of conventional pesticides for their potential to end up and persist in biosolids. The initial efforts focused on identifying pesticide uses with the greatest potential for releases down the drain (Table 9). Subsequently, efforts have focused on developing screening level models for evaluating the potential risks associated with pesticides in land-applied biosolids. One approach being evaluated is adapting the current Office of Water Biosolids Core Risk Assessment Model (BCRAM) for a screening level assessment. Other approaches being investigated include adapting existing OPP models (*e.g.*, PRZM) and exposure scenarios for evaluation of land applied biosolids.

Table 17. Pyrethroids and Chlorpyrifos in Effluent from Three California POTWs. (Source: Weston and Lydy (*19*))

POTW[1]	*Bifen.*	*Cyfl.*	*Cyp.*	*Delt.*	*Esfen.*	*Fenp.*	*L. Cyh*	*Perm.*	*Chlor.*
Maximum Concentration Detected (ng/L)									
Sacr.	2.7	1.7	17.0	0	3.7	0	5.5	17.2	24.1
Stock.	4.8	0	0	1.3	0	0	0	7.9	5.5
Vaca.	6.3	0	0	2.7	0	0	2.8	7.6	0
Overall Detection Frequency (n=18) [2]									
	39%	6%	6%	11%	6%	0%	17%	33%	40%
Frequency exceeding EC_{50} or LC_{50} [3]									
	22%	0	6%	NA	NA	NA	17%	0	0

[1] Sacr. = Sacramento; Stock. = Stockton; Vaca. = Vacaville. [2] Detection frequency = # samples > 1 ng/L/total samples from all 3 plants (n=18). [3] Frequency of exceeding EC_{50} or LC_{50} for *H. azteca* (Bif =3.3 ng/L; Cyf = 1.9 ng/L; Cyp = 1.7 ng/L; L. Cyh = 2.3 ng/L; Per =21.1 ng/L and chlor = 96 ng/L).

Table 18. Summary of Pyrethroid Measurements in Biosolids from 24 California POTWs. (Source: Markle *et al.* (55))

Chemical	*# of Detects*	*% Detected*	*LOQ (ng/g)*	*Max. (ng/g)*	*Min. (ng/g)*	*Average[1] (ng/g)*	*Median[1] (ng/g)*
Bifenthrin	50	96%	2.5	1100	ND	150	120
Cyfluthrin	45	87%	2.5	190	ND	34	29
Lambda-Cyhalothrin	27	52%	2.5	200	ND	29	28
Cypermethrin	47	90%	2.5	1000	ND	110	79
Deltamethrin	16	31%	5.0	78	ND	28	24
Esfenvalerate	16	31%	2.5	42	ND	15	14
Fenpropathrin	3	5.8%	2.5	71	ND	12	6.8
Permethrin	48	92%	25	11000	30	1500	1200

ND = Not detected. A total of 52 influent samples were collected. [1] Median and average values were calculated assuming the limit of quantitation for non-detects.

Conclusions

As part of the Registration Review Program in USEPA, the first pyrethroid ecological risk assessments are less than two years away. Their widespread and diverse urban use patterns present many challenges in conducting a national scale ecological risk assessment. The problem formulations and public comment process has been extremely valuable in focusing on issues that need to be addressed. The Pyrethroid Working Group (PWG) has conducted a number of studies in response to the Data-Call-In (DCI) from USEPA and California Department of Pesticide Regulation (CADPR). Analysis of data from some of these studies is presented in this chapter while other studies are currently being reviewed. These data along with a wealth of information from public literature would be used in conducting ecological risk assessments for urban use pesticides.

To assess the exposure estimates from outdoor urban uses, EFED is currently using the residential and impervious scenarios in PRZM/EXAMS which only provide screening level information. To further refine these urban scenarios, results obtained from studies submitted for pathway identification, impervious surfaces washoff/runoff, turfgrass runoff and others could be used. Additionally, quality monitoring data may be used in verifying modeled EECs. Other factors that should be considered in improving these urban scenarios include characteristics of the pesticide to be modeled such as expected solubility in natural/urban drainage waters and washability from varied types of impervious surfaces. Any other significant pesticide load from sources such as ground water, drift and airborne dust contaminated with pesticides should also be considered.

The available evidence indicates that uses of conventional pesticides are resulting in relevant loadings to and from POTWs in the U.S. Information on use patterns can be used to identify those uses which are more likely to result in releases down the drain. However, POTW monitoring studies have also identified the presence of some pesticides for which the occurrence in POTW effluents is not easily explained by their labeled use patterns. Less obvious practices such as container washing, pet washing and possibly improper disposal of unwanted pesticide may be leading to pesticide loadings to POTWs. Efforts to date to model pesticide loadings to POTWs have relied on coarse, screening level models (*e.g.,* E-FAST). Information to refine critical model input parameters (*e.g.,* % removal efficiency) has been collected for some pesticides and suggest reasonable agreement between predicted and measured model parameters. The need for more comprehensive surveys of pesticides in U.S. POTW effluent is clear, as no national level survey information was identified to date. Information from such surveys in Europe (*e.g.*, Loos *et al.* (*52*)) and pesticide use pattern can provide useful information for identifying candidate pesticides for additional monitoring.

DISCLAIMER: The content of this chapter does not necessarily represent the official views of the U.S. EPA.

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Chapter 11

Application of a Regional Screening Index for Chemical Leaching to Groundwater Vulnerability Analysis in the National Level

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This chapter describes a regional screening index for use in Hawaii which has been recently updated to assess groundwater vulnerability to contamination by volatile organic compounds and pesticides. Specifically, this chapter will discuss two issues: 1) how we assess the accuracy of a new screening index compared to an analytical solution for the movement of contaminants and 2) how we extend the regional index scheme into a national-scale vulnerability assessment. We found that the screening index was able to be used as an initial diagnostic tool for groundwater vulnerability assessment as it consistently provided a conservative estimate of the vulnerability to protect public health. The results of the national-scale assessment also showed that the groundwater vulnerability to agricultural chemicals varied widely among the conterminous 48 states, which demonstrated the feasibility of the regional screening index to a large-scale vulnerability assessment. We present two examples to illustrate the regional and national levels of groundwater vulnerability assessment.

Introduction

Agricultural chemicals such as pesticides and volatile organic compounds (VOC) are the major contaminants that impact national water quality in the United States (US) (*1*, *2*). Pesticides applied to or present near the soil surface undergo two primary processes: moving with runoff and leaching down the soil profile, respectively, and they have wide impacts on surface water and groundwater quality (*1*, *3*). During subsurface transport, pollutants move through soils with percolating water and eventually reach groundwater if they are not sufficiently attenuated by sorption and degradation within given soil layers (*4*, *5*). Chemical properties of a pollutant as well as environmental conditions such as soil and recharge characteristics are typically found to be the major factors that determine the degree of attenuation in soil (*6*).

Various index approaches, in contrast with the DRASTIC method that assesses aquifer vulnerability without consideration for individual pollutant characteristics, have been suggested to estimate the amount of attenuation of a chemical in subsurface transport (*7–9*). This index strategy is particularly useful when model parameters required to provide a detailed description of subsurface processes are difficult to obtain or are not available. Attenuation factor (AF) is one of popular indices, listed in initial pesticide evaluation step in Hawaii, that estimates the leaching potential of pollutants using three important properties, such as sorption, degradation, and recharge as discussed above (*4–7*). Other accepted methods are Screening Concentration In GROund Water (SCI-GROW) and Windows Pesticide Screening Tool (WIN-PST) which are recommended by US Environmental Protection Agency (US EPA ,) and US Department of Agriculture (USDA ,), respectively. Like the AF, these two indices use similar properties to examine aquifer vulnerability to pesticide contamination through either regression analysis or rating scale appraoch. Some of the main drawbacks with these two methods are a lack of their generalization ability and reliance on non-volatile compounds.

Recently, the State of Hawaii has adopted a regional screening index that revises the original AF for identifying vulnerable areas to VOC plus pesticides. This was done to account for volatilization loss which reduced the amount of pollutant leaching through soils as it was not addressed in the previous index approaches (*10*). Using the regional screening index, this chapter will explain: 1) how the contamination risk of volatile and non-volatile chemicals is evaluated at the state level, 2) how much accuracy can be expected from the screening index under local conditions in Hawaii, as compared to an analytical solution of volatile chemical transport, and 3) what steps should be taken to address the national level of groundwater vulnerability. With the examples presented, this chapter provides insight into the basic process of soil contamination and the application of geographic information system (GIS) tool in vulnerability analysis.

Materials and Methods

Regional Screening Index

The regional screening index (*RSI*) is a modification of the mass fraction model (i.e., M_r/M_0) that has been initially developed for evaluating the leaching of volatile chemicals in a dual-porosity model which divides soil porosity into two domains, macro- and micro-pores (*10*). After assuming 1 m of effective root zone as well as neglecting the terms water uptake (by root) and diffusive loss (to micro-pore) from the original equation of Hantush et al. (*10*), we can arrive at the following equation:

$$RSI = \frac{M_r}{M_0} = \frac{q}{q+\sigma} \cdot \exp\left\{ \frac{-\ln(2) \cdot \theta_{FC} \cdot d}{T_{1/2} \cdot q} \cdot \left(1 + \frac{\rho_b \cdot f_{oc} \cdot K_{oc}}{\theta_{FC}} + \frac{n_a \cdot K_h}{\theta_{FC}} \right) \right\}, \quad (1)$$

$$\sigma = \frac{K_h \cdot D_g}{l}. \quad (2)$$

where, M_0 and M_r are initial mass at the soil surface and residual mass at a reference depth d (m), respectively. The chemical-related parameters $T_{1/2}$, K_{oc}, K_h, and D_g, respectively, indicate the half-life (d), sorption coefficient (m^3/kg), dimensionless Henry's law constant (–), and gaseous diffusion coefficient (m^2/d). The soil-related properties ρ_b, f_{oc}, θ_{FC}, and n_a signify the bulk density (kg/m^3), organic matter fraction (–), moisture content at field capacity (–), and air-filled porosity (–), respectively. Lastly, q and l represent the groundwater recharge rate (m/d) and boundary layer thickness on top of the soil surface (m), respectively.

Compiling Databases

As shown in eq 1, the parameter information is required to evaluate the contamination risk of chemicals to groundwater. First, chemical properties of test compounds were obtained from around 800 references such as national and international pesticide databases (*11–13*). Table I shows a summary of key characteristics of 10 example compounds used for the groundwater vulnerability assessment. Next, two different levels of digital soil data (i.e., detailed and general soil maps in the US) which were retrieved from an online database were used for the groundwater vulnerability assessment at the state and national levels, respectively (*14*). This is because application of the detailed soil data to the 48 lower states needs a large amount of data storage capacity. Then, groundwater recharge maps for the State of Hawaii and the US were collected from state (*15*) and federal agencies (*16*), respectively. Specifically, the national recharge map was created to estimate contaminant loads (e.g., suspended sediments and nutrients) in US streams, whereas the statewide recharge map was generated from a numerical simulation study carried out under Hawaii's source water assessment program. Updating all the parameters enabled assessment of the vulnerability to groundwater contamination, which was then compared with the result of the

STANMOD program. The STANMOD contains a series of analytical solutions derived from advection and dispersion equations in soils including degradation and volatilization (*17*). Three required parameters K_{oc}, $T_{1/2}$, and K_h plus the value of D_g for each compound were identically used for the STANMOD, as applied to the regional screening index (see Table I). In both cases, l and d were set to 0.05 m and 0.5 m, respectively.

Results and Discussion

Regional-Scale Groundwater Vulnerability Assessment

A regional screening index (see eq 1) was applied to assess the groundwater vulnerability in the State of Hawaii. Figures 1a and 1b illustrate the contamination risk of two islands in Hawaii: chlorobenzene on the island of Molokai and 2,4-D on the island of Hawaii, respectively. The chemical properties of the two compounds used for the state-wide groundwater vulnerability assessment are described in Table I. These figures show that the chemicals are classified into four types of contamination levels: 1) no data (if information on the soil bulk density or moisture content is not available), 2) unlikely, 3) uncertain, and 4) likely. This risk categorization is established by a classification method which compares the contamination risk of a particular compound to that of a known leacher (e.g., atrazine) and a non-leacher (e.g., endosulfan determined from local groundwater monitoring studies. From the figure, it was determined that while the contamination risk of test chemicals in the two islands appeared to be generally uncertain, a high and low contamination risk was also observed sporadically in some areas. This is because local conditions such as the recharge and soil characteristics vary across different areas even though the chemical properties of the test compound are identically maintained in each island. Therefore, it can be suggested from these examples that the regional screening index can be successfully used for the regional-scale groundwater vulnerability mapping as long as it provides a reasonable estimate of pollutant leaching versus other similar models. Note that a careful review of reference chemicals (i.e., a leacher and non-leacher) from the monitoring studies is needed to increase its predictive validity at the state level as the index itself is not used as an independent prediction of leaching.

Model Validation with STANMOD

The STANMOD program, which provided a closed-form solution for predicting contaminant movement in soils, was used to examine accuracy of the regional screening index. Three soils on the island of Oahu were selected for validation of the regional screening index (see Figure 2a) because these soils were located inside the capture zones that were considered important to protect public water supply wells and groundwater resources (*15*). Here, the capture zone indicates the virtually delineated boundary within which groundwater in specific areas can travel to the wells. Table II presents the physical properties of three soils A, B, and C on this island which are averaged over topsoil, from the soil surface to a depth of 0.5 m. The recharge rates in the soils were obtained from the groundwater modeling study that was conducted to simulate flow and pollutant transport processes including the capture zone delineation, as discussed above (*15*). Figure 2b presents a result of comparison between the STANMOD and the regional screening index. In this figure, each data point indicates the contamination risk of 10 individual chemicals on three test soils (see Table I). It was found that the STANMOD typically overestimated the contamination risk of compounds than the regional screening index. It can be assumed that the STANMOD is generally more accurate than the regional screening index between low and medium recharge conditions, although both are not expected to outperform complex models. This is becuase the regional screening index is derived under the condition of an infinite Peclet number, i.e., advection dominated flows (*10*). The difference between them was smaller in Soils A and C than Soil B, as explained by the coefficient of determination, R^2. From the result, it is concluded that the regional screening index can still be used to evaluate the contamination risk of chemicals at initial vulnerability screening level, because it provides at least a vulnerability level that is safe to protect public health in both best- and worst-case scenarios.

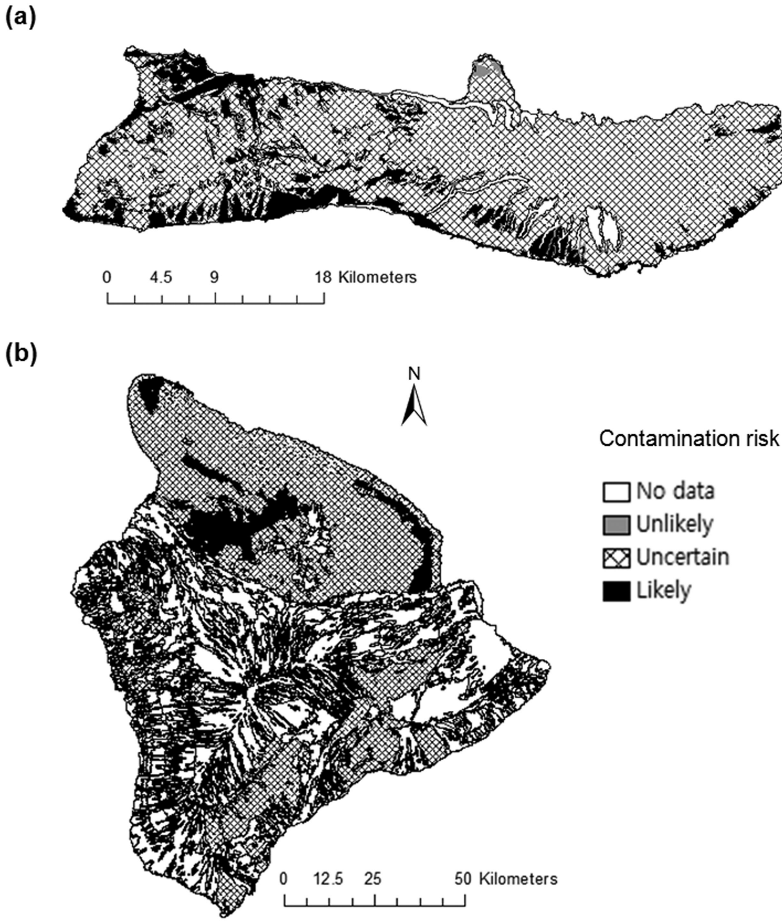

Figure 1. Examples of groundwater vulnerability assessment using the regional screening index: (a) chlorobenzene in Molokai Island and (b) 2,4-D in Hawaii Island.

Table I. Chemical properties of 10 compounds to compare the performance of the regional screening index and the STANMOD

Compounds[a]	K_{OC} *(m³/kg)*	$T_{1/2}$ *(days)*	K_h *(–)*	D_g *(m²/day)*
Atrazine*, [b]	0.126	61.6	2.50×10^{-7}	0.472
Carbofuran	0.048	43.4	6.29×10^{-4}	0.342
Carbon tetrachloride	0.146	148.8	$1.23 \times 10^{+0}$	0.654
Chlorobenzene*	0.260	73.4	1.53×10^{-1}	0.628
1,2-Dichloroethane	0.044	86.0	4.28×10^{-2}	0.846
DCM	0.018	23.8	1.01×10^{-1}	0.870
PCE	0.279	270.0	7.39×10^{-1}	0.560
1,1,1-Trichloroethane	0.248	259.3	7.78×10^{-1}	0.661
2,4-D*	0.053	11.7	6.22×10^{-7}	0.479
Xylenes (total)[c]	0.376	360.0	2.12×10^{-1}	0.646

[a] Other chemical names: DCM = Dichloromethane, PCE = Tetrachloroethylene, and 2,4-D = 2,4-Dichlorophenoxyacetic acid. [b] The chemicals used for regional and national vulnerability assessment are indicated by asterisk (∗). [c] Chemical characteristics of xylenes (total) were compiled from two isomers of *p*- and *m*-xylenes.

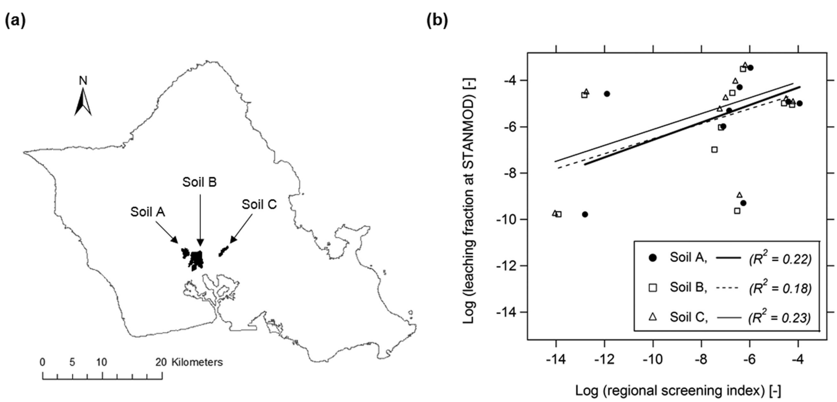

Figure 2. Validation of the regional screening index in assessing the contamination risk of chemicals: (a) three test soils in Oahu Island and (b) a comparison between the regional screening index and the STANMOD. Individual symbols in Figure 2b indicate different chemical compounds examined for three test soils (see Table I).

Table II. Physical properties of three test soils at 0.5 m depth used for validation of the regional screening index (see Figure 2a)

Soils	*MUKEY*[a]	N (–)	ρ_b (kg/m^3)	θ_{FC} (–)	f_{OC} (–)	q^b (m/day)
Soil A	468510	0.534	1,330	0.391	0.026	2.33×10^{-3}
Soil B	468393	0.615	1,100	0.303	0.021	2.05×10^{-3}
Soil C	468533	0.667	950	0.173	0.121	6.72×10^{-3}

[a] MUKEY refers to the map unit key (i.e., the soil indentifier) that associates soil polygons with tabular data, the physical and chemical characteristics of soils. [b] The recharge rates for specific soils are obtained from a Source Water Assessment Program in the State of Hawaii (*15*).

National-Scale Groundwater Vulnerability Assessment

Finally, the regional screening index was extended to assess groundwater vulnerability outside Hawaii as it only required the minimum number of parameters easily available (see eq 1). Figure 3 illustrates the procedure for evaluating the groundwater vulnerability to atrazine in the State of California in the US, where the soil and recharge information, except for the same chemical properties, is newly added to the regional screening index. In this example, the contamination risk of a chemical is classified into six types of contamination levels depending on the value of the regional screening index: from no data (0) through very low (< 0.0001) to very high (> 0.25). This is because selecting reference chemicals simply from the national groundwater monitoring studies may not correctly reflect the results of statewide monitoring data. In fact, some differences were observed in the contamination risk of atrazine in the State of California between the regional screening index and the regional (*18*) and national monitoring studies (*1*). The main reason is that the regional screening index does not account for heterogeneous geoenvironmental conditions, history of pesticide use, and groundwater level in the state and national levels. In addition, the regional screening index does not assess groundwater quality in monitoring wells. As discussed in the regional vulnerability assessment, a more rigorous procedure for selecting reference chemicals is, therefore, needed to ensure its prediction accuracy at the national level. However, implementation of such complex models within the GIS framework is not easy and we leave this for future study. In this way, the new databases containing soil and recharge properties in the 48 contiguous states were created for the national-scale groundwater vulnerability assessment. Figure 4 presents the contamination risk of atrazine in the lower 48 US states (see a solid black bar). In the figure, a gray bar indicates the number of soil polygons in each state compiled from a general soil map in the US. Based on the number of soil samples in the states, the mean and (95%) confidence interval of the regional screening index were estimated. It was shown that there existed a high degree of variation in the contamination risk of atrazine in individual states. Among them, three states such as California, Washington, and Montana represented the highest vulnerability to atrazine due largely to a high groundwater recharge provided (*16*). In Arizona, soil properties appeared to be more vulnerable to leaching than the remaining states. Conversely, some states such as Indiana and Minnesota also showed a high pollutant attenuation capacity resulted from the combined effect of chemical, recharge and soil properties. However, as the national groundwater monitoring studies showed medium to high occurence of this compound in those regions (*1*), additional investigation on the leaching mechanism is required. From this result, it is confirmed that the regional screening index can be used to the national-scale groundwater vulnerability assessment, although some efforts to adjust its prediction with the monitoring data appear to be needed. Finally, this will allow relative risk of contaminants between states to be rapidly assessed and summarized in GIS map.

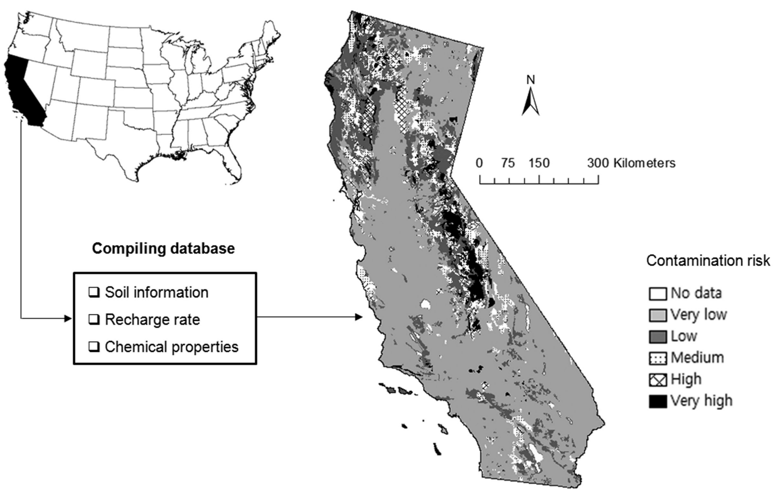

Figure 3. A procedure for assessing groundwater vulnerability on the national level. Shown in the sample is the contamination risk of atrazine in the State of California in the United States.

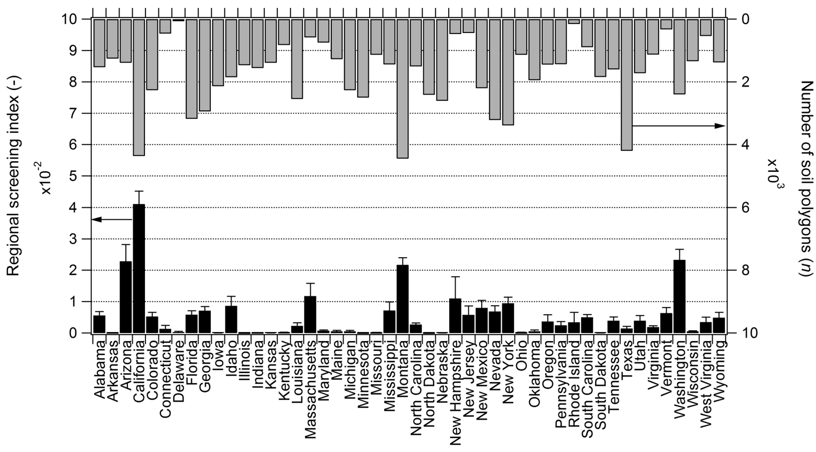

Figure 4. The contamination risk of atrazine at the lower 48 states in the United States (see the left/bottom axis). An error bar indicates the 95% confidence interval. A bar graph shown as gray presents the number of soil polygons in individual states (see the top/right axis).

Conclusion

In this study, the regional screening index that evaluates the leaching of volatile and non-volatile chemicals is applied to the state- and national-scale groundwater vulnerability assessment, i.e., in Hawaii and the conterminous 48 states. A few simple parameters were used to describe the contamination risk of agricultural chemicals to groundwater. Appropriate databases at the state and national levels were constructed to reflect variation in environmental conditions. Below are the major findings of the study.

1. The regional screening index was successfully applied to the state-wide groundwater vulnerability assessment in Hawaii. Groundwater vulnerability varies between the chemicals and local conditions such as the recharge and soil characteristics.
2. The accuracy of the regional screening index was tested with an analytical solution of the STANMOD program. Although the regional screening index shows weak agreement with the analytical solution, it is likely to offer an aquifer vulnerability in the safe level to the public by providing a conservative leaching potential than other models in the best condition for leaching.
3. Compiling new databases such as the soil and recharge information at the national level enabled the regional screening index to evaluate the contamination risk of chemicals in the 48 contiguous states. As shown in the statewide vulnerability assessment, the contamination risk differs considerably among states and each chemical. Therefore, we suggest a

new method be developed to evaluate the groundwater vulnerability to agrochemical contamination at both state and national levels, specifically for those that show dissipation and/or volatile emission in soils.

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Chapter 12

Sensitivity Analysis of Individual Parameters for Synthetic Pyrethroid Exposure Assessments to Runoff, Erosion, and Drift Entry Routes for the PRZM and AGRO-2014 Models

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This analysis focused on individual parameter sensitivity to identify pyrethroid variables that have the greatest impact on predicted runoff and erosion mass loadings from the PRZM model as well those expected to have a significant effect on the receiving water body concentrations predicted by the AGRO-2014 modeling system. This study showed the PRZM and AGRO-2014 models were highly sensitive to numerous individual parameters related to the amount of chemical applied to the field and drift onto the receiving water body, chemical field degradation parameters, factors that greatly influence the content of the edge-of-field runoff/erosion flows, and parameters related to pond geometry and water-sediment partitioning parameters.

Introduction

This sensitivity analysis focused on individual parameters to determine which input parameters in the models (PRZM and PRZM/AGRO-2014) were most sensitive. This analysis generated data showing the variation of a "base case" due to variation in each individual parameter. Other studies have also examined AGRO model sensitivity (*1*) and modeling sensitivity with respect to pyrethroids (*2*, *3*). A hypothetical pyrethroid (hypothrin) was developed for this analysis with properties and usage designed to be representative of the physicochemical characteristics, environmental fate profile, and crop use patterns of all the foliar applied pyrethroids. The United States Environmental Protection Agency (USEPA) standard pond scenario was used as the base case for simulating hypothrin use on cotton (MS) and lettuce (CA). These two scenarios were chosen because they represent wet (many erosion events) and dry (fewer erosion events) conditions. A parameter may be more sensitive for a scenario that is dominated by erosion loadings as opposed to a scenario where the loading is dominated by drift.

Simulation Methods and Modeling Inputs

Models

Chemical application, dissipation, and runoff/erosion were simulated using the Pesticide Root Zone Model (PRZM, version 3.12.2) (*4*). Aerial and ground application drift fractions were estimated using the AgDRIFT® model (version 2.0.10) (*5*). Residue dissipation and redistribution in the receiving water was estimated using the AGRO-2014 model (*6*) for the sensitivity analysis. Detailed information regarding the development of the AGRO-2014 conceptual model is provided in a separate report (*7*). The effect of the presence of a vegetative filter strip (VFS) between the field and the water body was demonstrated using the Vegetative Filter Strip Modelling System (VFSMOD-W), version 5.1.8 (*8*).

Base Scenarios

The base scenarios used in this assessment were the MS cotton and CA lettuce Tier II USEPA standard PRZM scenarios. The model scenarios used in the PRZM/AGRO-2014 sensitivity analyses were developed by the USEPA and represent vulnerable aquatic ecosystems for agricultural chemical use. The base scenarios simulated runoff and erosion mass of pesticide residues, as predicted by PRZM from a standard 10-ha field, and provided loadings to USEPA's standard pond (1 ha x 2 m deep), which was modeled using AGRO-2014. Models were run for the USEPA standard 30-year (1961-1990) period using daily weather data from the recommended SAMSON weather stations. Frequency analyses were conducted for the annual maxima across six different averaging durations (24-hr, 96-hour, 21-day, 60-day, 90-day, and annual average periods) for the concentrations (dissolved water, pore water and sediment) generated via AGRO-2014. Total mass loads that entered the water body from the PRZM model were also analyzed for parameter sensitivity.

Chemical

A hypothetical pyrethroid (hypothrin) was developed for this sensitivity analysis with properties and usage designed to be representative of the physicochemical characteristics, environmental fate profile, and crop use patterns of all the foliar applied pyrethroids. Hypothrin properties were based on properties from all the pyrethroids and best professional judgment. Table I below provides the physicochemical properties for hypothrin used in this analysis.

Table I. Hypothrin Physicochemical Properties

Property	*Hypothrin Value*
Molecular weight, g/Mole	420
Vapor pressure, mm Hg (at 25°C)	1.50×10^{-08}
Aqueous solubility, ppm (at 20°C)	0.05
Henry's Law Constant, atm-m^3/Mole	4.80×10^{-07}
K_{OC}, mL/g	500,000
LogKow	6.0862
Melting point, °C	60
Test temperature, °C	25
Soil photolysis half-life, days	Stable
Aqueous photolysis half-life, days	30
Aerobic soil half-life, days	66
Foliar half-life, days	5.3
Hydrolysis at pH 7, days	Stable
Aerobic aquatic half-life, days	12
Anaerobic aquatic half-life, days	70

Sensitivity Assessment

This assessment concentrated on the sensitivity of properties related to runoff, erosion and drift as well as receiving water body parameters that would be expected to affect the concentration in the pond based on best professional judgment and consideration of earlier studies (*1–3*). This included sensitivity to hypothrin application parameters, hypothrin environmental fate parameters, PRZM field parameters and AGRO-2014 receiving water body parameters. Drift loads were calculated using the regulatory version, 2.0.10, of the AgDRIFT® model (*5*) to estimate the drift fraction onto the water body for labeled buffer distances for each type of application (i.e. aerial and ground). Additionally, the effect of the 3-m (10-ft) vegetative filter strip was modeled for comparison with the base case. The base scenario parameters with the sensitivity run parameter ranges and values are shown in Table II.

Table II. Individual Parameter Sensitivity Analysis—Selection of Parameter Ranges

Parameter (units)	*Base Scenario*	*Sensitivity Run*
Hypothrin Application Parameters		
Number of applications (appl.)	MS Cotton: 6 CA Lettuce: 6	10, 4, 1 4, 2, 1
Application rate (kg a.i./ha)	0.056	0.028, 0.112
1st application dates	MS Cotton: 11-May CA Lettuce: 26-Feb	MS Cotton: May 1, 21, 31, June 10, 20, 30 CA Lettuce: Feb 16, March 8, 18, 28
Application interval (days)	MS Cotton: 5 CA Lettuce: 7	MS Cotton: 3, 7, 10, 14 CA Lettuce: 3, 5, 10, 14
Application type (aerial (A)/ground (G)/ incorporated (I))	Aerial (6 appl.)	Ground (6 appl.), I/G (1 appl. / 5 appl.) I/A (1 appl. / 5 appl.) I/G/A (1 appl. / 2 appl. / 3 appl.); I/G, I/A, and I/G/A only run for MS Cotton
Droplet size Aerial drift fraction based on ASAE droplet size Fine/Medium = F/M Medium/Coarse = M/C Coarse/Very Coarse = C/VC	M/C 150 ft = 0.0197	F/M 150 ft = 0.0385 300 ft = 0.0231 M/C 300 ft = 0.0108 C/VC 150 ft = 0.0119 300 ft = 0.0066 300 ft = 0.0066
Hypothrin Environmental Fate Parameters		
K_{OC} (mL/g) (PRZM)	500,000	200,000 2,000,000 4,000,000 13,000,000 41,000,000
Soil half-life (days)	66	1, 10, 100, 500
Soil photolysis in top 0.2 cm (days)	Stable (66 days in top 0.2 cm)	1, 10
Washoff factor (per cm rainfall)	0.5	0.1, 0.3
Solubility (g/m3)	0.05	0.000005, 0.00005, 0.005, 0.5

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Table II. (Continued). Individual Parameter Sensitivity Analysis—Selection of Parameter Ranges

Parameter (units)	*Base Scenario*	*Sensitivity Run*
K_{OC} (mL/g) (AGRO-2014)	500,000	200,000 2,000,000 4,000,000 13,000,000 41,000,000
Vapor pressure (mm Hg)	1.50E-08	9.3E-11, 1.9E-5
Degradation half-life in water (hours)	288 (12 days)	72, 1200, 4800, 24000 (3, 50, 200, 1000 days)
Degradation half-life in sediment (hours)	1680 (70 days)	600, 3600, 7200, 24000 (25, 150, 300, 1000 days)
Field Parameters		
Land slope (%)	6	1, 10
Length slope (LS) factor	1.34 (slope length of 370 ft)	0.34, 1.7
Hydrologic Soil Group (HSG)	MS Cotton: C (CN 86 and 89) CA Lettuce: D (CN 89 and 94)	MS Cotton: D (CN 90 and 92) B (CN 79 and 82) A (CN 69 and 73) CA Lettuce: C (CN 85 and 91) B (CN 78 and 86) A (CN 67 and 77)
Tillage practice	Conventional MS Cotton: CN 86 and 89	MS Cotton: No till: CN 77 and 80 Reduced till: CN 82 and 84
USLE P-factor	0.5	0.25, 1.00
Field organic carbon (%OC in top soil horizon)	MS Cotton: 1.28 CA Lettuce: 0.725	0.50, 2.00, 2.50
Field-to-Pond ratio	10:1	6:1, 50:1
Vegetative filter strip (VFS)	None	3-m (10-ft) VFS
Receiving Water Body Parameters		
Water surface area (m2)	10000	1000, 5000, 20000
Pond depth (m)	2	0.5, 1, 4
Sediment active layer depth (m)	0.05	0.025, 0.10
Suspended sediment (mg/L)	30	10, 90
Sediment particles (m^3/m^3)	0.5	0.25, 0.75

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Table II. (Continued). Individual Parameter Sensitivity Analysis—Selection of Parameter Ranges

Parameter (units)	*Base Scenario*	*Sensitivity Run*
Organic carbon fraction[a] in water including inflow water	0.067	0.02, 0.04, 0.08
Organic carbon fraction in sediment	0.04	0.02, 0.08
River water inflow and outflow (m3/h)	5	10, 25
Settling time 90% (days)	3.4	0.1, 7, 14
Resuspension percentage (% of deposition)	50	25, 75
Sediment-Water diffusion (m/h)	0.05	0.005, 0.17
Temperature (°C)	Weather files: MS-W03940 CA-W23273	Constant 8, 12, 25, and 30

[a] Organic carbon fraction in water refers to suspended sediment or TSS % Organic carbon = % organic matter x 0.58.

Application Parameters Considered in the Sensitivity Assessment

The hypothrin application parameters considered in this sensitivity analysis include: number of applications, application rate, application start date, application interval, application type (i.e. ground (G), incorporated (I) and aerial (A)), and application drift fraction. A brief description of these parameters is provided below.

Number of Applications

The number of applications for each crop varies between different pyrethroid labels; therefore, a range of number of applications was analyzed for sensitivity. The MS cotton base scenario had six applications and the numbers of applications were varied to one, four, and ten. CA lettuce applications varied from six (base) to four, two, and one application.

Application Rate

Application rates of one half and two times the base rate of 0.056 kg/ha were analyzed for sensitivity for both the MS cotton and CA lettuce scenarios.

Application Start Date

The standard EFED scenarios for MS cotton and CA lettuce have a default crop emergence date of May 1 and Feb. 16, respectively. The base scenarios were run with application starting dates that were 10 days after emergence. Alternative starting dates (+/- 10 day increments) were analyzed for model sensitivity (6 for MS cotton and 4 for CA lettuce).

Application Interval

The application interval for each crop varies between the different pyrethroid labels; therefore, a range of application intervals was analyzed for sensitivity. The application interval was varied from 3 days to 14 days (MS cotton base = 5 days; CA lettuce base = 7 days).

Application Type

For cotton use, most pyrethroid labels allow aerial (A) and/or ground (G) applications. The base scenarios were simulated with all six aerial applications. For cotton uses, specific pyrethroid labels also allow a soil incorporated (I) application (1-inch incorporation assumed; CAM 5 in PRZM). To analyze the sensitivity to the type of application, four additional model simulations were conducted for MS cotton: one with all six ground applications (99% efficiency and 0.0045 drift fraction), another with one incorporated application followed by five ground applications, a third with one incorporated application followed by five aerial applications, and lastly, an incorporated application followed by two ground applications and three aerial applications.

The pyrethroid labels allow only aerial and ground applications to lettuce and do not include a soil incorporated use pattern. Therefore, only the ground application (99% efficiency and 0.0045 drift fraction) was simulated for the CA lettuce scenario sensitivity (base was aerial applications).

Aerial Drift Fraction

The range of aerial drift fractions from the available AgDRIFT® Tier I droplet sizes were analyzed for model sensitivity. These included Fine/Medium, Medium/Coarse and Coarse/Very Coarse droplet sizes for two different setback distances of 150 ft and 300 ft. The base scenarios were simulated with the current pyrethroid label requirements of a Medium/Coarse droplet size and a 150-ft setback buffer resulting in an aerial drift fraction of 0.0197.

Environmental Fate Parameters Considered in the Sensitivity Assessment

The hypothrin environmental fate parameters considered in this sensitivity analysis include: PRZM organic carbon partition coefficient (K_{OC}), soil half-life, soil half-life combined with soil photolysis, foliar washoff factor, water solubility, receiving water body K_{OC}, vapor pressure, aerobic aquatic half-life and anaerobic aquatic half-life. A brief description of these parameters is provided below.

PRZM K_{OC}

The range of soil organic carbon-water partition coefficients (K_{OC}) evaluated in this sensitivity analysis was based on measured data from laboratory studies conducted on pyrethroids. The range of K_{OC} values in this assessment extended beyond the range of expected pyrethroid values (200,000 – 12,000,000 mL/g), with a base value of 500,000 mL/g. Typically, the same K_{OC} value is used for both the field (PRZM) and the receiving water body (AGRO-2014) for exposure modeling; however, the extremely hydrophobic characteristics of pyrethroids require the selection of appropriate K_{OC} values for different phases of the exposure modeling process. In the field runoff setting modeled by PRZM, it was most appropriate to use K_{OC} values developed using Liquid-Liquid Extraction (LLE) approaches since this is inclusive of the chemical adsorbed to dissolved organic carbon moving in the runoff phase. However, when estimating the free concentrations expected in pore water and the receiving water body water column, the most appropriate K_{OC} values to use were measured using Solid-Phase Micro-Extraction (SPME) technology since these reflect the partition to the freely dissolved phase. Therefore, this analysis measured the sensitivity of K_{OC} separately in each of the models simulated.

Soil Half-life

The range of aerobic soil degradation half-lives for pyrethroids varies across compounds, and a wide range of values was considered in this sensitivity analysis. The aerobic soil half-lives ranged from 1 to 500 days for this assessment which exceeded the range of expected pyrethroid values, with a base value of 66 days.

Soil Half-Life Combined with Soil Photolysis

The combined soil and soil-photolysis half-lives were considered in this sensitivity analysis. This was achieved by changing the degradation rate in the top 0.2 cm of the top soil horizon from the base value of 66 days (aerobic soil only) to 1 day and 10 days. The half-life in the remaining depth of the soil column was maintained at 66 days in all runs.

Foliar Washoff Factor

The foliar washoff factor is a parameter that estimates the flux of pesticide washoff (per cm rainfall) from plant surfaces based on crop, pesticide properties and application method. Foliar washoff factors ranging between 0.1 and 0.5 (base value) were considered in this sensitivity analysis.

Water Solubility

The range of solubilities considered in the sensitivity analysis was 0.000005 to 0.5 ppm with a base value of 0.05 ppm. This covered the measured pyrethroid range of solubilities. It is important to note that the AGRO-2014 model limits the water concentrations so they do not exceed the model solubility input value.

Receiving Water Body K_{OC}

The base K_{OC} for the AGRO-2014 model was 500,000 mL/g and was varied from 200,000 mL/g to 41,000,000 mL/g. The range of K_{OC} values in this assessment exceeded the range of expected pyrethroid values (200,000 – 12,000,000 mL/g). As stated previously, the K_{OC} sensitivity in the receiving water body was modeled separately from the field (PRZM).

Vapor Pressure

The vapor pressure values used in this analysis ranged from 9.3 x 10^{-11} to 1.9 x 10^{-5} mm Hg with the base vapor pressure 1.50 x 10^{-8} mm Hg. This range covered the measured pyrethroid range of vapor pressure values.

Aerobic Aquatic Half-Life

The water half-life variation was based on the range of aerobic aquatic laboratory half-life values from the pyrethroids (*9*, *10*). The aerobic aquatic half-lives ranged from 3 to 1,000 days for this assessment which exceeded the expected pyrethroid values, with a base value of 12 days.

Anaerobic Aquatic Half-life

The sediment half-life variation was based on the range of anaerobic aquatic laboratory half-life values from the pyrethroids (*9*, *10*). The hypothrin base sediment half-life was 70 days, and it was varied from 25 days to 1,000 days for the sensitivity assessment.

Field Parameters Considered in the Sensitivity Assessment

The PRZM field parameters that were considered in this sensitivity analysis include: land slope, length slope factor, hydrologic soil group, tillage practices, the universal soil loss equation (USLE) p-factor, organic carbon in soil, field to pond ratio, and inclusion of a 3-m (10-ft) vegetative filter strip. A brief description of these parameters is provided below.

Percent Land Slope

The percent land slope varies across growing regions as well as within a watershed. Therefore, a range of land slope from 1-10% (base = 6%) was evaluated in this analysis. The median slope for cotton in the South and lettuce in CA is 1% (*11*, *12*).

Length Slope (LS) Factor

The LS factor, also called the universal soil loss equation (USLE) topographic factor, is based on length and steepness of the slope of the field and was developed by the USDA. The base scenarios have a LS factor of 1.34 (based on a slope length of 370 ft.). The sensitivity range considered in this assessment was for a 6% slope with slope lengths of 25 ft and 600 ft resulting in LS factors of 0.34 and 1.7 ((*4*), Table 5.5).

Hydrologic Soil Group (HSG)

HSGs are assigned based on measured infiltration rates of a soil. Soils are assigned to one of four groups (A, B, C and D) according to the rate of water infiltration when soils are not protected by vegetation, are thoroughly wet, and receive precipitation from long-duration storms. HSG A soils have the lowest runoff potential (lower curve numbers) while HSG D soils have the highest runoff potential (higher curve numbers). The curve numbers for each HSG used in this analysis were derived from Table 5.10 of the PRZM Manual (*4*). MS cotton curve numbers were based on row crops average of poor and good hydrologic condition and average row crop and fallow. CA lettuce curve numbers were based on row crop good and fallow conditions.

The MS cotton curve numbers used in the HSG sensitivity runs were as follows for cropping and residue: D = 90, 92; C = 86, 89; B= 79, 82; A = 69, 73. The CA lettuce curve numbers used in the HSG sensitivity runs were as follows for cropping and residue: D = 89, 94; C = 85, 91; B= 78, 86; A = 67, 77.

Tillage Practice

The base scenarios were set up with conventional tillage practices. The curve numbers in the PRZM input file were decreased 5% for reduced tillage and 10% for no-till based on (*13*). The c-factors and Manning's N factors from the USDA Agricultural Handbook were used for MS cotton no-till and reduced till practices (*14*). CA lettuce did not have adjusted c-factors and Manning's N factors in the database for reduced till and no till; therefore, only MS cotton was analyzed for tillage practice sensitivity.

P-Factor

The P-factor, also called the USLE practice factor, was developed by the USDA to describe conservative agricultural practices. ((*4*), Table 5.6) Values used in this assessment ranged from 0.10 (extensive practices) to 1.0 (no supporting practices) with a base value of 0.5.

Percent Organic Carbon in Soil

The percent organic carbon in soil varies across soil types; therefore, a range of percent of organic carbon (0.5-2.5%) was evaluated in this sensitivity analysis. The base field organic carbon percent in the top soil horizon for the MS cotton and CA lettuce scenarios was 1.28% and 0.725%, respectively.

Field to Pond Ratio

The base field to pond ratio for both MS cotton and CA lettuce was 10:1. Additional field to pond ratios of 6:1 and 50:1 were evaluated in this sensitivity assessment.

Vegetative Filter Strip

The current pyrethroid agricultural product labels require a 3-m (10-ft) VFS to be maintained between the areas of application (field edge) and down gradient aquatic habitats. The base scenarios do not account for the presence of a properly maintained VFS. Therefore, the presence of the 3-m vegetative filter strip was modeled using VFSMOD (*8*) to simulate the impact of a grassed buffer between the PRZM field and the AGRO-2014 simulated receiving water system. No sensitivities associated with the VFS width or effectiveness were modeled since they are well documented elsewhere (*15–17*).

Receiving Water Body Parameters Considered in the Sensitivity Assessment

The receiving water body parameters considered in this sensitivity analysis include: pond area, pond depth, sediment layer depth, suspended sediment, sediment particle volume, organic carbon fraction in water, organic carbon fraction in sediment, water inflow/outflow rate, settling time 90%, resuspension percentage, sediment-water diffusion, and temperature. A brief description of these parameters is provided below.

Pond Surface Area

The base pond area was 1-ha in AGRO-2014. A range of pond areas from 0.1 ha to 20 ha were evaluated for the sensitivity analysis. For this analysis, the field area (10 ha), pond depth (2 m) and sediment depth (0.05 m) were kept constant to isolate the pond surface area parameter. The width of the pond remained the same which resulted in the same aerial drift fraction of 0.0197. In AGRO-2014, the water surface area and water volume in the "Environment" worksheet were modified to account for the pond area parameter changes. Table III below gives the base values and modified values for the range of pond areas included in the AGRO-2014 receiving water body.

Table III. Pond Surface Area and Related Parameter Ranges

Pond Surface Area (m^2)	*Pond Depth (m)*	*Water Volume (m^3)*	*Sediment Depth (m)*	*Sediment Volume (m^3)*
20,000	2	40,000	0.05	1,000
10,000 (base)	2	20,000	0.05	500
5,000	2	10,000	0.05	250
1,000	2	2,000	0.05	50

Pond Depth

The base pond depth was 2 meters in AGRO-2014. Additional pond depths were derived with a range of 0.5 – 4.0 meters (*18*) and evaluated for the sensitivity analysis. In AGRO-2014, the water volume in the "Environment" worksheet was modified to account for the pond depth parameter changes. Table IV below gives the base values and modified values for the range of pond depths included in the AGRO-2014 receiving water body.

Table IV. Pond Water Depth and Related Parameter Ranges

Pond Surface Area (m^2)	***Pond Depth (m)***	*Water Volume (m^3)*	*Sediment Depth (m)*	*Sediment Volume (m^3)*
10,000	**4**	40,000	0.05	500
10,000	**2 (base)**	20,000	0.05	500
10,000	**1**	10,000	0.05	500
10,000	**0.5**	5,000	0.05	500

Sediment Layer Depth

The base sediment layer depth was 0.05 meters in AGRO-2014. Additional sediment layer depths with a range of 0.025-0.10 meters were evaluated for the sensitivity analysis. In AGRO-2014, the sediment active layer depth in the "Environment" worksheet was modified to account for the sediment depth parameter changes. Table V below gives the base values and modified values for the range of sediment depths included in the AGRO-2014 receiving water body.

Table V. Pond Sediment Depth and Related Parameter Ranges

Pond Surface Area (m^2)	*Pond Depth (m)*	*Water Volume (m^3)*	***Sediment Depth (m)***	*Sediment Volume (m^3)*
10,000	2	20,000	**0.10**	1,000
10,000	2	20,000	**0.05 (base)**	500
10,000	2	20,000	**0.025**	250

Suspended Sediment

The base suspended sediment concentration (SS) in the water column was 30 mg/L in AGRO-2014 (this refers to the baseline suspended sediment concentration in AGRO-2014 rather than the SS concentration after runoff events). Additional baseline suspended sediment concentrations ranging from 10-90 mg/L were evaluated for the sensitivity analysis.

Sediment Particle Volumes

The base volume fraction of sediment particles in the benthic layer was 0.5. This parameter is the solid fraction of the sediment layer and is reported in m^3/m^3 units. The range of volume fraction of sediment particles was 0.25-0.75 for the sensitivity analysis.

Organic Carbon Fraction in Water

The base organic carbon fraction in the water column was 0.067 in AGRO-2014. The organic carbon fraction in water is the fraction of organic carbon based on the dry weight of suspended sediment in the bulk water column. Additional organic carbon fractions in water ranging from 0.02-0.08 were evaluated for the sensitivity analysis.

Organic Carbon Fraction in Sediment

The base organic carbon fraction in the sediment layer was 0.04 in AGRO-2014. The organic carbon fraction in sediment is the fraction of organic carbon based on the dry weight of sediment in the benthic layer. Additional organic carbon fractions in sediment ranging from 0.02-0.08 were evaluated for the sensitivity analysis.

Water Inflow and Outflow Rate

The base water inflow and outflow rate was 5.0 m^3/h in AGRO-2014. Additional water flow rates ranging from 10-25 m^3/h were evaluated for the sensitivity analysis.

Settling Time 90%

The settling time is the time for 90% of eroded sediment to deposit on the active sediment bed. The base settling time 90% value was 3.4 days in AGRO-2014. The range of settling velocities evaluated, based on various soil types in a 2 meter deep pond, was 0.1-14 days (*19*, *20*).

Resuspension Percentage

The resuspension percentage (% of deposition) is the percent of solid particles transferring out of the active sediment layer and back into the water column. The base resuspension percentage in AGRO-2014 was 50%, and the range of resuspension percentages evaluated was 25-75%.

Sediment-Water Diffusion

The sediment-water diffusion is the rate of diffusion between the active sediment layer and the water column. The base sediment-water diffusion rate was 0.05 m/h, and the range of sediment-water diffusion rates evaluated was 0.005-0.17 m/h.

Temperature

The base scenarios for MS cotton and CA lettuce were simulated using the meteorological weather station daily temperature value files from Jackson, MS and Santa Maria, CA, respectively. The degradation rates used in AGRO-2014 were adjusted to account for the difference in environmental and laboratory experimental temperatures (laboratory default is 25°C). Additional simulations were conducted using a constant temperature ranging from 8-30°C and evaluated for the sensitivity analysis.

Results

Model Output Data Processing

Total annual pyrethroid loadings to the AGRO-2014 pond from drift, runoff, and erosion were computed for each climatological year simulated. The annual total mass loadings (kg) from runoff and erosion were computed from the PRZM output by summing up the daily mass in runoff (kg/ha) or erosion (kg/ha) for each year and multiplying the value by 10 for the 10-ha field size. The drift for each year was computed by multiplying number of applications by the application rate by the drift fraction by the surface area of the pond (1 ha). The total annual loads resulting from runoff, erosion, and drift sources were then calculated.

Annual maximum and 90th percentile concentrations in the water column (dissolved), pore water, and sediment were generated by AGRO-2014 for six different TWA exposure durations (24-hour, 96-hour, 21-day, 60-day, 90-day, and annual average). Frequency analyses were performed to evaluate how often specific levels of hypothrin annual loadings or receiving water body concentrations might occur for each simulation. The analyses were conducted using the Weibull plotting position (*21*).

Sensitivity Results

For PRZM loading sensitivity, a comparison to the base scenarios (MS cotton and CA lettuce) of the 90th percentile annual total mass loading resulting from the variation in each parameter is provided in Figures 1and 2 for MS cotton and CA lettuce scenarios, respectively. A list of numerical results is presented elsewhere (*22*).

For PRZM/AGRO-2014 EEC sensitivity, the percent differences (+/-) from the base scenarios of the 90th percentile maximum 24-hr dissolved water and sediment EECs for each sensitivity run are shown graphically in Figures 3 thru 10. Additionally, for pore water and sediment, the 90th percentile year 21-day time-weighted average concentrations were evaluated. However, the percent differences observed from the 21-day base values were very similar to the sensitivities observed with the 24-hour values; therefore, only the 24-hr values are reported in this assessment.

The percent difference from the MS cotton and CA lettuce base 90th percentile year 24-hr dissolved water concentrations is provided graphically in Figure 3 for the application parameters, Figure 4 for the environmental fate parameters, Figure 5 for the field parameters and Figure 6 for the receiving water body parameters. Similar graphs for the 24-hr sediment concentrations are provided in Figures 7, 8, 9 and 10. Not all sensitivity runs are displayed in the figures to ensure legibility; however, the high and low extremes are included for comparison of each sensitivity parameter.

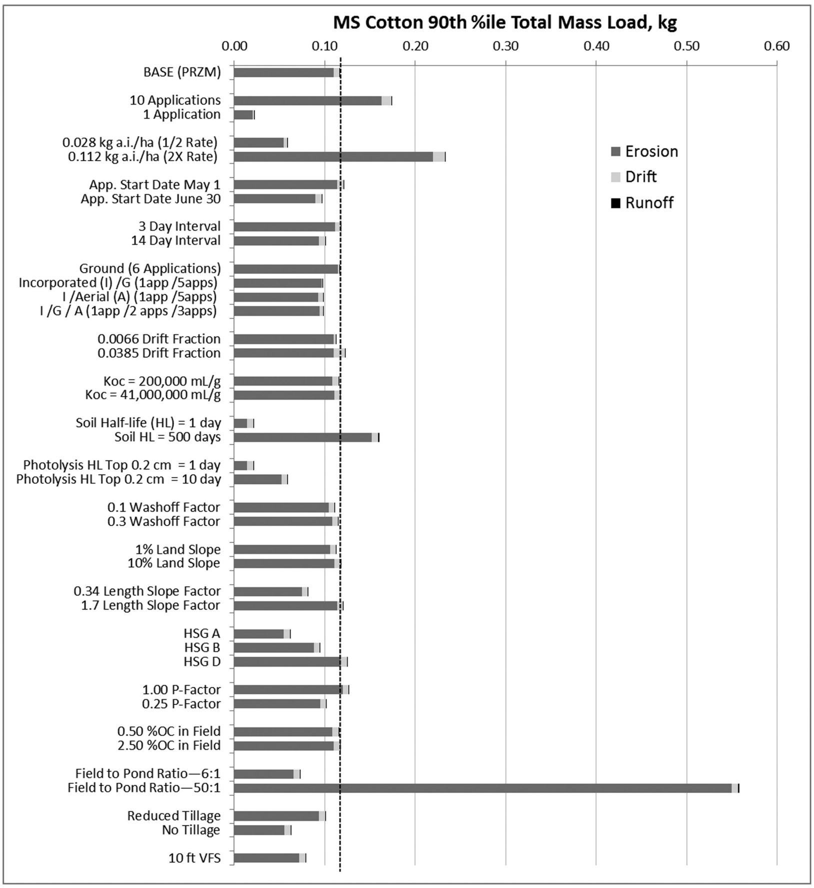

Figure 1. Comparison of 90th Percentile Annual Mass Loads for the MS Cotton Scenario as Potentially Sensitive Input Parameters Were Varied.

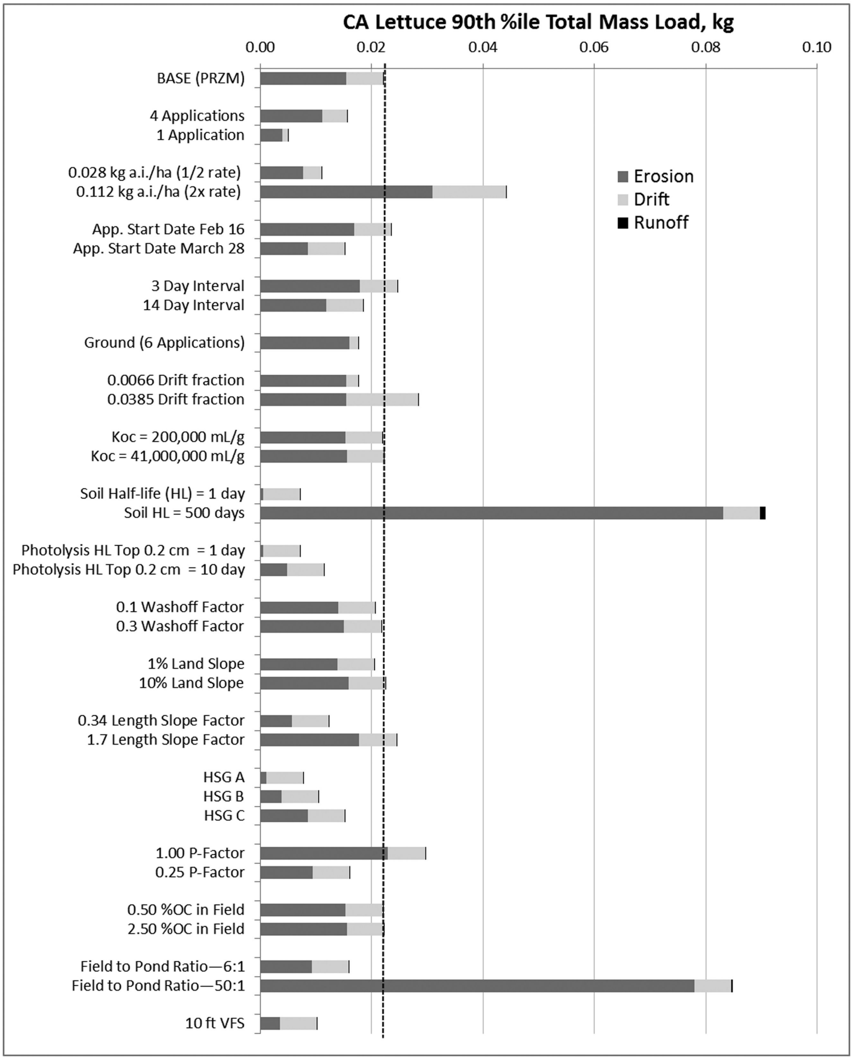

Figure 2. Comparison of 90th Percentile Annual Mass Loads for the CA Lettuce Scenario as Potentially Sensitive Input Parameters were Varied (note scaling difference from MS cotton graph in Figure 1.).

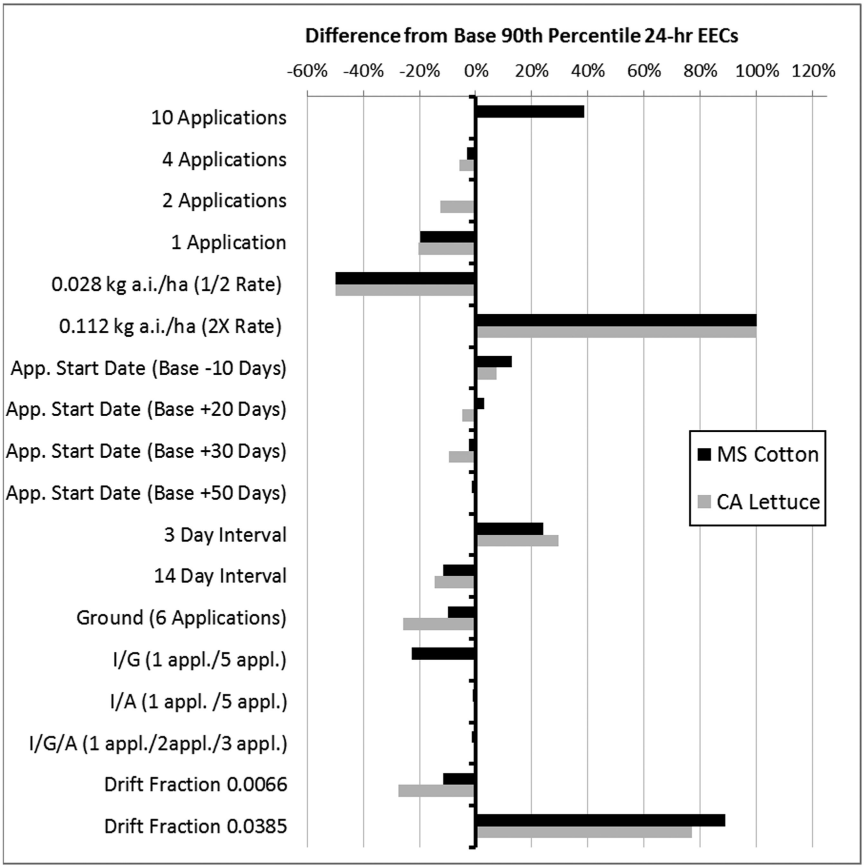

Figure 3. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Dissolved Water EECs from Varying Hypothrin Application Parameters (note scaling differences across figures).

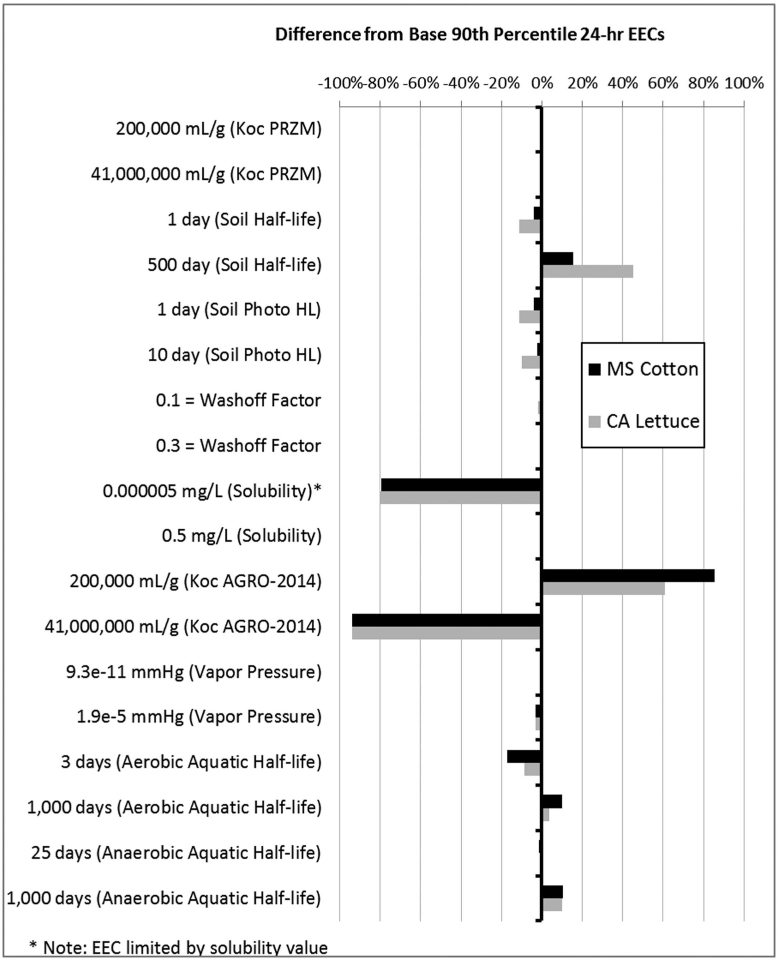

Figure 4. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Dissolved Water EECs from Varying Hypothrin Environmental Fate Parameters (note scaling differences across figures).

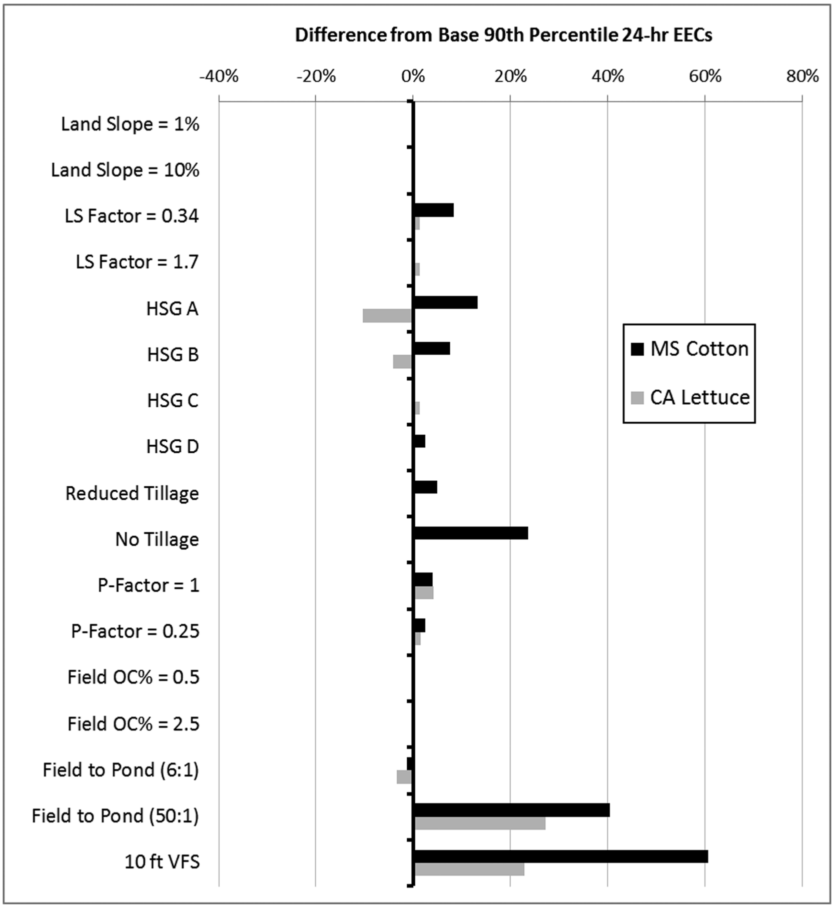

Figure 5. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Dissolved Water EECs from Varying Field Parameters (note scaling differences across figures).

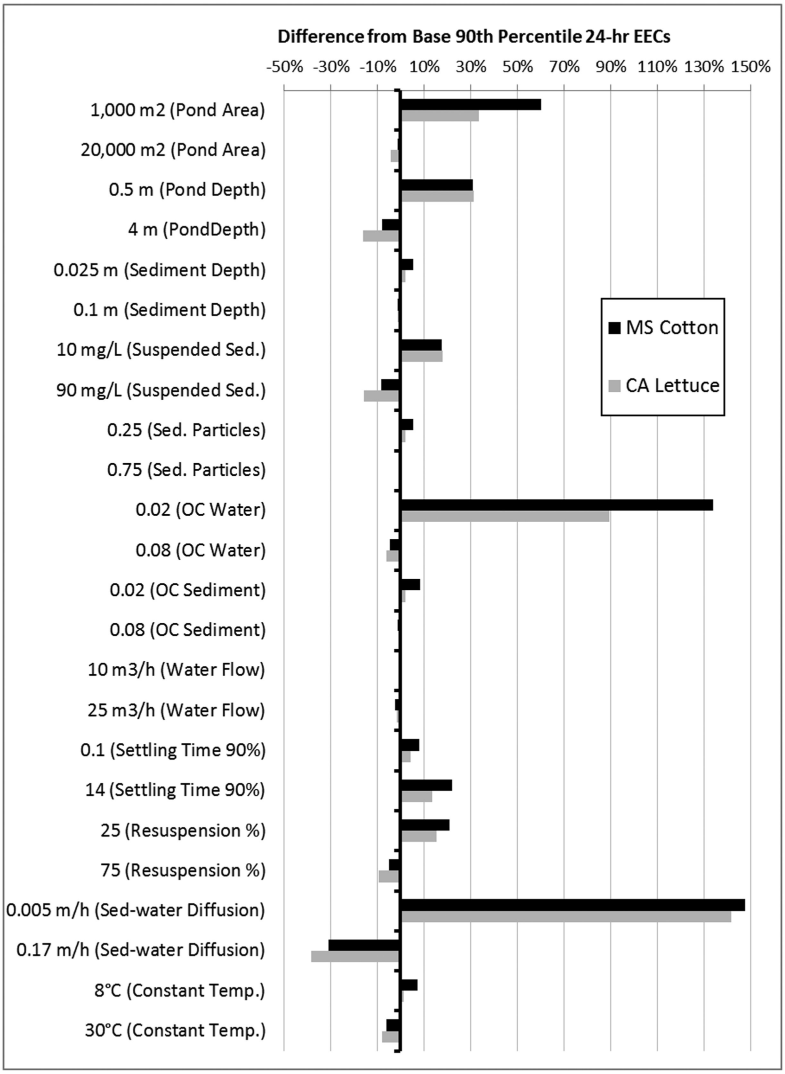

Figure 6. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Dissolved Water EECs from Varying Receiving Water Body Parameters (note scaling differences across figures).

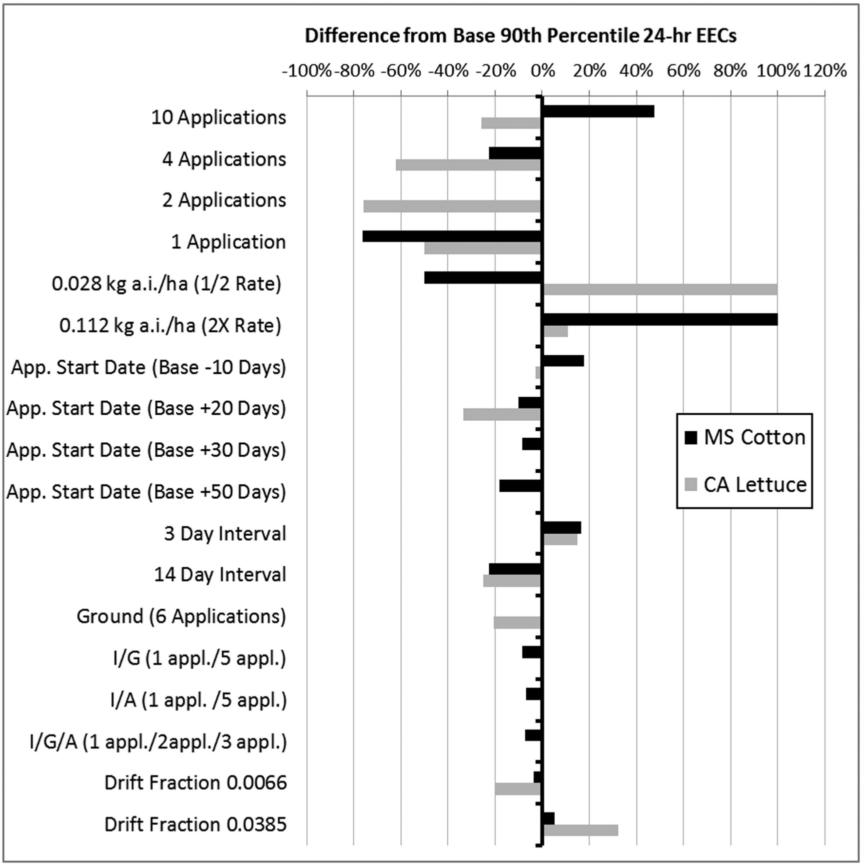

Figure 7. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Sediment EECs from Varying Hypothrin Application Parameters (note scaling differences across figures).

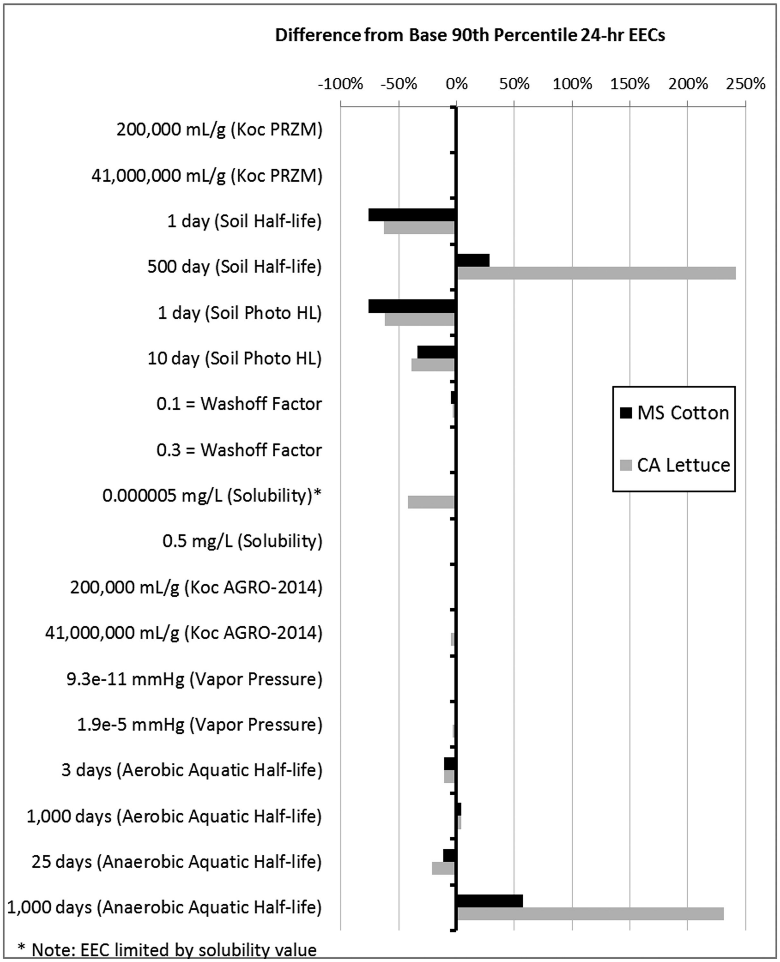

Figure 8. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Sediment EECs from Varying Hypothrin Environmental Fate Parameters (note scaling differences across figures).

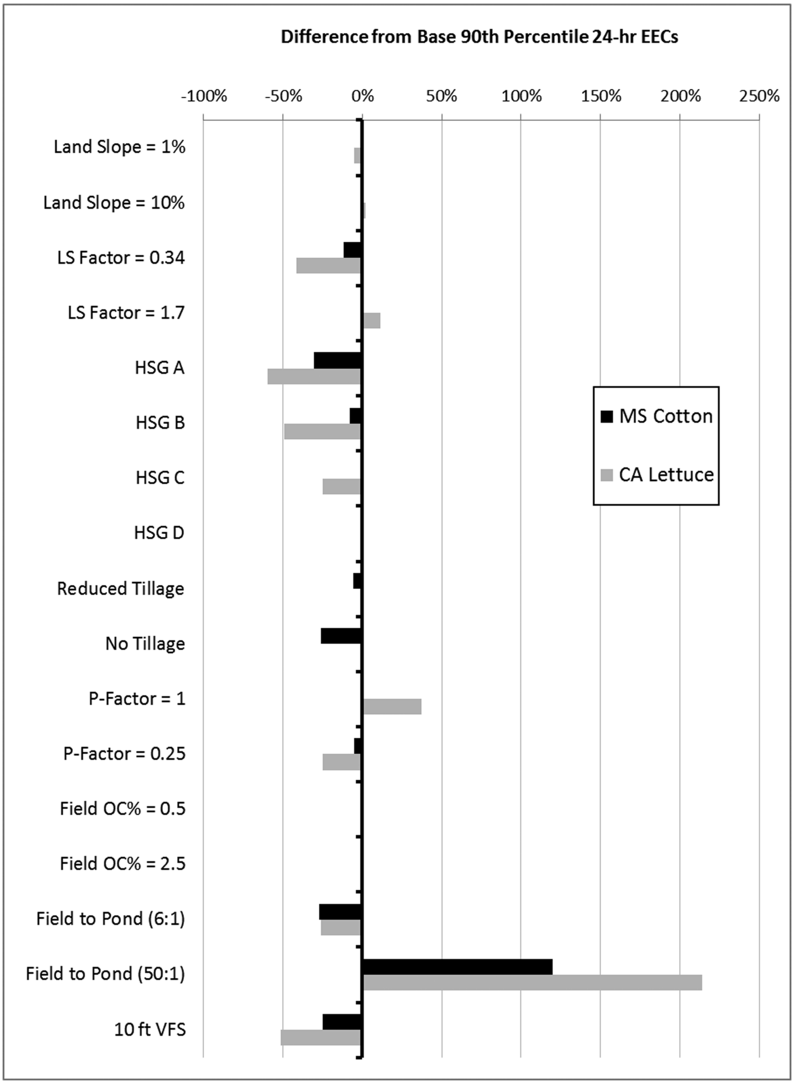

Figure 9. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Sediment EECs from Varying Field Parameters (note scaling differences across figures).

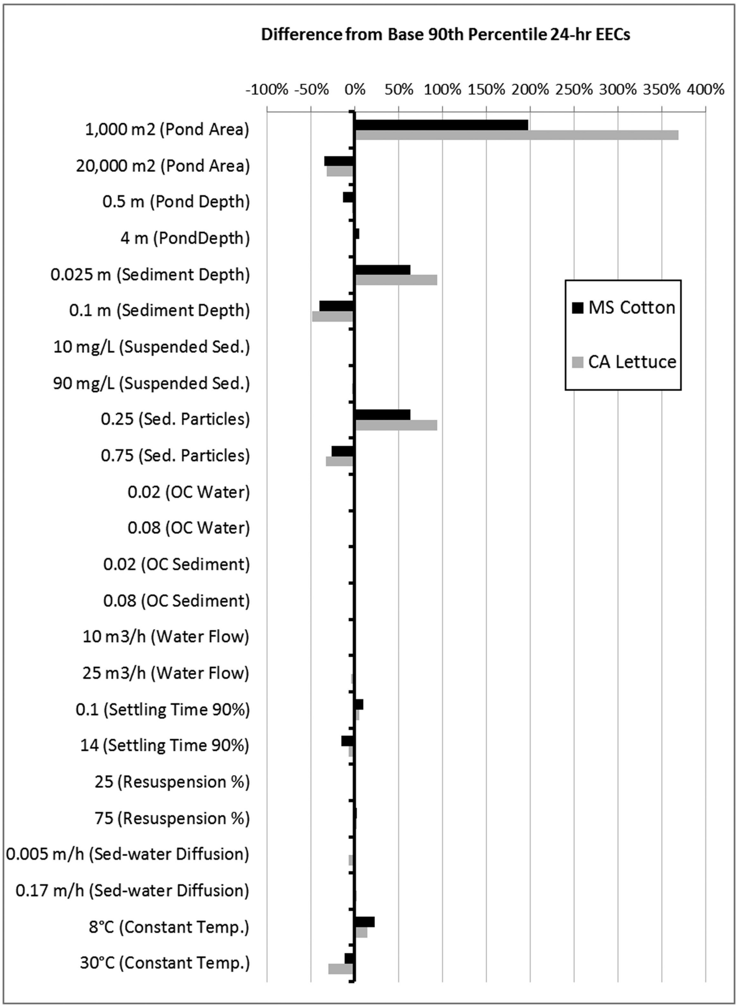

Figure 10. Percent Difference from the Base 90th Percentile PRZM/AGRO-2014 24-hr Sediment EECs from Varying Receiving Water Body Parameters (note scaling differences across figures).

Conclusions

The objective of this assessment was to identify the application, environmental fate and field parameters that have the greatest impact on predicted runoff and erosion mass loadings from PRZM as well as model input parameters that would be expected to have a significant effect on the receiving water body dissolved water column, pore water and sediment concentrations predicted by AGRO-2014 modeling systems. The pore water concentrations were evaluated in this assessment but are not shown in this paper because the pore water and sediment sensitivities were very similar for all parameters evaluated except the

AGRO-2014 K_{OC} and the organic carbon fraction in sediment. As expected, both of these parameters were highly sensitive for the pore water concentration and not sensitive in the sediment.

Results from the edge-of-field mass loading sensitivity indicated that the PRZM model was highly sensitive to the choice of scenario as well as individual parameters related to the amount of hypothrin applied to the field (e.g. application number and rate), hypothrin field degradation parameters (e.g. soil and combined soil and photolysis half-lives) and factors that greatly influence the content of the edge-of-field runoff/erosion flows (e.g. hydrologic soil group, field to pond ratio and inclusion of a vegetative filter strip). It is important to note that the sensitivities in this paper were evaluated only across the ranges of parameters expected for pyrethroid compounds. The PRZM K_{OC} is an example of a parameter that might be more sensitive if substantially lower K_{OC} coefficients (e.g. 100-2000 mL/g) were evaluated.

Results from the 24-hr estimated exposure concentration sensitivity indicated the PRZM/AGRO-2014 models were highly sensitive to mass loadings, as expected, as well as some additional pond related parameters related to its geometry (e.g. pond area and sediment depth), water-sediment partitioning (K_{OC} AGRO-2014, sediment particle volume, organic carbon fraction in water and sediment-water diffusion) and degradation rate (i.e. anaerobic aquatic half-life). Additionally, the AGRO-2014 model was highly sensitive to the aerial drift fraction parameter in the dissolved water column. In AGRO-2014, the dissolved water column annual maximum 24-hr EECs were primarily driven by drift events rather than erosion events in which eroded chemical does not release from the incoming sediment into the dissolved water column. Additionally, any pre-existing dissolved chemical quickly adsorbs to the increased presence of eroded sediment entering the water column as suspended sediment.

In the real-world, a wide range of values is possible for many of the input parameters examined here, either due to true site-to-site or compound-to-compound variability of the parameter or due to measurement error. As a result, the uncertainty associated with predicted hypothrin PRZM mass loadings and exposure concentrations in the receiving water bodies may be high. This sensitivity analysis provides the necessary data to permit an evaluation of the impact of key input variables to improve the understanding of the significance of default variable selection and the range of values expected for different regions, crops and scenarios.

Acknowledgments

This work was sponsored by the Pyrethroid Working Group, composed of AMVAC Chemical Corporation, BASF Corporation, Bayer CropScience LP, Cheminova A/S, DuPont Crop Protection, FMC Corporation, Syngenta Crop Protection, Inc., and Valent U.S.A. Corporation.

Additionally, the authors would like to acknowledge Dr. Paul Hendley of Phasera Ltd., who provided valuable ideas and expertise to the undertaking of this project.

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Chapter 13

Application of an Approach for Predicting Pesticide Concentrations in Static Water Bodies Using Spatially Explicit Hydrography, Landscape, and Pesticide Use Data

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The standard regulatory approach for predicting aquatic pesticide Expected Environmental Concentrations (EECs) in an ecological risk assessment is to use the PRZM/EXAMS model to simulate a ten hectare field draining into a one hectare pond. This approach assumes that 100% of the crop area draining into the pond is treated with the pesticide on a soil representative of the geographic region and crop. In reality, the characteristics of pond drainage areas vary widely over the geographic extent of interest for a typical exposure assessment. An approach that accounts for variability in soils, weather, percent cropped area, and pesticide use was developed to predict aquatic pesticide concentrations as part of an endangered species risk assessment. The approach used spatially explicit data and the PRZM/EXAMS model to predict a probability distribution of aquatic EECs reflective of the species habitat area and may be applied in exposure assessments required for other ecological risk assessments.

Introduction

The Pesticide Root Zone Model (PRZM) (*1*) is used by the US Environmental Protection Agency (EPA) to simulate pesticide transport in runoff and eroded sediment from agricultural and residential pesticide applications in their standard tiered environmental risk assessment process. The PRZM model's strength is in the simulation of pesticide fate and transport in homogenous, agricultural systems, for which it has been validated in studies by several authors (*2*, *3*). The EPA has developed many PRZM model standard scenarios designed to represent specific crops in a variety of geographic regions across the United States (*4*) which are used to predict aquatic pesticide concentrations in screening level risk assessments. The PRZM standard crop scenarios are based upon a single representative soil for a given crop linked to the EPA EXAMS standard farm pond. The EPA farm pond standard scenario assumes that 100% of the 10-hectare area draining to the 1-hectare pond is cropped and treated with the pesticide. In addition, spray drift is assumed to contribute pesticide to the farm pond at a constant rate for each pesticide application and assumes that the entire treated area is always directly upwind of the pond. As a screening approach, this represents a worst-case scenario; however, in order to more accurately assess potential pesticide exposure, an analysis more representative of the variability in actual environmental conditions is required to generate more accurate predictions.

There are many environmental conditions that affect potential pesticide exposure in static water bodies due to both runoff and spray drift. Critical factors that can affect runoff contribution to pesticide exposure include soil properties, land slope, weather, land uses (and percent cropped area), percent of area treated with the pesticide, and pesticide application timing. Spray drift contributions to pesticide exposure in static water bodies are impacted by weather conditions (e.g. wind speed and direction, air temperature, relative humidity), spray application technology (nozzles), and the spatial relationship of the treated area relative to the water body. Additionally, the concentrations of pesticide in a static water body will be heavily dependent upon the size of the upland area contributing to the water body (i.e., the watershed area) compared to the geometry of the pond (both surface area and volume). For a given geographical area of interest, (be it an entire country, state, or a species habitat area) simulation of the probability distribution of aquatic pesticide concentrations will be improved as more of the variability in these environmental conditions is accounted for.

An aquatic pesticide exposure assessment pertinent to the California red-legged frog (CRLF) was conducted using an approach for predicting pesticide aquatic exposure that accounts for the variability in several environmental conditions that influence the prediction of pesticide loads in runoff. The environmental conditions accounted for in the approach included soils, slope, weather, percent cropped area, and pesticide use, all of which were quantifiable from readily available datasets. Other factors, such as spray drift contributions to exposure, watershed contributing area, and pond geometry were less readily quantifiable and thus were not included in the approach developed in this study.

The approach developed allows for flexibility in the assumptions related to the extent of pesticide use, and three different assumptions are presented in this study.

The most conservative assumption is that pesticide is applied at the maximum label rate to the entire extent of the potential pesticide use sites. The second assumption is that pesticide is applied at the maximum label rate only to locations where use of the pesticide has been recorded historically in the California Department of Pesticide Regulation (CDPR) Pesticide Use Record (PUR) database (*5*). The final, most realistic assumption accounts for the probability of pesticide use occurring at specific location in any given year based on the historical records contained in the PUR.

The spatial analysis, development of model inputs, and the model simulation process will be presented following a short description of the study area (CRLF habitat) to which the exposure analysis approach was applied. In this example application, the CLRF habitat area serves to constrain the geographical extent of interest, but has no further role in defining the modeling approach. The results and discussion section will compare the probability distributions of pond Expected Environmental Concentrations (EECs) generated based on the different assumptions regarding pesticide use. These EEC distributions will also be compared to the aquatic EEC predicted using a single PRZM/EXAMS standard scenario as part of the screening level risk assessment. The results will demonstrate that the screening level EECs derived from a single model simulation represent a conservative prediction of exposure compared to predictions that include a more complete set of model inputs that account for the range of actual (and more realistic) environmental conditions that affect pesticide exposure in the region of interest.

Materials and Methods

Study Area

This study focused on an aquatic pesticide exposure assessment relevant to the CRLF habitat. The CRLF habitat spans a broad area from northern California (near Mount Shasta) south to an area between Los Angeles and San Diego (*6*). The CRLF habitat area was developed from several different data sources which represent different habitat classifications. These included:

- Known species occurrences from the Multi-Jurisdictional (MJD) Element Occurrence Database (*7*), and the California Natural Diversity Database (CNDDB) (*8*)
- Critical habitat areas from the US Fish and Wildlife Service (US FWS) (*9*)
- Refined currently occupied core areas from the US FWS (*6*). The US FWS core areas were refined using high resolution spatial datasets to remove those areas that did not correspond to the CRLF primary constituent elements.

The extent of the CRLF core areas, critical habitat areas, and CNDDB elemental occurrences are shown in Figure 1 (MJD elemental occurrences are not shown). The base map shown in Figure 1 is the 2012 Cropland Data Layer, which depicts areas of forest, grassland, and shrubland in shades of green, and diverse cropland in a broad range of other colors. There is some overlap in the areas of the different habitat classifications, with a combined area covering approximately 6,108,624 acres. The currently occupied core areas cover 5,430,288 acres, the critical habitat areas cover 1,640,288 acres, and the elemental occurrences cover 533,393 acres. Throughout the remainder of this report, references to the CRLF habitat areas refer to the combined extent of all the habitat designations just described.

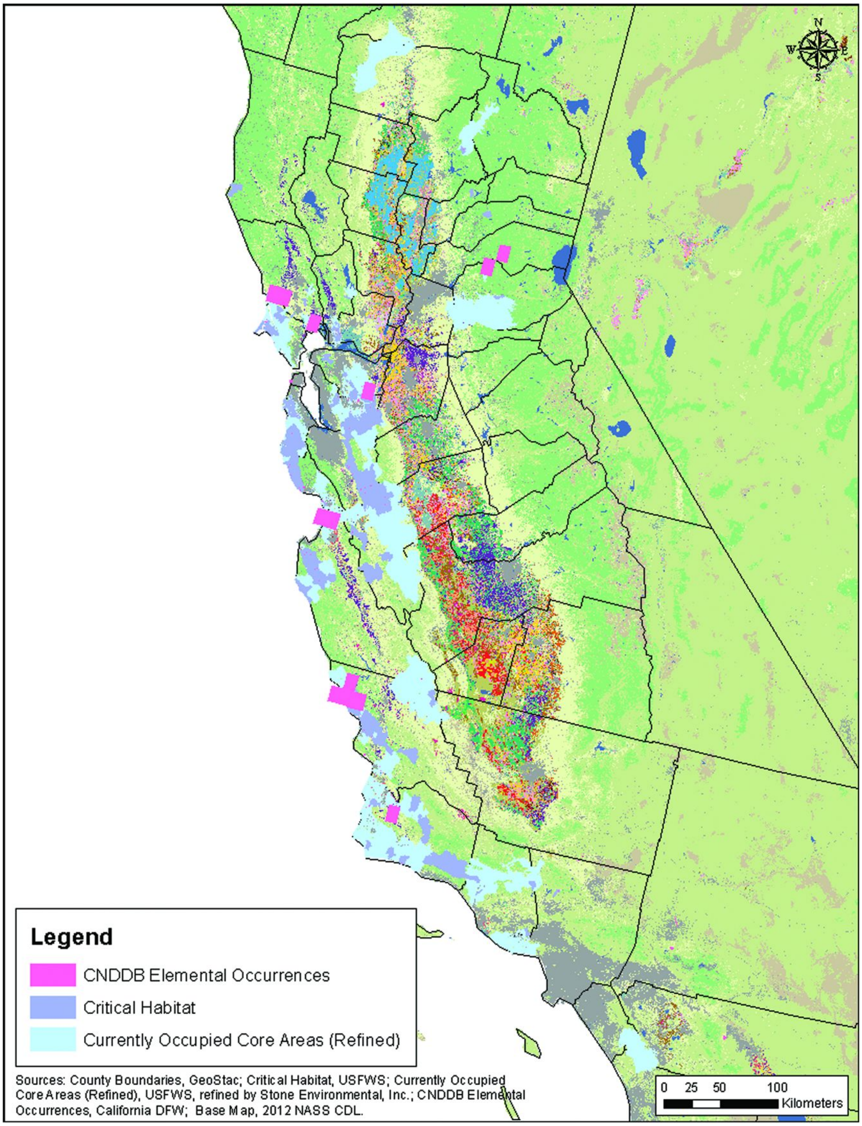

Figure 1. CRLF Habitat Areas. (see color insert)

Development of PRZM Model Inputs for Static Water Body Assessment

Selection of Crop Scenarios

The crops found within CRLF habitat area that are on the current Pesticide-A label included carrots, celeriac, cilantro, leafy petioles (celery, transplanted celery, Chinese celery, Florence fennel, and rhubarb), and parsley. Five crop scenarios were selected for PRMZM/EXAMS simulations and their associated baseline EPA standard scenarios are provided in Table I. For each of these crops, both potential and historical pesticide use site footprints were developed. From these pesticide use footprints, specific ponds and associated environmental conditions within the CRLF habitat area were developed. The development of potential and historical pesticide use site footprints are described in the next sections.

Table I. Crop Scenarios Simulated in PRZM/EXAMS for Actual Pond Analysis

Crop	*Baseline PZRM/EXAMS Scenario*
Carrots	CARowCropRLF_V2
Celeriac	CARowCropRLF_V2
Leafy petioles	CARowCropRLF_V2
Cilantro	CAlettuceSTD
Parsley	CAlettuceSTD

Potential Pesticide Use Sites

Potential pesticide use sites represent locations where, based on the current pesticide label, pesticide applications can potentially occur. This represents a conservative estimate of the actual extent of pesticide use, because in reality a pesticide will only be applied to a fraction of the crop area it is labeled for.

The spatial extent of potential Pesticide-A use sites was characterized for the labeled agricultural uses including carrots, celeriac, cilantro, leafy petioles, and parsley. The approach incorporated comprehensive spatial data including a five-year (2007 – 2011) composite of National Agricultural Statistics Service Cropland Data Layer (NASS CDL) datasets, a five-year (2006 - 2010) composite PUR dataset, the 2006 National Land Cover Dataset (NLCD) (*10*), the 2007 Census of Agriculture (*11*), as well as the USDA NASS Quick Stats from 2008 to 2011 (*12*). The approach also incorporated CDL crop grouping "cross-walks" that have been proposed by EPA (*13*) and recently refined by CropLife America (*14*). These crop groups represent a more generalized set of crops with similar cropping patterns that can account for crop rotations as well as some of the uncertainty inherent in CDL data when specifying potential areas where crops are grown.

The criteria by which a potential use site footprint for each crop was developed were as follows:

- To constrain the footprint of a particular crop to counties where ground-based crop reporting had occurred, a county-level crop dataset was developed for each labeled crop based on the USDA NASS 2007 Census of Agriculture and USDA NASS Quick Stats for 2008 through 2011. Counties with greater than zero (0) acres harvested based on the 2007 Census of Agriculture and 2008 to 2011 Quick Stats were included in the dataset to constrain the analysis. The 2007 Census of Agriculture data are available for most crops. The 2008 to 2011 Quick Stats data are only available for major crops. There are some cases where the 2007 Census of Agriculture was not able to disclose the actual county-level acreage harvested for a given crop, due to the small number of farms reporting the crop. These counties were included in the dataset, even though acreages harvested for the crop are expected to be very low. There are cases where the Census of Agriculture and Quick Stats reported zero (0) acres, but the PUR database reported use on the labeled crop for at least one application from 2006 to 2010 (2010 was the most recent data available at the time of the study). In these cases, the county where the chemical was applied was included in the dataset.
- A five-year composite CDL raster dataset was developed where each pixel (representing a 30 m by 30 m grid cell) preserved the CDL crop class from each year from 2007 to 2011. A pixel in the CDL composite raster was assigned to represent a specific crop class if it was classified as that crop in one or more of the five years. If the crop had an explicit CDL classification, then the five-year composite CDL raster dataset contributed to the potential use site footprint. Table II provides the explicit CDL classifications for labeled crops.
- A five-year CDL (2007-2011) composite for the 'crop group' associated with the specific crop of interest was created (e.g., 'vegetables and ground fruit' crop group). A five-year PUR composite dataset was developed that represents all Public Land Survey System (PLSS) sections where any pesticide record on the specific crop of interest has occurred within the last five years of available data (2006 – 2010). All CDL crop group pixels that fall within PLSS sections that reported use of ANY pesticide on the crop of interest contribute to the crop use site footprint. Table II provides the CDL crop group classifications for labeled crops.
- If selected PLSS sections remained where there are no 'crop group' pixels for the crop of interest, then the NLCD 2006 pixels (cultivated cropland –class 82 in the case of Pesticide-A agricultural uses) were extracted for those PLSS sections and added to the crop use site footprint.
- The resulting potential use footprint was compared with the acreage reported by the 2007 Census of Agriculture. If the potential use raster acreage was less than the 2007 Census of Agriculture reported acreage at the county level, the potential use grid was expanded to adjacent agricultural pixels within the county until the acreage met or exceeded

the 2007 Census of Agriculture reported acreage for the crop. The exception was in cases where there were no reported chemical uses (all chemical applications) on the labeled crop within the county over the five-year period, according to the PUR database, and no CDL pixels from the five-year composite for the explicit crop of interest. In these cases, there are no potential use sites within the county. This expansion of potential use site footprint area was done to ensure a broader (more conservative) extent of potential use consistent with the best available crop survey data (i.e., Census of Agriculture).

Table II. CDL Explicit Class and Crop Group by Labeled Crop

Labelled Crop	*CDL[1] Class*	*Explicit CDL Class Name*	*Crop Group Class*
Carrots	206	Carrots	Vegetables and ground fruit
Okra	N/A[2]	No explicit class	Vegetables and ground fruit
Leafy Petioles (Celery, Transplanted Celery, Chinese celery, Florence fennel, rhubarb)	245	Celery	Vegetables and ground fruit
Celeriac	N/A	No explicit class	Vegetables and ground fruit
Parsley	N/A	No explicit class	Other crops
Cilantro	N/A	No explicit class	Other crops

[1] CDL = Cropland Data Layer. [2] N/A = Not applicable.

The resulting potential use site footprint includes all CDL pixels specific to that crop over the 5 year period (2007-2011), as well as agricultural areas within PLSS sections where any pesticide applications occurred on that crop within the five year period. Figure 2 illustrates the potential use sites for all labeled crops including carrots, celeriac, cilantro, leafy petioles, okra, and parsley. There are two primary areas of overlap of potential use sites and CRLF habitat. These are located in the northern portion of the Salinas valley in Monterey County and the Santa Maria area in Santa Barbara County.

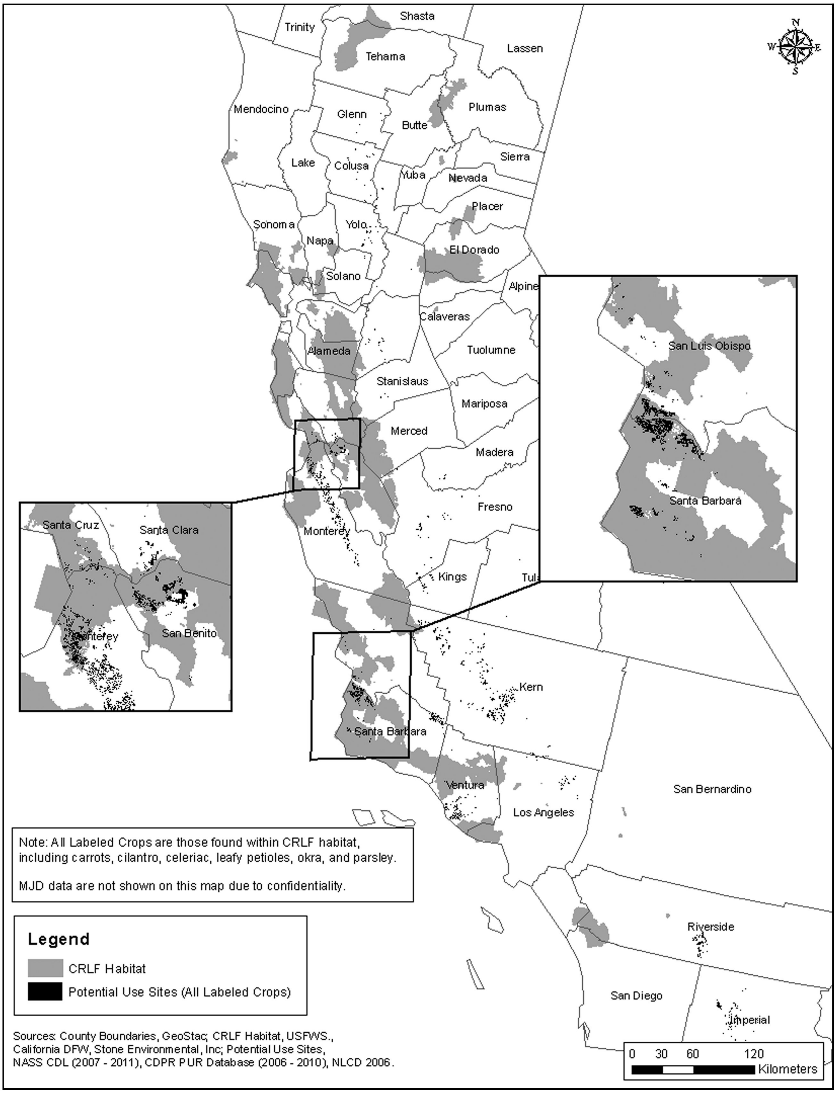

Figure 2. Potential Use Sites for All Pesticide-A Labeled Crops Relative to CRLF Habitat Areas.

Historical Pesticide Use Sites

Historic pesticide use was characterized by evaluating the recorded Pesticide-A use within California for carrots, celeriac, cilantro, leafy petioles, okra, and parsley. PUR records from 2006 to 2010 were extracted and used to identify PLSS sections where Pesticide-A was applied for individual labeled crops and all labeled crops combined in, at least one year between 2006 and 2010. Pesticide use is reported in the CDPR database at the PLSS section level. The database does not provide the information on where the Pesticide-A use took place within a PLSS section. This analysis assumes that use is evenly distributed across potential use site pixels within a PLSS section.

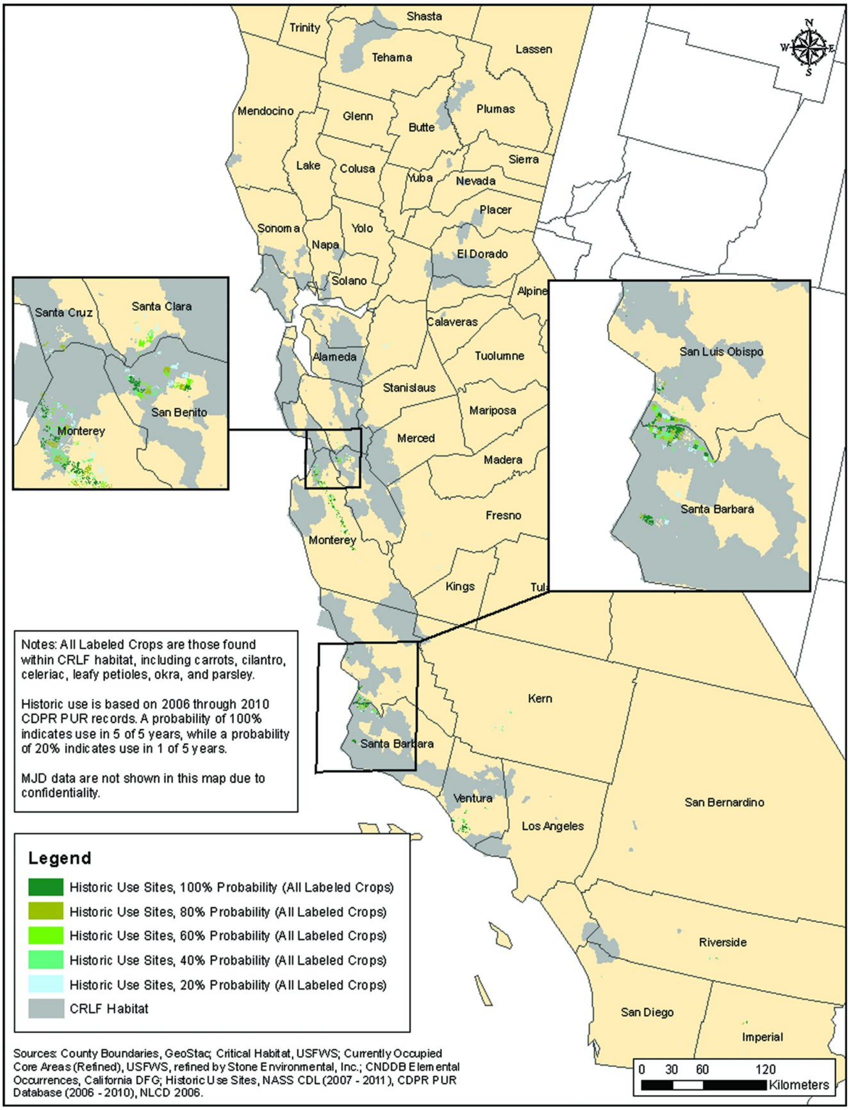

Figure 3. Historical Use Sites for All Pesticide-A Labeled Crops Relative to CRLF Habitat Areas. (see color insert)

The probability of historic use was also determined. For example, if Pesticide-A was applied on carrot sites for 2 out of 5 years in a PLSS section, there is a historic use probability of 40% within that PLSS section. Similarly, a historic use probability of 20% is equivalent to pesticide use in at least 1 of the past 5 years. Figure 3 illustrates the historic use pattern by probability for all labeled crops combined. Historic use sites overlap with CRLF habitat in the northern portion of the Salinas valley in Monterey County and the Santa Maria area in Santa Barbara County for leafy petioles and parsley. Carrots, cilantro, and okra have no Pesticide-A applications within the five-year period evaluated and therefore, do not have a historic use pattern in California. These crop uses were approved in 2011.

Identification of Soil and Weather Inputs

The soils database used to characterize the soils relevant to use of Pesticide-A within the CRLF habitat was the Soil Survey Geographic Database (SSURGO). The SSURGO database (*15*) is the highest resolution (typically 1:24,000 scale) national soils database for the US, with a typical minimum mapping unit size of approximately 1 to 10 acres. Each mapping unit consists of one or more soils, with one to three soils per mapping unit most common. The SSURGO database describes the percent area of the mapping unit that each soil occupies. In addition, each soil description contains information on multiple layers of the soil, including all the soil properties required as input to PRZM. In addition to the specific inputs required by PRZM, the surface soil texture class was also extracted and used to determine the appropriate Pesticide-A application rate for each soil. This was required because the Pesticide-A label specifies different application rates as a function on both soil texture and soil organic matter. The specific criteria used to determine the appropriate use rate for each soil is described in the forthcoming Pesticide Application Inputs section.

The soils associated with Pesticide-A use on the crops of interest were identified by overlaying the potential use site footprints for each crop with the SSURGO soils database soil mapping units. In performing this extraction, the area associated with the overlap of the SSURGO mapping units and the crop potential use sites within CRLF habitat was maintained.

The potential Pesticide-A use sites for all the crops in CRLF habitat areas were clustered in three areas. The Salinas area and the Santa Maria areas had the greatest intensity, followed by a much less significant region near Paso Robles. To cover the weather conditions for these areas, three weather stations having sufficiently complete records to construct 30-year daily time series were identified and downloaded from the National Climatic Data Center (NCDC) Climate Data Online web mapping application (http://www.ncdc.noaa.gov/cdo-web/, accessed 10/6/12). For the three stations selected, Santa Maria Public Airport, Salinas Municipal Airport, and Paso Robles Municipal Airport, spatial extents were drawn to determine which weather stations would be associated with each soil mapping unit. These spatial extents were delineated by hand to ensure the proper weather stations were assigned to different geographic areas with potential Pesticide-A use sites. A map of these three weather station locations is shown in Figure 4 relative to the historical use sites footprint for all crops.

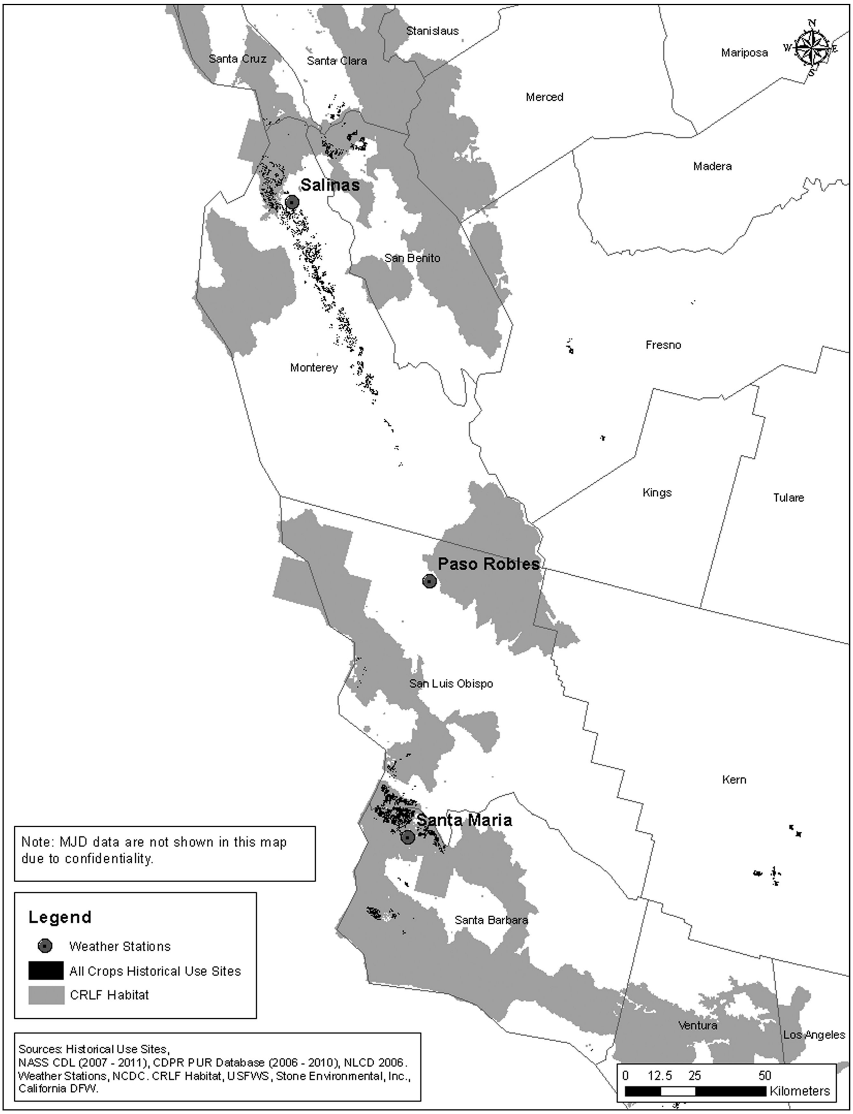

Figure 4. Weather Stations for PRZM/EXAMS Modeling.

Once the SSURGO mapping units associated with each crop were extracted, the specific soils associated with each of those mapping units were evaluated to determine if all the data required for PRZM modeling were available. For a soil to be selected for modeling, all of the required data parameters were required to be complete for all soil layers. Once this was determined, the required attributes associated with each soil were extracted and compiled for input to PRZM/EXAMS simulations.

Pesticide Application Inputs

The application timing of Pesticide-A on the different crops assessed was based on analysis of the PUR from the years 2006 – 2010. The application timing was characterized on a monthly basis in order to calculate the probability of an application occurring in each month. Only Pesticide-A applications occurring within CRLF habitat were considered in the assessment. Of the crops assessed, historical application of Pesticide-A within the CRLF habitat occurred on celery, fennel, and parsley. Therefore, in order to characterize application timing for the other crops (carrots, celeriac, and cilantro), the timing distribution of all the celery, fennel, and parsley combined was used. Table III provides a summary of the application timing distribution for each of the crops within CRLF habitat. As shown in the table, there is a clear peak in application during the summer months for the leafy petioles and a January peak for parsley. Because the majority of applications are on leafy petioles, the application timing distribution for all crops is more heavily weighted towards the leafy petiole pattern.

Table III. Monthly Distribution of Pesticide-A Applications

	Average Fraction of Annual Applications		
Month	***Leafy Petioles***	***Parsley***	***All Crops***
Jan	0.02	0.23	0.03
Feb	0.04	0.11	0.04
Mar	0.08	0.08	0.08
Apr	0.1	0.09	0.1
May	0.12	0.08	0.12
Jun	0.11	0.1	0.11
Jul	0.17	0.06	0.16
Aug	0.19	0.07	0.18
Sept	0.11	0.02	0.11
Oct	0.03	0.05	0.03
Nov	0.02	0.04	0.02
Dec	0.01	0.07	0.02

The historical PUR data suggests that Pesticide-A applications on the crops being assessed can occur throughout the entire year, with a concentration of applications occurring during the dry summer months when runoff potential is low. In order to account for all possible application dates, a PRZM/EXAMS simulation for each soil was made for every day of the year (January 1 through December 31). The monthly application distributions shown in Table III were used to derive application timing probability weights for each application date simulated. By assuming a uniform probability of applications occurring on any day within a given month, the monthly probabilities in Table III were divided by the number of days in the month to arrive at the final application timing weight by day. For example, based on a 10% probability of application in the month of April for leafy petioles (see Table III), the probability of an application on April 1st (or any day in April) is equal 10% / 30-days, which is equal to a probability of 0.33%.

The application rate for Pesticide-A is dependent upon soil texture and organic matter for celery and parsley, with a higher rate for "fine textured, low organic matter soils" and a lower rate for "coarse textured, high organic matter soils". The interpretation of what constitutes a "coarse" versus "fine" soil and "low" or "high" organic matter was required in order to assign appropriate application rates to each soil scenario. The matrix in Table IV provides the logic that was adopted in order to make this determination using best professional judgment.

Table IV. Application Rate Dependencies on Texture and Organic Matter

Texture	*Texture Class*	*Application Rate for OM <= 2%*	*Application Rate for OM > 2%*
Clay	Fine	High	High
Clay loam	Fine	High	High
Silty clay	Fine	High	High
Silty clay loam	Fine	High	High
Silt loam	Medium	Low	High
Sandy clay	Medium	Low	High
Silt	Medium	Low	High
Loam	Medium	Low	High
Sandy clay loam	Medium	Low	High
Sandy loam	Coarse	Low	Low
Loamy sand	Coarse	Low	Low
Sand	Coarse	Low	Low

Identification and Characterization of Actual Ponds in CRLF Habitat

Pond Selection

Static water bodies within the CRLF habitat area were selected from the "NHDWaterbody" feature class from the high resolution National Hydrography Dataset (NHD) for California (*16*). All static water body types were included in the initial selection, including perennial and intermittent ponds, swamps/marshes, and reservoirs. For convenience, the term "pond" or "static water body" is used to represent any of the water body types evaluated. The water bodies selected were then filtered by size. Because the objective was to identify static water bodies that were analogous to the EXAMS standard farm pond, the size constraint was set to be within one order of magnitude smaller or larger than the 1 hectare farm pond. Therefore, water bodies between 0.1 ha and 10 ha were selected. After applying the size filter, a total of 5,090 static water bodies were identified within CRLF habitat areas.

A significant number of these 5,090 ponds are located in non-agricultural areas, far away from potential Pesticide-A use sites. For this assessment, it was assumed that static water bodies with no potential Pesticide-A use sites within their "watershed" will have Pesticide-A EECs of 0 μg/L, with further analysis focused on ponds draining from potential Pesticide-A use areas. Because the goal of this assessment was to predict static water body EECs analogous to the standard farm pond (but accounting for soils and cropped areas around actual ponds), a simplified assumption regarding pond watershed area was developed based upon the watershed area for the standard farm pond. This assumption was that a pond's watershed boundary, regardless of pond size, was represented by a 178.4 meter perimeter around the pond. The 178.4 meter distance represents the radius of a circle with an area of 10 hectares (the watershed area for the EPA standard pond scenario). If a pond were a single point in space, then this 178.4-meter distance/radius around it would result in a 10-ha watershed. The ponds identified for evaluation in this exercise ranged in size from 0.1 to 10 hectares, which results in watershed areas (excluding the pond area) of greater than 10 hectares. It should be noted that although the watershed area used to characterize the soils and crops varied for each pond, it was the fractional area of the soils/crops for the watershed that was ultimately used as an adjustment factor to the pond EECs resulting from PRZM/EXAMS simulations. Therefore, the ratio of standard farm pond drainage area to pond area in the simulations remained 10:1. An example of a pond and its 178.4 meter perimeter watershed boundary is shown in Figure 5.

Of the 5,090 ponds initially identified within the CRLF habitat, a subset of those that were within 178.4 m watershed boundary perimeter of Pesticide-A potential use sites was selected. While the high resolution NHD dataset represents the best available spatial dataset of static water bodies, there are some errors in the data, namely depictions of water bodies that no longer exist. To address this issue, each of the ponds identified from the NHD were compared with the latest Bing Maps aerial imagery from Esri's ArcGIS (*17*). Upon comparison with Bing Maps imagery, if an NHD water body was determined to be clearly not a pond, or a swamp, or a marsh, or seasonal pool, then it was removed from the analysis. In cases where judgement of the NHD feature of a water body was uncertain, the NHD feature was kept as a water body in the analysis. In total, 251 NHD water body features whose watersheds contained Pesticide-A potential use sites were determined to meet the selection criteria and were included in the analysis.

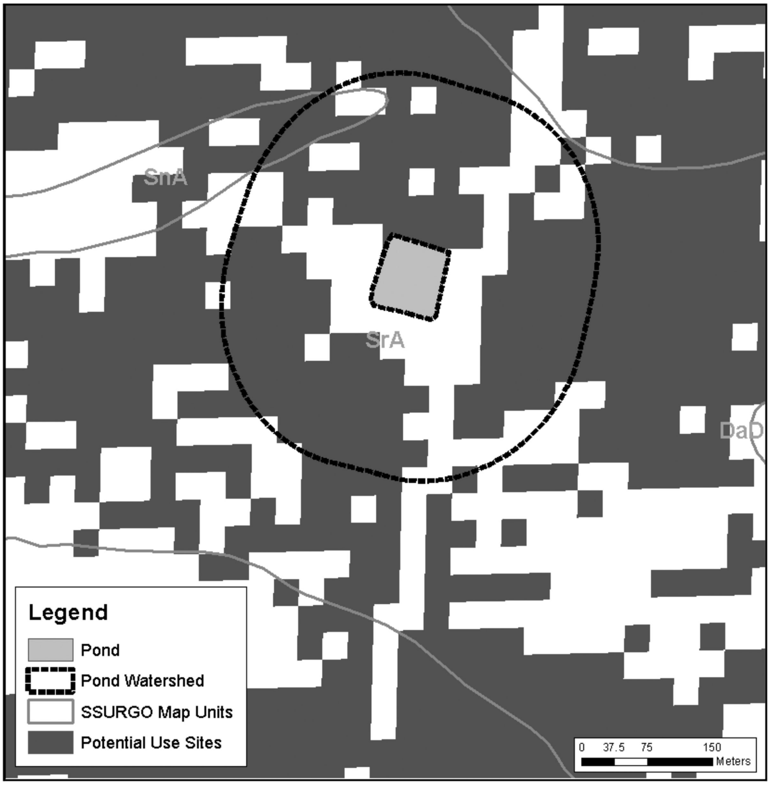

Figure 5. Example Pond, Pond Watershed, and Overlay with Soils and Potential Use Sites.

Pond Characterization

Watersheds for each pond were assumed to be the area within a 178.4 meter perimeter around the pond. The pond watersheds were then intersected with the SSURGO soils, the potential Pesticide-A use site footprints for each crop, and the historical Pesticide-A use site footprints for each crop. This spatial analysis resulted in a database that contained the fraction of every pond's watershed occupied by each soil and Pesticide-A use site crop. With PRZM/EXAMS simulations completed for each of these soil and crop combinations, EECs for each of the ponds could now be calculated based on the proportion the watershed receiving Pesticide-A applications, and the relative areas of the different soil types. A summary of the characteristics of the ponds evaluated in this analysis is provided in Table V. In addition, a cumulative distribution of pond watershed PCA for all crops lumped together is provided in Figure 6. Table V shows that there are a total of 251 static water bodies (ponds) with Pesticide-A use crops covering greater than 0% of the area within their 178.4 m perimeter (the assumed watershed area). These 251 ponds represent approximately 5% of the 5,090 static water bodies in the CRLF habitat with surface areas between 0.1 and 10 hectares. In addition, celery is by far the dominant crop. The median size of all the ponds evaluated is 0.37 ha, while the median watershed area of all the ponds is 14.63 ha. The PCAs for the ponds evaluated vary widely, as shown in Table V by the difference between the median and maximum PCAs for all ponds (12.07% and 98.2%, respectively) and illustrated in the cumulative distribution plot in Figure 6. The pond watershed PCA is one of the important factors in the calculation of ponds EECs, and based upon the wide range in PCAs observed in the CRLF habitat, the ranges in EECs can be expected to be broad as well.

Table V. Summary of Pond Characteristics

Crop	*Number of Ponds with PCA[1] > 0*	*Percent of All 5,090 Ponds in Habitat*	*Median Pond Size (ha)*	*Median Watershed Size (ha)*	*Median Watershed PCA (%)*	*Max Watershed PCA (%)*
Carrots	32	0.63	0.38	14.7	5.03	30.4
Celeriac	2	0.04	1.85	20.29	14.83	17
Celery	206	4.05	0.38	14.84	16.84	98.2
Cilantro	65	1.28	0.25	14.21	2.97	29.5
Parsley	44	0.86	0.34	14.94	2.48	22.71
All Crops	251	4.93	0.37	14.63	12.07	98.2

[1] Percent Cropped Area (PCA) based on a pond watershed represented by a 178.4 meter perimeter around the pond.

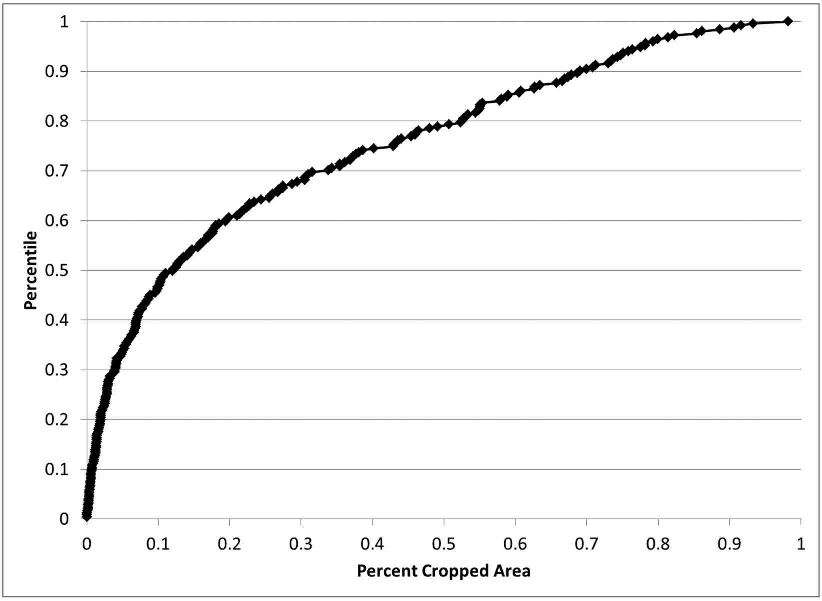

Figure 6. Cumulative Distribution of Pond Watershed Percent Cropped Area for 251 Ponds Assessed within CRLF Habitat.

Model Simulation and Data Post-Processing

Prediction of Standard Farm Pond EECs by Soil

The PRZM/EXAMS simulations for all the soil scenarios within the CRLF habitat were executed in batches associated with each crop. For each soil type, separate simulations for each possible Pesticide-A application date were run. Based on the application date data in the PUR, there were a total of 365 potential application dates for each crop. Carrots were an exception, because the carrot use pattern allows for 2 applications 14 days apart, so the latest date in the year for the 1st of two applications was December 17th, resulting in a total of 351 possible application dates. Once all simulations were completed, the maximum EECs of each exposure duration (e.g. peak, 21-day, 60-day) for each year of every simulated application date were compiled. The number of annual maximum EECs for each crop was then equal to the number of soil types multiplied by the number of application dates multiplied by 30 years.

The cumulative distributions of EECs for each exposure duration were calculated independently for each soil. These were determined by first sorting all the years of annual maximum EECs from each of the simulations (30 years per simulation, 365 application dates, resulting in 10,950 annual maximum EECs per soil) and then calculating a running summation of the application date weights associated with each simulation result. Application dates weights were calculated for each date based on the probability that an application would occur in that month (equal to the probability on an application during the month divided by the number of days in the month, which assumes equal probabilities for days within a given month). The percentile of each simulated annual maximum EECs was then calculated as the running summation of the simulation weights divided by the total sum of all the simulation weights. An example of this calculation is shown in Table VI below. For simplicity, this example assumes only five different application dates and two years of simulation. The table is sorted from lowest to highest EEC for each simulation year. The application date probabilities range from a high 0.3 for August 10th to a low of 0.1 for March 20th. Since there were only 2 years in each simulation in this example, the simulation year probability is 0.5. The total probability is equal to the product of the application date probability and the simulation year probability. Finally, the cumulative percentile is determined for each EEC value by summing the total probabilities. In this example, the 90th percentile annual maximum peak EEC is equal to 10.1 µg/L.

Table VI. Calculation of EEC Cumulative Distribution for a Single Soil/Weather Condition

Year	*App. Date*	*Annual Max Peak EEC[1] (µg/L)*	*Application Date Prob.[2]*	*Sim. Year Prob.*	*Total Prob.*	*Cumulative Percentile*
1960	15-Jul	1	0.2	0.5	0.1	0.1
1961	10-Aug	2	0.3	0.5	0.15	0.25
1960	10-Aug	3.5	0.3	0.5	0.15	0.4
1961	15-Jul	5.5	0.2	0.5	0.1	0.5
1961	1-May	6.7	0.2	0.5	0.1	0.6
1961	10-Apr	7.9	0.2	0.5	0.1	0.7
1960	10-Apr	8.7	0.2	0.5	0.1	0.8
1960	1-May	10.1	0.2	0.5	0.1	0.9
1960	20-Mar	12.1	0.1	0.5	0.05	0.95
1961	20-Mar	14.3	0.1	0.5	0.05	1

[1] EEC = Expected Environmental Concentrations [2] Prob. = Probability

Prediction of Actual Pond EECs

Aquatic EECs were simulated for each of the static water bodies identified within the CRLF habitat and falling within a size range of 0.1 to 10 hectares. Only those water bodies with potential Pesticide-A use sites within 178.4 meters of the water bodies were included in the assessment, as described above. These EECs were derived from PRZM/EXAMS standard farm pond simulations for the specific soils and associated weather conditions found in the watersheds of each of the ponds assessed. The calculation of EECs for each of the ponds required the following assumptions:

1. Each pond has the same geometry and hydrology as the standard farm pond. In other words, a pond with 1 hectare surface area that is 2 meters deep with static hydrology (no inflows or outflows).
2. The non-use site portions of the pond watershed contribute zero Pesticide-A load to the pond. This is equivalent to an actual percent cropped area (PCA) for the pond derived from the potential use site footprint.
3. The EEC associated with each soil and potential crop use site is taken to be the 90th percentile of the annual maximum EECs derived from the cumulative distribution for the crop/soil scenario.

The EECs for each pond were calculated based on both the potential and historical use site footprints for each crop. The derivation of the potential and historical use site footprints was discussed previously. The EEC associated with a single pond is calculated as the area weighted average of the PRZM/EXAMS EECs associated with the crop/soils within the pond watershed. The pond EECs based on the historical use site footprint were calculated using two different sets of assumptions. The first set of assumptions was that all areas having received Pesticide-A applications in at least one of the last five years were treated with Pesticide-A and that in areas of the pond watershed where the historical use sites for multiple crops co-occur (e.g., celery and parsley), the highest EEC of the multiple crops is assumed to represent the contributions from that section of the watershed. These assumptions are analogous to how the pond EECs based on potential use sites were calculated (i.e., the more expansive potential use site footprint defines the PCA). An example calculation of pond EECs based on these assumptions is shown in Table VII below. In this example, there are four soils with historical Pesticide-A use sites, four of which are associated with celery and three of which are associated with parsley. These areas account for 45% of the pond watershed, with the other 55 % of the watershed composed of land uses or crops that are not potential Pesticide-A use sites. For each soil, the maximum EEC from the crops associated with that area is taken to represent the soil. In the case of soil 1, it is the 20 μg/L EEC associated with the celery use pattern. To determine the EEC for the pond, the EEC for each soil is multiplied by the soil area fraction and then summed for all the soils within that pond watershed. In the case of this example pond, the resulting EEC is 9.6 μg/L. Note, that if the PCA for this watershed were 100% and the relative proportions of the 4 soils were the same, then the pond EEC would be 21.33 μg/L (calculated as 9.6 μg/L/ 0.45). In the context of historical use site analysis, this approach for calculating pond EECs will be referred to as the "un-weighted" approach, and is more conservative in that it assumes that all historical use sites are treated each year, even if the historical data suggests that applications occur in only a fraction of all years. Note that EECs based on potential use sites will be the most conservative in that this assumes that all potential use sites receive applications of Pesticide-A on the same day.

Table VII. Calculation of Pond EECs, Potential Use Site Assumptions

Soil	*Fraction of Watershed Area*	*Celery EEC (µg/L)[1]*	*Parsley EEC (µg/L)[1]*	*Max EEC (µg/L)*	*EEC Contribution to Pond (µg/L)*
1	0.15	20	18	20	3
2	0.05	35	37	37	1.85
3	0.1	25	22	25	2.5
4	0.15	15	0	15	2.25
Pond Total	0.45				**9.6**

[1] 90th percentile annual maximum Expected Environmental Concentrations (EECs)

The second set of assumptions used in the historical use sites pond EEC calculations adjusts the Pesticide-A contribution from a given area based on the probability of a Pesticide-A application for that area in any given year (ranging from 0.2 for areas that received Pesticide-A 1 of the past 5 years to 1.0 for areas receiving Pesticide-A in 5 of the past 5 years). An example calculation of a pond EEC based on the probability-weighted historical use pattern is shown in Table VIII below. The probability of use ranges from 0.4 to 0.8 for celery and from 0 to 0.8 for parsley. For each soil and crop, the probability weighted EEC is calculated by multiplying the EEC value by the use probability. Then, the EEC assigned to the soil area is the maximum value of the crops on that soil area. In the case of soil 1, this maximum value comes from the parsley use pattern with an EEC of 18 and a probability of 0.8 resulting in an EEC of 14.4 µg/L. The soil fraction of the watershed area is multiplied by the maximum EEC to obtain the EEC contribution to the pond, and then summed for all soils around the pond. In this example, this results in a pond EEC of 6.46 µg/L. This approach for calculating pond EECs will be referred to as the "probability-weighted" approach, and is most representative of actual Pesticide-A use practices around the ponds, and thus represents the "best available data." It represents exposure potential based on a range of actual observations of Pesticide-A use over a multi-year period, rather than hypothetical maximum potential use that has never been observed

Table VIII. Calculation of Pond EECs, Historical Use Site Assumptions

Soil	*Fraction of Watershed Area[1]*	*Celery EEC (μg/L)[2]*	*Celery Use Prob.[3]*	*Parsley EEC (μg/L)[2]*	*Parsley Use Prob.[3]*	*Max EEC (μg/L)*	*EEC Contrib.[4] to Pond (μg/L)*
1	0.15	20	0.4	18	0.8	14.4	2.16
2	0.05	35	0.8	37	0.4	28	1.4
3	0.1	25	0.8	22	0.4	20	2
4	0.15	15	0.4	0	0	6	0.9
Pond Total	0.45						6.46

[1] Fraction of watershed area with historical use on soil in at least one of 5 years. [2] 90th percentile annual maximum Expected Environmental Concentrations (EECs). [3] Prob. - Probability. [4] Contrib. - Contribution.

Results and Discussion

The 90th percentile annual peak EECs were calculated for the 251 ponds based on the three different pesticide use assumptions:

1. Potential Use Sites: Pesticide is applied at the maximum label rate to the entire extent of potential pesticide use sites (defined as the crop footprint extent of all labelled crops).
2. Historical Use Sites: Pesticide is applied at the maximum label rate to all potential use sites where the pesticide has been applied historically (as recorded in the PUR database).
3. Probability-Weighted, Historical Use Sites: Pesticide is applied at the maximum label rate to historical use sites, weighted by the probability of use in a given year derived from historical records in the PUR database.

Table IX summarizes how the pond 90th percentile annual peak EECs calculated for the population of actual ponds and the three different pesticide use assumptions compare to the highest 90th percentile annual peak EEC from a single PRZM/EXAMS standard scenario simulation. The single PRZM/EXAMS scenario used for comparison was the US EPA's CRLF Row Crops standard scenario using local weather data from 1981 – 2010 and a pesticide use pattern for carrots. This standard scenario resulted in the highest EEC value (49.17 μg/L) in the screening level exposure assessment. Based on the most conservative potential use sites assumptions, only 10 ponds (99.8% of the ponds within CRLF habitat) had 90th percentile annual peak EECs higher than the carrot scenario. When pesticide use is assumed to occur on all historical use sites, only 1 pond out of the population assessed had EECs higher than the carrot scenario. Finally, based on the more realistic probability-weighted historical use site assumptions, 100% of the EECs calculated for the actual ponds were lower than the carrot scenario.

Figure 7 provides plots of the cumulative distributions of pond 90th percentile annual peak EECs for the 251 ponds with PCA > 0% based on the three different pesticide use assumptions. Based on the most conservative assumption of pesticide applications to all potential use sites, more than 50% of the ponds have EECs below 10 µg/L, a substantially lower concentration than the single PRZM/EXAMS carrot scenario (49.17 µg/L). This shows that even with a worst case assumption for pesticide use (all labeled crops received pesticide), accounting for the variability in soils, slopes, weather, and land use results in substantially lower EECs compared to the highest 90th percentile annual peak EEC from the PRZM/EXAMS standard scenario simulations. When the assumptions regarding pesticide use extent are constrained to more realistic values based on the total historical use extent, the magnitude of the predicted EECs drops so that approximately 75% of the ponds have EECs below 10 µg/L. Finally, based on the most realistic set of pesticide us assumptions, (the probability-weighted historical use sites) approximately 90% of ponds have 90th percentile annual maximum EECs of 10 µg/L or less, with a median pond EEC of approximately 0.4 µg/L. In reviewing the shapes of the probability distributions in Figure 7, the most substantial change occurs between the potential use sites assumption and the historical use sites assumption. This demonstrates the importance of incorporating data on actual pesticide use into exposure assessments, as assessments that assume 100% of a crop is treated can often be unrepresentative of actual conditions for many pesticides.

Table IX. Actual Pond EECs Compared to Standard Scenario EEC

Pesticide Use Site Assumption[1]	***Number of Ponds Above Highest P/E[2] Standard Scenario EEC[3],[4]***	***Percent of All Ponds[5] Below Highest P/E[2] Standard Scenario EEC[3] (%)***	***Percent of Ponds with Potential Use[6] Below Highest P/E[2] Standard Scenario EEC[3] (%)***
Potential Use Sites	10	99.8	96.02
Historical Use Sites, Un-Weighted	1	99.98	99.6
Historical Use Sites, Probability Weighted	0	100	100

[1] "Un-Weighted" assumes all historical use sites from 2006 - 2010 receive pesticide applications; "Probability Weighted" weights the EECs by the likelihood of application in a single year. For example, a use site with a 60% probability of use would have a 60% likelihood of contributing pesticide to the pond in a given year. [2] P/E = PRZM-EXAMS. [3] EEC = Expected Environmental Concentration. [4] The highest 90th percentile peak EEC from P/E standard scenario was carrot with 49.17 µg/L. [5] Include all (5,090) ponds with an area of between 0.1 ha and 10 ha within CRLF habitat areas. [6] Includes all (251) ponds with an area of between 0.1 ha and 10 ha within CRLF habitat areas, that have potential pesticide use sites within 178.4 m.

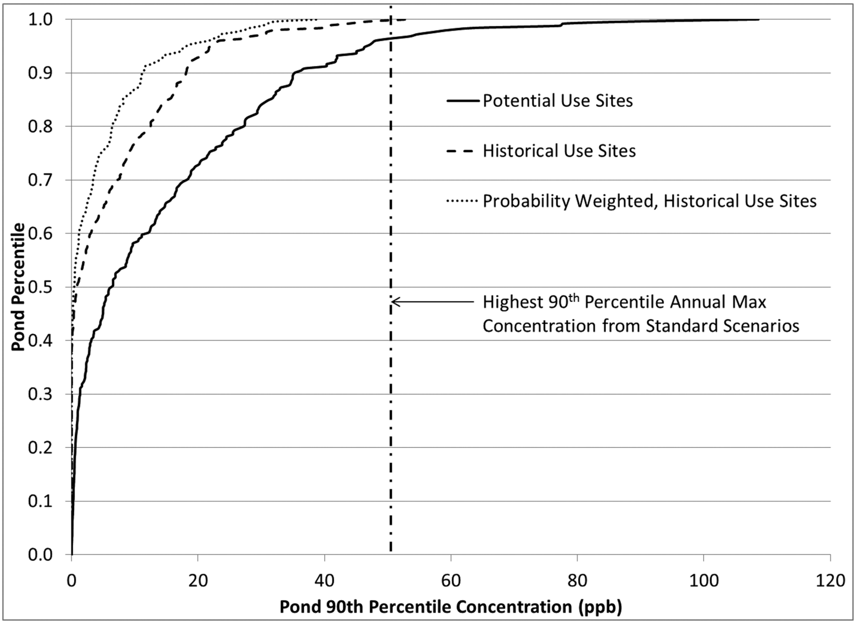

Figure 7. Cumulative Distribution of Pond 90th Percentile Annual Peak Concentrations Based on Different Pesticide Use Assumptions (Ponds with > 0% Percent Cropped Area).

This assessment of actual ponds has taken PRZM/EXAMS simulated EECs for the standard farm pond and refined the 90th percentile EEC values to account for the variability of soil characteristics, weather, and percent cropped areas within approximated pond watersheds. In addition, historical use of Pesticide-A was included as a component of the assessment to provide an indication of the most likely EECs given the recent actual use pattern of the pesticide. Several important conclusions can be made from this assessment:

- The vast majority of static water bodies within the CRLF habitat are not within close proximity (178.4 meters) of potential Pesticide-A use sites. For the size of ponds assessed (0.1 to 10 ha), only 251 ponds out of the 5,090 (4.9%) had any potential Pesticide-A use within their assumed watershed, with only 156 ponds (3.1%) having any historical Pesticide-A use.
- Based on the most conservative assumption that all potential Pesticide-A use sites receive applications on the same date, 99.8% of all ponds in CRLF habitat have EECs below the highest EECs from the PRZM/EXAMS standard scenario (49.17 µg/L for carrot).
- Based on the most realistic assumptions of actual PCA, soils, and historical use, 100% of ponds had annual peak EECs lower than the highest annual peak simulated from the standard PRZM/EXAMS simulations (49.17 µg/L for carrot). It must also be emphasized that even these most realistic assumptions maintain conservatism that make

the EECs higher than would likely occur. One of these assumptions is that for a given crop, the application date is the same for all fields surrounding the pond. In many cases, more than one field of a given crop may be located within the pond watershed, and applications to all fields on the same day may not occur. In addition, for ponds with multiple crops, it is assumed that the 90th percentile annual maximum EEC occurs on the same date for all crops within the pond watershed. In actuality, due to differences of application dates, the date in which the annual maximum EEC occurs will be different.

The results of this static water body assessment are applicable to static water bodies with geometric and hydrologic characteristics similar to the standard farm pond. The Pesticide-A loadings are representative of the soils and actual percent cropped areas and historical use for ponds of between 0.1 and 10 hectares found within the CRLF habitat. The results from this analysis would not necessarily be representative of either smaller or larger static water bodies, or of ponds with a drainage area to pond area ratio substantially different than the 10:1 ratio assumed here.

Conclusions

A method for refining screening level aquatic exposure estimates was developed which accounts for the variability in climate and landscape conditions relevant to CRLF aquatic habitats of interest. The method uses readily available spatial datasets and a straightforward approach for calculating EECs by area weighting contributions from different crop and soil conditions. The approach can be applied based on more conservative assumptions of pesticide applications to potential use sites, or on more realistic applications to historical use sites. Conservatism built into the method includes assumptions that, 1.) All areas of a given crop receive pesticide on the same day, 2.) Annual maximum EECs for different crops occur on the same date, and 3.) For landscape areas with multiple crops, EECs associated with the most vulnerable crop are assumed. The resulting exposure probabilities better reflect the variability of environmental conditions that affect aquatic pesticide exposure. In the future, the approach presented in this study may be extended by consideration of additional factors that impact pesticide exposure in static water bodies, such as spray drift variability, water body contributing area size, and pond geometry.

Acknowledgments

This work was sponsored by Syngenta Crop Protection. The authors would like to acknowledge Dr. Russell Underwood and Dr. Dan Campbell of Syngenta Crop Protection and Scott Teed of Intrinsik Environmental Sciences who provided valuable ideas and expertise throughout this project.

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