ACS SYMPOSIUM SERIES 1075

Pesticide Mitigation Strategies for Surface Water Quality

EDITED BY
Kean S. Goh, Brian L. Bret,
Thomas L. Potter, and Jay Gan

Pesticide Mitigation Strategies for Surface Water Quality

ACS SYMPOSIUM SERIES **1075**

Pesticide Mitigation Strategies for Surface Water Quality

Kean S. Goh, Editor
California Department of Pesticide Regulation

Brian L. Bret, Editor
Dow AgroSciences LLC

Thomas L. Potter, Editor
USDA-Agricultural Research Service

Jay Gan, Editor
UC Riverside

Sponsored by the
ACS Division of Agrochemicals

American Chemical Society, Washington, DC

Distributed in print by Oxford University Press, Inc.

Library of Congress Cataloging-in-Publication Data

Pesticide mitigation strategies for surface water quality / Kean S. Goh ... [et al.], editors ; sponsored by the ACS Division of Agrochemicals.
p. cm. -- (ACS symposium series ; 1075)
Includes bibliographical references and index.
ISBN 978-0-8412-2656-2
1. Pesticides--Environmental aspects--California--San Joaquin River Watershed. 2. Pesticides--Risk mitigation--California--San Joaquin River Watershed. 3. Agricultural pollution--California--San Joaquin River Watershed. 4. Water quality--California--San Joaquin River Watershed. 5. San Joaquin River Watershed (Calif.) I. Goh, Kean S. II. American Chemical Society. Division of Agrochemicals.
TD1066.P47P47 2011
628.5'29097948--dc23
2011036010

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, Inc.

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

This book compiles chapters developed from presentations at two symposia that addressed urban and agricultural pesticide uses and mitigation measures to prevent pesticide runoff and surface water contamination. The symposia were held at the 239th ACS International Meeting in the spring of 2010 in San Francisco with collaborative organizational efforts and presentations from industry, academia, government research organizations, and regulatory agencies. Selected chapters were also invited outside the symposia to more comprehensively cover the topic.

Pesticides are critical components of pest management programs that sustain food and fiber production and protect public health, homes and property. However, they are among the many non-point source pollutants that threaten surface water quality. Pesticide residues are being increasingly detected in surface water in agricultural and urban areas. In some cases water bodies are being listed under the Clean Water Act 303(d) as impaired and Total Maximum Daily Loads are required to address the impairments. Pesticides in surface waters are associated with runoff from irrigation and storm events and drift during application. Various pesticide classes have been detected including pyrethroid, organophosphate, and carbamate insecticides; acetanilide, triazine, urea, and phenoxy herbicides; and strobilurin fungicides. Although presence of pesticides in surface water does not mean toxicity or impairment, in many cases pesticides have been, and continue to be, detected at concentrations that do cause toxicity to aquatic invertebrates such as the daphnids, *Hyalella azteca*, and copepods. Thus, there are efforts by regulatory agencies, registrants, researchers, and end users to work together to understand the source and effects of such contaminations and to develop mitigation strategies.

To communicate the latest information on pesticide runoff, mitigation practices, and their effectiveness, we compiled this volume. Information presented covers fate and transport of pesticides leading to their runoff, modeling of various runoff and mitigation scenarios, and successes and challenges of mitigation tactics.

The first section of the book focuses on mitigation measures. Chapters describe field research conducted on vegetated ditches and buffer strips, constructed wetlands, settlement ponds, use of enzymes to degrade pesticides, application methods, and grower outreach. The second section focuses on modeling efforts in field crops, rice paddies, and urban turf testing various mitigation measures or comparing different models. The final section discusses some of the more problematic issues and challenges to implementing mitigation practices. It is the editors' expectation that the chapters included in this book will prove useful to both academics and practitioners, stimulate further research where

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

needed, and encourage development and implementation of mitigation measures resulting in improvements in surface water quality.

Kean S. Goh, PhD

California Department of Pesticide Regulation
1001 I Street
Sacramento, CA 95812
kgoh@cdpr.ca.gov (e-mail)

Brian L. Bret, PhD

Dow AgroSciences LLC
909 Thoreau Court
Roseville, CA 95747
blbret@dow.com (e-mail)

Jay Gan, PhD

Department of Environmental Sciences
University of California
Riverside, CA 92521
jgan@ucr.edu (e-mail)

Thomas L. Potter, PhD

USDA-Agricultural Research Service
Southeast Watershed Research Laboratory
P.O. Box 748
Tifton, GA 31793
tom.potter@ars.usda.gov (e-mail)

Chapter 1

Improving Surface Water Quality Through Grower-Led Coalition Program Using GIS Mapping and Grower Visits

Parry Klassen[1,*] and Michael L. Johnson, PhD[2]

[1]Executive Director, East San Joaquin Water Quality Coalition, 1201 L Street, Modesto, CA 95354
[2]President, Michael L. Johnson, LLC, 632 Cantrill Dr., Davis, CA 95618
[*]pklassen@unwiredbb.com

Surface water quality in the San Joaquin River watershed in the Central Valley of California is impacted by multiple stressors. To address water quality issues attributed to agricultural activities, the Central Valley Regional Water Quality Control (Water Board) enacted a regulatory program called the Irrigated Lands Regulatory Program (ILRP). The ILRP requires agricultural dischargers to identify if wastewater discharges are impacting downstream beneficial uses and impairing water quality. To comply with the requirement of the ILRP, agricultural interests in five northern San Joaquin Valley counties formed the East San Joaquin Water Quality Coalition (ESJWQC or Coalition). Coalition membership in 2010 stood at more than 2,400 landowners/operators responsible for over 559,000 irrigated acres on over 9,000 parcels. In 2004, the Coalition put in place a surface water monitoring program to determine compliance with state water quality criteria protective of beneficial uses. As a result of finding numerous exceedances of criteria, the Coalition developed in 2007 its initial Management Plan to address exceedances of those criteria. A modified approach was implemented in 2009 that targeted high risk lands identified through GIS mapping of pesticide use, downstream exceedances, cropping patterns, and proximity to water. The development of a grower-led program to monitor water quality, develop and implement

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

management plans and use of a targeted approach for selecting and implementing Best Management Practices resulted in improvements in water quality.

Background

Surface water quality in the San Joaquin River watershed in the Central Valley of California is impacted by multiple stressors (*1*) including discharges from irrigated agriculture. To address water quality issues attributed to agricultural activities, the Central Valley Regional Water Quality Control (Water Board) in 2003 adopted the Irrigated Lands Regulatory Program (ILRP) (*2*). This program imposes limits on agricultural discharges to waters of the state and requires monitoring and reporting to confirm that agriculture is in compliance with Porter-Cologne, the State of California's equivalent to the US Clean Water Act. To comply with the ILRP, landowners engaged in irrigated agriculture can seek coverage as an individual discharger or join a water quality coalition which represents growers to the Water Board. Coverage as an individual discharger is expensive and time consuming and the preferred method of compliance is as a member of a coalition of growers. Seven geographically-based coalitions currently operate in the Central Valley. The ILRP requires each coalition to operate a surface water monitoring and reporting program to determine if surface waters of the state are being degraded as a result of discharges from irrigated agriculture. If a coalition determines that any water quality objective is not being met, it must be reported to the Water Board within five days and later summarized in a yearly monitoring report. In addition, the coalitions are required to follow up with notification to growers regarding water quality issues and in some cases develop a management plan to specify all additional actions to reduce the impact of agricultural discharge on downstream water quality.

In the southern San Joaquin Valley, landowners and agricultural interests formed the East San Joaquin Water Quality Coalition (ESJWQC or Coalition) (*3*). The Coalition region encompasses irrigated lands east of the San Joaquin River within Madera, Merced, Stanislaus, Tuolumne, and Mariposa Counties and portions of Calaveras County. The Coalition currently includes more than 2,400 landowners/operators responsible for over 559,000 irrigated acres. To finance the monitoring and reporting program and pay mandatory state fees, members pay a nominal flat fee per farm plus an additional fee per acre for every parcel included in the program. Coalition monitoring and reporting activities include:

1. Monitoring to characterize agricultural discharge.
2. Evaluating water quality monitoring data against numerical values protective of downstream beneficial uses.
3. Reporting to the Water Board and coalition members the status of water quality and possible sources of beneficial use impairments.
4. Surveying and evaluating current management practices implemented by growers and track the implementation of new practices.

This paper describes the process employed by the ESJWQC to evaluate potential sources of water quality exceedances and work with members to improve water quality by various Best Management Practices. This paper describes early efforts which were only marginally effective in improving water quality in comparison to recent efforts which have resulted in reducing or eliminating water quality problems in targeted Coalition waterways.

Monitoring Program 2004 - 2008

Since 2004, the ESJWQC has monitored over 35 locations on 23 different waterways for numerous pesticides, nutrients, physical parameters such as salt / electrical conductivity, metals, fecal indicator bacteria, water column toxicity to algae, an invertebrate, and a fish, sediment toxicity, and field parameters such as temperature and dissolved oxygen. Water samples are collected monthly and all analyses are performed according to US EPA approved methods by National Environmental Laboratory Accreditation Program (NELAP) certified laboratories. The Quality Assurance-Quality Control Program conforms to EPA guidelines (e.g., "Laboratory Documentation Requirements for Data Validation", January 1990, USEPA Region 9) or to procedures approved by the Water Board (*4*).

Results are evaluated against water quality trigger limits to determine if there are impairments to downstream beneficial uses. Trigger limits are a combination of promulgated water quality objectives and narrative water quality criteria used by the Water Board to determine when impairment of any beneficial use is occurring. Under the ILRP, a management plan is required by the Water Board for a waterway when Coalition sampling finds any constituent exceeding a water quality trigger limit two or more times within a three-year period. A management plan is also required for just a single exceedance if there is an EPA approved Total Maximum Daily Load (TMDL) in place for that particular constituent (e.g. chlorpyrifos and diazinon).

Management plans must include the following (*5*):

1. Identification of irrigated agricultural source or a study design to determine the source of the constituent;
2. Identification of management practices to address the exceedances;
3. Management practice implementation schedule;
4. Waste-specific monitoring schedule;
5. A process and schedule for evaluating management practice effectiveness;
6. A schedule of reporting to the Water Board.

Monitoring Program Results

The Coalition exports data collected in compliance with the ILRP to the Central Valley Regional Data Center after each reporting year. The Central Valley Regional Data Center is one of four California data centers that standardize data to be integrated into the California Environmental Data Exchange Network. Data through 2009 can be viewed and downloaded from http://ceden.org (*6*).

The Coalition's monitoring program found exceedances of water quality trigger limits for a range of constituents including pesticides, metals, nutrients, physical parameters, bacteria and toxicity resulting in over 25 waterways requiring a management plan for one or more constituents (Table 1). Pesticide exceedances include chlorpyrifos, diazinon, malathion, diuron, simazine and thiobencarb. However, chlorpyrifos is the most common pesticide detected in concentrations above the water quality objective within the ESJWQC region and was found in 22% of samples from 2004 through 2008 (Table 2). Eighty-five out of 144 (59%) of those detections were above the chlorpyrifos water quality objective of 0.015 µg/L (Table 2).

Management Plan

As a result of the exceedances, the ESJWQC developed an overall management plan for all 27 waterways monitored between 2004 and 2008 (Table 1). Management plans were originally developed in 2006/07 and initial implementation occurred in 2007. These plans identified pesticides applied by agriculture as high priority for management. However, all water quality problems, e.g. low dissolved oxygen, elevated pH, and elevated specific conductivity, were included in the ESJWQC Management Plan. Water Board staff and Coalition representatives recognized the difficulty in managing these problems and the potential for other non-agricultural dischargers to contribute to these problems and consequently, constituents such as dissolved oxygen and pH were designated as a lower priority for outreach.

Despite the implementation of the management plan strategy from 2006 -2008 (described immediately below), pesticides such as chlorpyrifos were repeatedly found in water bodies in the Coalition region. In July of 2007, there were 10 exceedances of chlorpyrifos and in July of 2008 there were 7 exceedances (out of 18 sites monitored) indicating that the initial approach of addressing issues on a watershed basis was not effective. In 2008, the Coalition modified its Management Plan and adopted a new strategy of contacting growers individually (*7*). Both approaches are described below.

Implementing Management Plans 2006 - 2008

The initial ESJWQC Management Plan strategy involved identifying potential sources of pesticide exceedances, performing outreach to growers and applicators about pesticide management, and performing additional monitoring to evaluate the effectiveness of current management practices. The strategy involved treating pesticide management as a watershed issue without focusing on individual growers.

Table 1. List of ESJWQC monitored subwatersheds (sites) with management plans for specified constituents.

Constituent Category	*Number of Sites with Management Plans*
Physical Parameters	25
Pathogens	23
Nutrients	8
Metals	17
Pesticides	21
Water Column Toxicity	13
Sediment Toxicity	12

Table 2. Count of samples collected for chlorpyrifos analysis, count of chlorpyrifos exceedances and percentage of samples that exceeded the water quality objective (WQO) of 0.015 µg/L.

Years	*Number of Chlorpyrifos Samples*	*Number of Chlorpyrifos Detections*	*% Detections*	*Number of Chlorpyrifos Exceedances*	*% Exceedances*
2004	9	0	0%	0	0%
2005	72	9	13%	6	8%
2006	112	28	25%	17	15%
2007	154	35	23%	21	14%
2008	186	50	27%	27	15%
TOTAL	**663**	**144**	**22%**	**85**	**13%**

Identifying Sources

The Coalition identifies sources of water quality exceedances by linking pesticide exceedances to pesticide use within the watershed and identifying parcels with the potential to affect downstream water quality (i.e. via direct drainage or spray drift). In some cases upstream source monitoring is also used. Numerous resources are used to identify potential sources of water quality impairments in a watershed including:

1. Pesticide Use Reports from CA Department of Pesticide Regulation and County Agricultural Commissioner's offices (timing of applications relative to detections of pesticides in the water body);
2. Crop and parcel information;
3. Intensive spatial and temporal monitoring of water quality;
4. Grower interviews.

Grower Outreach

The Coalition's strategy from 2006 - 2008 was designed to utilize the Coalition's resources in an effective way and exceedances were addressed on a watershed basis. No attempt was made to link individual applications to water quality problems. Outreach activities focused on informing growers of problems in their watershed and providing information on effective management practices. Grower meetings, news articles in grower magazines, newsletters and other printed media, and direct mailings were used to create awareness of water quality issues, the need for changes in existing practices, and recommendations on Best Management Practices. Numerous BMP brochures were developed and distributed to growers and applicators (*8*). Information was provided online for those growers with the capability to utilize the internet, but all information was also provided in hard copy so that it was available to all growers.

Evaluation

Evaluation of the effectiveness of Coalition efforts consisted of documenting implementation of management practices and continued monitoring of water bodies to document improved water quality. Implementation of management practices by growers within each Management Plan watershed was determined by mailing surveys to growers across the Coalition region. Surveys questioned growers on what practices they currently had in place and what practices they might implement in the near future. Additional monitoring was performed at some upstream locations in an attempt to better isolate potential sources, and also more frequently during periods of high applications. Additional monitoring events and locations ensured the Water Board that if exceedances occurred, Coalition monitoring would detect them. It was the goal of this strategy to document improvement in water quality within two years of the initiation of the Coalition Management Plan. Unfortunately, grower response to the surveys was minimal and approximately half of the surveys were returned. In addition, water monitoring results in 2007 and 2008 did not indicate improvements in water quality especially in regards to chlorpyrifos exceedances (*9*, *10*).

Focused Approach 2009 - 2011

Results from the monitoring program demonstrated continuing exceedances in many watersheds despite the initial management plans and outreach using a watershed approach. Consequently, it was determined that outreach focused on individual growers (Figure 1) would provide greater progress toward improving water quality. This approach involved identifying high risk fields and following up with individual contacts and on-site farm visits. The identification of high risk properties involved GIS mapping of parcels applying pesticides upstream of locations where pesticides were detected. Pesticide use reports were obtained directly from the County Agricultural Commissioners within a few months after they were filed by growers. Coalition representatives developed a history of pesticide use by individual growers, a GIS map of parcels receiving applications relative to the water body in which the chemical was detected, and the water quality data from downstream of the grower. Coalition representatives provided the information to growers during their visits. A key component of this focused approach is to meet with the grower individually to perform a site assessment, discuss downstream monitoring results, farm management practices, and recommend implementation of specific BMPs tailored for each parcel of land (Figure 1). Although all constituents are addressed during site visits, the Coalition specifically discusses the management of chlorpyrifos with growers.

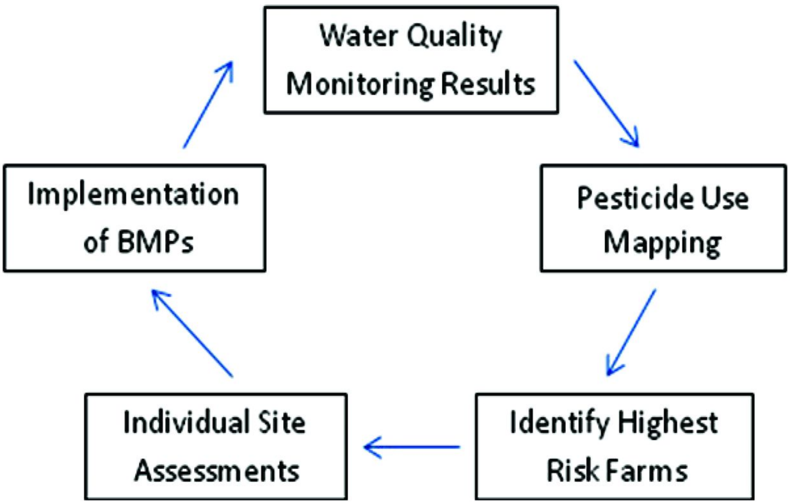


Figure 1. ESJWQC management plan strategy for focused approach.

The focused approach is time intensive and requires the participation of Coalition representatives that are familiar with farming practices. As a result, it was not possible to address water quality issues in all watersheds simultaneously. In 2009, the Coalition selected three watersheds as high priority based on the following criteria: waterways that had been monitored for at least three consecutive years; monitoring data showed multiple chlorpyrifos exceedances; and watersheds represented a range of conditions in the Coalition region. The watersheds and sample sites selected were Dry Creek (Stanislaus County), Prairie Flower Drain (Stanislaus County), and Duck Slough (Merced County) (*7*). The major crops in the Dry Creek subwatershed are almonds and grapes with some row crops like corn in the upper areas of the watershed (Figure 2). The Prairie Flower Drain watershed is located in the western portion of the Coalition region and has a very shallow groundwater table. Alfalfa and row crops like corn are the primary crops (Figure 3). Duck Slough has a combination of both orchards and row crops (Figure 4).

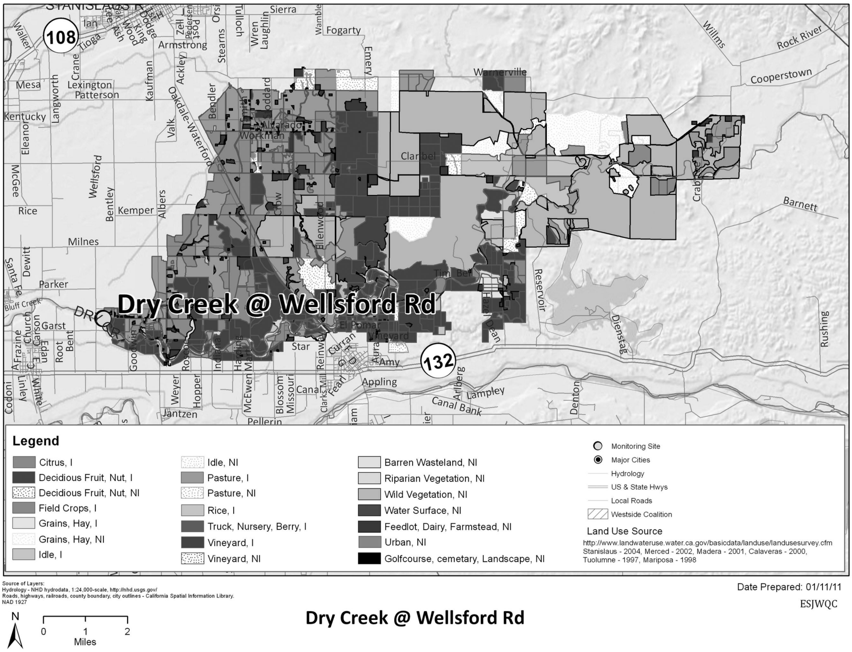


Figure 2. Dry Creek subwatershed land use map.

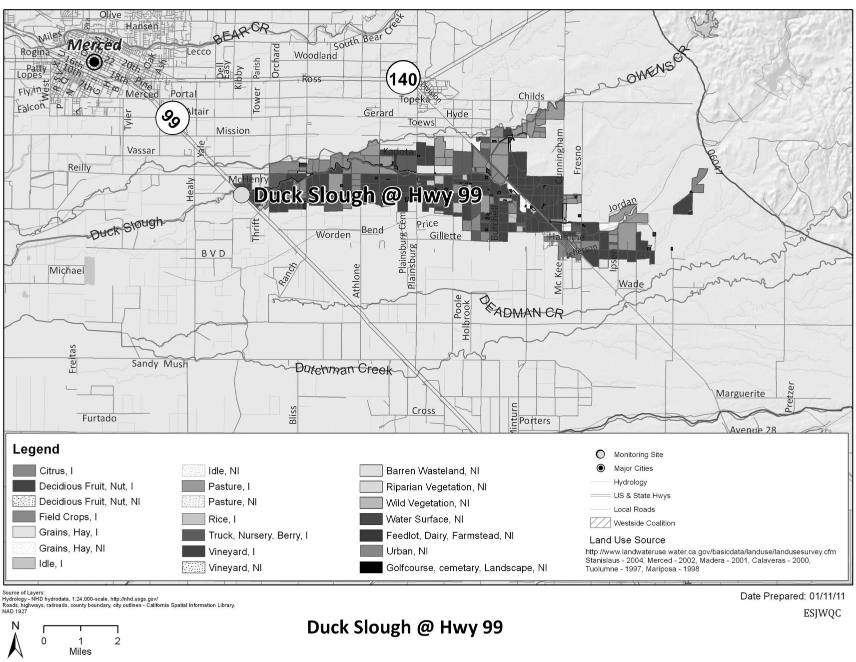


Figure 3. Duck Slough subwatershed land use map.

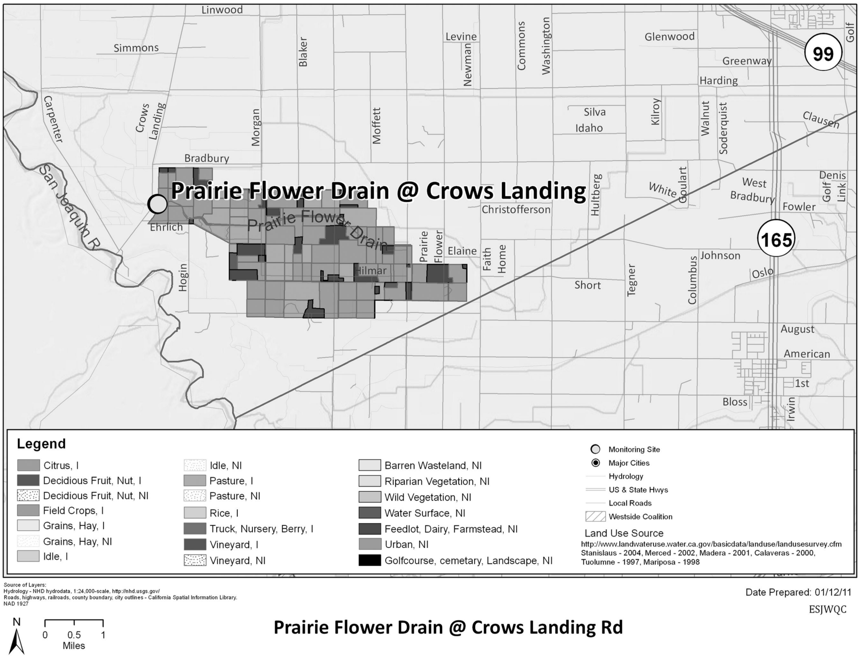


Figure 4. Prairie Flower Drain subwatershed land use map.

Step 1. Identifying High Risk Properties Adjacent to Waterways Using GIS Layers

In its initial effort, the Coalition focused on members with the potential to drain directly to the three waterways. The focus was on fields immediately adjacent to the waterway with the potential to drain during irrigation or winter storms as well as fields where spray drift could reach adjacent waterways. The Coalition also used information gathered by staff from the County Agricultural Commissioners who surveyed creeks and identified discharge points including pipes, drains, and eroded water pathways. The Coalition utilized GIS mapping to overlay drainage locations and fields with applications (Figure 5). An analysis of the concentrations detected in the creeks was used to determine if drift or direct runoff were more likely to be the source of chlorpyrifos.

Step 2. Individual Meetings with Property Owners

In 2009, each member was contacted through registered mail to schedule individual interviews. Between the three subwatersheds, the Coalition contacted and obtained management practice information from 52 members representing 11,273 acres (Table 3). Coalition representatives visited the member's farms to discuss downstream water quality issues, evaluate current management practices used on fields adjacent to waterways, and if appropriate propose management practices that could be implemented. Management practices recommended include spray drift management and farm site management practices to reduce the amount of pesticides and other products applied by agriculture from entering downstream water bodies.

Spray Drift Management

Because of the potential for spray drift from any field adjacent to a waterway, growers in all watersheds were encouraged to closely follow spray drift management practices including:

1. On the outer two rows adjacent to surface water, shut off outside nozzles and spray inward only;
2. Spray fields close to water bodies only when the wind is blowing away from them;
3. Make air blast applications when the wind is between 3-10 mph and downwind of surface water.

Farm Site Management Practices

Not all farms adjacent to waterways have irrigation drainage. For those that do, farm site practices can eliminate the potential for pesticides and other products to enter surface water. These practices include:

1. Installing tailwater return systems;
2. Installing sediment retention basins;
3. Developing vegetated ditches and grass row centers.

Tailwater systems re-circulate drain water back to the fields which eliminates discharge to surface waters, re-uses water, and retains pesticides on the farm. Basins for sediment retention can be used with or without tailwater return systems. Both basins and return systems require modifications to the drainage system and the installation of expensive equipment. Relatively few farms install tailwater return systems or sediment basins due to the high cost associated with their construction and maintenance. Vegetated ditches act as filter strips to remove certain constituents from the water column including suspended sediment and pesticides that tend to bind to organic material. Figure 6 indicates the types of practices recommended to growers within Dry Creek, Duck Slough and Prairie Flower Drain.

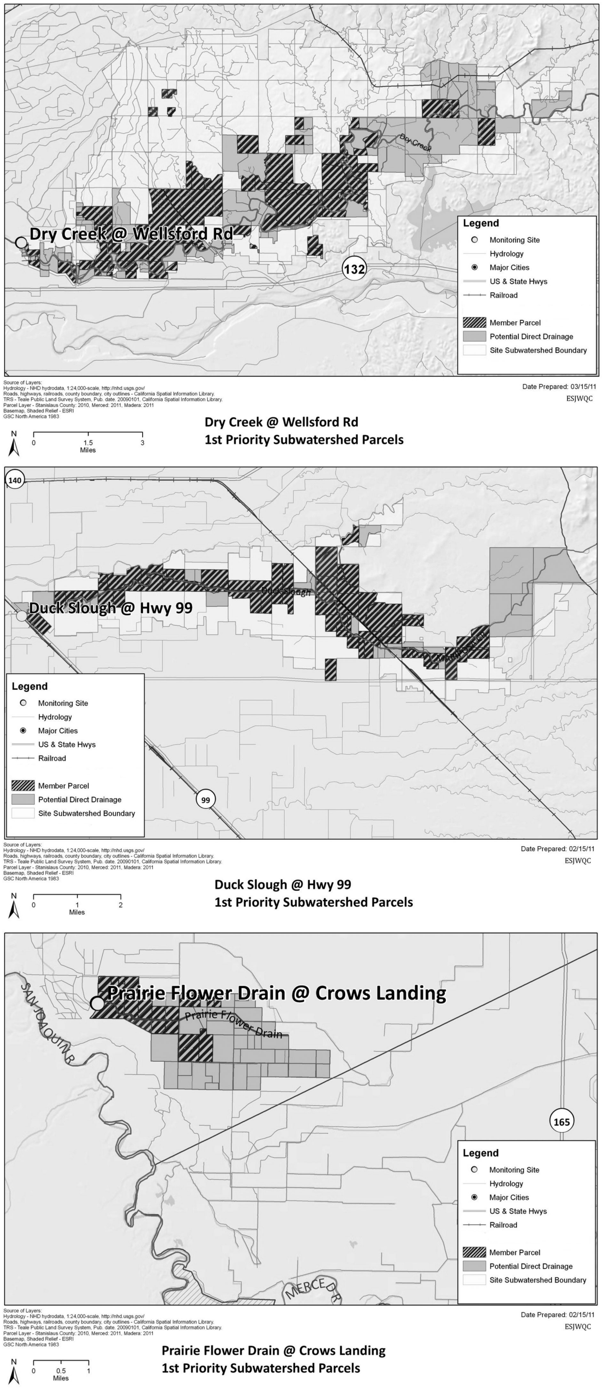


Figure 5. GIS maps- direct drainage parcels overlaid with past chlorpyrifos use for each subwatershed.

Table 3. Number of growers contacted in priority subwatersheds and the associated acreage for which management practices were recorded through surveys.

	Dry Creek	*Duck Slough*	*Prairie Flower Drain*	*Total*
Acreage of Members Contacted	6,392	4,016	865	11,273
Number of Individual Meetings/Surveys Completed	22	20	10	52
Number of Newly Implemented Management Practices Following Focused Approach	9	12	7	28
Percent of Members Implemented New Management Practices Following Focused Approached	36%	35%	50%	38%

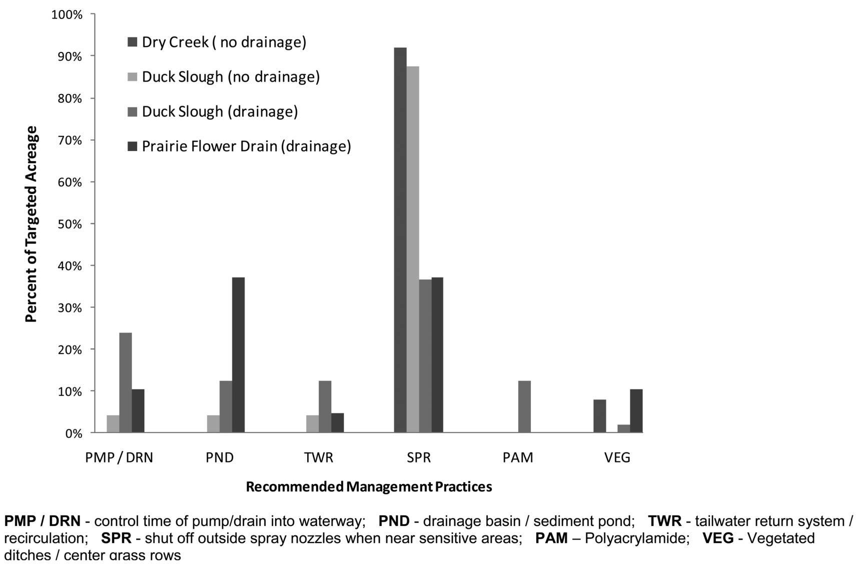


Figure 6. Percentage of targeted acreage with recommended management practices for Dry Creek, Duck Slough (acreage with no irrigation drainage), Duck Slough (acreage with irrigation drainage) and Prairie Flower Drain.

Step 3. Water and Sediment Monitoring

The ESJWQC Management Plan includes a monitoring strategy for prioritized constituents applied by agriculture (e.g. chlorpyrifos) during months when past exceedances occurred. For example, samples collected from Dry Creek exceeded

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

the chlorpyrifos water quality objective in July of 2007 and therefore is monitored for chlorpyrifos in subsequent Julys. This monitoring is in addition to the regular surveillance monitoring conducted by the Coalition on a monthly basis.

Step 4. Measuring Success

The Coalition evaluates success or effectiveness of the management plan strategy based on both the implementation of additional management practices by members and the downstream water quality results. Demonstrating the effectiveness of Coalition efforts in reducing the impact of agricultural practices on water quality is difficult because:

1. Not all landowners along a waterway are coalition members;
2. A field may be enrolled and regulated under the Regional Water Board Dairy Program and not contacted by the Coalition;
3. Direct source and "cause and effect" of a single exceedance is often difficult if not impossible to confirm.

Each of the three priority watersheds was unique in the number of irrigated acres, types of crops grown and management practices used on the fields. For example, growers along Prairie Flower Drain have the highest percentage of acreage (95%) with tailwater drainage. About half the acreage along Duck Slough/Mariposa Creek has tailwater drainage. Dry Creek has less than 15% of its acreage with tailwater drainage (Table 4). Thus management practices differ for growers in each watershed.

The type of crop grown and irrigation practice in each watershed tended to determine the amount of irrigation drainage. Orchard crops dominate the Dry Creek region, with most orchards using drip or microsprinklers. Row and field crops, which are typically flood or furrow irrigated, are the majority in the Prairie Flower Drain watershed. Duck Slough watershed is a mixture of orchards, row and field crops.

Dry Creek Watershed

Concentrations of chlorpyrifos detected in the creek were low despite substantial use in the watershed (e.g. May, June, July 2005, Figure 7). No relationship was seen between pounds of active ingredient applied and concentration (Figure 8, y= 0.01612x, $r^2 = 0.000$). The lack of tailwater and the low concentrations indicate that the most likely source of the chlorpyrifos in the water is drift from airblast applications in orchards. Therefore, preventing drift was the focus of discussions with growers in this watershed (Figure 6). Turning off outside nozzles when spraying outside orchard rows was recommended on 92% of the acreage (Figure 6). Planting vegetation along ditches was only recommended on 8% of the acreage (Figure 6).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table 4. Total subwatershed acreage, subwatershed acreage with direct drainage to surface waters, acreage of members with direct drainage, percent of growers contacted with direct irrigation drainage, and percent acreage with irrigation drainage for the first three prioritized subwatersheds with focused outreach.

Priority Subwatershed	*Acreage: Total Subwatershed*	*Acreage: Potential for Direct Drainage*	*Acreage: Members with Direct Drainage*	*% Direct Drainage Acreage Contacted*	*% Acreage with Irrigation Drainage*
Prairie Flower Drain	3,105.97	3,105.97	1,047.94	35.85%	95%
Duck Slough	17,559.00	5,767.00	4,440.15	83.10%	52%
Dry Creek	68,620.00	16,110.97	6,734.72	43.17%	14%

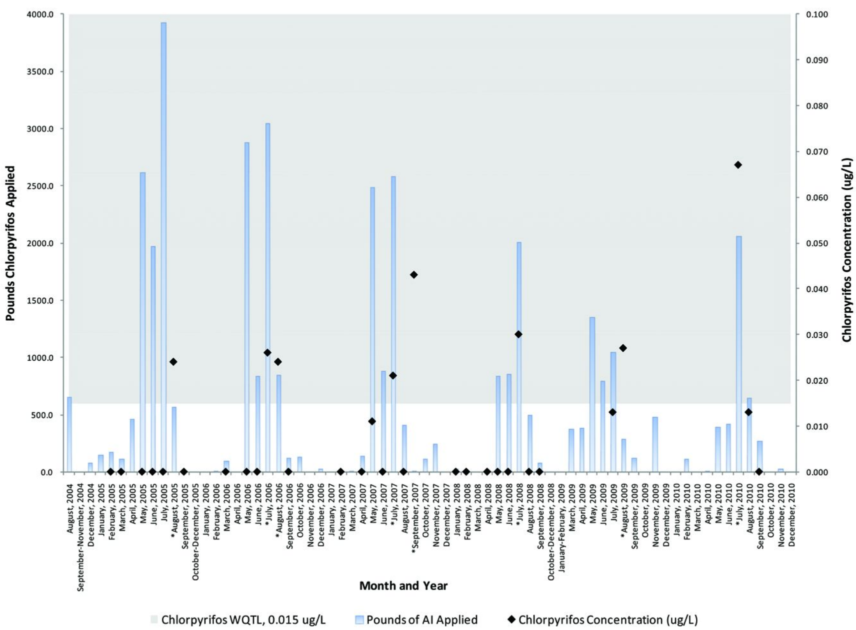


Figure 7. Pounds of chlorpyrifos applied within the Dry Creek subwatershed from 2004—2010. Asterisk (*) denotes months with exceedances.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

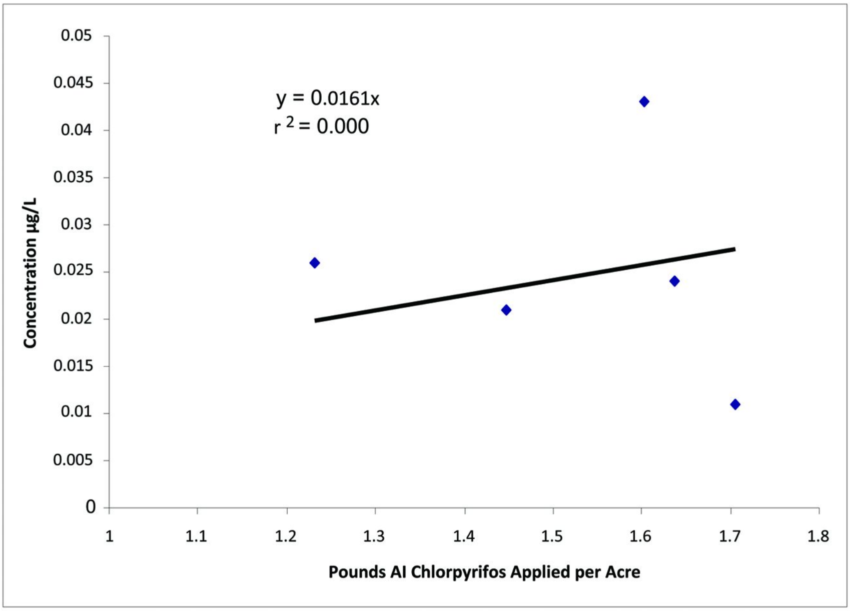


Figure 8. Chlorpyrifos concentrations in Dry Creek and applications of chlorpyrifos in the Dry Creek @ Wellsford Rd watershed. Applications are all within four weeks of sampling.

Duck Slough/Mariposa Creek Watershed

Management practices recommended in Duck Slough/Mariposa Creek watershed were tailored to meet the unique circumstances of each farm depending on whether off-site drainage occurred (Figure 6). There is a combination of fields with and without tailwater drainage within this watershed. The acreages without drainage contain orchards whereas the acreages with drainage are predominately field/row crops with some orchards and pasture land. There is a weak but positive relationship between the amount of chlorpyrifos applied and the amount detected in the water samples indicating that management of runoff and spray drift are both important practices to ensure downstream water quality (Figure 10, y= 0.0182x, $r^2 = 0.63$). However, even in this subwatershed there are occurrences of exceedances that don’t correspond to the highest use (i.e. September 2008, Figure 9) indicating that a mixture of spray drift and direct drainage was responsible for the detected concentrations of chlorpyrifos at the sampling location. For acreages with irrigation drainage to Duck Slough/Mariposa Creek discussions with members focused on a combination of spray drift management, control of storm drainage, allowing vegetation to grow in ditches and adding drainage basins/sediment ponds where needed (Figure 6). For acreages without irrigation drainage, discussions with members focused on spray drift management practices (Figure 6).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

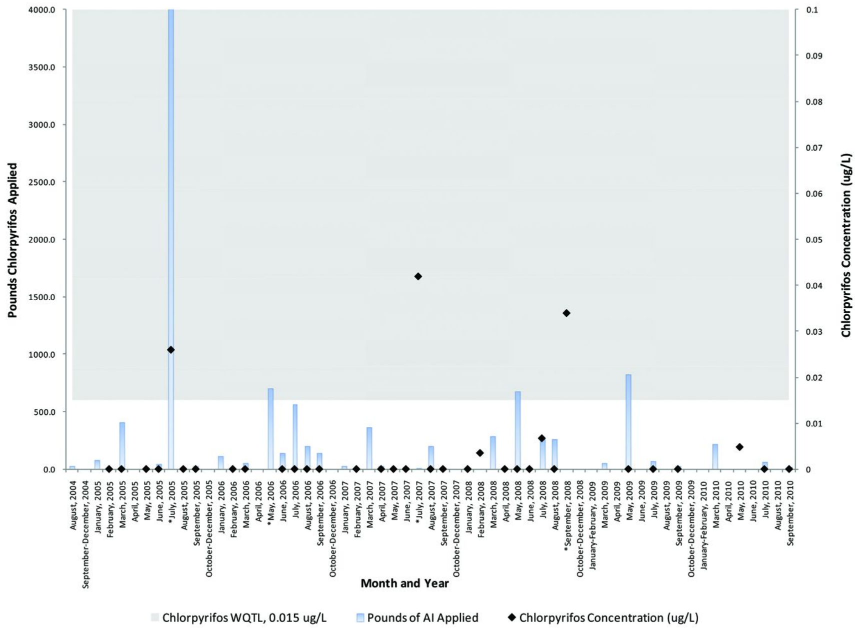


Figure 9. Pounds of chlorpyrifos applied within the Duck Slough subwatershed from 2004 - 2010. Asterisk (*) denotes months with exceedances.

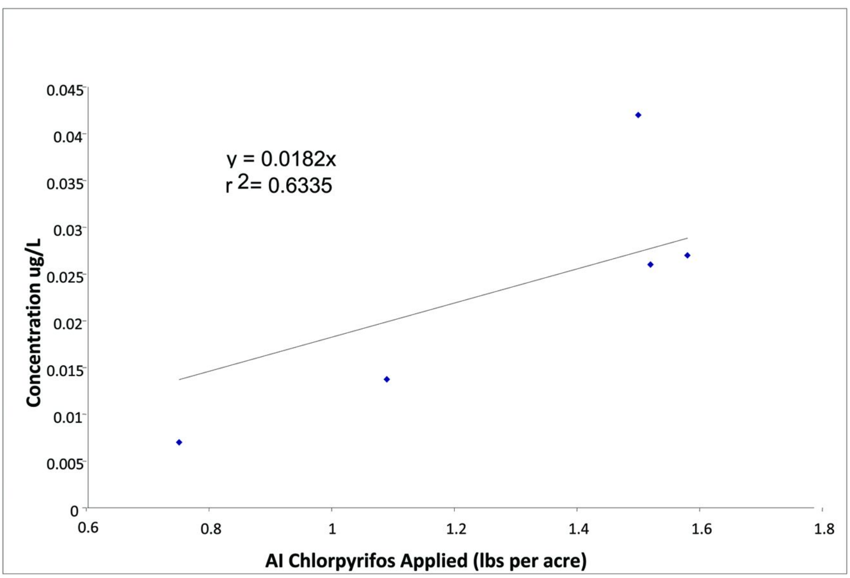


Figure 10. Chlorpyrifos loads and application rates for the Duck Slough site subwatershed for applications within four weeks of sampling.

Prairie Flower Drain Watershed

Fields adjacent to Prairie Flower Drain with drainage were predominantly field and row crops with flood or furrow irrigation (Figure 4). There were insufficient data for exceedances and pesticide applications to allow regression analysis so recommendations of practices relied primarily on tours of farms along the drain. Figure 11 shows the concentrations of chlorpyrifos in relation to amount of pounds applied within the subwatershed; there is no clear trend since there may be detections with no reported use (July and August 2007), relatively high use with no detections (July 2008) or high use and an exceedance (August 2005). Landowners were encouraged to adopt management practices such as controlling the timing of pumping or draining into the waterway following pesticide applications, allowing vegetation growth in drainage ditches, and constructing drainage basins/sediment ponds to hold field runoff (Figure 6).

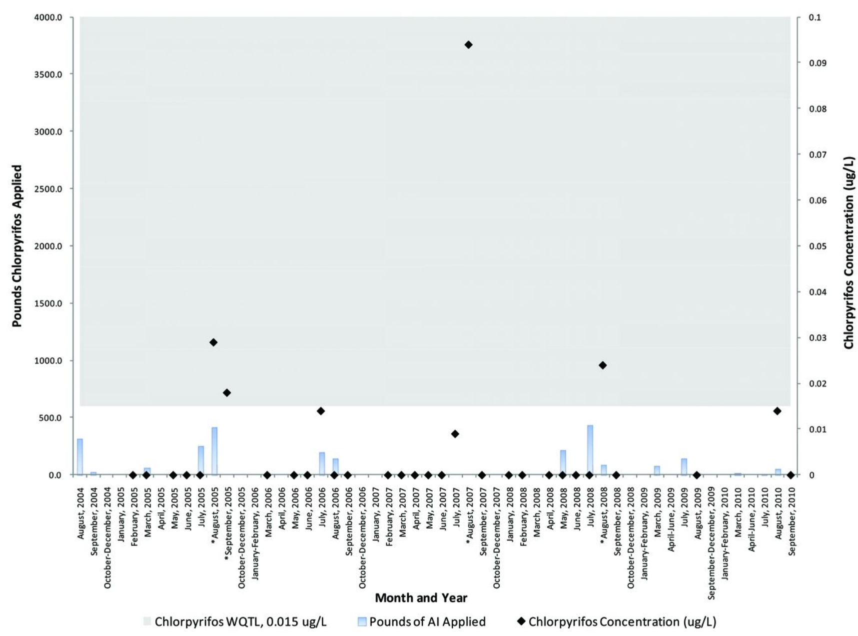


Figure 11. Pounds of chlorpyrifos applied within the Prairie Flower Drain subwatershed from 2004 - 2010. Asterisk (*) denotes months with exceedances.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Results of Focused Approach

Improved water quality can be determined as; 1) a reduction in the concentration of chlorpyrifos in water samples with detections, and 2) reduced number (or elimination) of detections of chlorpyrifos in the water. Management Plan monitoring results in 2009 and 2010 from the first three high priority locations indicated an overall improvement in water quality. Both Duck Slough and Prairie Flower Drain watersheds had no exceedances of any applied pesticides. Dry Creek samples contained concentrations of chlorpyrifos above the water quality trigger limit in just one sampling event in each year however the sources were determined to be due to discharges from landowners not participating in the ILRP.

Table 5. Dry Creek: acreage of recommended practices in relation to implemented practices in 2009.

Management Practice	*Acreage: Recommended Practices*	*Acreage: Implemented Practices*	*Percent of Recommended Acreage with Implemented Practices*
No drainage from property			
Shut off outside nozzles when spraying outer rows	523.7	523.7	100%
Vegetation is planted along or allowed to grow in ditches	45	0	0%
Recirculation - Tailwater return system	0	443	NA[a]
Drainage Basins (Sediment Ponds)	0	121.3	NA
Filter strips at least 10' wide around field perimeter	0	28	NA
Reduce amount of water used in surface irrigation	0	162	NA
Other (Not specified)	NA	1200.5	NA
Total (no drainage)	**568.7**	**2478.5**	**434%**
Yes, drainage from property			
Other (Not specified)	NA	2450	NA
Total (drainage)	**NA**	**2450**	**NA**

[a] NA = Not Applicable

Dry Creek

In the year following the first farm visit, the Coalition followed up with members to document implemented management practices (Table 5). One grower did not implement the recommended practice (vegetated ditches) because ditches were removed. All other growers implemented recommended practices. In addition, six growers who had not received any recommendations (their operation was determined to be managing applications appropriately) installed tailwater return systems, drainage basins, filter strips, or reduced the amount of water used for surface irrigation.

Dry Creek experienced exceedances of chlorpyrifos in August 2009 and July 2010. Based on pesticide use information associated with those two exceedances, it was determined the exceedances came from non-members who farm directly upstream of the monitoring location. Despite the fact that these nonmembers would not normally be entitled to Coalition services, the Coalition met with these growers and discussed spray drift and irrigation management practices to prevent further exceedances. In addition, due to change of ownership of properties in the watershed, the Coalition gained additional members in the watershed since 2008 and therefore is conducting additional outreach to those new members.

One outcome of the outreach is a reduction in the amount of chlorpyrifos used within the watershed (Figure 8, Table 6). Based on data from 2004 through 2010, the highest number of applications occurred in 2006 and the highest amount of pounds used occurred in 2005 (Table 6). Since 2006, the number of applications has decreased yearly (Table 6). Growers have determined that the proximity of streams to certain orchards means that additional BMPs must be followed in addition to following label requirements in order to keep the product out of the creek.

Table 6. Dry Creek: Chlorpyrifos use by year in the subwatershed, 2004—2010.

Year	*Number of Chlorpyrifos Applications*	*Pounds of Chlorpyrifos Applied*	*Acres Treated*
2004	17	736.4	665
2005	117	9996.5	6806
2006	137	8016.6	5776
2007	112	6901.1	4506
2008	88	4326.4	3287
2009	74	4879.6	2970
2010	71	3948.5	2757

Duck Slough/Mariposa Creek

In 2009, recommended practices were implemented on 53% of the acreage without drainage (Table 7). One grower indicated that he planned to implement additional practices in 2010 and another grower indicated he did not have the resources to install the recommended tailwater return system and drainage pond. There was also one grower who was unresponsive and did not return a follow up survey. For acreage with drainage, 100% of the recommended practices were implemented. In addition, members with drainage also implemented practices that were not recommended (Table 7). Additional practices not recommended but adopted included installing a device to control discharge, shutting off outside nozzles during spraying, and reducing the amount of water used in irrigation.

Duck Slough has had no exceedances of the chlorpyrifos water quality objective since the Coalition began its focused approach strategy. In addition there has been an overall reduction in the use of chlorpyrifos within the subwatershed since 2005 (Figure 9, Table 8) due to the close proximity to surface waters of certain parcels.

Table 7. Duck Slough: acreage of recommended practices in relation to implemented practices in 2009.

Management Practice	*Acreage: Recommended Practices*	*Acreage: Implemented Practices*	*Percent of Recommended Acreage with Implemented Practices*
No drainage from property			
Shut off outside nozzles when spraying outer rows next to sensitive sites	871.8	210	24.1%
Use air blast applications when wind is between 3-10 mph and upwind of a sensitive site	661.8	NA[a]	NA[a]
Recirculation - Tailwater return system	42	0	0%
Drainage basins (sediment ponds)	42	0	0%
Install device to control discharge	42	661.8	1575.7%
Total (no drainage)	**1659.6**	**871.8**	**53%**
Yes, drainage from property			
Recirculation - Tailwater return system	142	0	0%

Continued on next page.

Table 7. (Continued). Duck Slough: acreage of recommended practices in relation to implemented practices in 2009.

Management Practice	*Acreage: Recommended Practices*	*Acreage: Implemented Practices*	*Percent of Recommended Acreage with Implemented Practices*
Drainage basins (sediment ponds)	142	0	0%
Use Polyacrylamide(PAM)	142	0	0%
Install device to control discharge	269	485.5	592.1%
Vegetation is planted or allowed to grow along ditches	21	0	0%
Shut off outside nozzles when spraying outer rows next to sensitive sites	414.5	435.5	105.1%
Spray areas close to water bodies when the wind is blowing away from them	595.5	NA[a]	NA[a]
Reduce amount of water used in surface irrigation	0	764	NA
Microirrigation system	0	279	NA
Other (Not specified)	NA	451	NA
Total (drainage)	**1726**	**2415**	**140%**

[a] Management practice was not listed on follow up survey.

Table 8. Duck Slough: Chlorpyrifos use by year in the subwatershed, 2004—2010.

Year	*Number of Chlorpyrifos Applications*	*Pounds of Chlorpyrifos Applied*	*Acres Treated*
2004	1	29.9	20
2005	38	4790.4	1589
2006	35	1935.5	1436
2007	26	662.8	788
2008	37	1501.2	1747
2009	9	979.4	1011
2010	13	295.5	466

Prairie Flower Drain

One hundred percent of growers with recommended practices implemented them in 2009 (Table 9). In addition, members with drainage implemented practices that were not recommended including the installation of a device to control discharge and reducing the amount of water used in surface irrigation (Table 9).

Prairie Flower Drain has had no exceedances of the chlorpyrifos water quality objective since the Coalition began its focused outreach strategy. In addition, as in the other subwatersheds, there has been an overall reduction in the use of chlorpyrifos within the watershed since 2008 (Figure 11, Table 10).

Table 9. Prairie Flower Drain: acreage of recommended practices in relation to implemented practices in 2009.

Management Practice	*Acreage: Recommended Practices*	*Acreage: Implemented Practices*	*Percent of Recommended Acreage with Implemented Practices*
Yes, drainage from property			
Install device to control discharge	76.9	420.9	547%
Plant or allow vegetation along ditches	76.9	0	0%
Drainage basins (sediment ponds)	270.9	150	55%
Use Polyacrylamide(PAM)	270.9	150	55%
Reduce amount of water used in surface irrigation	0	270.9	NA
Recirculation - Tailwater return system	34	0	0%
Total (drainage)	**729.6**	**991.8**	**136%**

Table 10. Prairie Flower Drain: Chlorpyrifos use by year in the subwatershed, 2004—2010.

Year	*Number of Chlorpyrifos Applications*	*Pounds of Chlorpyrifos Applied*	*Acres Treated*
2004	6	343.5	351
2005	14	733.3	917
2006	8	361.5	438
2008	12	740.4	790
2009	4	238.9	310
2010	4	80.1	134

Conclusions

A grower-led coalition can be an effective way to inform, educate, and obtain commitment by growers to make changes necessary to address surface water quality issues. The greatest improvements in water quality were seen following a focused outreach approach that combined downstream water monitoring results with data on upstream pesticide use, identification of high risk parcels adjacent to waterways, and on-site farm evaluations with growers. Such a targeted approach enabled the identification and development of site-specific BMPs based on the cropping system, pesticide application methods, irrigation practices, and proximity to waterways. Tailoring BMPs for those growers whose farms were identified as most likely to contribute to exceedances resulted in improvements in downstream water quality. Coalition water and sediment quality sampling from summer and fall 2009 and 2010 in the three watersheds with focused outreach showed no exceedances of water quality standards for chlorpyrifos except for single samples in 2009 and 2010 from Dry Creek, both of which originated with growers who were not members of the Coalition. One grower subsequently joined the coalition and the other is a member of the Dairy Program. Two out of the three priority waterways had no exceedances of any farm inputs, in particular the targeted pesticides (chlorpyrifos, diuron and copper).

One of the biggest challenges with coalitions is getting all growers to participate. The East San Joaquin Water Coalition represents only approximately 55% of the irrigated agriculture in its region. The other 45% includes growers who should but choose not to join, growers who claim not to discharge to surface waters, and growers who are enrolled in the Dairy Program. These growers do not receive information from the Coalition about water quality issues, management practices, or funding sources to help finance management practice implementation. In many San Joaquin River watersheds, particularly Dry Creek and Prairie Flower Drain, considerable acreage is enrolled in the Water Board's Dairy Program which focuses on manure management and nutrient impacts on water quality. Landowners with fields covered by this program are not required to monitor pesticides in runoff from fields in production for forage. This complicates

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

the task of assessing the contribution of water quality impairments due to fields regulated under the Dairy Program versus fields regulated under the ILRP. Efforts are underway by the Water Board to close this accountability gap and ensure that dairy farmers are also held accountable for pesticide contributions to surface waters.

The Coalition considers the decrease in chlorpyrifos exceedances in 2009 and 2010 an important step in demonstrating the effectiveness of its management plan strategy that targets high risk parcels adjacent to surface waters. Growers farming these parcels are the target of focused outreach and site-specific recommendations. In addition, feedback from members on this strategy has been positive and encouraging. In all cases, growers have appreciated individual visits and become much more aware of downstream water quality concerns.

The ESJWQC members are continuing efforts to ensure that water quality within the region is not impaired by sources related to agricultural production. The Coalition is a resource to its members for information on management practices, grant funding to finance the installation of structural management practices (i.e. sediment ponds), and updates of local water quality monitoring results. In subsequent years, additional watersheds are the focus of targeted monitoring, source identification, and outreach. Within a decade, the Coalition will be able to address all surface water quality issues in all watersheds in which exceedances of water quality objectives have occurred. With the demonstrated success of its focused approach, future water quality issues can be addressed quickly and effectively.

References

1. http://www.swrcb.ca.gov/rwqcb5/water_issues/water_quality_studies/surface_water_ambient_monitoring/sjr_swamp.shtml
2. http://www.waterboards.ca.gov/centralvalley/water_issues/irrigated_lands/
3. http://www.esjcoalition.org/home.asp
4. http://www.swrcb.ca.gov/centralvalley/board_decisions/adopted_orders/waivers/r5-2005-0833.pdf
5. http://www.waterboards.ca.gov/centralvalley/board_decisions/adopted_orders/waivers/r5-2008-0005_mrp.pdf
6. http://ceden.org
7. East San Joaquin Water Quality Coalition. *Management Plan*. Submitted on September 30, 2008, to the Irrigated Lands Regulatory Program, Central Valley Regional Water Quality Control Board, Rancho Cordova, California, 2008; 420 pages.
8. http://curesworks.org/publications/ag.asp
9. East San Joaquin Water Quality Coalition. *Semi-Annual Monitoring Report*. Submitted on December 31, 2007, to the Irrigated Lands Regulatory Program, Central Valley Regional Water Quality Control Board, Rancho Cordova, California, 2007; 153 pages plus appendices.

10. http://www.waterboards.ca.gov/centralvalley/water_issues/irrigated_lands/monitoring_plans_reports_reviews/monitoring_report_reviews/coalitions/east_sanjoaquin_waterquality/index.shtml

Chapter 2

From Vegetated Ditches to Rice Fields: Thinking Outside the Box for Pesticide Mitigation

M. T. Moore,[1,*] R. Kröger,[2] J. L. Farris,[3] M. A. Locke,[1] E. R. Bennett,[4] D. L. Denton,[5] and C. M. Cooper[1]

[1]U.S. Department of Agriculture, Agricultural Research Service, National Sedimentation Laboratory, Oxford, MS 38655
[2]Mississippi State University, Department of Wildlife, Fisheries, and Aquaculture, Mississippi State, MS 39762
[3]Arkansas State University, Arkansas Biosciences Institute, State University, AR 72467
[4]Bioengineering Group, Salem, MA 01970
[5]U.S. Environmental Protection Agency, Region IX, Sacramento, CA 95814
[*]matt.moore@ars.usda.gov

Pesticide contamination of surface waters has been a global concern for decades. In agricultural areas, pesticides enter receiving waters through irrigation and storm runoff, spray drift, or even atmospheric deposition. Management practices incorporating vegetation and phytoremediation have demonstrated success in reducing pesticide loads to rivers, lakes, and streams. This chapter will focus on a variety of vegetative management practices (e.g. constructed wetlands, drainage ditches, and rice fields) which have been studied in the intensively cultivated Mississippi Delta. Summaries of research results will be presented, as well as potential future directions for additional research.

Introduction

The current world population is estimated at over 6.89 billion people, growing at a rate of nearly three people each second (*1*). Agriculture is under increasing stress to produce more food and fiber to meet growing population needs, while

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

also reducing its potential impacts upon the environment. Farmers continue to use pesticides on their crops in order to maximize yield on the landscape. In 2001, approximately 547 million kg of pesticide active ingredient were used in the United States, while worldwide pesticide use was estimated at 2.3 billion kg (*2*).

Even with advances in application technology, a portion of the applied pesticide, through spray drift, will end up in an unintended area such as an adjacent aquatic ecosystem. Additionally, during storm events, pesticides may be mobilized either in the dissolved or particulate phase (with sediments) via runoff. As a result, potential damage to downstream receiving systems may occur. Nationwide, only about 3% (1,865) of the Clean Water Act 303(d) listed impairments are due to pesticides. Individual states' monitoring programs vary greatly, so it is possible that some states fail to monitor for pesticides at a resolution high enough to determine their presence. In states such as California, pesticides are the most prevalent contaminant reported, responsible for nearly 18% of the state's 303(d) impairments (*3*).

To prevent pesticides entering the receiving water environment at concentrations of concern, various management practices, both in-field and edge-of-field, have been suggested. Popular practices include, but are not limited to, winter cover crops, stiff-grass hedges, constructed wetlands, conservation tillage, slotted-inlet pipes, and grassed waterways. Given today's difficult agricultural economy, many farmers are hesitant to implement any management practice that (1) removes valuable land from production or (2) is not economically-beneficial (i.e. cost-sharing opportunities). With those two factors in mind, various management practices using phytoremediation techniques have been examined in the intensively agricultural area of the lower Mississippi Alluvial Plain. Vegetation is an important element within these practices, since plants aid in physical filtration, bed sediment stabilization, and provide increased or enhanced surface area for microbial attachment (*4*). This chapter will examine research on both traditional (constructed wetlands) and innovative (ditches and rice fields) management practices used to achieve pesticide mitigation. Just as water quality in agricultural settings is becoming a challenge, scientists, farmers, and conservationists must be willing to think "outside the box" to develop both successful preventative and mitigation strategies.

Constructed Wetland Studies

Wetlands are ecotones (transition zones) between upland areas and aquatic systems such as rivers, lakes, or streams (*5*). Estimates of wetlands in the conterminous United States from the early 1600s suggest over 89 million ha existed; however, within nearly four centuries, over half of those wetlands, some 48 million ha, had been lost due to development or agriculture (*6*). This severe loss of wetland habitat is at least partially responsible for a decline in water quality throughout the nation. Since the latter part of the 20th century, efforts have been made to construct wetlands in areas that once housed natural wetland systems. Reintroduction of these systems, especially in agricultural areas, serves to improve water quality following storm runoff or irrigation controlled-releases. Although some studies on the ability of wetlands to remove pesticides were conducted in the 1970s and 1980s, Rodgers and Dunn (*7*) were the first to suggest a method for developing design guides for constructed wetlands targeted specifically at pesticide removal. Their series of eight experimental wetland cells were constructed at the University of Mississippi's Field Station in the late 1980s and early 1990s. Out of this experimental design came three primary studies which were some of the first to suggest necessary wetland lengths for various levels of pesticide mitigation.

In the first experiment, constructed wetland cells (59-73 x 14 x 0.3 m) were amended with the organophosphate insecticide chlorpyrifos at three different concentrations: 73, 147, and 733 μg/L. These concentrations represented theoretical chemical runoff of 0.1, 1, and 5% of applied pesticides on a 32-ha field. For 12 weeks, water, sediment, and plant samples were collected spatially throughout the length of the constructed wetlands. Plants, consisting of the emergent soft rush *Juncus effusus*, accounted for approximately 25% of the measured chlorpryifos mass, while 55% of the mass was located in sediments. The wetland buffer length necessary to reduce the aqueous chlorpyrifos concentrations to 0.02 μg/L (no observed effects concentration or NOEC) ranged from 184 m to 230 m, depending on the initial concentration (*8*).

A second experiment was later conducted by amending wetland cells with a mixture of the herbicides atrazine and metolachlor at concentrations of 73 and 147 μg/L, representing a 0.1 and 1% theoretical chemical runoff (*9*, *10*). Water, sediment, and plant (*J. effusus*) samples were collected spatially and temporally for 35 d. Results indicated atrazine concentrations were below detection (0.05 μg/kg) in all sediment and plant samples, while only 10% of the measured metolachlor mass was present in plant samples. As with atrazine, metolachlor concentrations in sediment were below detection limits (0.05 μg/kg). According to Huber (*11*), 20 μg/L is the suggested atrazine concentration below which is not expected to adversely affect aquatic ecosystem health. Conservative wetland buffer lengths necessary to reduce the atrazine aqueous concentration to 20 μg/L ranged from 100 m to 280 m, depending on the initial atrazine concentration. For metolachlor, to reduce the aqueous concentration to 40 μg/L, necessary wetland buffer lengths ranged from 100 m to 400 m, depending on the initial concentration (*9*, *10*).

These first generation studies laid the foundation for later investigations which focused constructed wetland research on the influence of plants in pesticide mitigation. In 2003, 10 m x 50 m constructed wetlands were used to evaluate the fate of methyl parathion (*12*) in vegetated and non-vegetated systems. A storm event simulating 1% pesticide runoff from a 20-ha contributing area was used as an amendment. As with earlier studies, water, sediment, and plant samples were collected spatially and temporally for 120 d. Additionally, semi-permeable membrane devices (SPMDs) were placed near the outflow of each wetland cell. Only 30 min after the initial exposure, methyl parathion was detected in all spatially collected samples within the non-vegetated wetland replicates. In the same time frame, methyl parathion had only travelled 20 m in the vegetated cell. After examining SPMD results, it was noted that only the non-vegetated replicate cells had measurable concentrations of methyl parathion in the outflow. Utilizing chemical fate and distribution formulas, it was determined that a wetland length of 18.8 m would be required to reduce the inflow concentration (8.01 mg/L) to

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

0.1% of its original in vegetated systems. Alternatively, in non-vegetated systems, a wetland length of 62.9 m would be required to reduce the inflow concentration to 0.1% of the original. These data provided further evidence of the benefits of vegetation in mitigation of pesticides.

Following the success of these studies, a constructed wetland was designed and placed in the Beasley Lake watershed, a 915-ha agricultural experimental watershed in Sunflower County, Mississippi (*13*, *14*). The entire system was 30 m wide x 180 m long and included a sediment retention basin followed by two separate vegetated treatment cells. Ten collection sites were established spatially along the system. A simulated storm event containing the pesticides diazinon and cyfluthrin, as well as suspended sediment (403 mg/L) and surface water from Beasley Lake, was amended into the constructed wetland system. Water, sediment, and plant samples were collected over 55 d at each site. The percentage of individual measured pesticide mass found in vegetation was 43% (diazinon), 49% (lambda-cyhalothrin), and 76% (cyfluthrin) (*15*, *16*). Based on conservative effects concentrations and regression analyses, to mitigate 1% of the pyrethroid (lambda-cyhalothrin and cyfluthrin) runoff from a 14-ha contributing area would require a constructed wetland 30 m wide x 215 m long (*16*).

While the environmental benefits of using constructed wetlands to mitigate pesticide runoff have been demonstrated, there was still the challenge of implementation due to the costs. Aside from any construction cost of the wetland (which may be cost-shared with government programs in certain instances), there was a loss of production land associated with the construction. Based on data generated from Moore et al. (*16*), approximately 5% of the contributing area would be needed for a constructed wetland to effectively mitigate pesticide runoff from that land. Using that information, a cost table (Table 1) was generated from data collected from the 2009 Mississippi state agricultural overview (*17*).

Table 1. General agricultural economic impact of using a constructed wetland for pesticide mitigation for field sizes of 8 ha, 16 ha, and 32 ha[a]

			Annual Gross Profit Loss (5%)		
Crop	*Average Yield*	*Average Price*	*32 ha*	*16 ha*	*8 ha*
Soybeans	94 bu/ha	$9.15 / bu	$1,376	$688	$344
Corn	311 bu/ha	$3.70 / bu	$1,841	$921	$461
Rice	7510 kg / ha	$0.28 / kg	$3,364	$1,682	$841
Cotton	772 kg / ha	$1.53 / kg	$1,890	$945	$472

[a] bu = bushel

Not only would a farmer lose 5% of his production landscape, but he would also lose 5% of his potential annual gross profits. In an era of economic uncertainty, this risk is unacceptable to many farmers and landowners. Therefore, it was necessary to design innovative management practices that were environmentally efficient, and also economically palatable to farmers and landowners. One had to look no further than the agricultural fields themselves and the surrounding landscape. Investigations began immediately into the potential of vegetated agricultural drainage ditches for pesticide mitigation.

Vegetated Agricultural Drainage Ditch Studies

Historically, agricultural ditches have primarily served a hydrologic purpose: facilitate drainage from production acreage following storms. Little thought or value was placed on their maintenance or design. Closer examination of these ecosystems showed they can, to some degree, mimic wetland areas with their hydric soils, hydrophytes, and a measurable hydroperiod. Conventional wisdom then deduced these areas could be managed and manipulated similarly to constructed wetlands. The use of agricultural drainage ditches was attractive because they were often prevalent features in the farming landscape that required no additional acreage removal from production to realize their mitigation potential. Research was needed to confirm drainage ditch ability of pesticide mitigation.

In 1998, a small-scale study was initiated to evaluate the transport and fate of the pesticides atrazine and lambda-cyhalothrin in an agricultural drainage ditch. A 50 m portion of a ditch within the Beasley Lake watershed (Mississippi) was chosen for the experiment. Using a diffuser, the pesticides were amended directly into the ditch, and water, sediment, and plant samples were collected spatially and temporally for 28 d. Within one hour of initiation of the simulated storm event, 61% and 87% of the measured atrazine and lambda-cyhalothrin concentrations, respectively, were associated with the ditch vegetation as opposed to the sediment or aqueous phases. At the 28 d sampling, 86% and 97% of the measured atrazine and lambda-cyhalothrin, respectively, were associated with the ditch vegetation (*18*). Using linear regression analysis of the maximum observed pesticide concentrations in water, it was determined that both atrazine and lambda-cyhalothrin could be mitigated to a no observed effects concentration (NOEC) ($\leq$ 20 µg/L for atrazine; $\leq$ 0.02 µg/L for lambda-cyhalothrin) within the 50 m reach of the ditch (*18*).

Following the success of this initial study, further examinations into the potential of vegetated agricultural drainage ditches for pesticide mitigation were conducted. A longer ditch (650 m) within the Thighman Lake watershed (Mississippi) was chosen for the next set of experiments. A spatial and temporal sampling scheme, similar to those previously detailed from other studies was used. Two pyrethroid insecticides, lambda-cyhalothrin and bifenthin were released in a slurry mixture to simulate a storm runoff event. Three hours following the initiation of the event, 95% and 99% of the measured lambda-cyhalothrin and bifenthin concentrations, respectively, were associated with ditch vegetation. Aqueous concentrations of lambda-cyhalothrin and bifenthrin at the inlet site (site 0) at 3 h were 374 and 666 µg/L, respectively. During the same time frame, but 200 m downstream, aqueous concentrations were 5.23 and 7.24 µg/L, respectively, for lambda-cyhalothrin and bifenthrin. Samples collected at the 400-m collection site indicated no chemical residues. Using regression analyses, it was determined that

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

both lambda-cyhalothrin and bifenthin aqueous concentrations could be reduced to 0.1% of their original concentration within 280 m of the vegetated drainage ditch. Mass balance calculations confirmed the significance of pesticide sorption to plant material as the major sink for the system (*19*).

A second study was initiated a year later in the same 650-m ditch in the Thighman Lake watershed. During this experiment, the pyrethroid insecticide esfenvalerate was mixed with suspended sediment (400 mg/L) to simulate a storm runoff event. Spatial and temporal water, sediment, and plant collections were similar to those described by Bennett et al. (*19*). Three hours following the initiation of the event, 99% of the measured pesticide was associated with the ditch vegetation. Excluding the injection site (which had no vegetation), measured esfenvalerate concentrations were associated more in plants than in sediment by a ratio of 6:1. Regression analyses determined that a ditch length of 509 m would be necessary to reduce the maximum aqueous pesticide concentration at the injection site to 0.1% of its original concentration (*20*).

Although three successful pesticide mitigation studies had been conducted in the Mississippi Delta with vegetated drainage ditches, the concept was still untested in sites outside the midsouthern US. Scientists in California were interested in the potential demonstrated by the management practice, especially given the state's pesticide concerns caused by organophosphate and pyrethroid insecticide runoff. Two ditches (100 m in length) were constructed along the edge of a tomato field in Yolo County, California. Both ditches had V-shaped cross-sections, which is commong to the growing region. One of the V-ditches was vegetated with annual ryegrass (*Lolium multiflorum*) and barley (*Hordeum vulgare*). Lamb's quarter (*Chenopodium album*), an invasive weed, was prevalent within the vegetated ditch. The second ditch was maintained with no vegetation (bare). A simulated irrigation runoff event containing a mixture of diazinon, permethrin, and crushed, sieved soil (45 kg) was amended equally into both of the ditches. To compare transport and fate of the pesticides, spatial and temporal sampling of water, sediment, and plants occurred as with previous experiments. Differences in half-distances (distance required to reduce initial concentration by 50%) were noted among the two V-ditches, indicating the importance of vegetation in pesticide mitigation. For the *cis-* and *trans-* isomers of permethrin, half- distances in the V-vegetated ditches ranged from 21-22 m. However, in the non-vegetated V-ditch, half distances for the same pesticide more than doubled to 50-55 m. The greatest difference was noted in diazinon half-distances. The half-distance for diazinon in V-vegetated ditches was 56 m, while nearly tripling to 158 m in the non-vegetated V-ditch (*21*). Due to the success and collaborative nature of this research, the California state office of the USDA Natural Resources Conservation Service (NRCS) agreed to designate vegetated agricultural drainage ditches (VADDs) as an eligible cost-share management practice within the Environmental Quality Incentives Program (EQIP). Within this program, farmers and landowners can apply for up to 75% cost-sharing for installing practices improving natural resource conditions. As a result of this research, this practice is listed in the state's electronic field office technical guide (eFOTG) as 607A – Surface Drainage, Field Ditch – Vegetated Agricultural Drainage Ditch. While not listed officially in Mississippi's eFOTG, NRCS engineers continue to promote practice 607A to improve runoff water quality (*22*).

Rice Fields – A Dual Benefit?

Continuing to think outside the box and, after the success of both constructed wetland and vegetated drainage ditch research, the question was posed, "Is there a practice that combines beneficial aspects of both wetlands and ditches?" Research plans were then focused on the pesticide mitigation potential of diverting storm runoff through rice (*Oryza sativa*) fields. This situation provides the potential benefits of phytoremediation without loss of valuable production acreage. One obvious question, however, is whether or not any pesticides sorbed by the rice would be translocated to the harvested (and consumed) seed. This separate question is currently being examined using separate smaller-scale studies.

To initially address the possibility of rice fields for pesticide mitigation, three ponds were chosen at the University of Mississippi Field Station. Two ponds were planted with equal densities of rice, while one pond remained non-vegetated to serve as a control. A simulated storm runoff event containing diazinon was amended equally to each of the three ponds. The event simulated runoff of 0.05% of the recommended pesticide application rate from a 32 ha field. Water, sediment, and rice (where applicable) samples were collected spatially and temporally for the duration of the experiment (72 h). The experiment was conducted twice, once during the typical rice growing season (pre-harvest), and once after rice had begun to senesce (post-harvest). Significant ($p < 0.05$) decreases in aqueous diazinon concentrations were noted between the inflow and outflow of both ponds planted with rice, during the pre-harvest and post-harvest experiments. Actual pesticide sorption to rice was minimal (1-3% of mass distribution); however, temporal sampling indicated that diazinon reached the sediment of outflow samples twice as fast in the non-vegetated pond when compared to either rice pond. Decreases in sediment diazinon concentrations of 77-100% from inflow to outflow were noted in the rice ponds, while diazinon sediment concentrations decreased less than 2% from inflow to outflow in the non-vegetated pond (*23*). Diazinon adsorption to rice tissue was further tested with rice senescence. Senescence to rice tissues showed significant decreases in tissue mass ($r^2=0.985$); however, there were no corollary increases in diazinon concentrations in the water column. Control vegetation placed within the treatment rice field showed negligible diazinon concentrations throughout senescence suggesting a lack of mobility and transfer of diazinon from senescing tissues (*24*).

Conclusion

Potential contamination of aquatic receiving systems from agricultural pesticide runoff is a challenging issue, requiring a preventative approach for a successful outcome. Additionally, multiple management practices should be considered together, rather than seeking one silver bullet solution. Solutions begin on the field, with more efficient pesticide application technology to reduce spray drift and attempts to confine applications to the most opportune weather conditions. Even with the most cautious application management approach, sudden weather events causing storm runoff are out of the control of the farmer. The challenges then shift toward management practices that intercept runoff, reducing the potential for pesticides to contaminate aquatic systems. This chapter has discussed some traditional (constructed wetlands) and innovative (vegetated ditches and rice fields) methods by which to mitigate pesticides in storm runoff. Although these basic practices have demonstrated great potential, little is known about the specific mechanisms of why these systems work. How does the hydrology affect the success of these management practices? How do variations in vegetation affect the pesticide reduction? How responsive can ditch mitigation become under more conservative water use practices and under changing climatic conditions? What is the role of the microbial community in these systems? These are just some of the questions future research needs to address. With a difficult economic future, solving the problems of pesticide pollution in agricultural runoff will require scientists and farmers to closely interact and think “outside the box” for possible solutions

Acknowledgments

Authors thank the countless students, technicians, and support staff who have made these projects possible over the last fifteen years. Thanks also to the landowners who graciously provided access throughout the growing season. Special thanks to the University of Mississippi Field Sta;tion and staff, particularly Mark Baker and David Mathis, who were instrumental in the success of many of the wetland studies. Although this chapter has been reviewed and approved in accordance with U.S. EPA requirements, its contents do not necessarily reflect U.S. EPA views or policy.

References

1. US Census Bureau. World Vital Events. http://www.census.gov/cgi-bin/ipc/pcwe, 2011.
2. Kiely, T.; Donaldson, D.; Grube, A. *Pesticides Industry Sales and Usage 2000 and 2001 Market Estimates*; EPA-733-R-04-001; Office of Prevention, Pesticides, and Toxic Substances: Washington, D.C., 2004; 33 pp.
3. US Environmental Protection Agency. 2006 Section 303(d) List Fact Sheet for California. http://iaspub.epa.gov/waters10/state_rept.control?p_state=CA&p_cycle=2006#TPOL, 2010.
4. Brix, H. *Water Sci. Technol.* **1994**, *29*, 71–78.
5. Mitsch, W. J.; Gosselink, J. G. *Wetlands*; Van Nostrand Reinhold: New York, NY, 1993; 722 pp.
6. Dahl, T. E.; Allord, G. J. *History of Wetlands in the Conterminous United States*; National Water Summary on Wetland Resources, United States Geological Survey Water Supply Paper 2425, 1997.
7. Rodgers, J. H., Jr.; Dunn, A. *Ecol. Eng.* **1992**, *1*, 83–95.

8. Moore, M. T.; Schulz, R.; Cooper, C. M.; Smith, S., Jr.; Rodgers, J. H., Jr. *Chemosphere* **2002**, *46*, 827–835.
9. Moore, M. T.; Rodgers, J. H., Jr.; Cooper, C. M; Smith, S., Jr. *Environ. Pollut.* **2000**, *110*, 393–399.
10. Moore, M. T.; Rodgers, J. H., Jr.; Smith, S., Jr.; Cooper, C. M. *Agric., Ecosyst. Environ.* **2001**, *84*, 169–176.
11. Huber, W. *Environ. Toxicol. Chem.* **1993**, *12*, 1865–1881.
12. Moore, M. T.; Bennett, E. R.; Cooper, C. M.; Smith, S., Jr.; Farris, J. L.; Drouillard, K. G.; Schulz, R. *Environ. Pollut.* **2006**, *142*, 288–294.
13. Locke, M. A; Knight, S. S.; Smith, S., Jr.; Cullum, R. F.; Zablotowicz, R. M.; Yuan, Y.; Bingner, R. L. *J. Soil Water Conserv.* **2008**, *63*, 430–442.
14. Weaver, M. A.; Zablotowicz, R. M.; Locke, M. A. *Chemosphere* **2004**, *57*, 853–862.
15. Moore, M. T.; Cooper, C. M.; Smith, S., Jr.; Cullum, R. F.; Knight, S. S.; Locke, M. A.; Bennett, E. R. *Water, Air, Soil Pollut.* **2007**, *184*, 313–321.
16. Moore, M. T.; Cooper, C. M.; Smith, S., Jr.; Cullum, R. F.; Knight, S. S.; Locke, M. A.; Bennett, E. R. *Environ. Pollut.* **2009**, *157*, 250–256.
17. US Department of Agriculture National Agricultural Statistics Service. 2009 State Agricultural Overview – Mississippi. http://www.nass.usda.gov/Statistics_by_State/Ag_Overview/AgOverview_MS.pdf, 2010.
18. Moore, M. T.; Bennett, E. R.; Cooper, C. M.; Smith, S., Jr.; Shields, F. D., Jr.; Milam, C. D.; Farris, J. L. *Agric., Ecosyst. Environ.* **2001**, *87*, 309–314.
19. Bennett, E. R.; Moore, M. T.; Cooper, C. M.; Smith, S., Jr.; Shields, F. D., Jr.; Drouillard, K. G.; Schulz, R. *Environ. Toxicol. Chem.* **2005**, *24*, 2121–2127.
20. Cooper, C. M.; Moore, M. T.; Bennett, E. R.; Smith, S., Jr.; Farris, J. L.; Milam, C. D.; Shields, F. D., Jr. *Water Sci. Technol.* **2004**, *49*, 117–123.
21. Moore, M. T.; Denton, D. L.; Cooper, C. M.; Wrysinski, J.; Miller, J. L.; Reece, K.; Crane, D.; Robins, P. *J. Environ. Qual.* **2008**, *37*, 486–493.
22. US Department of Agriculture Natural Resources Conservation Service. 607A-Vegetative Agricultural Drain Farm Bill Implementation – Water Quality; MS-ENG-607A-01 (JS) Engineering – Area 4; 2008.
23. Moore, M. T.; Kröger, R.; Cooper, C. M.; Cullum, R. F.; Smith, S., Jr.; Locke, M. A. *Pest Manage. Sci.* **2009**, *65*, 1182–1188.
24. Kröger, R.; Moore, M. T.; Cooper, C. M.; Holland, M. M. *Water, Air, Soil Pollut.* **2009**, *201*, 209–218.

Chapter 3

Use of Constructed Wetlands as Best Management Practice To Reduce Pesticide Loads

Robert Budd*

California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA 95814
***rbudd@cdpr.ca.gov**

The demand to find cost-effective methods to mitigate the effect of urban and agricultural runoff on surface water quality is increasing. Constructed wetlands (CW) have been proposed as a potential mitigation measure to treat a variety of contaminants. Both surface and subsurface CWs have demonstrated potential to retain chemicals with a wide range of physicochemical properties. From published results, it appears a reduction of at least 50% in outflow pesticide concentrations can be expected with minimum residence times of 100 hours. A robust vegetative community is a critical component of an effective mitigation system. Constructed wetlands have proven an effective best management practice to reduce aqueous pesticide concentrations through enhanced retention and transformation processes. However, more research is justified addressing the potential long-term effects of using CWs as natural contaminant filters.

Introduction

Constructed wetlands (CW) have gained popularity in recent years as a cost effective best management practice (BMP) to reduce contaminant loading to receiving waterways from both agricultural and urban sources. The potential forces involved in contaminant removal are physical (sorption, sedimentation, volatilization), chemical (hydrolysis, oxidation) and biological (biological degradation, plant uptake) processes (*1*). The design characteristics of constructed

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

wetlands vary considerably and are often governed by the water management program goals, as well as the topography, flows and availability of land. Due to the low cost of running and maintaining these systems, studies have been conducted evaluating their ability to mitigate a wide range of common water quality contaminants. In addition to pesticides, CWs have been shown to effectively mitigate solvents (*2*), pharmaceuticals (*3*, *4*), and metals (*5*). CWs can be broadly categorized into two flow regimes: surface flow and subsurface flow systems.

Surface Flow Constructed Wetlands

Surface flow CWs (SFCW) defining characteristic is that effluent movement is above the sediment bed layer. Although design characteristics vary considerably, a typical SFCW employs an initial sedimentation (settling) basin, followed by one or more vegetative wetland cells (*6–8*). SFCWs are often larger than subsurface flow systems and receive higher flow rates. These systems often include both open water and vegetated sections, which can change over time with new plant growth and subsequent senescence. The temporal variability in biomass has dramatic impacts on flow patterns and removal efficacies (*7*, *9*). The CWs are generally characterized by heterogeneous vegetation species, percent cover, and flow patterns throughout the systems. Several studies world wide representing an array of environmental conditions have shown the potential of SFCWs to reduce pesticide concentrations in outflows. Two SFCWs receiving agricultural runoff in northern California, USA, were shown to reduce outflow concentrations of five pyrethroids between 52-94% over the course of an entire irrigation season (*7*). Another SFCW receiving agricultural runoff built along a tributary of the Lourens River in South Africa was shown to reduce incoming azinphos-methyl concentrations by 91% (*10*). In Adelaide, Australia, herbicides were reduced by half within a system receiving inputs from industrial and residential sources, while removal efficiencies were greater than 79% for both mecoprop and MCPA over a two-year period in a wetland designed to treat effluent from a wastewater treatment plant in northeastern Spain (*3*, *11*).

Subsurface Flow Constructed Wetlands

As the name implies, flow through subsurface-flow CWs (SSCW) is primarily below the bed layer. Flow can be primarily horizontal or vertical through the substrate. They are often much smaller systems than SFCWs, with more homogenous physical parameters such as vegetation and substrate (i.e. gravel, sand). There are several contaminant removal processes that can be amplified in SSCWs. In addition to a greater control of vegetation density and biomass, retention times are often easier to adjust in SSCWs. This allows for greater pesticide contact time with emergent vegetation, substrate, as well as maximizing the potential for both microbial degradation and plant uptake. SSCWs have been utilized to reduce concentrations of commonly used triazine herbicides, which generally have moderate water solubility and low to moderate K_{OC} values. In a 4.9-m system vegetated with *Scirpus validus*, simazine removal rates were 77%

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

over a two-year period (*12*). In another trial, ametryn was removed at a lower rate (39%) over a longer flow path (24 m) vegetated with the common cattail *Typha latifolia* (*13*). Small mesocosms (1 m × 0.6 m) sown with *Phragmites autralis* displayed a high rate of chlorpyrifos removal, with an average 93% reduction in concentrations (*14*). One of the common disadvantages of SSCWs is the limitations on inflow rates, which might limit their applicability under larger field runoff operations. The highest flow rate observed in the reviewed studies was 0.12 $m^3 h^{-1}$, in comparison to 632 $m^3 h^{-1}$ observed in surface systems (*12*, *15*).

The SSCW and SFCW studies reviewed here span a wide range of environmental conditions, wetland characteristics and pesticide physicochemical properties. To examine the claim that constructed wetlands are a viable BMP under variable conditions, a synopsis of reported pesticide removal efficiencies (ratio of outlet/inlet concentrations) was conducted. Figure 1 represents the average wetland performance under surface and subsurface flow conditions, as well as the observed reductions by pesticide class. Reported efficacies were taken as individual data points, which may skew the results for studies with multiple observations. For example, multiple removal efficacy rates were reported for simazine in similarly designed SSCWs with varying flow rates and retention times (*12*). However, the overall results demonstrate high average removal efficiencies for both surface (61%) and subsurface (72%) systems. The effect appears to span across the major pesticide classes as well, with average removal of fungicides (42%), herbicides (61%), and insecticides (80%) (Figure 1).

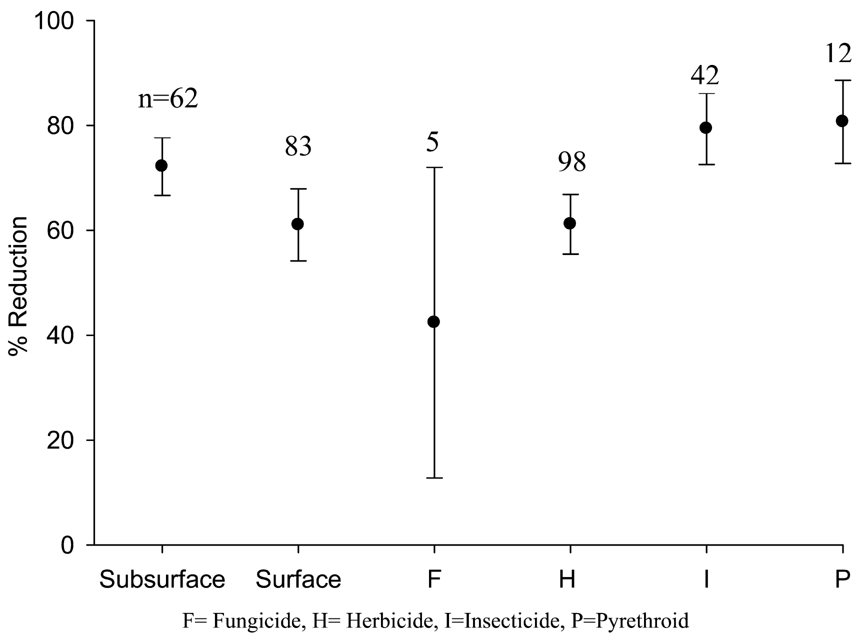


Figure 1. Average (± 95% CI) reductions in pesticide concentrations by flow type and chemical class. Note: Data points represent each reported % Reduction with a study

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Toxicity

In addition to chemical concentrations, toxicity is a common endpoint to measure wetland performance. Several studies have observed reduced toxicity of pesticides in the outputs of CWs (Table 1). The studies represent a wide range of contaminants and test species. Survival of the arthropod *Chironomus tentans* deployed in a 50-m vegetated (*Juncus effusus*) CW increased from 0 at the inlet to 100% at the outlet following a simulated runoff event of methyl parathion applied to a 50-ha field and a post application storm of 6.35 mm (*16*). In another CW toxicity study, the mortality of midges (*Chironomus* sp.) attributed to azinophos-methyl in runoff from adjacent fields was reduced from 43.8% at the inlet to 3.2% (average of two trials) at the outlet (*10*). A small (1.9 m) mesocosm study observed a >98% reduction in toxicity to *Ceriodaphnia dubia* and *Pimephales promelas* from a chlorpyrifos (19 µg l^{-1}) and chlorothalonil (296 µg l^{-1}) mixture after a 72 h retention period (*17*).

Although pesticide concentrations are typically lower after passing through the system, mitigation of aquatic toxicity is not always observed. Hunt et al. (2008) observed a 100% *C. dubia* mortality in water samples collected at the outlet of a 48-m CW receiving a mixture of pesticides in runoff from surrounding agricultural fields (*18*). Researchers at the National Sedimentation Laboratory have used a three-cell vegetated CW system to evaluate the toxicity of input water spiked with various pesticides (*6*, *19*, *20*). Moore et al. (2007) simulated a 1.3-cm rainfall event on a 14-ha agricultural field with input water spiked with 9 ng mL^{-1} lambda-cyhalothrin and 39 ng mL^{-1} cyfluthrin. Water concentrations remained at toxic levels to *H. azteca* within the secondary cell (farthest away from inlet) 61-d after initial dosing (*19*). Complete (100%) mortality of *C. dubia* continued within the secondary cell until the end of the 26-d study period following a second simulated event with diazinon amended runoff (*6*). Observed prolonged toxicity might be a result of additive or synergistic effects of pesticide mixtures, even at low concentrations (*21*). The additive or synergistic effect of mixtures of pesticides commonly found in waterways is in need of more research. Also, as discussed below, certain pesticides may elicit toxic effects long after being retained within the system.

Parameters Influencing Pesticide Removal

The overall efficacy of a wetland to retain contaminants from the water column is dictated by the interactions between the physicochemical properties of the contaminant and the environmental conditions of the system. Water quality parameters such as temperature, pH, and salinity all affect sorption potentials (*22*). In addition, the binding of hydrophobic contaminants are not only influenced by the quantity of suspended particles, but also the quality (i.e. aromaticity) of the organic carbon fraction (*23*, *24*). In a previous review of constructed wetland performance, a positive relationship was noted between log K_{ow} values and observed pesticide removal rates. The analysis concluded that a >50% reduction in pesticide concentrations were obtained in most systems for chemicals with log

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

K_{ow} values >4.2 (*25*). Although the factors mentioned above are all important considerations in partition behavior, this discussion will focus on the parameters with the possibility of adjustment by design or management.

Vegetation

It is widely accepted that vegetation is an integral component in the contaminant removal process (*7*, *9*). The presence of vegetation can increase macrophyte populations and organic matter available for pesticide sorption, enhance the physical trapping of contaminant-laden particles, and reduce flow velocity leading to increased sedimentation (*26*, *27*). Several studies have observed improved pesticide removal efficacy in systems with vegetation in comparison to their non-vegetated counterparts. Wetlands planted with the common bulrush (*Scirpus validus*) at 600 stems m^{-2} were able to increase the retention of metolachlor and simazine by 19 and 13%, respectively, compared to non-vegetated systems (*12*). In a second system, spiked methyl parathion was detected throughout the non-vegetated wetland, while undetected at the outlet of the wetland cell with >90% cover (*27*).

Knowledge of optimized vegetation parameters (species, biomass, density) would be informative for managing systems intended for pesticide retention. While several laboratory studies have evaluated sorption of organic chemicals to plant materials (*28*, *29*), there are few data for comparing the effect of specific vegetation factors such as species on wetland performance. Interestingly, one study observed little difference in permethrin removal between mesocosms planted with common wetland species *Typha latifolia*, *Sparganium americanum*, *Thalia dealbata*, and *Leersia oryzoides* (*30*). Although our knowledge of the complex interactions with vegetation is incomplete to optimize load reduction, it is well established that vegetation plays a role in both direct and indirect removal processes.

Researchers at the Mississippi Field Station, USA, have used constructed wetlands designed specifically to evaluate the fate of pesticides transported with agricultural runoff into the system. These vegetated flow-through systems allow direct measurement of pesticide phase partitioning in soil, water and plants. In the first set of experiments, amended runoff was discharged into vegetated mesocosms (59-73 m long) consisting primarily of *Juncus effusus*, *Leersia* sp., and *Luwigia* sp. While 25% of the chlorpyrifos mass was retained by plant material, atrazine concentrations were below detection levels for all plant samples (*26*, *31*). Two separate partitioning studies were conducted within a three-cell wetland system with multiple dominant species. Simulated pesticide amended runoff was introduced into the sediment basin and concentrations of pesticides were monitored in aqueous, sediment, and plant media throughout the system. The estimated mass of contaminants partitioning to plants were high for both the organophosphate diazinon (43%), as well as the pyrethroids lambda-cyhalothrin (49%) and cyfluthrin (76%) (*8*, *32*). These studies demonstrate that partitioning to plant materials is variable among pesticides.

Table 1. Observed toxicity to test species within surface flow constructed wetlands

Ref	*Input (amended)*	*Media*	*Test Species*	*Main Findings*
(*6*)	Diazinon	Water	*C. dubia*	100% mortality in second cell 9 h - 26 d after introduction
		Sediment	*C. dilutus*	20% (14 d) - 98% (26 d) survival in cell 2
(*18*)	Mixed runoff	Water	*C. dubia*	100% mortality at outlet during 5 surveys
		Sediment	*H. azteca*	72% mortality at outlets
(*18*)	Mixed runoff	Water	*C. dubia*	Significantly toxicity at outlets in 4 out of 5 surveys
		Sediment	*H. azteca*	100% mortality at outlet
(*19*)	Cyfluthrin, Cyhalothrin	Plant, Sediment, Water	*H. azteca*	~100% mortality in all media after 61 d in 2nd wetland cell
(*15*)	Mixed runoff	Water	*Chironomus sp.*	Mortality reduced 89% at outlet during runoff event
(*16*)	Methyl parathion	Water	*C. tentans*	100% survival after 40 m
(*17*)	Chlorpyrifos, Chlorothalonil	Water	*C. dubia, P. promelas*	>98% decrease in mortality after 72 h retention
(*20*)	Diazinon	Water	*H. azteca*	97% mortality in 2nd cell 27 d post treatment
		Sediment	*H. azteca*	53% survival (48 h) increased to 100% (27 d)
(*10*)	Azinphos-methyl	Water	*Chironomus sp.*	Mortality reduced 93% at outlet during two drift events

Although the majority of system studies have focused on emergent vegetation, other aquatic species common within wetland systems have shown promise in pesticide mitigation. Duckweed communities (*Landoltia punctata* and *Lemna minor*) actively depleted concentrations of 2,4-D in laboratory tests (*33*). In another laboratory study common microalgae species (*S. obliquus* and *S. quadricauda*) have been found to reduce aqueous fungicide and herbicide concentrations 10 – 58% over 96 h through phytoremediation processes (*34*). These studies suggest that a robust composition of heterogeneous aquatic species typically found in natural wetlands might be the best community structure to optimize mitigation of pesticide mixtures from the water column.

In addition to providing an emergent substrate for which contaminants may bind, the presence of vegetation has dramatic effects on the hydraulics of a system. The presence of vegetation increases drag, thereby decreasing flow velocity resulting in increased retention times (*35*). Channelized flow and shortcutting is common in systems void of vegetation (*36*). The optimal retention time was severely reduced within a section of a SFCW which had become channelized due to a lack of emergent vegetation. It was concluded that the lack of vegetation was the primary cause of uninhibited transport of pyrethroid laden sediment downstream (*7*). Regardless of the responsible removal process (sorption, phytoremediation, sedimentation) it is imperative that wetland managers maintain a healthy vegetative biomass and reduce shortcutting of flows whenever possible. The use of ‘hummocks’, or shallow planting beds situated perpendicular to flow, is a fairly new design component intended to improve hydraulic performance by providing variable water depths and promoting a more balanced cycle of plant growth and decomposition (*37*, *38*).

Hydrology

The hydrologic and hydraulic properties of a wetland have dramatic effects on the transport of pesticides through the system (*39*). Pesticide removal efficiency has been shown to decrease considerably with increasing flow (*12*). Many factors influence the hydraulic conditions of flow through systems, including the shape, length to width ratio, depth, topography, as well as the presence of islands, baffles, and vegetation (*40*). Consideration of these aspects in the design will allow for maximizing the residence time of the system.

The residence time represents the time frame in which the pesticide remains in the wetland and are subject to attenuation. The residence time also directly influences sedimentation processes (*36*). Sedimentation is a critical removal process for hydrophobic compounds which are typically transported bound to particles in the water column (*7*, *8*). Although residence time has been cited as a critical parameter in contaminant retention, little guidance exists for wetland managers desiring an estimate of expected contaminant mitigation based on the physical characteristics of the system. Pesticide loading into receiving waters are often complex mixtures, the composition of which dependent upon the demands of local agricultural and industrial entities for pest management (*7*). Because of the heterogeneous nature of contaminant loads, it would be helpful to establish relationships between design characteristics and wetland performance independent of the physicochemical properties of the pesticides of concern.

The effect of system length and residence time on removal efficiency (%) was evaluated in a meta-analysis with available data from reviewed studies. There were too few data to evaluate other design parameters such as vegetation species, biomass, and flow rates. One difficulty in performing such an exercise is the discrepancies in reported data. Not all studies reviewed reported physical characteristics of the system or removal efficiency. For the purposes of this evaluation some efficacy rates were estimated using the maximum reported input and output concentrations. Also, some of the studies did not report any outflow, effectively becoming closed systems. In these instances the "retention time" was recorded as the span of the sampling period. Although not truly representing flow through systems, they provide data representing comparative holding times necessary for effective transfer or degradation processes to occur to reduce aqueous concentrations. Both surface and subsurface flow systems were evaluated, but displayed separately. The studies encompassed a variety of system types, with system flow paths ranging from mesocosm in size (1 m) to large ponds (720 m). The analysis includes the removal efficiencies of 36 pesticides spanning a large range of physicochemical properties. Solubilities of monitored pesticides ranged from 0.001 mg L^{-1} (esfenvalerate) to 2.5 x 105 mg L^{-1} (mecoprop), while partitioning coefficient log K_{ow} values ranging from -1.88 (dicamba) to 7.3 (bifenthrin) (*41*). Removal efficiencies, as percent reduction in concentrations, were plotted against both retention time and flow path lengths. Any negative reported removal efficiencies were plotted as a 0% reduction.

Increasing the length of the system was expected to improve pesticide removal. Surprisingly, no trend between the two parameters could be inferred (Figure 2). One potential explanation is preferential sorption of hydrophobic pesticides. Pesticides with high Koc values have been shown to preferentially sorb to lighter particles with high organic carbon content such as clays and decomposed plant material that are more resistant to sedimentation compared to sand particles (*42*, *43*). Due to this behavior, bound pesticides have been found to be transported farther downstream than sedimentation rates would suggest (*7*, *42*, *44*).

A positive relationship was observed between retention time and reductions in pesticide aqueous concentrations (Figure 3). With one exception, there was a >50% reduction in all instances with system retention times of greater than 100 h. Although partitioning of a pesticide is ultimately influenced by specific environmental parameters, this exercise gives a starting point in evaluating one of the primary physical characteristics of the system. As mentioned, the reviewed pesticides and systems span a wide range of physical and chemical characteristics. The 100-h retention time should therefore represent a conservative estimate to achieve a desired reduction of ≥50% in initial aqueous pesticide concentrations.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

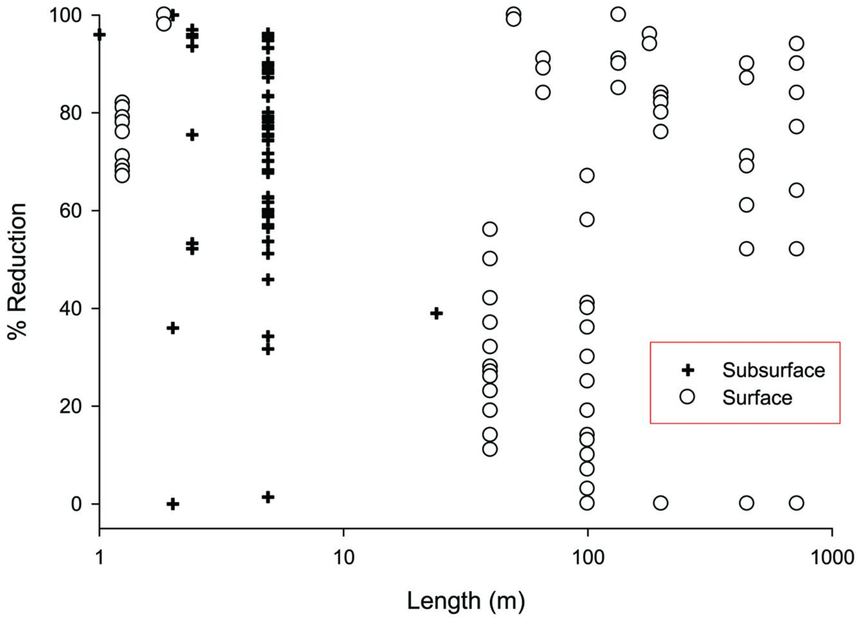


Figure 2. Reduction (%) in pesticide concentrations vs. flow path length (m) of system

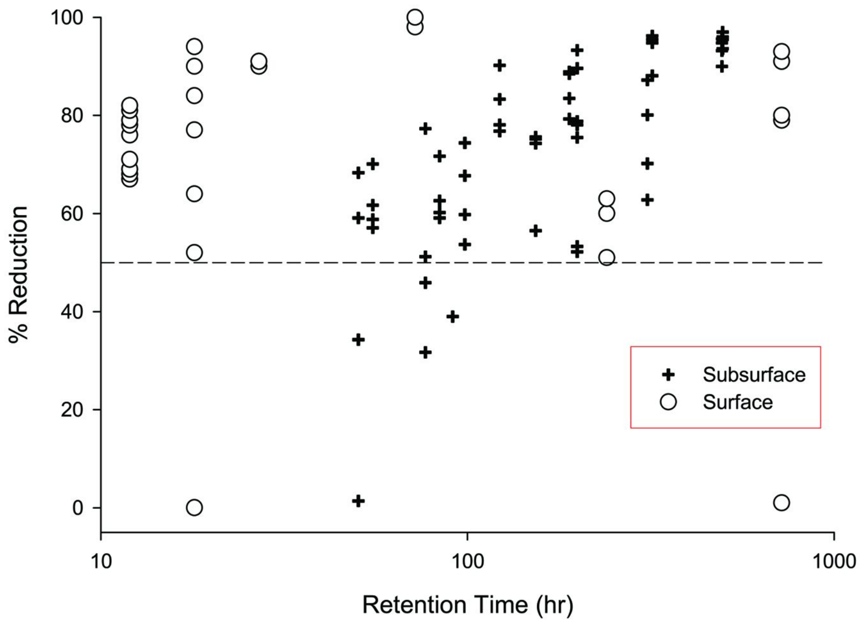


Figure 3. Reduction (%) in pesticide concentrations v. the system retention time (hr).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Long-Term Effects

Few studies have addressed the long-term ecological effects resulting from contaminant retention within the CW. As CWs act as natural filters for a wide range of contaminants, there is a concern that pesticides may accumulate to levels of ecological concern to wildlife using the wetland as habitat. Sorption to sediment, a mechanism responsible for lowering concentrations in the overlying water, has been found to subsequently act as a source of toxicity long after initial binding (*8*). This is of particular concern for hydrophobic pesticides such as pyrethroids. Several studies have observed invertebrate toxicity due to wetland sediment pyrethroid concentrations. A survey study of twenty-one wetlands receiving urban runoff located in southern California found that the macroinvertebrate communities of 86% of wetlands were at risk from deposited contaminants. Sediment concentrations from half of those surveyed were toxic to the bottom dwelling amphipod *H. azteca.* Toxicity identification evaluation (TIE) tests indicated that pyrethroids, primarily bifenthrin, were responsible for invertebrate mortality (*45*). In another study, the observed sediment toxicity from samples collected at the outlets of vegetated cells receiving agricultural runoff was attributed to pyrethroids as well (*18*).

The long-term potential toxicity of a chemical is ultimately controlled by rate of degradation or transformation processes. Degradation processes within the wetlands are influenced by the sediment redox potential, salinity, and the microbial community present (*46–48*). A recent study observed the dissipation behavior of pesticides in field contaminated sediment deposited within CW systems under aerobic and anaerobic conditions. For several of the pyrethroids, no measurable degradation was observed under *in situ* conditions over a 96 d period (*42*). It has been suggested that the strong sorption of some hydrophobic pesticides to sediments high in organic carbon may render them unavailable to microbial degradation, therefore increasing their persistence (*46*, *49*).

Conclusions

This review summarized available data on the ability of constructed wetlands to remove pesticides from the water column. Although variability in removal efficacies exists, the majority of studies observed high removal rates. This positive effect was observed between chemical classes with large differences in physicochemical properties, as well as systems with variable flows and vegetative cover. With proper design to maximize retention time, constructed wetlands may be used as an effective mitigation measure with little maintenance. However, care must be taken to ensure a healthy vegetative community, and minimizing shortcutting and channelized flow to maximize benefits. More research is necessary to further explore the long-term effects of pesticides that are retained but have the potential for prolonged toxicity within the systems. However, constructed wetlands have proven a viable best management practice to accomplish the management goal of reducing pesticide loads to receiving waters.

References

1. Imfeld, G.; Braeckevelt, M.; Kuschk, P.; Richnow, H. H. *Chemosphere* **2009**, *74* (3), 349–362.
2. Grove, J. K.; Stein, O. R. *Water Res.* **2005**, *39* (16), 4040–4050.
3. Matamoros, V.; Garcia, J.; Bayona, J. M. *Water Res.* **2008**, *42* (3), 653–660.
4. Dordio, A.; Pinto, J.; Dias, C. B.; Pinto, A. P.; Carvalho, A. J. P.; Teixeira, D. M. *Int. J. Environ. Anal. Chem.* **2009**, *89* (8−12), 835–848.
5. Cheng, S.; Grosse, W.; Karrenbrock, F.; Thoennessen, M. *Ecol. Eng.* **2002**, *18*, 317–325.
6. Bouldin, J. L.; Farris, J. L.; Moore, M. T.; Smith, S.; Cooper, C. M. *Arch. Environ. Contam. Toxicol.* **2007**, *53* (2), 174–182.
7. Budd, R.; O'Geen, A.; Goh, K. S.; Bondarenko, S.; Gan, J. *Environ. Sci. Technol.* **2009**, *43* (8), 2925–2930.
8. Moore, M. T.; Cooper, C. M.; Smith, S.; Cullum, R. F.; Knight, S. S.; Locke, M. A.; Bennett, E. R. *Environ. Pollut.* **2009**, *157* (1), 250–256.
9. Rose, M. T.; Sanchez-Bayo, F.; Crossan, A. N.; Kennedy, I. R. *Chemosphere* **2006**, *63* (11), 1849–1858.
10. Schulz, R.; Peall, S. K. C.; Hugo, C.; Krause, V. *Ecol. Eng.* **2001**, *18* (2), 239–245.
11. Page, D.; Dillon, P.; Mueller, J.; Bartkow, M. *Chemosphere* **2010**, *81*, 394–399.
12. Stearman, G. K.; George, D. B.; Carlson, K.; Lansford, S. *J. Environ. Qual.* **2003**, *32* (4), 1548–1556.
13. Borges, A. C.; Calijuri, M. D.; de Matos, A. T.; de Queiroz, M. *Water SA* **2009**, *35* (4), 441–445.
14. Agudelo, R. M.; Penuela, G.; Aguirre, N. J.; Morato, J.; Jaramillo, M. L. *Ecol. Eng.* **2010**, *36* (10), 1401–1408.
15. Schulz, R.; Peall, S. K. C. *Environ. Sci. Technol.* **2001**, *35* (2), 422–426.
16. Schulz, R.; Moore, M. T.; Bennett, E. R.; Farris, J. L.; Smith, S.; Cooper, C. M. *Environ. Toxical. Chem.* **2003**, *22* (6), 1262–1268.
17. Sherrard, R. M.; Bearr, J. S.; Murray-Gulde, C. L.; Rodgers, J. H.; Shah, Y. T. *Environ. Pollut.* **2004**, *127* (3), 385–394.
18. Hunt, J.; Anderson, B.; Philips, B.; Tjeerdema, R.; Largay, B.; Beretti, M.; Bern, A. *Environ. Pollut.* **2008**, *156* (2), 348–358.
19. Moore, M. T.; Lizotte, R. E.; Smith, S. *Bull. Environ. Contam. Toxicol.* **2007**, *78* (3−4), 245–248.
20. Smith, S.; Lizotte, R. E.; Moore, M. T. *Bull. Environ. Contam. Toxicol.* **2007**, *79* (1), 58–61.
21. Relyea, R. A. *Oecologia* **2009**, *159* (2), 363–376.
22. Strangroom, S.; Lester, J.; Collins, C *Environ. Technol.* **2000**, *21*, 845–863.
23. Ahmad, R.; Nelson, P.; Kookana, R. *Eur. J. Soil Sci.* **2006**, *57*, 883–893.
24. Oliver, D.; Baldock, J.; Kookana, R.; Grocke, S. *Chemosphere* **2005**, *60*, 531–541.
25. O'Geen, A.; Budd, R.; Gan, J.; Maynard, J.; Parikh, S.; Dahlgren, R. *Adv. Agron.* **2010**, *108*, 1–76.

26. Moore, M. T.; Schulz, R.; Cooper, C. M.; Smith, S.; Rodgers, J. H. *Chemosphere* **2002**, *46* (6), 827–835.
27. Schulz, R.; Moore, M. T.; Bennett, E. R.; Milam, C. D.; Bouldin, J. L.; Farris, J. L.; Smith, S.; Cooper, C. M. *Arch. Environ. Contam. Toxicol.* **2003**, *45* (3), 331–336.
28. Chen, B.; Johnson, E.; Chefetz, B.; Zhu, L.; Xing, B. *Environ. Sci. Technol.* **2005**, *39* (16), 6138–6146.
29. Chen, B.; Li, Y.; Guo, Y.; Zhu, L.; Schnoor, J. *Environ. Sci. Technol.* **2008**, *42* (5), 1517–1523.
30. Moore, M. T.; Kroger, R.; Cooper, C. M.; Smith, S. *Arch. Environ. Contam. Toxicol.* **2009**, *57* (2), 282–288.
31. Moore, M. T.; Rodgers, J. H.; Cooper, C. M.; Smith, S. *Environ. Pollut.* **2000**, *110* (3), 393–399.
32. Moore, M. T.; Cooper, C. M.; Smith, S.; Cullum, R. F.; Knight, S. S.; Locke, M. A.; Bennett, E. R. *Water, Air, Soil Pollut.* **2007**, *184* (1−4), 313–321.
33. Reinhold, D.; Vishwanathan, S.; Park, J. J.; Oh, D.; Saunders, F. M. *Chemosphere* **2010**, *80* (7), 687–692.
34. Dosnon-Olette, R.; Trotel-Aziz, P.; Couderchet, M.; Eullaffroy, P. *Chemosphere* **2010**, *79* (2), 117–123.
35. Jadhav, R. a. S. B. *Ecol. Eng.* **1995**, *5*, 48–496.
36. Fennessy, M. S.; Brueske, C. C.; Mitsch, W. J. *Ecol. Eng.* **1994**, *3* (4), 409–428.
37. Keefe, S.; Daniels, J.; Runkel, R.; Wass, R.; Stiles, E.; Barber, L. *Water Resour. Res.* **2010**, *46* (W11518), 1–13.
38. Thullen, J.; Satoris, J.; Nelson, M. *Ecol. Eng.* **2005**, *25*, 583–593.
39. Braskerud, B. C.; Haarstad, K. *Water Sci. Technol.* **2003**, *48* (5), 267–274.
40. Persson, J. a. H. W. *Ecol. Eng.* **2003**, *21*, 259–269.
41. IUPAC, I.U.o.P.a.A.C. Available from: http://sitem.herts.ac.uk/aeru/iupac/.
42. Budd, R.; O'Geen, A.; Goh, K.; Bondarenko, S.; Gan, J. *Chemosphere* **2011**, *83* (11), 1581–1587.
43. Luo, J. P.; Ma, M.; Liu, C.; Zha, J. M.; Wang, Z. J. *J. Soils Sediments* **2009**, *9* (3), 180–187.
44. Gan, J.; Lee, S.; Liu, W.; Haver, D.; Kabashima, J. *J. Environ. Qual.* **2005**, *34*, 836–841.
45. Brown, J. S.; Sutula, M.; Stransky, C.; Rudolph, J.; Byron, E. *J. Am. Water Resour. Assoc.* **2010**, *46* (2), 367–384.
46. Lee, S.; Gan, J. Y.; Kim, J. S.; Kabashima, J. N.; Crowley, D. E. *Environ. Toxicol. Chem.* **2004**, *23* (1), 1–6.
47. Lin, T.; Wen, Y.; Jiang, L. G.; Li, J. B.; Yang, S. L.; Zhou, Q. *Chemosphere* **2008**, *72* (1), 122–128.
48. Munoz-Leoz, B.; Garbisu, C.; Antiguedad, I.; Alonso, M.; Alonso, R.; Ruiz-Romera, E. *Soil Sci.* **2009**, *174* (4), 220–228.
49. Bondarenko, S.; Gan, J. Y. *Environ. Toxicol. Chem.* **2004**, *23* (8), 1809–1814.

Chapter 4

Efficacy of Sediment Basins for Reducing Sediment and Pyrethroid Transport in Almond Orchards

James C. Markle,*,[1] Tamara E. Watson,[1] Terry L. Prichard,[2] and P. Klassen[1]

[1]CURES, 531-D North Alta Avenue, Dinuba, CA 93618 USA
[2]University of California Cooperative Extension, 2101 East Earhart Avenue, Suite 200, Stockton, CA 95206 USA
***jcmarkle@sbcglobal.net**

This study examined the effectiveness of sediment basins for reducing sediment and pyrethroid residues in tailwater in two different trials conducted on a section of a large-scale commercial orchard in the Central Valley of California planted with nonpareil almonds. The first trial was conducted under typical tailwater flow conditions with no PAM added to the irrigation water. The second trial was conducted under slightly higher flow rates with PAM added at the point of irrigation input resulting in a five-fold reduction in total suspended solids (TSS) entering the sediment basin. In both trials, the total mass of the sediment leaving the sediment basin was reduced 79%-84% at the discharge point of the basin. Although PAM did not appear to significantly impact the total mass of pyrethroid leaving the field in this study, the sediment basin reduced the total pyrethroid load by 38%-61%.

Introduction

Off-site movement of pesticides and sediment from flood-irrigated agriculture has been a significant concern in the Central Valley of California. It is estimated that about 1.2 million tons per year of sediment are carried into the San Joaquin River by irrigation runoff from just West Stanislaus County farmland alone (*1*). These sediments may potentially carry pesticides, nutrients, metals and salts

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

trapped in the soil matrix and degrade surface water quality. In California's Central Valley there are 11 water body segments listed as "impaired" under the draft 2008 Clean Water Act Section 303(d) list, due to sediment toxicity of agricultural origin (*2*). Pyrethroid insecticides, which are widely used in California (*3*), are commonly found in sediments in creeks and agricultural drains at concentrations toxic to sensitive aquatic species (*4–6*). These compounds are highly hydrophobic and readily bind to the sediment.

Two best management practices (BMPs) recommended by the Natural Resource Conservation Service (NRCS) to retain soil on croplands and mitigate the transport of sediments are the use of sediment basins (Conservation Standard Practice No. 350) and polyacrylamide or PAM (Conservation Standard Practice No. 450).

If sediment basins are designed correctly, they may trap up to 70-80% of the sediment that flows into them (*7*). The sediment basins reduce flow rates and briefly retain water allowing deposition of the heavier suspended particles. Compounds that are highly hydrophobic such as the organochlorine pesticides, polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons, and pyrethroids bind readily to the sediment and are removed from the runoff water as the sediment settles. Although a number of papers have investigated the transport of highly hydrophobic compounds into agricultural streams with the sediment (*8*, *9*), to date few data exist on the effectiveness of sediment basins for the removal of pyrethroid residues from agricultural runoff.

Polyacrylamide (PAM) is a water soluble, high molecular weight, synthetic organic polymer. Since 1995, its first year of commercial use for irrigation-induced erosion control, it has been used on about one million hectares worldwide (*10*). It has also been used as a flocculent in municipal water treatment, paper manufacturing and food processing (*11*). PAM interacts with soil particles to stabilize both soil surface structure and pore continuity (*12*, *13*). Under experimental field-trial conditions, proper application of PAM with the first irrigation has substantially reduced soil erosion in furrow systems with benefits that include reduced topsoil loss, enhanced water infiltration, improved uptake of nutrients and pesticides, reduced furrow-reshaping operations, and reduced sediment-control requirements downstream of the field (*14*). By increasing soil flocculation, PAM has been shown to be effective in reducing sediment erosion through runoff and increasing water infiltration (*15*). A recent study has found that PAM applications to furrow irrigated crops reduced sediment erosion by over 90 percent (*16*). As reductions in sediment transport are achieved, reductions in pesticides such as dicofol that are highly absorbed to soil particles also occur (*17*). Broadcast applications of PAM were also found to be significantly effective in increasing water infiltration and reducing sediment transport (*18*).

To reduce in-row erosion, a grower may apply polyacrylamide (PAM) using the "patch method" at each irrigation event. The "patch method" involves applying PAM at the point in the furrow where the water first hits the soil; spreading it for a length of about 1-2 meters down the furrow to reduce the risk of the PAM becoming buried in the furrow or washing down the furrow where its effectiveness is reduced. The patch method creates a sort of gel-slab at the top of the furrow where the water slowly dissolves the PAM and carries it down the row furrow.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Growers have indicated that without the use of PAM in erodible soils, a sediment basin can quickly fill with sediment and therefore they would have to excavate the basin and dispose of the accumulated soil more frequently. Polyacrylamide products are commercially available for $4 to $5.50/lb (*11*) and are thus attractive to many farmers who perceive an erosion problem, regardless of other economic considerations

This study examines the efficiency of sediment basins with and without the use of PAM at reducing lambda-cyhalothrin residues in irrigation drainage water following a lambda-cyhalothrin application to almonds at the rate of 0.045 kg ai/ha. Pyrethroids, including lambda-cyhalothrin, are typically applied to the orchards as either a winter dormant spray or as in-season spray to control various pests. It is a companion study to a previous study conducted in tomatoes (*19*) which also appears in this symposium series. Data from these studies will be used to evaluate the effectiveness of using these technologies as Best Management Practices (BMPs) in reducing the off-site transport of pyrethroids in irrigation drain waters. The purpose of these studies was not to repeat the body of research that has already confirmed the efficacy of PAM and sediment basins in reducing total suspended solids (TSS), but to learn more about how these practices might mitigate pyrethroid transport in these systems.

Materials and Methods

Study Site and Irrigation

The study site is a 57 hectare almond orchard near Chowchilla in the San Joaquin Valley. The field is divided into numerous blocks, 16 hectares of which are planted to nonpareil almonds. The site is relatively flat with a 1-2 percent slope. The National Resource Conservation Service (NRCS) has classified the soil type as a mixture of Chino fine sandy loam and Traver loam.

The field is surface irrigated using district canal water (see Figure 1). Each row in the field is provided with irrigation water from a single orchard irrigation head located at the top of the row and the rows are bermed on each side. The row is 6.7 m between berms and 366 m in length. At the bottom side of the field block is an interception ditch installed to capture irrigation drainage water which is subsequently directed to a sediment basin. The basin is basically rectangular in shape and measures 5.8 m by 49 m and averages 2.1 m deep. It has an estimated holding capacity of approximately 600,000 liters. Opposite the inlet side of the pond is a recirculation pump that returns the water for reuse to other parts of the orchard.

Application of Lambda-Cyhalothrin

Lambda-cyhalothrin is typically applied to almonds in this region at the hull split nut growth stage to control navel orangeworm (*Amyelois transitella*) and other chewing insects. In this study, lambda-cyhalothrin was applied by ground as Warrior® with Zeon Technology™ using an air blast sprayer at the rate of 0.045

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

kg ai/ha on the morning of July 27, 2009. One entire block of 16 ha was treated for a total target mass of 0.72 kg ai.

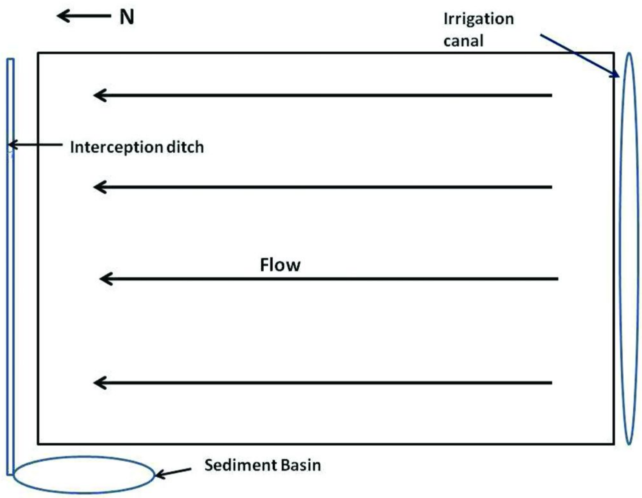


Figure 1. Plot diagram of the 16 hectare plot used for the study

Study Design

This study consisted of two trials:

- Sediment basin alone without the use of PAM
- Sediment basin in combination with PAM application

In the first trial, rows 1-16 were irrigated but no PAM was applied. Irrigation water was added at the top of the field through an orchard irrigation valve located at the top of each row. The tailwater from each row was collected in a drainage ditch at the bottom of the field. The tailwater then passes through a 15.2 cm PVC pipe and is discharged into the sediment basin. Water from the sediment basin is pumped out of the opposite side of the basin through a 10.2 cm diameter steel pipe and is recirculated back for reuse to other locations in the orchard. Duplicate 250 mL samples (one for pyrethroid analysis and one for TSS) of drainage water were taken every hour at the entrance to the sediment basin. Once water began to flow out of the sediment basin, samples were collected hourly at the sediment basin exit.

In the second trial, rows 32-40 were irrigated and approximately 180 g of PAM was applied to each row at the top of the block where the irrigation water enters the field. The product used was Soil Fix IR (CIBA Specialties) which contains 90% PAM. The nominal rate applied was approximately 750 g/ha. Duplicate 250 ml samples of drainage water were taken every hour at the entrance and exit (upon initiation of flow) of the sediment basin.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Sample Collection

Tailwater samples were sampled either by hand or with a pole sampler (Wildco 3.5 m swing sampler, 165-C10) hourly for 10 hours from the exit side of a 15.2 cm pipe located between the interception ditch at the base of the field and the entrance to the sediment basin and from the field drain (10.2 cm) at the end of the sediment basin. At each sampling interval and location, a sample of approximately 250 mL was collected for lambda-cyhalothrin analysis in a 500 mL amber Boston round glass (Fisher Scientific, P/N 02-911-738) and another sample of approximately 250 mL was collected for measuring total suspended solids in a 500 mL Nalgene polypropylene bottle (Fisher Scientific, A71841086). Within five minutes of collection, the samples were placed in a cooler filled with ice and kept on ice until delivery to the analytical laboratory. Samples were kept in ice chests for a maximum period of 6 days prior to delivery to the analytical laboratory where they were immediately placed in refrigerators for storage until extraction.

Sample Analysis-Lambda-Cyhalothrin

All samples were delivered to Morse Laboratories, Inc., in Sacramento, California for analysis. Samples were extracted within 21 days and analyzed within 24 days of receipt.

To extract samples prior to lambda-cyhalothrin analysis, 100 mL of MeOH and 25 mL of hexane were added to each sample bottle. The samples were shaken on a mechanical shaker for approximately 10 minutes and the solvent layers were allowed to separate. A 5.0 mL aliquot of the upper hexane layer was transferred to a test tube (13 x 100 mm) and concentrated to ~0.2 mL using an N-evap evaporator set to ≤40 ^{o}C. The samples were manually evaporated to dryness with nitrogen. To each sample, 2.0 mL hexane were added, mixed well and sonicated. The sample was transferred to a 500 mg Varian Silica Bond Elut solid phase extraction cartridge with a 1.0 mL rinse of hexane. The cartridge was eluted under gravity or low pressure and the eluate discarded. A 10 mL collection tube was placed under each cartridge and the cartridge was eluted with 6 ml of a hexane/diethyl ether [9:1, v/v] solution. The eluate was concentrated to dryness under a stream of dry, clean air in a heating block set to 40^{o}C. The sample was redissolved in acetone +0.1% peanut oil solution with ultrasonication. The sample was transferred to an autosampler vial for final determination by GC-MSD/NICI.

Note: The 0.1% peanut oil in acetone solution is used to minimize the effect of matrix related to GC-MSD response enhancement and to minimize possible peak tailing due to adsorption.

Final Determination by GC-MSD

The following instrument and conditions have been found to be suitable for analysis. Other instruments can also be used, however optimization may be required to achieve the desired separation and sensitivity. The Limit of Determination (LOD) for the analytical method was 0.01 ug/L.

Instrument Conditions

GC system	Agilent 6890 with split/splitless injector
MSD system	Agilent 5973 with negative ion chemical ionization
Injection temperature	275°C
Injection liner	4 mm i.d. double gooseneck splitless liner (unpacked)
Column	Varian CPSil 8 30 m × 0.25 mm, 0.25 µm film thickness (5% diphenyl, 95% dimethylpolysiloxane)
Column flow rate	0.9 mL min^{-1} constant flow
Injection mode	Pulsed splitless, 30 psi for 1 min, purge flow to split vent 50 psi @2 min
Injection volume	2 µL
Column temperature program	80°C for 1 min then program at 40°C/min to 180°C, hold for 0 min then program at 5 °C/min to 305 °C, hold for 0 min.

Under these conditions, lambda-cyhalothrin has retention times of 19.6 and 19.9 minutes for the two resolved diastereomers.

Sample Analysis-Total Suspended Solids

The analysis of tailwater samples for Total Suspended Solids (TSS) was based on Method 2540 D "Total Suspended Solids Dried at 103-105^{o}C" as described in Standard Methods for Examination of Water and Wastewater (*20*).

The glass fiber filter and planchet were weighed prior to filtration. The filter disk was inserted into the filtration apparatus. The sample of tailwater water was added to the filter and rinsed with three successive 10 mL portions of reagent grade water. Continuous suction was allowed for about 3 minutes after filtration was complete. The filter and planchet were removed from the filtration unit and dried in an oven at 103 to 105^{o}C for one hour. The sample was cooled in a desiccator to balance temperature and weighed. This cycle of drying, desiccation and weighing was repeated until a constant weight is obtained. The Limit of Determination (LOD) for the analytical method was 0.25 ug/L. The total weight of suspended solids in each sample was calculated using the following formula.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

mg total suspended solids = (weight of filter + dried residue) – (weight of filter)

Calculation of Water, Sediment, and Pyrethroid Discharges

Amounts of water, suspended solids, and pyrethroids entering and leaving the sediment basin were calculated for each sampling interval. Using the Doppler flow meter for measuring the water velocity in the pipes and knowing the cross-sectional area of the inlet and outlet pipes, flow volumes between each interval can be calculated. This volume is then multiplied by the residue concentration in ug/L for the pyrethroid mass load (mg) and the mg/L concentration to determine the mass load (g) of total suspended solids. We assume that the flow velocity is relatively constant between each sampling interval

Results and Discussion

Flow Rates

During the study, considerable variability in drainage flows occurred between trials and among irrigation rows within a trial which must be considered in the interpretation of the study results. In addition, the grower consciously conserves his water by turning rows off as they reach the end of the row and adds subsequent new rows to the irrigation cycle for maximum efficiency. As a result, the flows do not exhibit a typical bell-shaped curve with flow building up at the inlet as rows enter the interception ditch and gradually decline once irrigation is stopped. Instead, we observed a more constant flow throughout the day of the trial with a series of pulses to the flow as new rows were started and come on line.

We monitored the daytime sets from two consecutive irrigation days. On the first day of the study, Trial #1 (rows 1-16) tested the efficacy of the sediment basin alone (no PAM) in reducing sediment loads and pyrethroid residues. On the second day of the study, Trial #2 (rows 32-40) tested the efficacy of using PAM when used in conjunction with the sediment basins. Two other irrigations sets (rows 17-31 and rows 41-56) were run at night and no samples were collected. Flows were measured throughout the course of the irrigation cycle (day and night). Total volume of runoff from the field as measured at the inlet to the sediment basin was approximately 590,000 gallons (2.2 million liters). This volume equates to approximately 14% of the nominally applied amount. This closely equates with the estimated runoff from other irrigations in the field.

Nominal volume applied = 40 acres x 27,154 gallons/acre-inch x 6 inches
= 4.1 million gallons applied (1.6 million liters)

Flow rates at the inlet to the basin varied from 0 to 1291 liters/ minute during the course of the study. At the outlet, the flow was regulated by a discharge pump that was kept at a constant 662 liters/minute. The pump was started when the levels in the basin reached approximately 0.6 meters above the bottom of the basin and were turned off when the basin went below this level.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

At the start of the first trial, there was some water in the interception ditch from an irrigation that had been completed in another part of the orchard earlier the same week. It is recognized that this may dilute the absolute concentration in the tailwater samples (TSS or pyrethroid). However, it should not affect the mass balance differential between the inlet and outlet of the sediment basin on which we draw conclusions about the basin's effectiveness. It took approximately five hours from the start of irrigation until the runoff water reached the interception ditch (about a quarter of a mile from discharge to row end). Samples for TSS and pyrethroid analyses were collected each hour from the start of runoff (12:45 am) through 11:00 pm. The night time irrigation set (rows 17-31) was started at 10:45 pm.

Flow rate in Trial #1 ranged from a low of 3.785 liters/minute to a maximum of 1124 liters/minute at the inlet. Total flow observed at the inlet was 384,000 liters (101,584 gallons) during the 10 hours of monitoring, or 38,400 liters/hour.

In the second trial, water from the previous night's irrigation was still draining into the sediment basin although this dramatically tapered off by the time the irrigation for Trial #2 was started (9:50 am). PAM was applied to each irrigation row using the "patch" method described above. By 3:00 pm (five hours after the start of irrigation), water from the top of the field began to drain into the interception ditch. Samples were collected each hour until 12:00 pm. Irrigation was switched to the night time set (rows 41-56) at 11 pm.

Flow in the second trial was generally higher than the first perhaps due to the fewer number of rows irrigated. The flow rate ranged from 261 liters/minute to a maximum of 1291 liters/minute. Total flow observed was 590,000 liters (155,878 gallons) during the 9 hours of monitoring, or 65,555 liters/hour, almost twice the volume of the first trial.

Lambda-Cyhalothrin Residues and Total Suspended Solids (TSS)

With each set of analyses for lambda-cyhalothrin, two untreated water/sediment samples were fortified at two different rates to validate the analytical set. The average recovery of lambda-cyhalothrin was 103 ± 12.7% over the course of the study. Lambda-cyhalothrin residue levels in the samples from the study conducted without adding PAM to the irrigation runoff ranged from 0.555 to <0.01 ug/L at the field exit (prior to entering the sediment basin) and 0.185 to 0.012 ug/L at the exit of the sediment basin. Levels of total suspended solids ranged from 1280 mg/L to 50 mg/L prior to entering the sediment basin and 300 mg/L to 50 mg/L at the exit of the sediment basin. The results show a decline in both TSS and pyrethroid concentration during the time the sediment basin was discharging.

In the second trial, lambda-cyhalothrin residue levels in the samples from the study conducted with PAM added to the irrigation water ranged from 0.33 to 0.21 ug/L at the entrance to the sediment basin and from 0.50 to 0.11 ug/L at the exit of the sediment basin. At the same time, the concentrations of TSS ranged from 280 to 10 mg/L at the entrance to the sediment basin and 35 to <0.25 mg/L at the exit of the sediment basin.

Estimation of Efficiency for Removing Residues

Using the flow measurements and the concentrations of sediment and pyrethroids, the amount of water, sediment, and pyrethroids entering and leaving the sediment basin were calculated as a function of time using the methods as described earlier.

A plot of the total TSS (in g) residues entering and leaving the sediment basin in Trial 1 (no PAM) is shown in Figure 2. A significant amount of sediment (206 kg) enters the sediment basin, but only 43 kg (79% efficiency) remained in the runoff water at the basin exit.

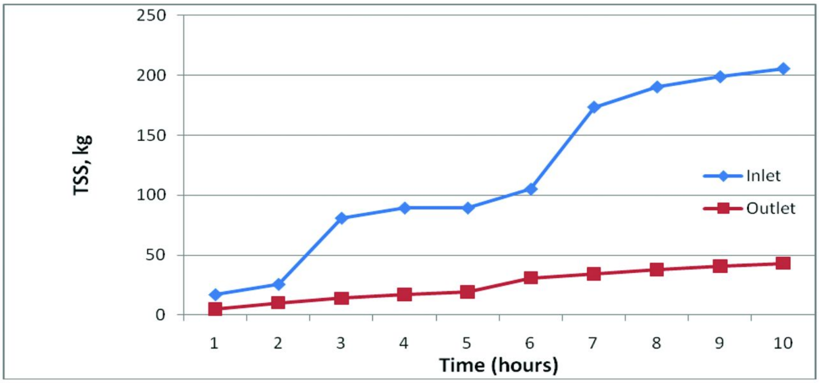


Figure 2. Total Suspended Solids (TSS) in the Inlet and Outlet of the Sediment Basin in Trial 1 (without PAM)

Similarly, a plot of the total lambda-cyhalothrin (in mg) entering and leaving the sediment basin for Trial 1 was plotted in Figure 3. A total of 108 mg of lambda-cyhalothrin enters the sediment basin and 43 mg remained in the water exiting the basin.

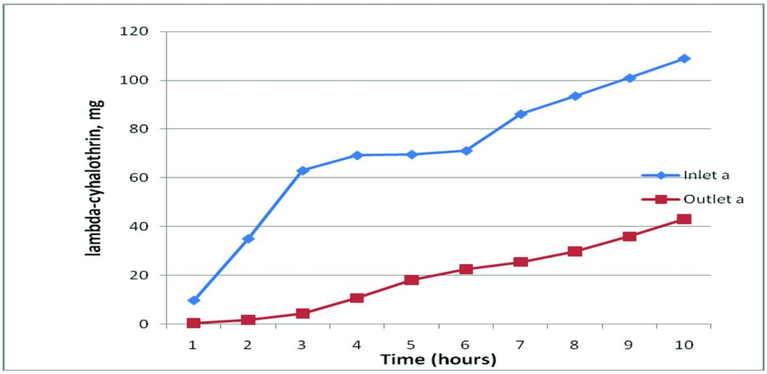


Figure 3. Total lambda-cyhalothrin residues in the Inlet and Outlet of the Sediment Basin in Trial 1 (without PAM)

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Although only low levels of lambda-cyhalothrin left the treated field (0.05% of applied), the levels found in runoff water are high enough to be of biological significance to some aquatic species. As a result, developing methods for reducing pyrethroid discharges continue to be of importance. In this trial, there was a 61% reduction of lambda-cyhalothrin with the sediment basin, presumably because of the adherence to the sediment particles as they settle out. The fact that the reduction is not to the same degree as that observed for the sediment suggest that either some pyrethroid is left in solution (unlikely given the hydrophobic nature of lambda-cyhalothrin (water solubility-0.004 mg/L)) or that loss may be occurring by adherence to fine, low weight sediment particles that have not settled out. In this study, no attempt was made to measure the size of the soil particles entering and exiting the sediment basin.

In the second trial (with PAM) a plot of total TSS residues (Figure 4) showed a similar pattern to that seen in Trial 1. Although the flows were higher, the levels of sediment entering the sediment basin were significantly reduced when compared to the first trial by almost a 5X factor (38 kg) presumably due to the application of PAM. In addition, the sediment basin removed an additional 84% of the sediment from the runoff as measured at the basin exit (6 kg).

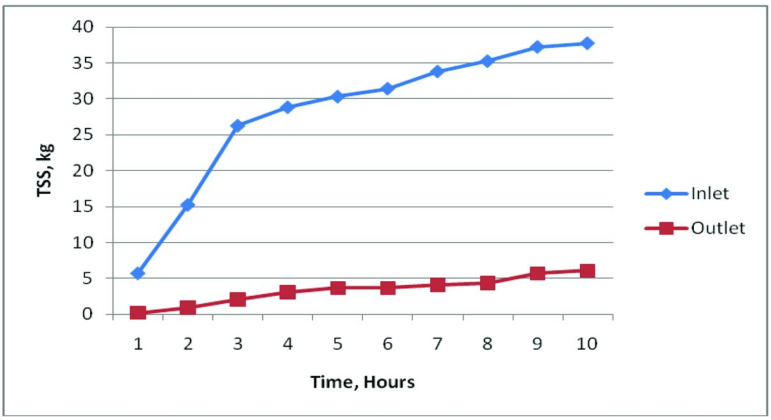


Figure 4. Total Suspended Solids (TSS) in the Inlet and Outlet of the Sediment Basin in Trial 2 (with PAM)

For lambda-cyhalothrin residues (see Figure 5), the higher flow rates resulted in more chemical reaching the entrance to the sediment basin (0.12 % of applied). Again, presumably due to the higher flow rates, the reduction of pyrethroid residues was significant (38%), but not as great as those observed in the previous trial.

The results of these calculations are summarized in Table I.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

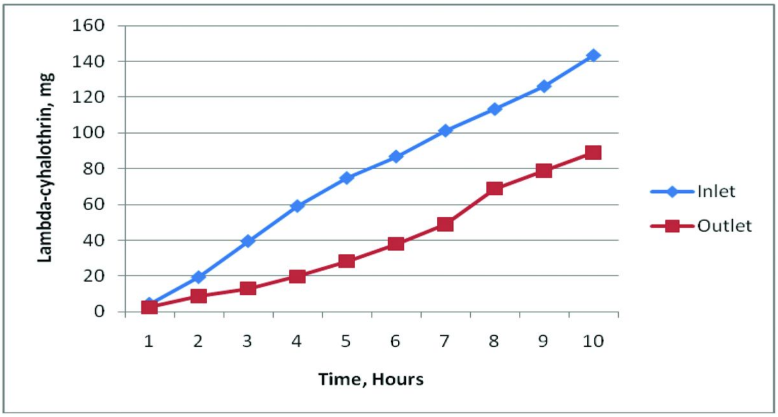


Figure 5. Total lambda-cyhalothrin residues in the Inlet and Outlet of the Sediment Basin in Trial 2 (with PAM)

Table I. Overall Summary for Both Trials

	Trial 1 (no PAM)	*Trial 2 (with PAM)*
Treated Area	4.7 hectares (11.6 acres)	2.6 hectares (6.4 acres)
Pyrethroid Applied	210 g ai (0.464 lb ai)	116 g ai (0.256 lb ai)
Pyrethroid Entering Basin (% of applied)	108.8 mg ai (0.05%)	143.2 mg ai (0.12%)
Pyrethroid Leaving Basin	43.0	88.9
Pyrethroid Reduction from Basin (%)	61%	38%
Sediment Entering Basin	206 kg	38 kg
Sediment Leaving Basin	43 kg	6 kg
Sediment Reduction (%)	79%	84%

Conclusions

Sediment basins can play an important role in mitigating the irrigation transport potential for both soil and pyrethroid residues. In this trial, 79-84% of the total suspended sediment entering a sediment basin was removed from the runoff. Given the hydrophobic nature of the pyrethroids as a class of insecticides, they will be transported as a chemical bound to sediments and these residue-bearing particles will be removed from the runoff stream as the sediment settles out. Although removal of the pyrethroids was 38% to 61%, the levels observed were not as high as the sediment response. This, possibly, may be due

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

to either the low water solubility of lambda-cyhalothrin (0.004 mg/L) or to the absorption of lambda-cyhalothrin residues to lighter weight clay particles which did not have a chance to settle out in this trial. These data also suggest that flow rate might impact both sediment and pesticide runoff. Future research on irrigation practices might help determine if decreasing flow rate could help reduce sediment and pesticide runoff.

The use of polyacrylamide (PAM) at each irrigation event can also reduce the levels of sediment leaving the field. Under the conditions observed in this study, a fivefold increase in sediment retention and subsequently sediment transport reduction from the field was observed. The sediment that did make it off the field was effectively removed with the sediment basin. Although application of PAM did not have as dramatic an effect on the total amount of pyrethroid residues leaving the field, any field management measures taken to reduce the total sediment loads leaving the orchard would be expected to have a positive effect on pyrethroid residue mitigation.

Acknowledgments

This work was generously sponsored by a grant from the Almond Board of California.

References

1. McCutchan, M.; Osterli, P.; Letey, J. Polymers check furrow erosion, help river life. *Calif. Agric.* **1993**, *47* (5), 10–11.
2. Long, R. F.; Hanson, B. R.; Fulton, A.; Weston, D. P. Mitigation techniques reduce sediment in runoff from furrow-irrigated cropland. *Calif. Agric.* **2010**, *64* (4), 135–140.
3. PUR. *Summary of Pesticide Use Reporting Data-2009 Indexed by Chemical*; Annual report from the California Department of Pesticide Registration, 2009.
4. Weston, D. P.; You, J.; Lydy, M. J. Distribution and toxicity of sediment-associated pesticides in agricultural-dominated water bodies of California's Central Valley. *Environ. Sci. Technol.* **2004**, *38*, 2752–2759.
5. Weston, D. P.; Zang, M; Lydy, M. J. Identifying the cause and source of sediment toxicity in an agriculture-influence creek. *Environ. Toxicol. Chem.* **2008**, *27* (4), 953–962.
6. Phillips, B. M.; Anderson, B. S.; Hunt, J. W. Solid-phase sediment toxicity identification in an agricultural stream. *Environ. Toxicol. Chem.* **2006**, *25* (6), 1671–1676.
7. California Stormwater Quality Association. *Stormwater Best Management Practice Handbook for New Development and Redevelopment*; 2003.
8. Pereira, W. E.; Domagalski, J. E.; Hostettler, F. D. Occurrence and Accumulation of Pesticides and Organic Contaminants in River Sediment, Water and Clam Tissues from the San Joaquin River and Tributaries, California. *Environ. Toxicol. Chem.* **1995**, *15* (2), 172–180.

9. Van Metre, P. C.; Callender, E.; Fuller, C. C. Historical Trends in Organochlorine Compounds in River Basins Identified Using Sediment Cores from Reservoirs. *Environ. Sci. Technol.* **1997**, *31* (8), 2339–2344.
10. Sojka, R. E.; Lentz, R. D.; Ross, C. W.; Trout, T. J.; Bjorneberg, D. L.; Aase, J. K. Polyacrylamide effects on infiltration in irrigated agriculture. *J. Soil Water Conserv.* **1998**, *53* (4), 325–331.
11. Sojka, R. E.; Lentz, R. D. Reducing Furrow Irrigation Erosion with Polyacrylamide (PAM). *J. Prod. Agric.* **1997**, *10* (1), 47–52.
12. De Boodt, M. F. In *Soil colloids and their associations*; NATO ASI series B: Physics; De Boodt, M. F., Hates, M. H. B., Herbillon, A., Eds.; Plenum: New York, 1990; Vol. 215.
13. Malik, M.; Letey, J. Adsorption of polyacrylamide and polysaccharide polymers on soil materials. *Soil Sci. Soc. Am. J.* **1991**, *55* (2), 380–383.
14. Sojka, R. E.; Lentz, R. D. Polyacrylamide for Furrow-Irrigation Erosion Control. *Irrigation Journal* **1996**, *46* (1), 8–11.
15. Lentz, R. D.; Steiber, T. D.; Sojka, R. E. Applying polyacrylamide (PAM) to reduce erosion and increase infiltration under furrow irrigation. In *Proceedings of Winter Commodity Schools--1995*; Robertson, L. D., Nolte, P., Vodraska, B., King, B., Tindall, T., Romanko, R., Gallian, J., Eds.; University of Idaho Cooperative Extension: Moscow, ID, 1995; pp 79−92
16. Orts, W. J.; Roa-Espinosa, A.; Sojka, R. E.; Glenn, G. M.; Imam, S. H.; Erlacher, K.; Pedersen, J. S. Use of synthetic polymers and biopolymers for soil stabilization in agricultural, construction, and military applications. *J. Mater. Civ. Eng.* **2007**, *19* (1), 58–66.
17. Singh, G.; Letey, J.; Hanson, P.; Osterli, P.; Spencer, W. F. Soil erosion and pesticide transport from an irrigated field. *J. Environ. Sci. Health* **1996**, *B3* (1), 25–41.
18. Abu-Zreig, M. Control of Rainfall-Induced Soil Erosion with Various Types of Polyacrylamide. *J. Soils Sediments* **2006**, *6* (3), 137–144.
19. Jones, R. L.; Markle, J. C.. Management Practices for Reducing Discharge of Pyrethroids and Sediment in Irrigation Water from Row Crops. In *Pesticide Mitigation Strategies for Surface Water Quality*; ACS Symposium Series 1075; American Chemical Society: Washington, DC, 2011; Chapter 5, doi: bk-2011-1075.ch005.
20. Greenberg, A.; et al. *Standard Methods for the Examination of Water and Wastewater*, 18th ed.; 1992; Method 2540 D Total Suspended Solids Dried at 103-105^{o}C.

Chapter 5

Management Practices for Reducing Discharge of Pyrethroids and Sediment in Irrigation Drainage Water from Row Crops

Russell L. Jones*[,1] and James C. Markle[2]

[1]Bayer CropScience, 17745 South Metcalf, Stilwell, KS 66085 USA
[2]CURES, 531-A North Alta Avenue, Dinuba, CA 93618 USA
***russell.jones@bayer.com**

The use of polyacrylamide (PAM) and sediment basins have long been recognized as effective management practices for reducing pesticide and sediments in drainage water from irrigated agriculture. Their effectiveness has been confirmed by many independent studies. This study examined transport of pyrethroids and sediment from tomato fields under two sets of conditions representing a wide range of sediment transport potential. The study results show that management practices that reduce water and sediment from the field (e.g. PAM and more careful irrigation flow control) and also technologies that remove sediment from edge of field tail waters (e.g. sediment basins) are also effective in reducing pyrethroid transport, with reductions of up to 80 % demonstrated in these trials.

Introduction

Previous research indicates that sediment basins can play an effective role in the reduction of sediment and pesticide runoff from agricultural fields. If sediment basins are designed correctly, they may trap up to 70-80% of the sediment that flows into them (*1*). Compounds that are highly hydrophobic such as the organochlorine pesticides, polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons, and pyrethroids bind readily to the sediment and are removed from the runoff water as the sediment settles. Although a number of papers have investigated the transport of highly hydrophobic compounds into agricultural

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

streams with the sediment (*2*, *3*) no published data existed on the effectiveness of sediment basins for the removal of pyrethroid residues from agricultural runoff.

Polyacrylamide (PAM) is a water soluble, synthetic organic polymer. It has been used in agriculture for soil erosion control on about one million hectares worldwide (*4*). It has also been used as a flocculent in municipal water treatment, paper manufacturing and food processing (*5*). PAM interacts with soil particles to stabilize both soil surface structure and pore continuity (*6*, *7*). Under experimental field-trial conditions, proper application of PAM with the first irrigation has substantially reduced soil erosion in furrow systems with benefits that include reduced topsoil loss, enhanced water infiltration, improved uptake of nutrients and pesticides, reduced furrow-reshaping operations, and reduced sediment-control requirements below the field (*8*). By increasing soil flocculation, PAM has been shown to be effective in reducing sediment erosion through runoff and increasing water infiltration (*9*). A recent study has found that PAM applications to furrow irrigated crops reduced sediment erosion by over 90 percent (*10*). As reductions in sediment runoff are achieved, reductions in pesticides such as dicofol that are highly absorbed to soil particles also occur (*11*). Broadcast applications of PAM were also found to be significantly effective in increasing water infiltration and reducing sediment runoff (*12*).

This study examines the use of sediment basins with and without the use of PAM to reduce pyrethroid residues in agricultural runoff following a pyrethroid (lambda-cyhalothrin) application to processing tomatoes. Data from this study will be used to evaluate the effectiveness of using these technologies as Best Management Practices (BMPs) in reducing the off-site movement of pyrethroids in irrigation tailwaters. The purpose of the study was not to repeat the body of research that has already confirmed the efficacy of PAM and sediment basins in reducing total suspended solids (TSS), but to learn more about how the pyrethroids behave with respect to the sediment in these systems.

Materials and Methods

Study Site and Irrigation

The study was conducted on a 184-ha commercial farm located near the city of Patterson, California in the San Joaquin Valley. The farm lies on the eastern slope of the Coastal Range (western side of the San Joaquin Valley). At the initiation of this trial, the farm was divided into numerous blocks, 121 ha of which were planted in processing tomatoes with the balance in spinach and dry beans. The National Resource Conservation Service (NRCS) classified the soil type as about 94 % being a Vernalis clay loam (fine-loamy, mixed, superactive, thermic calcic Haploxerepts) with the balance as Zacharias clay loam (fine-loamy, mixed, superactive, thermic typic Haploxerepts), which has been laser planed to 1-2 percent slope. At the base of each block is a sediment basin and sump to capture the irrigation drainage water (or tailwater) which is then directed to a master sump and sediment basin. Water in the master sump is then re-circulated by pumping the water back to the blocks where fresh water is added to make up for any water lost during irrigation and evaporation.

In the 26.3-ha block used for both trials (Figure 1), irrigation is applied to about 5.26 ha at a time (26 rows). Irrigation is applied at the west end of the block with water introduced via an irrigation ditch that runs along the entire length of the west end of the block. Siphons are used to remove water from the ditch and introduce water into the irrigation furrows. Irrigation water flows in the irrigation furrows towards the east end of the block, a distance of approximately 780 m. There is also an irrigation pipe running north-south through the block half-way between the east and west ends. This pipe has simple gate valves built into the pipe so that when opened, water is introduced into the irrigation furrow.

Drainage water (tailwater) from all irrigation furrows in the 26.3 ha block empties into an interception ditch along the east end of the block which flows into the sediment basin located in the northeast corner. A rectangular weir was installed in the ditch and the height of the water over the weir was measured at various intervals during the study. The flow was calculated using the rectangular weir equation (*13*). The sediment basin when filled measured 38.7 m in length and 9.1 m in width. The depth was approximately 2.4 m when full. Due to the irregular shape and depth, no estimate was made of the volume of water in the sediment basin when filled. At the end of the basin was a standpipe (0.24 m in diameter), which acted as the field drain.

The 26.3-ha block used for the trial was bedded up and transplanted with canning tomatoes on April 18, 2007. The transplants were initially irrigated in 24-hour sets at least every seven days. The beds were cultivated for weed control on May 9, 2007 and June 25, 2007. As the plants reached approximately 0.46 m in height and began to impede the flow of water in the furrows, the grower switched to a 12-hour set to prevent the beds from becoming too wet.

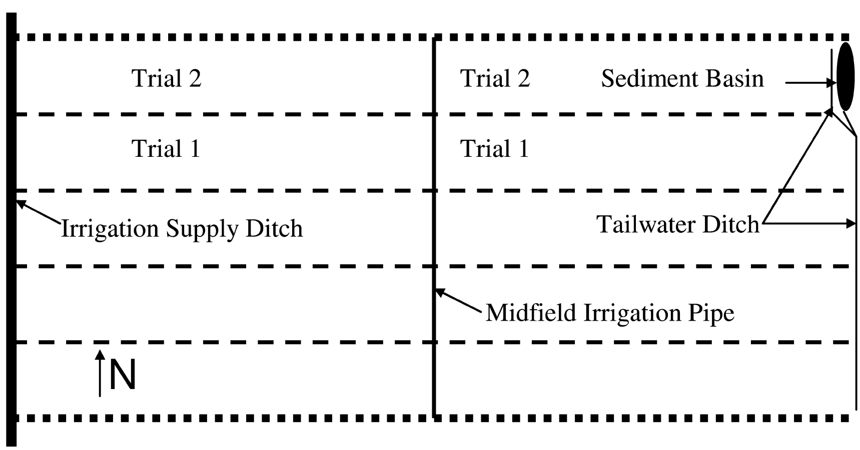


Figure 1. Diagram of the 26.3-acre Block in which the Trials were Conducted

To reduce erosion, the grower typically applies polyacrylamide (PAM) using the “patch method” at each irrigation event (including irrigation events that occurred prior to the application of the pyrethroid). The "patch method" involves

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

placing PAM at the point in the furrow where the water is introduced; applying it for a length of about 1-1.5 m down the furrow to reduce the risk of the PAM becoming buried in the furrow or washing down the furrow with little to no effect. The patch method creates a layer of gel at the top of the furrow where the water slowly dissolves the PAM and carries it down the furrow. The use of PAM at this farm prevents the need for frequent excavation of the sediment basins due to the highly erodible soil, saving both the cost of excavation and the cost to re-laser and re-level the field beds. At this farm, the cost of PAM is approximately $7/acre ($17/ha) each year.

Application of Lambda-Cyhalothrin

Lambda-cyhalothrin is typically applied to tomatoes in this region several times during the growing season to control chewing insects. In this study, lambda-cyhalothrin was applied by air as Warrior® with Zeon Technology™ at the rate of 22 g ai/ha (0.02 lb ai/A) on the morning of July 15, 2007. The entire block of 26.3 ha was treated for a total target mass of 590 g ai applied (118 g ai per irrigation section).

Study Design

This study consisted of two sequential trials. Trial 1 was conducted with only a sediment basin, without the use of PAM. Trial 2 was conducted with the same sediment basin, in combination with applications of PAM.

In the first trial, 26 rows were irrigated but no PAM was applied. Supplemental irrigation was also added at the middle of the field. Samples of drainage water flowing over the weir in the ditch entering the sediment basin were taken every hour. Once water began to flow out of the sediment basin, samples were collected hourly at the exit of the sediment basin.

In the second trial, 26 rows adjacent to those in the first trial were irrigated and about 250 mL of PAM was applied to the upper end of each furrow where the irrigation water enters the field. Due to unexpected water use restrictions, no irrigation water was added from the pipe at the middle of the field. The product used was Soil Fix IR (CIBA Specialties) which contains 90% PAM. Samples of drainage water were taken every two hours at the entrance and exit (upon initiation of flow) of the sediment basin. The longer sampling intervals in this trial were due to the lower flows observed.

Sample Collection and Analysis

Water samples were collected manually from the flow over the weir located in the ditch draining into the sediment basin and from the exit of the sediment basin. At each sampling interval, a sample of approximately 250 mL was collected for pyrethroid analysis in a 500mL Teflon-FEP bottle and another sample of approximately 250 mL was collected for measuring total suspended solids in a 500 mL Nalgene polypropylene bottle. Teflon-FEP containers were selected for use in this study, based on the work of Robbins (1997, unpublished report) which

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

showed a recovery of lambda-cyhalothrin of 89 percent after 57 days. Samples were placed immediately into coolers fill with ice and kept on ice until delivery to the analytical laboratory where they were immediately placed in refrigerators for storage until extraction. Pyrethroid samples were extracted and analyzed within 29 days of collection.

Samples were analyzed for lambda-cyhalothrin by extraction with a 4:1 (v:v) methanol hexane mixture and then transfer to an acetone solution with 0.1 % peanut oil (to minimize matrix effects) for analysis by GC-MSD/NICI. Analysis of samples for TSS was by standard filtration techniques (Method 2540 D (*14*)).

With each set of analyses for lambda-cyhalothrin, two untreated water samples were fortified at two different rates to validate the analytical set. The average recovery of lambda-cyhalothrin was 108 ± 11.7% over the course of the study. The Limit of Determination (LOD) for the analytical method was 0.01 µg/L of the water and sediment solution.

Calculation of Water, Sediment, and Pyrethroid Discharges

Amounts of water, suspended solids, and pyrethroids entering and leaving the sediment basin were calculated by performing a numerical integration. This numerical integration assumed that the flow of tailwater into the basin was zero at the time of the first sample (the first sample was taken just as flow began to start) and then varied linearly between flow measurements. Water flow out of the sediment basin was assumed to be equal to the flow of water into the basin during times when the basin was discharging. This assumption may overestimate the amount of material leaving and underestimate TSS and pyrethroid reductions since other processes (e.g., infiltration and evaporation) were assumed not to be significant. In the second trial the flow was assumed to be constant after the last flow measurement since all rows were discharging at that time. TSS and pyrethroid concentrations were assumed to vary linearly between sample times. Therefore, water flow rates and concentrations of TSS and pyrethroids could be estimated at one minute intervals using these assumptions. The numerical integration was performed using a one minute time step. The amount of tailwater flow during each time step was estimated using the average volumetric flow rate during the minute (flow at the start of the minute plus flow at the end of the minute divided by two). Amounts of TSS and pyrethroid mass for each minute were estimated by multiplying the amount of water flow for each minute times the average concentration (concentration at the start of the minute plus concentration at the end of the minute divided by two). The tailwater flows and amounts of TSS and pyrethroid for each minute were summed over appropriate study intervals.

Results and Discussion

Flow Rates

During the study considerable variability in the onset of runoff and the drainage flows occurred between trials and among irrigation furrows within a trial. This variability must be considered in the interpretation of the study results.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

In the first trial, irrigation water reached the lower end of the irrigation furrows approximately 2-3 hours after the irrigation was started. Starting the irrigation in the various furrows at the west end of the block was not an instantaneous process, but required approximately an hour to set the siphons at the west end and turn on the gate valves in the middle of the field. At the time the water in the drainage ditch reached the weir at the inlet to the sediment basin and sampling began, water from only 3 of 26 furrows had reached the end of the row and was contributing to tailwater flow. Two hours later, only 14 of the 26 furrows were draining into the ditch leading to the sediment basin. Five hours after the start of sampling, all but three of the furrows were draining. However, the final furrow did not start draining until about ten hours after the first furrows began draining. This resulted in increasing flow rates through the weir during the majority of the trial (Figure 2).

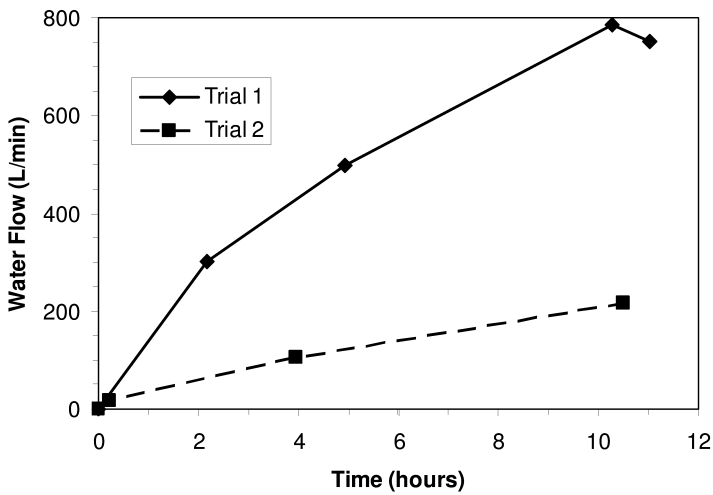


Figure 2. Flows Measured at the Weir during the Trials.

Between the 9 and 10-hour samples in the first trial, a stream of water was observed entering the sediment basin from another ditch. The water level in the irrigation ditch at the upper end of the field had been slowly rising during the night and had begun to flow over the ditch bank into row 1 at the northern end of the ditch. Therefore, the measurements at the weir no longer represented the discharge out of the sediment basin and the concentration of TSS and pyrethroids in the second stream were unknown. As a result, the interpretation of the study results was based on the data collected through nine hours, although the data from the later time intervals have been included in the figures.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

The intent was to conduct the second trial with flow rates similar to those used in the first trial. However, due to government water restrictions, less water was available for the second trial than for the first trial so additional irrigation water could not be added at the middle of the block. In the first trial, tailwater flow rates peaked at about 800 L/min, while the peak tailwater flow in the second study was only about 30 percent of that in the first trial. Therefore, the second trial provides information about the operation of the sediment basins under quite different operating conditions. First the sediment basin in the second trial was nearly full of water and contained TSS and pyrethroids from the first trial. Second, as mentioned earlier the flow rates in the second trial were only about 30 percent of that observed in the first trial. As a result, conclusions can not be drawn about the percent reduction in TSS or pyrethroids resulting from the use of PAM alone.

In the second trial about five hours was required between the start of irrigation and the onset of tailwater discharge into the ditch leading to the sediment basin. The pattern of increasing flow in the second trial was similar to that observed during the first trial, with all 26 rows contributing to tailwater after about 10 hours. At the same time as the 14-hour samples were collected, the tailwater ditch began to overflow and flood the access road, so a second entrance into the sediment basin had to be opened. Water entering via this second entrance bypassed the weir. Therefore, the study results were interpreted based on the data collected through 14 hours. However, the calculations were also performed for the 16-hour period, assuming no change in flow rate, and the amount of pyrethroids leaving the sediment basin expressed as percent of entering pyrethroids was essentially the same during the 16 hour period as for the 14 hour period.

Lambda-Cyhalothrin Residues and Total Suspended Solids (TSS)

The concentration of lambda-cyhalothrin (expressed in μg/L) and TSS levels (expressed in mg/L) for each runoff sample can be found in Figures 3−6. Concentrations of both pyrethroids and TSS appear to be spiky. This is probably the result of the flush that occurs when new rows begin to deliver tailwater and associated TSS and pyrethroid residues. However, the sediment basin seems to be effective in reducing the higher levels of TSS and pyrethroid residues in this first flush since the concentrations in the water entering the sediment basin during the first few hours are higher than the initial concentrations leaving the sediment basin.

Lambda-cyhalothrin residue levels in the runoff samples from the study conducted without adding PAM to the irrigation runoff ranged from 2.005 to 0.191 μg/L at the field exit (prior to entering the sediment basin) and 0.135 to 0.102 μg/L at the exit of the sediment basin. At the same time, the levels of total suspended solids ranged from 860 mg/L to 390 mg/L prior to entering the sediment basin and 535 mg/L to 85 mg/L at the exit of the sediment basin. The results show a decline in TSS and pyrethroid concentrations during the time the sediment basin was discharging. Also the maximum concentrations observed in the inlet are higher than in the outlet stream.

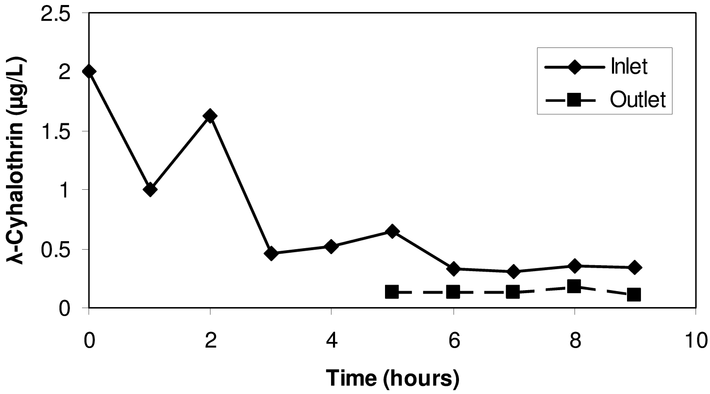


Figure 3. Lambda-Cyhalothrin Residues in the Inlet and Outlet of the Sediment Basin in Trial 1 (without PAM).

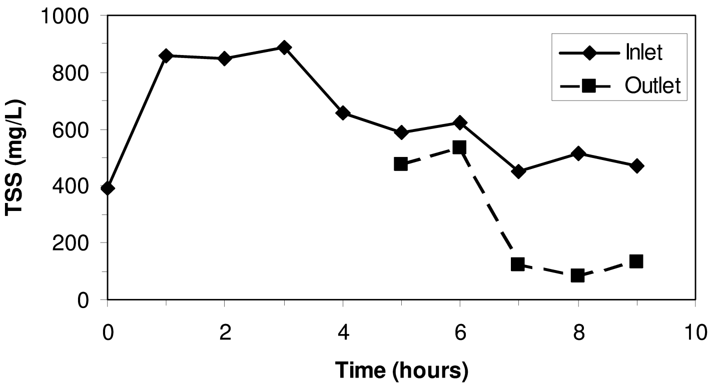


Figure 4. Total Suspended Solids (TSS) in the Inlet and Outlet of the Sediment Basin in Trial 1 (without PAM).

The pattern of results is slightly different for the second trial (with PAM). Pyrethroid concentrations in the runoff samples from the study conducted with PAM added to the irrigation water were lower and ranged from 1.32 to 0.106 µg/L at the entrance to the sediment basin and 0.144 to 0.0416 µg/L at the exit of the sediment basin. In this case maximum concentrations in the inlet and outlet streams still show a significant difference for pyrethroids and there also appears to be a reduction in concentrations during the time the sediment basin is discharging. However, the concentrations of TSS are largely unchanged between the inlet and outlet streams over the entire test period (although there is variability in the concentrations of both streams). The cause of the spike in TSS residues TSS in the 12 hour inlet sample and the 14 hour outlet sample is unknown.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

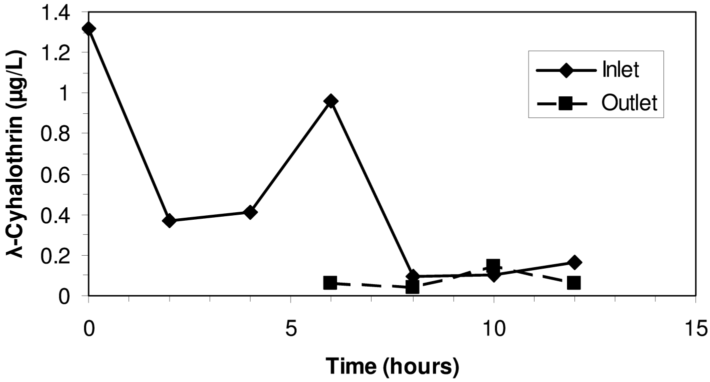


Figure 5. Lambda-Cyhalothrin Residues in the Inlet and Outlet of the Sediment Basin inTrial 2 (with PAM).

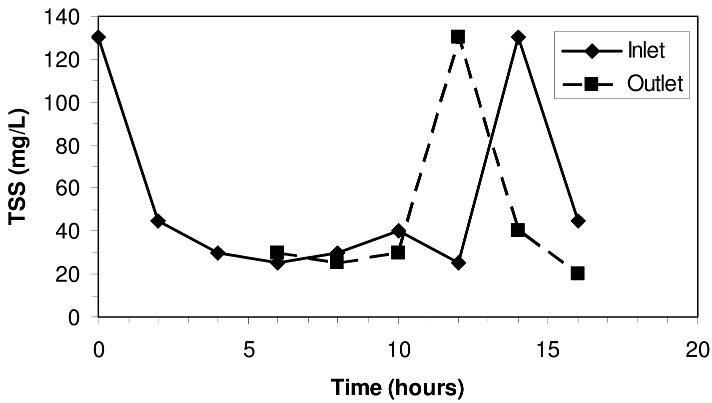


Figure 6. Total Suspended Solids (TSS) in the Inlet and Outlet of the Sediment Basin in Trial 2 (with PAM).

Estimation of Efficiency for Removing Residues

Using the flow measurements and the concentrations of TSS and pyrethroids, the amount of water, TSS, and pyrethroids entering and leaving the sediment basin were calculated as a function of time (Tables I and II) using the numerical integration process described earlier and used to estimate the removal of TSS and pyrethroids.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table I. Summary of Calculated Flows for Trial 1 (no PAM)[a]

Time Period (hours)	*Water Flow (L)*	*TSS (kg)*		*Pyrethroids (g)*	
		Into Basin	*Out of Basin*	*Into Basin*	*Out of Basin*
0-1	4,000	3	-	0.006	-
1-2	13,000	11	-	0.017	-
2-3	20,000	17	-	0.020	-
3-4	24,000	18	-	0.012	-
4-5	28,000	18	-	0.017	-
5-6	32,000	19	16	0.015	0.0041
6-7	35,000	19	11	0.011	0.0045
7-8	38,000	18	4	0.013	0.0059
8-9	41,000	20	4	0.014	0.0058
9-10	45,000	21	-	0.023	-
10-11	46,000	20	-	0.020	-
Total 0-9	235,000	144	36	0.125	0.0204

[a] There was no flow out of the sediment basin for the first 5 hours. Water flow for 9-10 and 10-11 hours does not include the contribution of the second stream to sediment basin inflow or outflow. The TSS and pyrethroid flows into the basin for these same sample intervals do not include the contribution from the second stream.

In Trial 1 (without PAM) 20 times as much TSS was transported in approximately 1.5 times the volume of runoff compared to Trial 2 (with PAM). In Trial 1 about 0.11 percent of the pyrethroid applied was transported into the sediment basin, while in the second trial approximately 0.043 percent of the pyrethroid was transported into the sediment basis or about 40 percent of the amount in Trial 1.

In Trial 1 (without PAM), 75 to 84 percent of the TSS and pyrethroid, respectively, were retained in the sediment pond. In trial 2 (with PAM), concentrations of pyrethroids were lower in the outflow than the inflow and approximately 80-85 percent of the pyrethroid was retained in the sediment basin. In trial 2 the differences in TSS levels flowing into and out of the sediment basin were too small and variable to allow reliable estimates of retention of sediment in the basin.

These results are consistent with other published data on sediment basins. Interpretation of these results requires consideration of factors such as starting volume of water in the sediment basin, initial pyrethroid content from earlier runoff events, starting TSS content, and volumetric flow of streams into and out of the sediment basin

Table II. Summary of Calculated Flows for Trial 2 (with PAM)[a]

Time Period (hours)	*Water Flow (L)*	*TSS (kg)*		*Pyrethroids (g)*	
		Into Basin	*Out of Basin*	*Into Basin*	*Out of Basin*
0-2	4,000	0.33	-	0.0031	-
2-4	10,000	0.37	-	0.0039	-
4-6	15,000	0.41	-	0.0104	-
6-8	19,000	0.52	0.52	0.0097	0.0010
8-10	23,000	0.81	0.63	0.0023	0.0022
10-12	26,000	0.84	2.07	0.0035	0.0027
12-14	26,000	2.01	2.20	0.0082	0.0014
14-16	26,000	2.27	0.78	0.0093	0.0014
Total 0-14	123,000	5.28	5.43	0.0412	0.0072
Total 0-16	149,000	7.54	6.20	0.0505	0.0086

[a] There was no flow out of the sediment basin for the first 6 hours. Values for 14-16 hours assume that the total flow into the sediment basin remained constant and that the concentrations of pyrethroids and sediment in both streams entering the sediment basin were the same.

Conclusions

This study has demonstrated that pyrethroid residues transport with a portion of the sediment that is eroded from the field under conditions of both high and low erosion potential. Importantly, the data also show that methods established to reduce water and sediment from the field (e.g. PAM and more careful irrigation flow control) and also technologies demonstrated to remove sediment from edge of field tail waters (e.g. sediment basins) are both effective in reducing pyrethroid transport in addition to their well documented benefits for reducing sediment transport.

Acknowledgments

This work was sponsored by the Pyrethroid Working Group, composed of AMVAC, Bayer, DuPont, FMC, Pytech, Syngenta, and Valent.

References

1. California Stormwater Quality Association. *Stormwater Best Management Practice Handbook for New Development and Redevelopment*; 2003.
2. Pereira, W. E.; Domagalski, J. E.; Hostettler, F. D. *Environ. Toxicol. Chem.* **1995**, *15* (2), 172–180.

3. Van Metre, P. C.; Callender, E.; Fuller, C. C. *Environ. Sci. Technol.* **1997**, *31* (8), 2339–2344.
4. Sojka, R. E.; Lentz, R. D.; Ross, C. W.; Trout, T. J.; Bjorneberg, D. L.; Aase, J. K. *J. Soil Water Conserv.* **1998**, *53* (4), 325–331.
5. Sojka, R. E.; Lentz, R. D. *J. Prod. Agricul.* **1997**, *10* (1), 47–52.
6. De Boodt, M. F. In *Soil colloids and their Associations*; De Boodt, M. F., Hates, M. H. B., Herbillon, A., Eds.; NATO ASI Series B: Physics; Plenum: New York, NY, 1990; Vol. 215; p 628.
7. Malik, M.; Letey, J. *Soil Sci. Soc. Am. J.* **1991**, *55* (2), 380–383.
8. Sojka, R. E.; Lentz, R. D. *Irrig. J.* **1996**, *46* (1), 8–11.
9. Lentz, R. D.; Steiber, T. D.; Sojka, R. E. In *Proc. Winter Commodity Schools—1995*; Robertson, L. D., Nolte, P., Vodraska, B., King, B., Tindall, T.;, Romanko, R., Gallian, J., Eds.; University of Idaho Cooperative Extension: Moscow, ID, 1995; pp 79−92.
10. Orts, W. J.; Roa-Espinosa, A.; Sojka, R. E.; Glenn, G. M.; Imam, S. H.; Erlacher, K.; Pedersen, J. S. *J. Mater. Civ. Eng.* **2007**, *19* (1), 58–66.
11. Singh, G.; Letey, J.; Hanson, P.; Osterli, P.; Spencer, W. F. *J. Environ. Sci. Health, Part B* **1996**, *B3* (1), 25–41.
12. Abu-Zreig, M. *J. Soils Sediments* **2006**, *6* (3), 137–144.
13. Brater, E. F.; King, H. W. *Handbook of Hydraulics for the Solution of Hydraulic Engineering Problems*, 6th ed.; McGraw Hill: New York, NY, 1982.
14. Greenberg, A.; Clesceri, L. S.; Eaton, A. D. *Standard Methods for the Examination of Water and Wastewater*, 18th ed.; Am. Public Health Assoc.: Washington, DC, 1992.

Chapter 6

Mitigating Pesticide Runoff from Nurseries

Julie Newman,*[,1] Salvatore Mangiafico,[2] Don Merhaut,[3] Laosheng Wu,[4] Jianhang Lu,[5] Darren Haver,[6] Ben Faber,[1] and Jay Gan[4]

[1]University of California Cooperative Extension, Ventura, CA 93003
[2]Rutgers Cooperative Extension of Salem County, Woodstown, NJ 08098
[3]Department of Botany and Plant Sciences, University of California, Riverside, CA 92521
[4]Department of Environmental Sciences, University of California, Riverside, CA 92521
[5]South Coast Air Quality Management District, Science & Technology Advancement, Diamond Bar, CA 91765
[6]University of California South Coast Research & Extension Center, Irvine, CA 92618
***jpnewman@ucdavis.edu**

Pesticide use and intensive irrigation in commercial nurseries can result in runoff that poses risks to downstream aquatic ecosystems. A variety of cultural practices are discussed in this chapter that can limit off-site movement of pesticides, such as improving irrigation efficiency, uniformity, methods, and timing; reducing chemical inputs by establishing an IPM program; applying pesticides safely and establishing protocols for cleaning spills and leaks; and retaining sediment and runoff on nursery property. Because many pesticides are transported after adsorbing to suspended sediment, detention basins and runoff capturing or recycling systems may effectively retain pesticides on site. In the second half of this chapter, we present a study evaluating the performance, costs, and pesticide removal efficiency of detention basins and water recycling practices at 11 commercial nurseries in southern California.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Introduction

Pesticide use in commercial nurseries may often be more intensive than for other agricultural crops. Exceptional pest management practices are required because consumers have low tolerance for pest damage on ornamental plants. The nursery industry is also responsible for intra- and interstate movement of potentially infested plants, and quarantine protocols for exotic pests mandate use of specific pesticides, application rates, and frequency. Furthermore, many major pests attacking ornamental crops are known to be resistant to one or more pesticides, which may result in higher application rates or frequency.

Heavy pesticide use poses significant risk of surface water contamination because pesticides may move off site in runoff produced by either irrigation or precipitation (*1*, *2*). For example, as much as 70 to 75% of irrigation water may run off packed gravel beds or impervious surfaces when nursery plants are watered by an overhead irrigation system (*3*). Summer use of pesticides is relatively heavy (compared to winter months) and is coupled with intensive irrigation; winter use of pesticides can also be substantial (*4*) and occurs when storm events are more likely.

Sources of pesticides in nursery runoff include pesticides injected into irrigation water, leachate from containers, and application drift (*5*–*7*). Deposition of sprayed pesticides between pots and within aisles has been noted for containerized foliage plants (*8*). Spills of potting media during production and transportation were identified as a main source for pesticides such as bifenthrin because these are incorporated directly into potting materials before transplanting (*5*).

The actual risk of nonpoint source pollution closely depends on the environmental conditions and management practices of each specific nursery. A variety of cultural practices such as improved irrigation efficiency and pest management have been implemented to limit pesticide and nutrient runoff (*5*, *7*, *9*). Developing sound management practices is dependent on understanding the factors that influence the actual outcome of pesticide applications, including soil properties, water movement, and pesticide properties (*4*).

Management Practices for Reducing Pesticide Use and Runoff

Some of the most important practices to reduce pesticide use and pesticide runoff from nurseries are summarized below. Refer to Newman et al. (*10*) and Haver (*11*) for detailed information on best management practices (BMPs) to reduce runoff.

Irrigation Practices

Under dry weather conditions, irrigation is the single most important factor affecting the volume of runoff that may contain pesticides. Irrigation efficiency, irrigation uniformity, methods of irrigation, and timing of irrigation events can all play a role in pesticide runoff.

Proper irrigation scheduling and timing is based on environmental conditions and plant water requirements; as conditions or plant requirements change, irrigation scheduling is adjusted and refined. In addition, the required amount of water is applied only to the locations desired. To reduce runoff when using overhead irrigation, containers are placed as closely as possible without reducing plant quality. With drip systems, irrigators ensure that each emitter is located in a pot to prevent runoff. When containers are moved, such as during harvesting operations or in retail areas, plants are reconsolidated and irrigation is turned off in unused portions. Irrigators note spray patterns to ensure water is being applied only to plants, not to walkways or roads. Hand watering is performed carefully to avoid creating runoff between pots and on walkways.

Regular system maintenance is critical. Irrigators inspect and repair all leaks and replace worn, outdated, or inefficient components and equipment. Maintenance also includes flushing and unclogging lines, emitters, and sprinkler heads and regularly cleaning filters.

Integrated Pest Management (IPM) Programs

Another important way to mitigate pesticide runoff is to reduce chemical inputs by establishing an IPM program. A key component is ongoing monitoring (scouting) to detect pests before crop damage occurs. Monitoring records include pest counts, degree of injury, and other data needed to determine pest pressure and population trends. Environmental parameters can also be monitored to predict growth of pest populations and for disease forecasting. Economic thresholds are established to determine when the benefit of controlling a pest is worth the cost of control methods and the associated potential hazards. Pesticides are applied only when justified by pest population size and crop damage threshold levels, resulting in fewer pesticide applications and reduced pesticide drift and runoff. Directed and spot-spray applications as well as the use of adjuvants such as spreader-stickers can also reduce the amount of pesticides applied. Pesticide resistance can be avoided by rotating pesticides from different modes of action and using the lowest effective application rate.

Preventive Control and Good Sanitation Practices

Pesticide use in the nursery and therefore pesticide runoff can be reduced by practicing preventative control techniques, such as good sanitation, use of resistant plant varieties, and proper plant culture. These practices prevent spread and infection to other plants and reduce the size of areas requiring treatment.

Good sanitation begins with plants that are free of pests and pathogens. All plant material brought to the nursery, therefore, is inspected. Any infested plants are treated or discarded. New plants are also quarantined whenever possible before introducing them into growing areas. Certified or culture-indexed stock—plants that are tested to confirm they are free of specific pathogens—is available for some plant species. Use of certified plant material is especially important when selecting propagation stock.

A clean environment must also be maintained for plant growth. Planting beds and recycled container media are heat steamed or chemically treated before establishing a new crop to eliminate pest problems from previous crops. Tools are also sterilized between uses on infected or highly susceptible crops. Employees remove soil from their shoes before entering propagation areas and feet are not allowed on propagation benches. Weeds are removed because they may host pests and plant disease vectors. Pulled weeds, pruned clippings, plant refuse, and culled plants are collected in sealed bags and disposed in covered dumpsters away from and downwind of healthy plants and production areas.

Another method of preventing pest problems is to select plants that are tolerant or resistant to pests and diseases; these plants have physical or biochemical characteristics that make them less susceptible to pests and diseases or are less likely to suffer appreciable damage. For example, natural resistance genes exist for various diseases including powdery mildew, *Verticillium,* and *Fusarium* and for some bacteria, nematodes, and viruses.

Many pest problems can be prevented by providing environmental and cultural conditions that are optimal for the species—healthy plants are more likely than unhealthy ones to resist or withstand pest infection or infestation. Plants require a good growing medium, proper fertilization, good air circulation, and good drainage and water management. Standing water and prolonged periods of leaf wetness should be avoided.

Non-Chemical Control

The use of non-chemical control strategies slows the development of pesticide resistance and reduces pesticide pollutant loads that can contaminate the environment. Non-chemical strategies include cultural controls (e.g., locating susceptible varieties in a specific area to intensify pest management, separating older plantings from new ones to minimize movement of pests to newer crops), mechanical control (e.g., hand-pulling weeds, applying mulch for weed control, installing screens to exclude insects), environmental control methods (e.g., heat treatments to control soil-borne pests, altering humidity and temperature to control foliar pathogens, improving drainage and aeration of planting media to prevent pathogenic problems), and biological control.

Reduced-Risk Pesticides

When pesticides are selected, it is important to check the label to determine if the product is registered for use on the target pest and host plant, and for instructions on product use. The pesticide label also provides hazard warnings, including information about potential environmental risks. Moreover, online resources may be consulted to select products with reduced runoff potential and toxicity, such as WIN-PST, a pesticide environmental risk screening tool supported by the USDA-NRCS National Water and Climate Center (http://www.wsi.nrcs.usda.gov/products/W2Q/pest/winpst.html), The University of California PesticideWise website (http://www.pw.ucr.edu/), the “Water Quality Compare Treatments” provided in the University of

California IPM Pest Management Guidelines (http://www.ipm.ucdavis.edu/PMG/crops-agriculture.html), or the Pesticide Action Network Pesticide Database (http://www.pesticideinfo.org/Search_Chemicals.jsp). Whenever possible, pesticides that would potentially contaminate surface water are avoided. These pesticides include some organophosphates (OPs) (e.g., chlorpyrifos, diazinon), carbamate insecticides (e.g., carbaryl), and synthetic pyrethroids (e.g., bifenthrin, cyfluthrin, permethrin). Additionally, pesticides that are the most selective for the target pest species are selected over broad-spectrum pesticides whenever possible, which minimizes disruption of natural population control mechanisms.

Safe Application of Pesticides

Pesticides should be applied according to their label. In addition, the exact location of the area to be treated and the site conditions must be known, including the potential hazard of spray drift or subsequent pesticide movement to surrounding areas. Pesticide applications are scheduled to avoid off-target pesticide movement. Pesticides are not applied before scheduled irrigations, unless the product must be activated by moisture and indicated in the label instructions. When applying pesticides outdoors, it is important to consider weather conditions (e.g., fog, rain, wind). Pesticide spraying equipment is calibrated to ensure the best coverage and accurate application rates. The volume of spray needed is properly calculated and pesticides are accurately measured to apply the labelled rate as well as to eliminate disposal problems associated with excess spray solutions. Pesticide use records (the amount and type of pesticides applied) are maintained, and aid in planning future pest control measures and limiting pesticide accumulation.

Pesticide Spills and Leakage

Leaks or spills can occur during pesticide transportation, usage, and storage. For this reason, pesticide storage structures are located as far away from waterways as possible, with a concrete pad and curb to contain spills and leaks. They are also protected from rainfall or irrigation. An up-to-date inventory of stored pesticides including a Material Safety Data Sheet (MSDS) for each pesticide is available at the facility, along with a spill kit that includes detergent, hand cleaner, and water; absorbent materials such as absorbent clay, sawdust, or paper to soak up spills; a shovel, broom, dustpan, and chemical resistant bags to collect contaminated materials; and a fire extinguisher. Any pesticide spills are cleaned immediately according to a predetermined protocol and with reference to the product MSDS.

Pesticide mixing and loading operations are conducted on an impermeable surface such as a concrete floor. If pesticides are mixed into container media before potting, concrete curbs or sand bags are used to isolate these areas so that media is not washed away. Any spilled potting media that contains pesticide residues is collected to avoid off-site movement by wind or water. Any runoff from areas where pesticides are used is contained or directed to a treatment area (see subsequent sections).

The pesticide label is consulted for disposal instructions of leftover pesticide materials. Empty, rinsed plastic pesticide containers are taken to pesticide container recycling facilities or to sanitary landfills.

Practices that Retain Pesticides On Site

Bare soil and hillsides in nonproduction areas must be protected from concentrated flows of water that cause erosion. Establishing plant covers such as landscaping reduce the amount and speed of runoff and trap sediment, thereby reducing soil losses and pesticide movement. Alternatively, ground covers such as mulch and gravel or sediment barriers such as sand bags, straw wattle, and synthetic hay bales can be used to curtail runoff and reduce erosion. Areas susceptible to erosion can also be treated with polyacrylamides (PAM) to improve stabilization (*12*).

If irrigation or storm water is discharged from the nursery, pollution must be mitigated. This may be achieved by treating runoff with vegetative buffers before discharge. Vegetative buffers such as constructed wetlands reduce runoff flow velocity, take up excess nutrients, and remove pesticides by trapping sediment, providing time for decomposition. Other mitigation practices include the use of landscaping, cover crops, slow sand filtration, sediment barriers, diversions, and underground outlets. Moreover, water bodies and drainage channels located on the nursery property should be protected by vegetated filter strips, strips of land used between production areas and waterways to trap sediment particles and stabilize the banks (*5*, *7*, *12*).

Wind erosion wears away topsoil and has a direct effect on the productivity of the nursery land, as well as impacting water quality. Furthermore, wind erosion from nurseries may contribute to air pollution, which could exceed air quality standards enforced by local regulatory agencies. Wind erosion is minimized by maintaining good soil structure and using plant covers. Additionally, trees, shrubs, or other vegetation are planted as windbreaks (shelterbelts) along the upwind boundaries of production fields to reduce wind erosion. Storing container media in a location sheltered from wind and away from drainage channels reduces the risk of media blowing into waterbodies.

Capturing Pesticide Runoff and Recycling Water

Technologies that capture runoff water and sediment are considered for mitigating pesticide movement because water serves as the carrier for dissolved and adsorbed pesticides. Many types of impoundments are used in nurseries for capturing runoff water. For example, sediment basins intercept large amounts of sediment-laden runoff; the runoff is temporarily detained under quiescent conditions, allowing sediment to settle out before the runoff is discharged. Impoundments are also constructed to collect large runoff flow and “detain” it temporarily (detention basin, infiltration basin) or “retain” it for longer periods (e.g., retention basins, ponds, recycling systems, tailwater recovery systems, and reservoirs). Water dissipates by evaporation and by infiltration into the ground from unlined impoundments. Seepage into the ground could be problematic and should be considered in the design of the impoundment (see next section).

Impoundments may not, however, have the capacity to store all rainfall from precipitation events and there may be overflow across the impoundment structure. For detention basins, a water outlet structure is used to provide controlled discharge from the basin to prevent overflow and damage to the structure. Discharges and overflow are treated to prevent polluted runoff from off-site movement, as described in the previous section. Overflow may be alleviated by using the collected water to irrigate landscapes and other non-crop areas, or by recycling it for irrigating crops.

Design and Maintenance Considerations

Impoundments should be designed to meet all federal, state, and local laws, rules, and regulations. There are many technical design considerations such as length-to-width ratio, inlet and outlet location, depth-to-surface area, and the need for baffles (*12*). Impoundments should also be designed to prevent seepage, a source of groundwater contamination. In areas with sandy soils or a high groundwater table, ponds can be lined to avoid groundwater contamination.

There may also be legal stipulations regarding the holding capacity of the basin or pond. Holding regular irrigation runoff is considered minimum capacity and is determined by the size of the area that drains to the structure and the irrigation methods used. For impoundments used in tailwater recovery systems (see next section), the amount of water to be recycled also is considered in determining the holding capacity.

Impoundments should be located so that runoff can be directed to the basins by gravity. After construction, permanent native vegetation on surrounding slopes and a 15 to 25-foot “chemical free” zone around the impoundment edge is established and maintained (*12*). Production wastes such as leaves and grass clippings are not to be placed near impoundments or dumped into the ponds (*12*).

Impoundments require on-going maintenance, including periodic removal of sediment to maintain design capacity and efficiency. Best practices include an annual inspection of the basin and dredging when sediment accumulation exceeds 6 to 12 inches. Sediment from traps or storage facilities is removed before rain seasons because large storms can move sediment and accumulated pesticides into creeks and streams (*7*).

Both dredged sludge from storage facilities and sediment removed from traps are considered hazardous and are carefully disposed. One method is to incorporate small amounts into container substrate mixes. An incorporation rate of less than 5% should not affect the overall properties of the media (*11*).

Tailwater Recovery Systems

In some nurseries, captured runoff water is regularly analyzed for nutrients and pathogens; it is then treated accordingly and used to irrigate crops. In addition to mitigating runoff, tailwater recovery systems have the advantage of conserving both water and fertilizers. Runoff for recycling can be collected by gravity flow into a reservoir or pumped from a settling pond into a reservoir. The major steps for recycling runoff water include: 1) collection and storage of runoff water; 2) removal of floating debris and suspended solids; 3) removal of suspended colloidal material (organic matter and clay); 4) sanitation/treatment of pathogens (e.g., *Phytophthora, Pythium*, and fungal pathogens) using slow sand filters, chemicals (e.g., chlorine, chlorine dioxide, or ozone), or radiation (e.g., UV); 5) fertilizer injection; 6) blending of fresh water with the treated runoff water to reduce the salt concentration to levels that will not damage plants; and 7) storage of treated water (*13*). Factors that determine whether a nursery builds a simple or sophisticated recycling system are the quality of the water collected; necessary treatment of the water to be recycled; contaminants in the water such as disease organisms, salts, organic material, and pesticides; and the type of plant material to be irrigated.

Barriers that Limit Industry-Wide Implementation

Technologies that capture runoff effectively reduce runoff volumes, sediment loads, and nutrient loads in agricultural situations (*14–16*) and urban settings (*17*, *18*). Both runoff capture (*12*, *19*) and the recycling of drainage water (*13*, *20–22*) have been advocated for production nurseries. Tailwater recovery systems, in particular, are often mentioned as the primary best management method for eliminating problems arising from container nursery runoff (*19*).

Because many pesticides are associated with sediment and organic matter in runoff water (*6*), technologies that capture these constituents may also be effective in reducing off-site movement of pesticides. However, the efficacy of these technologies in reducing pesticide runoff is not well-documented. Further studies are also required to determine the various costs of installing, operating, and monitoring these systems. Moreover, information on the social, economic, and environmental costs and benefits associated with implementing these technologies would greatly aid in describing the full benefit of runoff capture.

Detention and Recycling Basins – A Case Study

Site Descriptions, Sampling, and Chemical Analysis

Runoff was monitored from 11 production nurseries employing either recycling or detention basins. These nurseries, located in Ventura and Los Angeles counties in southern California, varied in production area size, crop types (including container plants, field-grown flowers, and large containerized trees), production facilities (including greenhouse, shadehouse, and outdoor facilities), and water application methods (including microirrigation, overhead irrigation, and handwatering). Many nurseries had several crop types, and utilized multiple production facilities and water application methods. Production area is listed by nursery in Table I. Samples of runoff water that flowed into detention or recycling basins were collected as manual grab samples or as composites of sequential samples taken with auto-samplers. Samples included runoff from both irrigation and precipitation events. Pesticide analysis was conducted on unfiltered whole

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

water samples using solvent extraction and gas chromatography with electron capture detector (GC–ECD) for four classes of pesticides: pyrethroids, OPs, organochlorines (OCs), and carbamates, following methods consistent with EPA methods 3510C, 8141, and 8081 (*23*).

Table I. Production area, number of samples, and percent samples with detections of pesticides in runoff entering detention or recycle basins for 11 production nurseries in southern California. SOURCE: Reproduced with permission of the American Society for Horticultural Science, from Mangiafico, S. S.; Newman, J.; Merhaut, D.; Gan, J.; Wu, L.; Lu, J.; Faber, B.; Evans, R. Detention and recycling basins for managing nutrient and pesticide runoff from nurseries. *HortScience 43,* 393-398, copyright 2008, permission conveyed through Copyright Clearance Center, Inc.

Nursery	*Production area (ha)*	*Number of Samples*	*Pyrethroids (%)*	*OPs (%)*	*OCs (%)*
a	8.10	3	100	0	0
b	68.80	12	100	33	25
c	6.48	6	17	0	0
d	20.20	11	64	18	27
e	3.24	9	22	11	33
f	28.70	1	100	100	0
g	3.64	4	0	75	0
h	11.70	5	100	40	20
i	18.20	11	73	64	36
j	7.29	6	50	83	67
k	16.20	8	63	25	13

Water Use and Costs

Water use data for nurseries were collected from municipal water company records or on site from inline water usage meters for wells or recycling systems. The amounts of water saved by using recycling systems were estimated by calculating the percentage of recycled water used in relation to the total water use for a period of time. Total water use was calculated as the sum of recycled water and fresh water used. A duration of one year was used when possible. However, in cases where recycling basins or water use meters were recently installed, a shorter duration was used, and data were extrapolated to annual use without adjustments for seasonal differences. Water use data were collected only from those nurseries employing recycling systems. Water use could be reliably estimated for five out of eight sites with recycling systems (Table II).

Table II. Water use (10^6 L ha^{-1} yr^{-1}) for eight production nurseries employing water recycling systems in southern California. SOURCE: Reproduced with permission of the American Society for Horticultural Science, from Mangiafico, S. S.; Newman, J.; Merhaut, D.; Gan, J.; Wu, L.; Lu, J.; Faber, B.; Evans, R. Detention and recycling basins for managing nutrient and pesticide runoff from nurseries. *HortScience 43,* 393-398, copyright 2008, permission conveyed through Copyright Clearance Center, Inc.

Nursery	*Production area, (ha)*	*Total water use*	*Recycled water*	*Recycled water, %*
a	8.10	8.85	1.27	14
b	68.80	15.40	6.47	42
c	6.48	7.61	N/A[a]	N/A
d	20.20	N/A	N/A	N/A
e	3.24	2.79	0.44	16
f	28.70	N/A	N/A	N/A
g	3.64	39.70	21.1	53
h	11.70	N/A	N/A	N/A
Median		8.85	3.87	29

[a] N/A is data not available.

Cost data were gathered from receipts furnished by cooperators at the nursery sites and from estimates of expenses developed by cooperators. Estimates included all costs associated with completing a detention basin or recycling system, including planning, permitting, design, materials, labor, and necessary supporting activities, such as grading and laying weed cloth. However, operational costs, such as maintenance, energy consumption, or chemical inputs, were not included. Cost data were available for recycling systems at six locations and for detention basins at two adjacent sites.

Statistical Analysis

The high proportion of samples with pesticide concentrations below detection limits precluded the determination of simple statistics of central tendency of concentrations such as means or medians in some cases (*24*). Therefore, detection frequency was the primary dependent variable used in analyses. The number of detections and non-detections were pooled across sites and a categorical linear model analysis was performed to determine the effects of event (irrigation or precipitation) and basin type (detention or recycle) and the interaction of these two effects. Regression analysis determined the relationship between the frequency of pesticide detection and the production area across sites. A linear regression analysis was performed to determine the relationship between production area and per-hectare water use, per-hectare recycled water use, and percentage of water recycled. A similar analysis was performed for recycling system costs as the dependent factor. A first-order inverse relationship ($y = a + b/x$) was determined relating per-hectare recycling system costs and production area, which is the appropriate model after determining a linear relationship with intercept between total costs and production area. Analyses were performed using the Statistical Analysis Software (SAS) package (SAS Institute, Cary, NC) using the REG, GLM, NLIN, or CATMOD procedures. Regression models were checked for homoscedasticity, normality of residuals, and independence of residuals (*25*).

Pesticide Detections and Concentrations

Pyrethroids were found in runoff at 10 out of 11 sites (Table II). OPs and OCs were found at 9 and 7 sites, respectively. No significant correlation was found between percent of samples with pesticide detections, by pesticide class, and production area ($P \geq 0.05$). Carbamate pesticides were not detected in any runoff sample. With samples pooled across sites, pyrethroid detections were common (63 and 58% for irrigation and precipitation events, respectively) while detections for OPs and OCs were less common (48 and 8%, and 29 and 17%, respectively) (Figure 1). No differences in the frequency of detection were found between samples taken during irrigation events and precipitation events for either pyrethroids or OCs (Figure 1; $P \geq 0.05$). However, for OPs, a significant difference in detection frequency was found between irrigation events and precipitation events (Figure 1, $P < 0.0001$; 48% and 8% for irrigation and precipitation events, respectively). Concentrations for detected pesticides are given in Table III. These observations suggest that managing runoff from both irrigation and precipitation events would be important in mitigating potential impacts to surface water. Common detections and high concentrations of pyrethroids in nursery runoff suggest that conventional insecticides such as OPs and carbamates are being replaced with pyrethroid products. This is a concern because pyrethroids typically have high acute aquatic toxicities (*26*, *27*).

Detention and Recycle Basin Performance

No runoff from irrigation events was observed after completion of detention basin and recycling projects. The ability of these basins to collect and detain runoff during storm events, however, was not adequately assessed by this study. For some sites, few precipitation events occurred after the completion of basins and before the completion of the study.

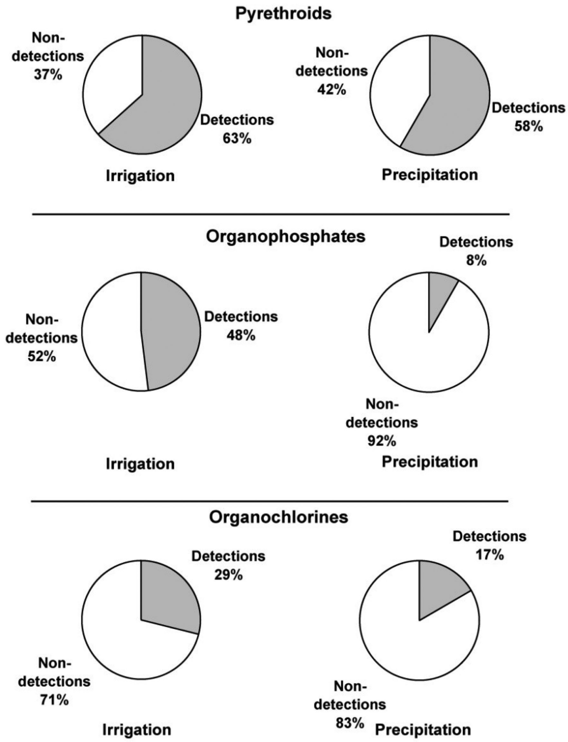


*Figure 1. Percent of samples with detections and non-detections for three classes of pesticides in runoff for 11 production nurseries in southern California. Reproduced with permission of the American Society for Horticultural Science, from Mangiafico, S. S.; Newman, J.; Merhaut, D.; Gan, J.; Wu, L.; Lu, J.; Faber, B.; Evans, R. Detention and recycling basins for managing nutrient and pesticide runoff from nurseries. HortScience 43, 393-398, copyright **2008**, permission conveyed through Copyright Clearance Center, Inc.*

Detection frequencies for pyrethroids prior to the installation of the detention and recyle basins were similar to those found by a survey of surface waters in agricultural watersheds in California, which found pyrethroids in 61% of samples, mostly in sediments (*28*). Similarly, pyrethroids and OCs were commonly detected in sediments of surface waters and tailwater ponds in the agricultural inland valleys of California (*29*) but certain OPs were infrequently detected (*30*). For pesticides that are strongly associated with particulate matter, differences in detection frequency in these studies may reflect the amounts of particles and organic matter in water samples (*6*, *31*).

Table III. Frequencies of detections and concentrations (ng L^{-1}) of pesticides in runoff entering detention or recycle basins for 11 production nurseries in southern California, number of samples=76. Reproduced with permission of the American Society for Horticultural Science, from Mangiafico, S. S.; Newman, J.; Merhaut, D.; Gan, J.; Wu, L.; Lu, J.; Faber, B.; Evans, R. Detention and recycling basins for managing nutrient and pesticide runoff from nurseries. HortScience 43, 393-398, copyright 2008, permission conveyed through Copyright Clearance Center, Inc.

	Detection (%)	*Median concentration*	*75th percentile*	*90th percentile*	*Maximum concentration*
Pyrethroids					
Bifenthrin	41	n/d[a]	31	235	20063
Fenpropathrin	33	n/d	29	223	1267
cis-Permethrin	26	n/d	3	89	1061
trans-Permethrin	22	n/d	n/d	56	1588
Cyhalothrin	7	n/d	n/d	n/d	1532
Cyfluthrin	12	n/d	n/d	5	889
Cypermethrin	1	n/d	n/d	n/d	2
Esfenvalerate	4	n/d	n/d	n/d	396
Deltamethrin	7	n/d	n/d	n/d	68
Organophosphates					
Diazinon	24	n/d[b]	n/d	712	17416
Chlorpyrifos	25	n/d	1	197	1595
Organochlorines					
trans-Chlordane	11	n/d[c]	n/d	1	29
Endosulfan sulfate	7	n/d	n/d	n/d	67
β-Endosulphane	3	n/d	n/d	n/d	9
Aldrin	7	n/d	n/d	n/d	21
Heptachlor	3	n/d	n/d	n/d	8
Dieldrin	1	n/d	n/d	n/d	20
α-BCH	3	n/d	n/d	n/d	5
γ-BCH	3	n/d	n/d	n/d	2
pp′-DDT	8	n/d	n/d	n/d	277

Continued on next page.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table III. (Continued). Frequencies of detections and concentrations (ng L^{-1}) of pesticides in runoff entering detention or recycle basins for 11 production nurseries in southern California, number of samples=76

	Detection (%)	*Median concentration*	*75th percentile*	*90th percentile*	*Maximum concentration*
pp′-DDE	5	n/d	n/d	n/d	91
pp′-DDD	1	n/d	n/d	n/d	6

[a] Detection limits for pyrethroid pesticides varied, but were less than 10 ng L^{-1}. [b] Detection limits for diazinon and chlorpyrifos were 5 and 1 ng L^{-1}, respectively. [c] Detection limits for organochlorine pesticides varied between 1 and 5 ng L^{-1}.

Pesticides detected in runoff from some nursery sites in this case study would have been of concern without the implementation of detention or recycle basins. The ability of detention and retention basins to capture runoff from precipitation events will depend on the capacity of the basins relative to the size, intensity, and frequency of precipitation events. In cases for which mitigation of runoff from precipitation events is desired, proper engineering of basin capacity for expected precipitation events is critical. Even in cases where larger precipitation events cause basin overflow, basins may serve to slow water and settle sediments, mitigating the discharge of sediment-bound nutrients and pesticides.

Water Use

For sites with recycling systems where water use data were available, use ranged from 2.79 to 39.7 million L ha^{-1} yr^{-1} (Table II), with a median of 8.85 million L ha^{-1} yr^{-1}. The highest water use was for a greenhouse hydroponic facility (Nursery *g*). The median percentage of water recycled was 29%, which corresponded to a savings of 3.87 million L ha^{-1} yr^{-1}. These values are comparable with water use for three container nurseries in southern California, which ranged from 1.05 to 31.4 million L ha^{-1} yr^{-1} (*32*). In this study, we found no significant linear relationship between production area and per-hectare water use, per-hectare recycled water use, or percentage of water recycled ($P \geq 0.05$). When data for the hydroponics facility was ignored, recycled water use on a per-hectare basis was positively linearly related to production area ($P = 0.039$, $r^2 = 0.996$, $n = 3$). This relationship suggests that larger facilities may benefit more from a recycling system than smaller ones in terms of volumetric water savings. Factors other than production type and production size that may also affect water use such as site characterisitics and irrigation system efficiency were not evaluated in this study.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Costs

Based on a study of six nurseries in southern California, median costs for water recycling systems were \$203,000, with a range of \$96,000 to \$1,000,000 (Figure 2A). Costs for recycling systems were positively linearly related to production area (Figure 2A, P = 0.0048, r^2 = 0.889, n = 6). Median costs for recycling systems were \$20,000 per hectare with a range of \$9,200 to \$43,000 per hectare (Figure 2B), and per-hectare costs were related by first-order inverse function to production area (Figure 2B, P = 0.042, r^2 = 0.686, n = 6), suggesting that larger nurseries may benefit from positive economies of scale in the installation of recycling systems. This observation is corroborated by a survey of production nurseries in Alabama which showed that runoff recycling was more common in larger nurseries (*19*). However, two relatively small nurseries (3.24 and 3.64 ha) in our study successfully implemented runoff recycling (Table I). Median costs to construct a detention basin were \$31,000 per hectare of production area (data not shown).

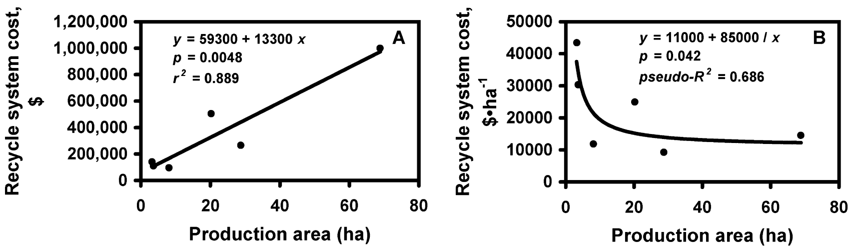


Figure 2. Recycling system costs for six production nurseries in southern California in relation to production area. (A) Costs were linearly related to production area; (B) Per-hectare costs were related by first-order inverse function to production area. Reproduced with permission of the American Society for Horticultural Science, from Detention and recycling basins for managing nutrient and pesticide runoff from nurseries; Mangiafico, S. S.; Newman, J.; Merhaut, D.; Gan, J.; Wu, L.; Lu, J.; Faber, B.; Evans, R. HortScience 43, 393-398, copyright ***2008,*** *permission conveyed through Copyright Clearance Center, Inc.*

Conclusions

Commercial nurseries represent quasi-point source pollution, as the intensive use of pesticides and irrigation water may lead to substantial dry-weather runoff that contains high levels of nutrients and pesticides. A variety of management practices may be used individually or integratively to effectively mitigate dry-weather runoff. In particular, structurally-based practices, such as retention basins and recycle systems, may offer the potential for completely eliminating dry-weather runoff while reducing water and fertilizer use. When properly constructed and maintained, these systems may also help to significantly curtail rain-induced runoff.

References

1. Briggs, J. A.; Riley, M. B.; Whitwell, T. Quantification and remediation of pesticides in runoff water from containerized plant production. *J. Environ. Qual.* **1998**, *27*, 814–820.
2. Mahnken, G. E.; Skroch, W. A.; Leidy, R. B.; Sheets, T. J. Metolachlor and simazine in surface runoff water from a simulated container plant nursery. *Weed Technol.* **1999**, *13*, 799–806.
3. Beeson, R. C.; Know, G. W. Analysis of efficiency of overhead irrigation in container production. *Hortscience* **1991**, *26*, 848–857.
4. Gan, J.; Haver, D.; Newman, J. Pesticide use and water quality protection. In *Greenhouse and Nursery Management Practices to Protect Water Quality*; Newman, J., Ed.; Publ. 3508; University of California Division of Agriculture and Natural Resources: Oakland, CA, 2008; Chapter 6, pp 73−82.
5. Kabashima, J. N.; Lee, S. J.; Haver, D. L.; Wu, L.; Goh, K.; Gan, J. Pesticide runoff and mitigation at a commercial nursery site. In *Pesticide Decontamination and Detoxification*; Gan, J., Zhu, P., Aust, S. A., Lemley, A. T., Eds.; ACS Symp. Ser. 863; American Chemical Society: Washington, DC, 2003; pp 213−230.
6. Gan, J.; Lee, S. J.; Liu, W. P.; Haver, D. L.; Kabashima, J. N. Distribution and persistence of pyrethroids in runoff sediments. *J. Environ. Qual.* **2005**, *34*, 836–841.
7. Lao, W. J.; Arye, G.; Ernst, F.; Xu, Y. P.; Bondarenko, S.; Haver, D.; Kabashima, J.; Gan, J. Reduction of pyrethroid runoff from a commercial nursery. In *Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments*; Gan, J., Spurlock, F., Hendley, P., Weston, D., Eds.; ACS Symp. Ser. 991; American Chemical Society: Washington, DC, 2008; pp 426−445.
8. Wilson, C.; Strimple, P.; Wilson, S.; Albano, J. Non-target deposition of methiocarb applied to a foliage plant staging area. *Bull. Environ. Toxicol.* **2005**, *74*, 509–517.
9. Mangiafico, S. S.; Newman, J.; Mochizuki, M.; Merhaut, D. J.; Faber, B. Nurseries surveyed in Southern California adopt best practices for water quality. *Calif. Agric.* **2010**, *64*, 26–30.
10. Newman, J.; Haver, D.; Mellano, V.; Robb, K. Management goals and management practices to mitigate runoff and leaching. In *Greenhouse and Nursery Management Practices to Protect Water Quality*; Newman, J., Ed.; Publ. 3508; University of California Division of Agriculture and Natural Resources: Oakland, CA, 2008; Chapter 2, pp 11−28.
11. Haver, D. L. *Sediment management goals and management practices for nursery and floriculture*; Publ. 8124; University of California Division of Agriculture and Natural Resources: Oakland, CA, 2004.
12. Lu, J.; Wu, L.; Faber, B. Erosion control and runoff management. In *Greenhouse and Nursery Management Practices to Protect Water Quality;* Newman, J., Ed.; Publ. 3508; University of California Division of Agriculture and Natural Resources: Oakland, CA, 2008; pp 83−96.

13. Merhaut, D. Water recycling in nurseries. In *Greenhouse and Nursery Management Practices to Protect Water Quality*; Newman, J., Ed.; Publ. 3508; University of California Division of Agriculture and Natural Resources: Oakland, CA, 2008; Chapter 8, pp 97−114.
14. Cooper, C. M.; Knight, S. S. Nutrient trapping efficiency of a small sediment detention basin. *Agric. Water Manage.* **1990**, *18*, 149–158.
15. Edwards, C. L.; Shannon, R. D.; Jarrett, A. R. Sedimentation basin retention efficiencies for sediment, nitrogen, and phosphorus from simulated agricultural runoff. *Trans. ASAE* **1999**, *42*, 403–409.
16. Fiener, P.; Auerswald, K.; Weigand, S. Managing erosion and water quality in agricultural watersheds by small detention ponds. *Agric., Ecosyst. Environ.* **2005**, *110*, 132–142.
17. Oberts, G. L.; Osgood, R. A. Water-quality effectiveness of a detention/wetland treatment system and its effect on an urban lake. *Environ. Manage.* **1991**, *15*, 131–138.
18. Sherwood, D. A. Effects of a vegetated stormwater-detention basin on chemical quality and temperature of runoff from a small residential development in Monroe County, New York; WRIR 01-4099; U.S. Geol. Surv.: 2001. http://www.monroecounty.gov/p/eh-WMVegetatedStormwater.pdf.
19. Fain, G. B.; Gilliam, C. H.; Tilt, K. M.; Olive, J. W.; Wallace, B. Survey of best management practices in container production nurseries. *J. Environ. Hortic.* **2000**, *18*, 142–144.
20. Skimina, C. A. Recycling irrigation runoff on container ornamentals. *HortScience* **1986**, *21*, 32–34.
21. Molitor, H. The European perspective with emphasis on subirrigation and recirculation of water and nutrients. *Acta Hortic.* **1990**, *272*, 165–173.
22. Skimina, C. A. Recycling water, nutrients, and waste in the nursery industry. *HortScience* **1992**, *27*, 968–971.
23. U.S. Environmental Protection Agency. *Test methods for evaluating solid waste, physical/chemical methods*, 3rd ed.; SW-846; Office of Solid Waste Management: Washington, DC, 1997. http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm.
24. U.S. Environmental Protection Agency. *Data quality assessment: statistical tools for practitioners*; QA/G-9S; Office of Environmental Information: Washington, DC, 2006. http://www.epa.gov/QUALITY/qs-docs/g9s-final.pdf.
25. Tabachnick, B. G.; Fidell, S. F. *Using multivariate statistics*, 4th ed; Allyn and Bacon: Boston, MA, 2001.
26. Clark, J. R.; Goodman, L. R.; Borthwick, P. W.; Patrick, J. M., Jr.; Cripe, G. M.; Moody, P. M.; Moore, J. C.; Lores, E. M. Toxicity of pyrethroids to marine invertebrates and fish: a literature and test results with sediment-sorbed chemicals. *Environ. Toxicol. Chem.* **1989**, *8*, 393–401.
27. Hill, I. Aquatic organisms and pyrethroids. *Pestic. Sci.* **1989**, *27*, 429–464.
28. Starner, K.; White, J.; Spurlock, F.; Kelley, K. Pyrethroid insecticides in California surface waters and bed sediments: concentrations and estimated

toxicities. California Department of Pesticide Registration: Sacramento, CA, 2006. http://www.cdpr.ca.gov/docs/sw/swposters/starner_pyreth06.pdf.

29. Weston, D. P.; You, J.; Lydy, M. J. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley. *Environ. Sci. Technol.* **2004**, *38*, 2752–2759.
30. Starner, K.; Spurlock, F.; Gill, S.; Goh, K.; Feng, H.; Hsu, J.; Lee, P.; Tran, D.; White, J. Pesticide residues in surface water from irrigation-season monitoring in the San Joaquin Valley, California, USA. *Bull. Environ. Contam. Toxicol.* **2005**, *74*, 920–927.
31. Budd, R.; O'Geen, A.; Goh, K.; Bondarenko, S.; Gan, J. Efficacy of constructed wetlands in pesticide removal from tailwaters in the Central Valley, California. *Environ. Sci. Technol.* **2009**, *43*, 2925–2930.
32. Kabashima, J. N. Innovative irrigation techniques in nursery production to reduce water usage. *HortScience* **1993**, *28*, 291–293.

Chapter 7

Effectiveness of Cultivation Practices To Minimize the Off-Site Transport of Pesticides in Runoff from Managed Turf

Pamela J. Rice,[†,*] Brian P. Horgan,[‡] and Jennifer L. Rittenhouse[†]

[†]U.S. Department of Agriculture - Agricultural Research Service, 1991 Upper Buford Circle, St. Paul, Minnesota 55108
[‡]University of Minnesota, Horticulture Department, 1970 Folwell Avenue, St. Paul, Minnesota 55108, USA
[*]To whom correspondence may be addressed (pamela.rice@ars.usda.gov).

Pesticides associated with the turfgrass industry have been detected in stormwater runoff and surface waters of urban watersheds. The detection of pesticides at locations where they have not been applied along with reported effects of pesticides to non-target organisms at environmentally relevant levels has raised the need to provide methodologies to control their off-site transport. We designed experiments to evaluate the effectiveness of cultivation practices to mitigate the off-site transport of herbicides in runoff from turf managed as a golf course fairway. Overall hollow tine core cultivation (HTCC) showed a reduction in runoff relative to the no core cultivation (NCC), solid tine core cultivation (STCC) and verticutting (VC). Likewise the percentage of applied herbicides measured in the runoff were smaller from turf managed with HTCC. These trends were statistically significant for dicamba, MCPP, and 2,4-D when comparing HTCC versus STCC at 2d following core cultivation, for 2,4-D when comparing HTCC with STCC at 63d following core cultivation, and for 2,4-D when comparing HTCC with VC. Results of this research provide quantitative information that will allow for informed decisions on management practices for turf that can maximize pesticide retention at the site of application; improving pest control while minimizing environmental contamination and adverse effects

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

associated with the off-site transport of pesticides to surface waters.

Introduction

Over 30% of pesticide use in the United States results from non-agricultural pest control; including applications to protect structures, control weeds at roadsides and right-of-ways, repel and control nuisance and disease carrying pests, and maintain lawns, landscapes and gardens (*1*). More than 16 million hectares of land in the United States is estimated to be covered by tended lawn (*2*). Managed turf is found in both private and public settings; as residential, commercial and public lawns, on golf courses and athletic fields, as sod farms, and in parks and cemeteries. Highly managed systems such as golf course turf often require multiple applications of pesticides at rates that exceed those typically found in agricultural or home environments (*3*, *4*). Pesticides associated with the turfgrass industry have been detected in surface waters of urban watersheds (*5*, *6*). Examples include reports of dicamba, mecoprop- p (MCPP) and 2,4-dichlorophenoxyacetic acid (2,4-D) in 85% of evaluated storm runoff events, and spring and summer detections of carbaryl and diazinon at levels that exceeded criteria for the protection of aquatic life (*7–9*). These findings have led to greater suspect of contaminant contributions from residential, urban, and recreational sources, in addition to the traditional agricultural inputs. The off-site transport of pesticides with runoff is both an agronomic and environmental concern resulting from reduced control of target pests in the area of application and contamination of surrounding ecosystems.

Golf courses and recreational fields are subject to foot and vehicle traffic that causes soil compaction and turf wear, reducing water infiltration and increasing turf stress (*10*, *11*). While thatch is beneficial to enhance turf durability, moderate soil temperatures and lessen weed invasion, an excessive thatch-mat can reduce cold temperature tolerance, increase disease and pest pressure and reduce water infiltration and hydraulic conductivity (*12–16*). Golf course fairways and putting greens are often managed with core cultivation or verticutting to alleviate surface compaction, control thatch, stimulate root and shoot growth and enhance water infiltration (*10*, *12*, *13*, *17–22*). Cultivation with hollow tines typically involves removing cores from the turf, which are air-dried and brushed back into the open holes (*23*). Solid tine core cultivation does not remove a core, requires a reduced amount of labor and is less disruptive to the surface of the turf but is believed to cause localized compaction (*23*).

Management practices have been shown to reduce runoff and pesticides transported with runoff from agricultural crops (*24–26*). A number of studies have evaluated management and cultural practices for turfgrass and their influence on turf quality (*23*, *27–29*), runoff volume (*30*, *31*) and nutrient and pesticide transport with leachate (*32–34*) and runoff (*30*, *31*, *35–37*). The goal of the present study was to evaluate the capacity of cultural practices to reduce the off-site transport of pesticides with runoff from creeping bentgrass turf managed as golf course fairway. Specific objectives were to quantify runoff volumes and

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

mass of pesticides transported in runoff comparing: hollow tine core cultivation (HTCC) with no core cultivation (NCC), HTCC with solid tine core cultivation (STCC), and HTCC with verticutting (VC). Evaluation of established and emerging cultural practices is important in order to understand their effectiveness and sustainability. As benefits and improvements in management strategies are discovered they can be implemented; while practices with unexpected adverse consequences can be modified or replaced.

Materials and Methods

Site Description

Experiments were conducted at the University of Minnesota Turf Research, Outreach and Education Center, Saint Paul, MN, USA. The soil was characterized as Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed superactive, mesic Typic Hapludolls; 3% organic carbon, 29% sand, 55% silt, and 16% clay), which was graded to a 4% slope running east to west and covered with L-93 creeping bentgrass (*Agrostis palustris* Huds.) sod 14 months prior to initiation of the reported studies (*38*).

Runoff Collection System

The 976 m^2 site was divided into 6 plots (24.4 m x 6.1 m, length x width) prepared in an east to west direction. Runoff collection systems, modified from the design of Cole et al. (*35*), were constructed at the western edge of each plot and are described in detail elsewhere (*38*). In summary, stainless steel flashing guided the runoff from the turf into polyvinyl chloride (PVC) gutters which lead to a large stainless steel 60° V-trapezoidal flume (Plasti-Fab, Tualatin, OR) equipped with a bubble tube port and two sample collection ports. Flume shields and gutter covers prevented dilution of runoff with precipitation. Prior to simulated precipitation events, plots were hydrologically isolated with removable berms, constructed from horizontally-split 10.2-cm schedule 40 PVC pipe, inverted to rest on the cut edges. Observations during runoff events showed no water movement under the PVC berms.

Management Practices

Creeping bentgrass turf was managed as a fairway with 1.25 cm height of cut (3 times weekly, clippings removed), topdressed with sand (weekly, 1.6 mm depth) and irrigated to prevent drought stress. The quantity of water applied with the maintenance irrigation was not enough to produce surface runoff. Specific management practices that were evaluated in side-by-side comparisons are provided in Table I and outlined below.

Table I. Description of management practices and simulated precipitation.

Management Practices (Treatments) Compared				
Treatment A	Hollow Tine Core[a]	Hollow Tine Core[a]	Hollow Tine Core[a]	Hollow Tine Core[a]
Treatment B	No Aerification	Solid Tine Core Cultivation[b]	Solid Tine Core Cultivation[b]	Verticut[c]
Time from Management Practice to Precipitation (d)	28	63	2	7
Time from Pesticide Application to Precipitation (d)	0.9 ± 0.1	1.4 ± 0.2	0.8 ± 0.1	0.8 ± 0.5
Simulated Precipitation Duration (min)	106 ± 3	106 ± 3	117 ± 9	105 ± 2
Simulated Precipitation Applied (mm)	76 ± 5	60 ± 6	47 ± 09	78 ± 7

[a] Hollow tines (0.95 cm internal diameter x 11.43 cm depth with 5 cm x 5 cm spacing)

[b] Solid tines (0.95 cm diameter x 11.43 cm depth with 5 cm x 5 cm spacing)

[c] Blades (2mm, 3.8 cm spacing x 1.9 cm depth)

Hollow Tine Core Cultivation (HTCC) versus No Core Cultivation (NCC)

All plots were rolled 2 times per week (Smithco Tournament Ultra-4 Greens roller, Smithco, Cameron, WI, USA) in addition to the general management listed above. Twenty-eight days prior to simulated precipitation, three of the 6 plots were aerated with hollow tines (0.95 cm internal diameter x 11.43 cm depth with 5 cm x 5 cm spacing) (Ryan Greensaire II Aerator, Ryan, Barrington, IL, USA). Cores removed with the hollow tines were allowed to dry, broken into smaller pieces, and worked back into the turf. A back-pack blower and leaf rake removed the turf and thatch from the plot surface. Sand topdressing was not performed immediately after core cultivation or within a week of simulated precipitation and generation of runoff.

Hollow Tine Core Cultivation (HTCC) versus Solid Tine Core Cultivation (STCC)

Plots were aerated twice (Julian day 172: 63 d prior to the first simulated precipitation and Julian day 272: 2 d prior to the second simulated precipitation) with either solid tines (0.95 cm diameter x 11.43 cm depth with 5 cm x 5 cm spacing, plots 1, 3 and 6) or hollow tines (0.95 cm internal diameter x 11.43 cm depth with 5 cm x 5 cm spacing, plots 2, 4 and 5) (Ryan Greensaire II Aerator, Ryan, Inc., Barrington, IL). Cores removed with the hollow tines were air dried and worked back into the turf as previously described. Sand top dressing was not performed within a week of simulated precipitation or immediately following core cultivation.

Hollow Tine Core Cultivation (HTCC) versus Verticutting (VC)

Seven days prior to simulated precipitation and runoff three of the 6 plots were aerated with hollow tine core cultivation as described previously or sliced (verticut) with 2mm blades (spaced 3.8 cm apart, slicing to a 1.9 cm depth) (Graden GS04 Verticutter, Graden USA, Inc., Richmond, VA).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Pesticide Application

Commercially available pesticide products were tank mixed and applied at label rates to all plots perpendicular to runoff flow. Trimec® Bentgrass Formula herbicide (PBI Gordon, Kansas City, MO, USA) containing 9.92% mecoprop-p (dimethylamine salt of (+)-(R)-2-(2-methyl-4-chlorophenoxy) propionic acid) (MCPP), 6.12% 2,4-D (dimethylamine salt of 2,4-dichlorophenoxyacetic acid), and 2.53% dicamba (dimethylamine salt of 3,6-dichloro-*o*-anisic acid) are reported in the present publication. Properties of the active ingredient are provided in Table II. Application was completed 22 ± 10 h prior to initiation of each rainfall simulation. No irrigation or natural precipitation occurred between completion of the pesticide application and initiation of simulated precipitation. Details on the tank mixed fungicide (flutolanil) and insecticide (chlorpyrifos), application equipment and spray characteristics are reported elsewhere (*38*).

Table II. Pesticide physiochemical properties.[a]

Pesticide	Water Solubility (20°C) (mg/L)	K_{OC}[b] (ml/g)	Half Life (d) Soil	Water-Sediment	Water Phase
Dicamba	250,000	12	8	41	40
MCPP[c]	860	31	8	50	37
2,4-D[d]	23,180	56	10	29	29

[a] http://sitem.herts.ac.uk/aeru/footprint/en/index.htm
[b] Soil organic carbon partition coefficient
[c] Mecoprop-P
[d] 2,4-dichlorophenoxyacetic acid

Simulated Precipitation

A rainfall simulator was constructed following the design of Coody and Lawrence (*39*), which delivered precipitation with a droplet size spectrum, impact velocity, and spatial uniformity characteristic of natural rainfall. The base of the simulator consisted of 5-cm schedule 40 PVC pipes, which surrounded two 24.4 m x 6.1 m plots, and guided water to eighteen 2.54-cm schedule 40 PVC risers. Risers were spaced 3.7 m apart and each was equipped with a pressure regulator (Lo-Flo, 15 psi), nozzle (No. 25) and standard PC-S3000 spinner (Nelson Irrigation, Walla Walla, WA) suspended 2.7 m above the turf. Simulated precipitation events occurred for 2.0 ± 0.5 h at rates of 29 ±6 mm/h, similar to storm intensities recorded in Minnesota, USA, during July through October with recurrence interval of 25 years (*40*).

Prior to initiation of simulated precipitation (48 h), each plot was pre-wet with the maintenance irrigation beyond soil saturation to allow for collection of background samples and to ensure uniform water distribution. Irrigation water samples and resulting background runoff were collected for analysis. The following day the turf was mowed (1.25 cm height, clippings removed) and runoff collection gutters and flumes were cleaned and covered with plastic sheeting to prevent contamination during pesticide application. Prior to chemical application, Petri dishes (glass, 14-cm) were distributed across the plots to verify pesticide delivery and application rates. Plastic sheeting and Petri dishes were removed following chemical application and 12-cm rain gauges (Taylor Precision Products, Las Cruces, NM) were distributed throughout each plot to quantify simulated precipitation. Plots were hydrologically isolated with removable berms, constructed from horizontally-split 10.2-cm schedule 40 PVC pipe, inverted to rest on the cut edges. Wind speeds were monitored with a hand-held meter (Davis Instruments, Vernon Hills, IL). Once wind speeds dropped and remained below 2.2 m/s rainfall simulations were initiated and continued until runoff had been generated for a minimum of 90 min. Overall, simulated precipitation was initiated 26 ± 13 h after pesticide application when the wind speeds averaged 0.8 ± 0.7 mps (1.8 ± 1.6 mph).

Runoff Collection

Within 3 h prior to initiation of simulated precipitation soil moisture was measured with a soil moisture meter (Field Scout TDR 300, Spectrum Technologies, Plainfield, IL). Automated runoff samplers (model 6700) equipped with flow meters (model 730) (Teledyne Isco, Lincoln, NE) recorded runoff flow rates every minute, calculated total runoff volumes and collected time-paced (5 min) runoff samples into glass bottles. Water samples were removed from the samplers and stored at -20 °C until laboratory analysis. Irrigation source water, background runoff water, and background runoff spiked with known quantities of pesticides served as blank and positive control samples.

Pesticide Analysis

Runoff samples (3 ml) were filtered through a 0.45 μm nylon syringe filter (Whatman) followed by methanol (0.5 ml) to rinse the filter. Each runoff sample was analyzed for pesticides. No samples were combined. Petri dishes, containing pesticide residues for determination of actual application rates, were rinsed with methanol and the filtered rinsate (0.45 μm nylon filter) was diluted with laboratory-grade organic-free water to 14% methanol to mimic the methanol and water content of the filtered runoff samples. Runoff and application rate samples were processed in groups of 10 with an untreated laboratory-grade organic-free water sample and a laboratory-grade organic-free water sample fortified with the target analytes at the beginning and end of each filtration batch. Concentrations of each pesticide were measured by direct injection (500 μl) onto a high performance liquid chromatograph (Waters model 717plus autosampler and model 1525 binary pump) with a photodiode array detector (Waters model 2996: Waters Corp., Milford, MA) set at 230nm. Analytes were eluted from an Agilent C-18 column (150 mm long, 4.6 mm diameter, 5 μm packing) using two solvents [solvent A: laboratory-grade organic-free water (0.17% trifluoroacetic acid); solvent B: 82:18 methanol:acetonitrile] at a rate of 1 ml/min. Initial conditions, 60% B, were held for 2 min followed by a gradient ramped from 60 to 95% B in 23 min, a 3 min hold, then back to 60% B in 10 min with a 5 min hold. Recoveries were: dicamba 102 ± 6%, MCPP 104 ± 7% and 2,4-D 105 ± 11%. Method detection limits ranged from 2.5 to 3.7 μg/L. Limits of quantification for the target analytes were: dicamba 5.1 ± 0.6 μg/L, MCPP 5.3 ± 0.9 μg/L and 2,4-D 4.5 ± 0.8 μg/L.

Calculation of Pesticide Loads

Pesticide loads (μg/m^2) transported with runoff for each time point were calculated from the measured pesticide concentration (mg/L) in the filtered runoff water, the flow rate at the time of sampling (L/min) and the time between samples (min) for the area of the turf plot (m^2). Graphical representation of runoff volumes and pesticide loads for individual samples throughout a runoff event are presented as hydrographs and chemographs, along with cumulative values, in the first four figures.

Statistical Analysis

The rainfall simulator delivered precipitation to two plots simultaneously. Therefore a randomized complete block design was used to assign one of each paired management practices to a treatment to a block, providing three replicate side-by-side comparisons. Analyses of variance were performed to evaluate runoff volumes and chemical loads, with the management practice as the single criteria of classification for the data. Statistical significance between treatment means was confirmed by least significant difference (LSD, 0.05 = error degrees of freedom and 0.05 probability to determine two-tailed t values). Coefficients of determination (r^2) were calculated to evaluate the association of runoff volume and chemical concentration to chemical load and factors that influence the percentage of applied precipitation as runoff and percentage of applied herbicides in runoff (*41*).

Results

Precipitation

Simulated rainfall and evaluation of resulting runoff occurred during the months of August and September while the turf was actively growing (mean air temperatures: high 26 °C, low 15 °C). A description of the management practices evaluated and details of the simulated precipitation events are provided in Table I. Precipitation was initiated within 36 h (1.4 d) following pesticide application and terminated 90 min after the onset of runoff totaling 76 ± 5 mm, 78 ± 7 mm, 60 ± 6 mm and 47 ± 9 mm of precipitation (mean ± standard deviation), respectively. Calculated rainfall rates were 24 ± 4 to 46 ± 4 mm/h. Variations in generated rainfall rates for the different runoff events were the result of changes in pressure at the water source during the time of simulated precipitation. Measured coefficients of uniformity for the rainfall simulator were 82 to 84%.

Runoff Volume and Mass of Herbicides Transported with Runoff

Side-by-side comparisons of paired management practices revealed the influence of turf management on runoff volume and the mass of herbicides transported in the runoff. Analysis of the source water applied as maintenance irrigation and simulated precipitation confirmed that the water supply did not contain the herbicides of interest. Dicamba, MCPP and 2,4-D were detected in the initial runoff sample and throughout the runoff event for all management practices evaluated.

With or Without Hollow Tine Core Cultivation

Plots managed with hollow tine core cultivation (HTCC) displayed a 40% reduction in runoff volume compared to plots that received no core cultivation (NCC) (cumulative volume: NCC = 1,560 ± 725 L; HTCC = 943 ± 876 L) (Figure 1A). This resulted in a 4 to 7% reduction in the off-site mass transport of dicamba, MCPP and 2,4-D (cumulative loads: dicamba, NCC = 1,693 ± 589 $\mu g/m^2$, HTCC = 1,127 ± 1,088 $\mu g/m^2$; MCPP, NCC = 374 ± 67 $\mu g/m^2$, HTCC = 260 ± 249 $\mu g/m^2$; 2,4-D, NCC = 642 ± 289 $\mu g/m^2$, HTCC = 405 ± 409 $\mu g/m^2$) (Figure 1B-D). Although a repeating trend was observed in both the hydrographs and chemographs where greater than 72% of the replicate means (n > 115) were reduced with HTCC compared to NCC, the mean cumulative runoff volumes and loads were not statistically significant. Analysis of chemical loads with runoff volumes and chemical concentrations revealed that herbicide loads were attributed to runoff volume more than chemical concentrations (NCC, volume r^2 = 0.67, concentration r^2 = 0.05; HTCC, volume r^2 = 0.76, concentration r^2 = 0.14).

Hollow Tine Core Cultivation versus Solid Tine Core Cultivation

The influence of HTCC versus solid tine core cultivation (STCC) on runoff volume and pesticide transport in the runoff was evaluated at two time points following core cultivation. The first runoff event occurred on Julian days 234-236, ~ 63 d following core cultivation, and the second event occurred on Julian days 272-273, ~ 2 d following the second core cultivation (~ 101 d following the first core cultivation). Overall, runoff volume was lessened in fairway turf plots managed with HTCC relative to STCC. For both time points the hydrographs displayed reductions in runoff volume from plots aerated with HTCC compared to STCC for more than 80% of the recorded data (63 d = 81%, 2 d = 87%, n > 130 for each treatment replicate). Calculation of cumulative runoff volumes from plots receiving core cultivation 63d prior to rainfall simulation demonstrated a 10% reduction in cumulative runoff volume with hollow tines relative to solid tines (HTCC = 3,149 ± 932 L; STCC = 3,490 ± 1,107 L) (Figure 2A). The same trends were observed and enhanced when plots received core cultivation 2 d prior to simulated rainfall resulting in a 55% reduction in cumulative runoff volume from hollow tine plots (HTCC = 1,856 ± 139 L; STCC = 4,164 ± 1,698 L) (Figure 3A).

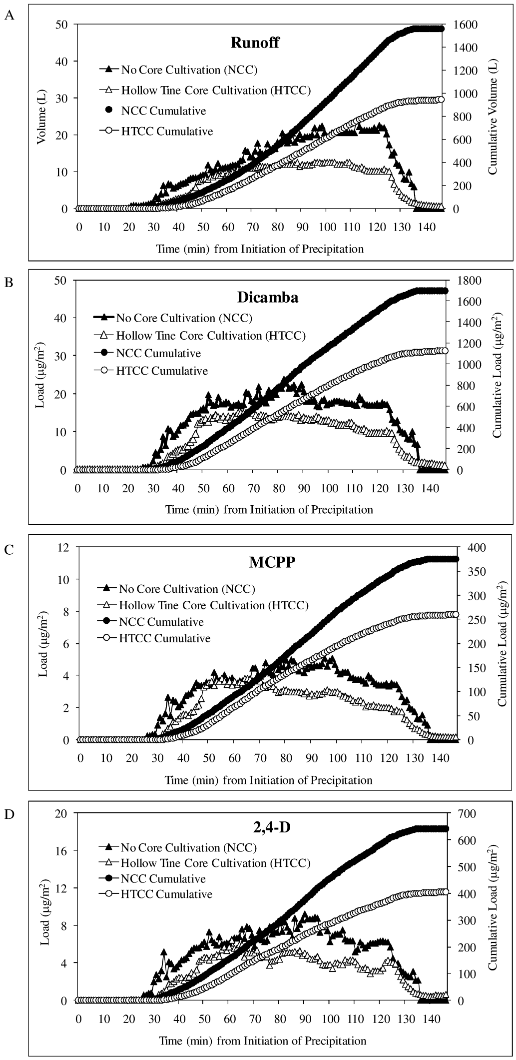


Figure 1. Runoff hydrograph and cumulative runoff volume (A) and chemographs and cumulative loads of dicamba (B), mecoprop-p (MCPP) (C), and 2,4-dichlorophenoxyacetic acid (2,4-D) (D) measured in runoff from turf plots managed with hollow tine core cultivation or no core cultivation 28d prior to simulated precipitation and runoff.

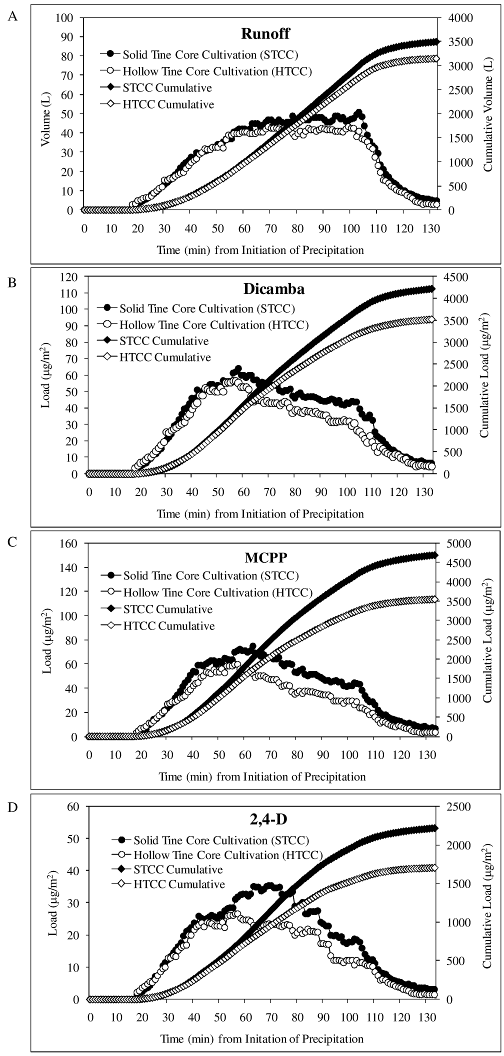


Figure 2. Runoff hydrograph and cumulative runoff volume (A) and chemographs and cumulative loads of dicamba (B), mecoprop-p (MCPP) (C), and 2,4-dichlorophenoxyacetic acid (2,4-D) (D) measured in runoff from turf plots managed with hollow tine core cultivation or solid tine core cultivation 63d prior to simulated precipitation and runoff.

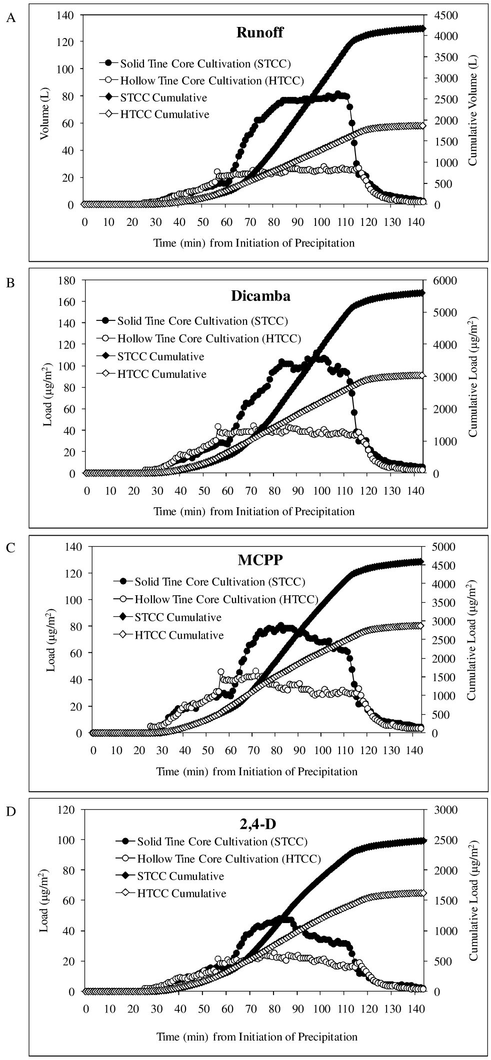


Figure 3. Runoff hydrograph and cumulative runoff volume (A) and chemographs and cumulative loads of dicamba (B), mecoprop-p (MCPP) (C), and 2,4-dichlorophenoxyacetic acid (2,4-D) (D) measured in runoff from turf plots managed with hollow tine core cultivation or solid tine core cultivation 2d prior to simulated precipitation and runoff.

The cumulative mass or load of chemicals transported with runoff from plots managed with solid tines exceeded that of plots managed with hollow tines. Chemographs and cumulative chemical loads for the runoff events occurring 63 d and 2 d following core cultivation are presented in Figures 2B-D and Figures 3B-D. Plots receiving HTCC to manage thatch 63 d prior to runoff showed a 17, 24 and 23% reduction in cumulative dicamba, MCPP and 2,4-D loads, respectively (dicamba: HTCC = 3,519 ± 453 μg/m^2, STCC = 4,222 ± 270 μg/m^2; MCPP: HTCC = 3,555 ± 1,273 μg/m^2, STCC = 4,693 ± 1,995 μg/m^2; 2,4-D: HTCC = 1,700 ± 663 μg/m^2, STCC = 2,219 ± 803 μg/m^2) (Figure 2B-D). Greater reductions in herbicide transport with runoff from HTCC relative to STCC were observed 2 d following core cultivation with 46, 37 and 35% decline in cumulative loads of dicamba, MCPP and 2,4-D (dicamba: HTCC = 3,043 ± 76 μg/m^2, STCC = 5,602 ± 1,788 μg/m^2; MCPP: HTCC = 2,878 ± 350 μg/m^2, STCC = 4,585 ± 596 μg/m^2; 2,4-D: HTCC = 1,617 ± 122 μg/m^2, STCC = 2,478 ± 515 μg/m^2) (Figure 3B-D). These observed trends were significant (LSD, 0.05) for the 2d data. Analysis of pesticide loads with runoff volumes and pesticide concentrations revealed that pesticide loads were attributed to runoff volume more than chemical concentrations for both management practices (HTCC 63 d, volume r^2 = 0.66, concentration r^2 = 0.13; STCC 63 d, volume r^2 = 0.74, concentration r^2 = 0.08; HTCC 2 d, volume r^2 = 0.90, concentration r^2 = 0.20; STCC 2 d, volume r^2 = 0.92, concentration r^2 = 0.06).

This greater association of pesticide load with runoff volume explains in part the increased pesticide transport associated with the STCC plots compared to HTCC plots and the increased difference in pesticide loads between cultivation practices at 2 d compared to 63 d.

Hollow Tine Core Cultivation versus Verticutting

Runoff volume and pesticide mass transport with runoff were compared from plots managed with HTCC or verticutting (VC). Hydrographs and chemographs showed reductions in runoff volume and chemical loads with runoff from plots managed with HTCC compared to VC for 63 to 87% of the data (n = 152) (Figure 4A-D). Plots with HTCC showed a 16% decline in cumulative runoff volume (HTCC = 3,266 ± 1,209 L; VC = 3,878 ± 1,910 L) and 28, 39 and 33% decline in cumulative loads of dicamba, MCPP and 2,4-D (dicamba: HTCC = 4,519 ± 2,417 μg/m^2, VC = 6,236 ± 3,637 μg/m^2; MCPP: HTCC = 1,604 ± 933 μg/m^2, VC = 2,643 ± 1,617 μg/m^2; 2,4-D: HTCC = 1,805 ± 1,159 μg/m^2, VC = 2,803 ± 1,634 μg/m^2), respectively. Despite these observed trends the mean cumulative runoff volumes and loads were not statistically significant. Analysis of chemical loads with runoff volumes and chemical concentrations showed that herbicide loads were attributed to runoff volume more than chemical concentrations for HTCC (volume r^2 = 0.70, concentration r^2 = 0.12) and comparable for VC (volume r^2 = 0.67, concentration r^2 = 0.70).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

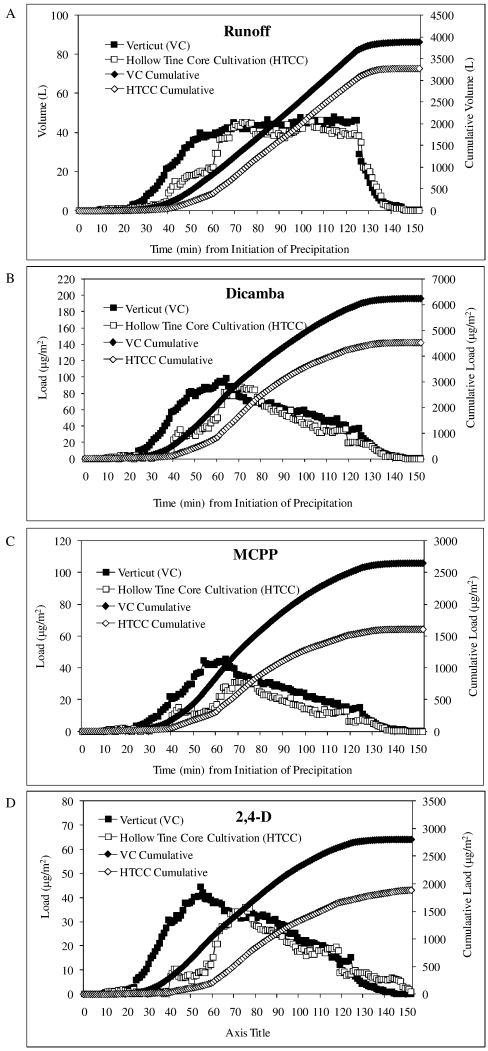


Figure 4. Runoff hydrograph and cumulative runoff volume (A) and chemographs and cumulative loads of dicamba (B), mecoprop-p (MCPP) (C), and 2,4-dichlorophenoxyacetic acid (2,4-D) (D) measured in runoff from turf plots managed with hollow tine core cultivation or verticutting 7d prior to simulated precipitation and runoff.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Discussion

In order to compare trends between management practices and field seasons the runoff and pesticide data were converted to the percentage of applied precipitation as runoff or percentage of applied herbicide transported with runoff (Figure 5 A-D). Runoff represented 8 to 62% of the simulated precipitation, which was influenced by soil moisture (r^2 = 0.62) more than precipitation depth (r^2 = 0.23), precipitation rate (r^2 = 0.06) or time from management practice to runoff (r^2 = 0.03) (Table II, Figure 5). A direct relationship between runoff volume and soil moisture at the time of precipitation events has been reported (*42*). Overall HTCC showed a reduction in runoff relative to the other management practices; with the least to greatest difference being NCC < VC < STCC (63 d) < STCC (2 d). This is the result of improved infiltration with HTCC as well as a difference in soil compaction compared to VC and STCC. Other researchers have reported enhanced water infiltration in turf managed with HTCC compared to untreated turf (*27*, *28*) and greater air porosity and saturated water conductivity in turf managed with HTCC compared to STCC (*23*). Verticutting and STCC displace soil with blades and solid tines, respectively, resulting in localized compaction. In contrast HTCC removes cores with hollow tines, returning soil to the turf while removing excess thatch. Studies have shown that STCC results in localized compaction with the greatest compaction at the base of the zone of cultivation (*23*). Cultivation with HTCC has also been shown to result in compaction along the sidewalls and base of the core channel; however, sidewall compaction diminished while base compaction remained after 95 d (*43*). In the present study the greatest distinction in soil physical properties between plots managed with STCC or HTCC was evident soon after cultivation and lessened with time as compaction dissipated, roots grew and holes were filled or covered. As a result the greatest divergence in percentage of precipitation measured as runoff was observed at 2 d (Figure 5C) following cultivation compared to 63 d (Figure 5B). We suspect that soil compaction resulting from VC was less than STCC as differences in observed runoff from HTCC were more representative of STCC after 63 d when time from VC to runoff was only 7d (Figure 5D versus 5B compared to Figure 5D versus 5C). The average percentage of applied precipitation as runoff, for all evaluated management practices, was 31 ± 17%. This is in line with the findings of Shuman (*42*) where 37 to 44 % of applied precipitation (50 mm) was reported as runoff from fairways of Tifway bermudagrass (*Cynodon dactylon* (L.) Pers.), 2 d following irrigation to field capacity.

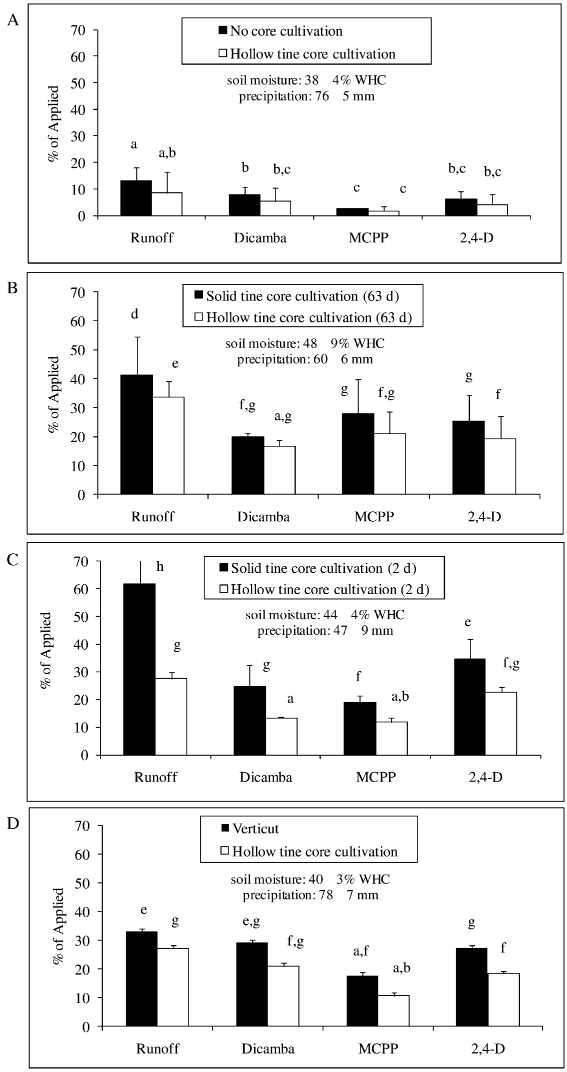


Figure 5. Mean percentage of applied precipitation measured as runoff and mean percentage of applied dicamba, mecoprop-p (MCPP) and 2,4-dichlorophenoxyacetic acid (2,4-D) measured in runoff from turf plots managed with hollow tine core cultivation or no core cultivation 28d prior to simulated precipitation and runoff (A), hollow tine core cultivation or solid tine core cultivation 63d prior to simulated precipitation and runoff (B), hollow tine core cultivation or solid tine core cultivation 2d prior to simulated precipitation and runoff (C), and hollow tine core cultivation or verticutting 7d prior to simulated precipitation and runoff (D). Error bars represent the standard deviation of the mean. Means that do not share the same lowercase letter are statistically different ($p < 0.05$).

Quantities of herbicides detected in the runoff represent 5 to 29% of applied dicamba, 2 to 28% of applied MCPP, and 4 to 35% of applied 2,4-D; which was influenced by percentage of applied precipitation as runoff (r^2 = 0.78) and water solubility of the herbicide (r^2 = 0.54) more than the soil organic carbon partition coefficient (K_{OC}) of the herbicide (r^2 = 0.25) (Figure 5, Table II). Chemical degradation was not influential in the present study as the time from chemical application to runoff (22 ± 10 h) was much less than the reported half lives of the compounds of interest (192 to 984 h; 8 to 41 d) (Table II). Ma et al. (*44*) observed that runoff from bermudagrass plots managed as a fairway contained 9, 10, and 15% of applied 2,4-D, MCPP, and dicamba, respectively. This concurs with the findings of Cole et al. (*35*) who measured less than 3 to 15% of applied 2,4-D, MCPP and dicamba in runoff from bermudagrass turf. Armbrust and Peeler (*45*) reported less than 3% of 2,4-D in runoff from Tifway bermudagrass that received simulated precipitation 24 h after application. These values are in range with those measured in our study comparing HTCC with NCC (Figure 5A: 2 to 8% of applied herbicides) where the soil moisture was 38% WHC. The larger percentages of applied herbicides measured with runoff in the studies comparing HTCC with STCC (Figure 5B: 16 to 41%; Figure 5C: 12 to 62%) and HTCC with VC (Figure 5D: 11 to 33%) are most likely related to the greater soil moisture (44, 48 and 40 % WHC) prior to pesticide application. Increased transport of dicamba, mecoprop and 2,4-D with runoff from turf has been noted with greater pre-application soil moistures (*35*).

When the influence of management practices were compared, the percentage of applied herbicides measured in runoff were less from turf managed with HTCC than NCC, VC, or STCC (Figure 5A-D). These trends were statistically significant ($p < 0.05$) for dicamba, MCPP, and 2,4-D when comparing HTCC versus STCC at 2d following core cultivation (Figure 5C), and for 2,4-D when comparing HTCC with VC (Figure 5D) and HTCC with STCC at 63d following core cultivation (Figure 5B). As previously discussed, HTCC removes the cores and returned the soil back to the turf while STCC and VC pushes the soil aside to create the channels or slices. Consequently one would anticipate greater soil compaction with the STCC and VC relative to HTCC as well as increased accessibility of soil adsorptive sites with the HTCC. This would influence hydraulic conductivity and infiltration (*23*, *27*, *28*) as well as pesticide availability for transport (*33*, *46*, *47*). Others have shown pesticide residues can be found in thatch where they may be sorbed (*48–50*) resulting in reduced mobility to underlying soil (*33*, *51*). It is important to point out that numerous environmental and management factors contribute to the availability of pesticides for movement with overland flow, of which only a few were considered in this study. The use of simulation models that consider environmental and management factors in addition to chemical properties can extend predictions of pesticide availability and transport beyond evaluated experimental constraints, as well as estimate ecological benefits and risks (*44*, *52*, *53*).

Acknowledgments

The present research was funded in part by the U.S. Golf Association, Green Section Research. We thank Christina Borgen, Troy Carson, Mike Dolan, Shari Greseth, Andrew Hollman, Craig Krueger, Jeff Lanners, Matthew McNearney, Carl Rosen, Jon Sass, Alex Seeley and Karli Swenson, and Nelson Irrigation.

Mention of specifice products or supplies is for identification and does not imply endorsement by U.S. Department of Agriculture to the exclusion of other suitable products or supplies.

References

1. Kiely, R.; Donaldson, D.; Grube, A. *Pesticide industry sales and usage, 2000 and 2001 market estimates*; Office of Pesticide Programs, U.S. Environmental Protection Agency: Washington, DC, 2004. http://www.epa.gov/opp00001/pestsales/01pestsales/usage2001.htm#3_1.
2. Milesi, C.; Running, S. W.; Elvidge, C. D.; Dietz, J. B.; Tuttle, B. T.; Nemani, R. R. *Environ. Manage.* **2005**, *36*, 426–438.
3. Gianessi, L. P.; Anderson, J. E. *Pesticide use in U. S. crop production*. National Data Report. National Center for Food and Agricultural Policy: Washington, DC, 1996.
4. Barbash, J. E.; Resek, E. A. *Pesticides in Groundwater: Distribution, Trends, and Governing Factors;* Lewis: Boca Raton, FL, 1996.
5. Cohen, S.; Svrjcek, A.; Durborow, T.; Barnes, N. L. *J. Environ. Qual.* **1999**, *28*, 798–809.
6. Gilliom, R. J.; Barbash, J. E.; Crawford, C. G.; Hamilton, P. A.; Martin, J. D.; Nakagaki, N.; Nowell, L. J.; Scott, J. C.; Stackelberg, E.; Thelin, G. P.; Wolock, D. M. *Pesticides in the nation's streams and ground water, 1992-2001*; Ci no. 1291, Revised Feb 2007; U.S. Geological Survey National Water-Quality Assessment Program: Reston, VA, 2006. http://pubs.usgs.gov/circ/2005/1291.
7. Hoffman, R. S.; Capel, P. D.; Larson, S. J. *Environ. Toxicol. Chem.* **2000**, *19*, 2249–2258.
8. Wotzka, P. J.; Lee, J.; Capel, P. D.; Lin, M. *Pesticide concentrations and fluxes in an urban watershed*; AWRA Technical Publication Series TPS-94-4; American Water Resources Association: Herndon, VA, 1994; pp 135−145.
9. U.S. Environmental Protection Agency. *National recommended water quality criteria*; EPA 822-Z-99-001; Washington, DC, 1999.
10. Dunn, J. H.; Minner, D. D.; Fresenburg, B. F.; Bughrara, S. S.; Hohnstrater, C. H. *Agron. J.* **1995**, *87*, 891–894.
11. Baldwin, C. H.; Liu, H.; McCarty, L. B.; Luo, H.; Toler, J.; Long, S. H. *HortScience* **2008**, *43*, 922–926.
12. Beard, J. B. *Turfgrass: Science and Culture*; Prentice-Hall: Engelwood Cliffs, NJ, 1973.
13. White, R. H.; Dickens, R. *Agron. J.* **1984**, *76*, 19–22.
14. Murray, J. J.; Juska, F. V. *Agron. J.* **1977**, *69*, 365–369.

15. Harris, J. R. In *Modifications of Soil Structure*; Emerson, W. W., Ed.; John Wiley & Sons: Chichester, England, 1978.
16. Miller, R. W. *Weeds, Trees, Turf* **1965**, *4*, 10–18.
17. Turgeon, A. J. *Turfgrass Management*, 2nd ed.; Reston Publishing: Reston, VA, 1985.
18. Carrow, R. N.; Johnson, B. J.; Burns, R. E. *Agron J.* **1987**, *79*, 524–530.
19. Callahan, L. L.; Sanders, W. L.; Parham, J. M.; Harper, C. A.; Lester, L. D.; McDonald, E. R. *Crop Sci.* **1998**, *38*, 181–187.
20. Rowland, J. H.; Cisar, J. L.; Snyder, G. H.; Sartain, J. B.; Wright, A. L. *Agron. J.* **2009**, *101*, 1565–1572.
21. Vargas, J. M.; Turgeon, A. J. *Poa annua: Physiology, culture, and control of annual bluegrass*; John Wiley & Sons: Hoboken, NJ, 2004.
22. Barton, L.; Wan, G. C. Y.; Buck, R. P.; Colmer, T. D. *Agron. J.* **2009**, *101*, 67–74.
23. Murphy, J. A.; Rieke, P. E.; Erickson, A. E. *Agron. J.* **1992**, *85*, 1–9.
24. Rice, P. J.; Harman-Fetcho, J. A.; Sadeghi, A. M.; McConnell, L. L.; Coffman, C. B.; Teasdale, J. R.; Abdul-Baki, A. A.; Starr, J. L.; McCarty, G. W.; Herbert, R. R.; Hapeman, C. J. *J. Agric. Food. Chem.* **2007**, *55*, 1377–1384.
25. Potter, T. L.; Truman, C. C.; Bosch, D. D.; Bednarz, C. *J. Environ. Qual.* **2004**, *33*, 2122–2131.
26. Hansen, N. C.; Moncrief, J. F.; Gupta, S. C.; Capel, P. D.; Olness, A. E. *J. Environ. Qual.* **2001**, *30*, 2120–2126.
27. Baldwin, C. M.; Liu, H.; Brown, P. J. *HortTechnol.* **2006**, *16*, 265–269.
28. McCarty, L. B.; Gregg, M. F.; Toler, J. E. *Agron. J.* **2007**, *99*, 1530–1537.
29. McCarty, L. B.; Gregg, M. F.; Toler, J. E.; Camberato, J. J.; Hill, H. S. *Crop Sci.* **2005**, *45*, 1529–1535.
30. Kauffman, G. L.; Watschke, T. L. *Agron. J.* **2007**, *99*, 141–147.
31. Moss, J. Q.; Bell, G. E.; Martin, D. L.; Payton, M. E. *J. Appl. Turfgrass Sci.* **2007**, DOI: 10.1094/ATS-2007-0125-02-RS.
32. Starrett, S. K.; Christians, N. E.; Austin, T. A. *J. Environ. Qual.* **1996**, *25*, 566–571.
33. Gardner, D. S.; Branham, B. E.; Lickfeldt, D. W. *Crop Sci.* **2000**, *40*, 1333–1339.
34. Smith, A. E.; Bridges, D. C. *Crop Sci.* **1996**, *36*, 1439–1445.
35. Cole, J. T.; Baird, J. H.; Basta, N. T.; Huhnke, R. L.; Storm, D. E.; Johnson, G. V.; Payton, M. E.; Smolen, M. D.; Martin, D. L.; Cole, J. C. *J. Environ. Qual.* **1997**, *26*, 1589–1598.
36. Wauchope, R. D.; Williams, R. G.; Marti, L. R. *J. Environ. Qual.* **1990**, *19*, 119–125.
37. Evans, J. R.; Edwards, D. R.; Workman, S. R.; Williams, R. M. *Trans. ASAE* **1998**, *41*, 1323–1329.
38. Rice, P. J.; Horgan, B. P.; Rittenhouse, J. L. *Environ. Toxicol. Chem.* **2010**, *29*, 1215–1223.
39. Coody, P. N.; Lawrence, L. J. Method and system for conducting meso-scale rainfall simulations and collecting runoff; U.S. Patent 5,279,151; U.S. Patent Office: Washington, DC, 1994.

40. Huff, F. A.; Angel, J. R. Rainfall Frequency Atlas of the Midwest, Bulletin 71, MCC Research Report 92-03, Midwest Climate Center and Illinois State Water Survey, Champaign, IL, 1992. http://www.isws.illinois.edu/pubdoc/B/ISWSB-71.pdf.
41. Steel, R. G. D.; Torrie, J. H.; Dickey, D. A. *Principles and Procedures of Statistics: A Biometrical Approach*, 3rd ed.; McGraw-Hill: New York, 1997.
42. Shuman, L. M. *J. Environ. Qual.* **2002**, *31*, 1710–1715.
43. Petrovic, A. Dissertation abstract, ADG80-06178, Michigan State University, Lansing, MI, 1979. http://guides.lib.msu.edu/page.phtml?page_id=1312.
44. Ma, Q. L.; Smith, A. E.; Hook, J. E.; Smith, R. E.; Bridges, D. C. *J. Environ. Qual.* **1999**, *28*, 1463–1473.
45. Armbrust, K. L.; Peeler, H. B. *Pest. Manage. Sci.* **2002**, *58*, 702–706.
46. Liu, L. X.; Hsiang, T.; Eggens, J. L. *Agron. J.* **1995**, *87*, 272–275.
47. Raturi, S.; Islam, K. R.; Caroll, M. J.; Hill, R. L. *Environ. Sci. Health, Part B* **2005**, *40*, 697–710.
48. Neimczyk, H. D.; Krueger, H. R. *J. Econ. Entomol.* **1987**, *80*, 950–952.
49. Dell, C. J.; Throssell, C. S.; Bischoff, M.; Turco, R. F. *J. Environ. Qual.* **1994**, *23*, 92–96.
50. Lickfeldt, D. W.; Branham, B. E. *J. Environ. Qual.* **1995**, *24*, 980–985.
51. Branham, B. E.; Wehner, D. J. *Agron. J.* **1985**, *77*, 101–104.
52. Ma, Q.; Hook, J. E.; Wauchope, R. D.; Dowler, C. C.; Johnson, A. W.; Davis, J. G.; Gascho, G. J.; Truman, C. C.; Sumner, H. R.; Chandler, L. D. *Soil Sci. Soc. Am. J.* **2000**, *64*, 2070–2079.
53. Haith, D. A. *J. Environ. Qual.* **2001**, *30*, 1033–1039.

Chapter 8

Encouraging Adoption of Integrated Pest Management in Non-Agricultural Settings

Cheryl A. Wilen,*,[1] Chris A. Geiger,[2] and Wanda Y. MacLachlan[3]

[1]University of California, Statewide IPM Program and UCCE, 5555 Overland Ave. Ste. 4101, San Diego, CA, USA 92123
[2]Department of the Environment, City & County of San Francisco, 11 Grove St., San Francisco, CA 94102
[3]University of Maryland, University of Maryland Extension, Central Maryland Research & Education Center, 11975 Homewood Road, Ellicott City, MD, USA 21042
*cawilen@ucdavis.edu

Pesticides used in non-crop areas, such as those used to control nuisance pests around structures and cosmetic use in landscapes and turf, contribute to surface water pollution. In this chapter we describe two general approaches to reducing pesticides in surface waters: *leading by example* through implementation of pesticide restrictions on municipal properties and limiting use of pesticides by governmental agencies, and *outreach* on the use of safer pest management alternatives. As shown by the case studies included here, these approaches are rooted in integrated pest management (IPM) and feature educational efforts designed to guide people toward less chemical-intensive approaches. Adoption of IPM techniques by both pest management professionals and home users can be influenced by education, demonstrations, and in some situations, imposing penalties. Pest management professionals, landscapers, and home gardeners will use information regarding IPM to reduce pesticide and fertilizer runoff when shown that implementing IPM will have a benefit to themselves or the environment.

Introduction

Wherever pesticides are applied there is the chance that they will move offsite through a number of mechanisms, one of them being surface water runoff. When pesticides are applied on or near impervious surfaces such as streets, driveways, sidewalks, and concrete around homes, the likelihood that pesticides will be carried offsite is even greater. However, even pesticide applications onto pervious surfaces such as lawns will move off the target site, onto the street and into storm drains where they are ultimately carried to local waterways, lakes, and the ocean.

This problem affects water bodies throughout the world. Nonessential use of pesticides, particularly in urban areas (cities and suburban areas where the local economy is not primarily based on agriculture), have been shown to contribute to surface water pollution and is described in other chapters of this book. Much of this unnecessary use can be attributed to nuisance pests around structures and applications solely for cosmetic purposes

Municipalities often deal with this issue by *leading by example*, where governmental agencies establish model programs on their own properties that limit pesticide use to prescreened products, and by *outreach* to the public and professional pesticide applicators, where residential use of pesticides is not restricted but users are strongly encouraged to use alternative methods to control pests.

Included in both these approaches is a very large educational and training component to help people transition away from depending on pesticides as their primary pest control method. Ways to select and apply pesticides that will reduce runoff and have the least environmental impact are also important factors for the user to consider if they do choose to use pesticides. Therefore, education about the use of integrated pest management (IPM) is an essential component to success of these programs.

In this chapter we describe two types of programs developed to educate non-agricultural pesticide users about the impact that pesticides can have on water quality and human health and how they can use alternative practices, such as IPM, to reduce that negative impact. Evaluation data regarding the impact of the training on knowledge or behavior change, when available, is also presented.

Leading by Example: Implementing a Model Program

Local governments in the U.S. generally lack the authority to directly regulate pesticide use by the general population. Under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), only the U.S. Environmental Protection Agency may approve the use of specific pesticide products or change the wording on pesticide product labels - which constitute the definitive legal documents affecting pesticide use. Furthermore, local governments in some states are prohibited from additional limits or bans on pesticide use, due to specific pre-exemptions under State law or by court precedent.

While local governments cannot legally regulate their residents' use of pesticides, they can regulate their own operations. As a result, some governments have chosen to lead by example through restrictions of pesticide use on their own properties. The City & County of San Francisco is a widely emulated example of this approach.

In October 1996, the San Francisco Board of Supervisors passed one of the strongest pesticide ordinances in the nation. Driven by public outcry over pesticide use in City parks, the Board passed an Integrated Pest Management Ordinance intended to phase out all use of all pesticides on City-owned properties by 2000, with an immediate halt in using US EPA Category I products and all known carcinogens and reproductive toxins. The ordinance also required the following actions:

Posting of all pesticide use on City properties, beginning three days before and extending to four days after each application.

Preparation of IPM plans by all City departments, for submission to the City's Department of the Environment.

Use of the IPM approach by City contractors. This was accomplished through the development of specific contracting requirements.

Recordkeeping and data requirements, including the submission of pesticide use data to the Dept. of the Environment.

By most accounts, the early version of the Ordinance was too blunt in its restrictions, although it caused an immediate drop in pesticide use. The Board amended the ordinance three times (*1*) in the following four years to allow:

Blanket exemptions for products registered for improving or maintaining water quality (such as disinfectants used in drinking water treatment plants), and for pesticides registered as antimicrobials or disinfectants.

Establishment of a Reduced-Risk Pesticide List of pesticides "commonly used as part of an IPM strategy" and allowed for use under specific situations. This list is created annually by the Department of the Environment and approved by the Commission on the Environment, its citizen oversight body.

One-year and "limited-use" exemptions granted by the Department of the Environment for products not currently on the Reduced-Risk Pesticide List

As a result of the Ordinance, total pesticide use, as measured by total pounds of product, dropped by 81% from 1996 (the year implementation began) to 2009. Total pesticide active ingredients used dropped by 76% during that period (Figure 1) (*2*). Those pesticide products designated as most hazardous ("Tier I"), have been gradually eliminated from the City's Reduced-Risk Pesticide Lists, and the Tier I products that remain are significantly safer than those used before 1996. City operations no longer use any pesticide active ingredients of concern under the U.S. Clean Water Act, specifically copper, diazinon, pyrethroids, and chlorpyrifos. While pest management effectiveness is more difficult to quantify than pesticide use, effectiveness appears to have remained within an acceptable range based on number of complaints from the public. Pest management effectiveness is more difficult to quantify than pesticide use, and no data exists that would allow a direct comparison of pest suppression now with pre-1996 levels. However, with the exception of the program's first two years (before implementation of the Reduced Risk Pesticide list), long-time City gardeners report no significant difference in the number of public complaints about inadequate pest suppression.

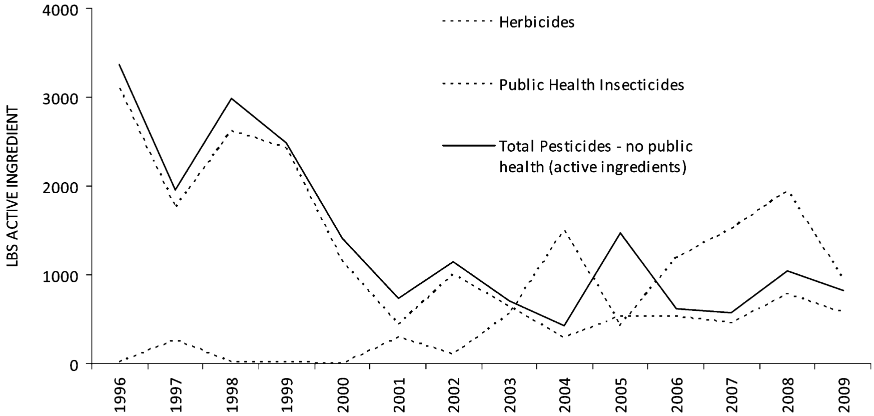


Figure 1. Total pesticides used on City properties, San Francisco, California, 1996-2009, in pounds of active ingredient. "Total pesticides" includes herbicides, insecticides, fungicides, rodenticides and molluscicides. "Public health insecticides" are mosquito larvicides. (Reproduced from (2)).

Both the IPM Ordinance and program strongly emphasize the importance of traditional IPM precepts: *Knowing the biology of the pests, taking preventive measures, establishing action thresholds, conducting monitoring, and reserving chemical control options for a last resort*. The last point presents the most significant communications challenge. For those not familiar with IPM, it is easy to confuse IPM with a mere set of tools, and forget that it is actually a decision-making process. For this reason, city departments seeking an exemption to use non-listed pesticides are required to answer a series of questions, to ensure than they are engaged in IPM rather than merely pesticide selection:

- *Justification for use*
- *Explanation of efforts to find alternatives*
- *Strategy to prevent future exemptions*

San Francisco's IPM Ordinance set into motion several processes that may have been more important than the ordinance itself in reducing pesticide use and enhancing adoption of IPM beyond the boundaries of city operations. Foremost among these has been the establishment of a strong, cross-jurisdictional IPM Technical Advisory Committee (TAC). The TAC began meeting in the 1997 and continues to meet monthly to this day. Typically, the TAC meetings feature IPM training or invited speakers as well as informal pest management "problem-solving" sessions, where IPM staff can discuss the prevailing challenges and possible solutions. The TAC has also plays a central role in organizing the biannual San Francisco Urban IPM Conference, which draws a wide audience of government agencies, nonprofits organizations, pest management professionals, and interested residents, thus moving the IPM message to parties outside the staff of the City & County of San Francisco

Activist groups, as well as the City's own staff, were at first wary of San Francisco's IPM ordinance, but have now become strong advocates of the IPM Program. For example, Beyond Pesticides (*3*) and the Natural Resources Defense Council (*4*) have both cited San Francisco's program as a model of urban IPM. In addition, IPM staff from other public agencies, such as the National Park Service, University of California, San Francisco Unified School District, and Presidio Trust, as well as some private property management firms, have joined the core group of the TAC, further extending its reach.

Although it is not a formal deliberative body, the IPM TAC now takes a central role in developing and updating the City's Reduced-Risk Pesticide List (*5*) each year, with the Dept. of Environment conducting background research and facilitating the process. The Department of Environment uses its own pesticide hazard screening system to develop the Reduce-Risk Pesticide List. This system was originally developed in 1999 by Dr. Phillip Dickey of the Washington Toxics Coalition as a first step in evaluating products and classifies products into one of three tiers, based on a wide variety of health and environmental hazards (*4*). With regard to surface and ground water hazards, for example, the screening system looks for active ingredients listed on the federal Clean Water Act 303(d) list, for high Groundwater Ubiquity Scores (GUS), and for product label language on potential groundwater contamination. Any pesticides flagged for these or other environmental hazards will automatically be cast as "Tier I," the highest hazard tier, and therefore avoided on the City's pesticide lists.

Once the draft Reduced-Risk Pesticide list has been revised, an annual public hearing is organized to simultaneously finalize the list, hear City residents' concerns on City pesticide use issues, and hear City departments' justifications for use of the most hazardous pesticides. Departments are also required to justify any exemptions granted to them during the previous year. The public hearings were not required under the original IPM Ordinance, but were considered important enough in promoting transparency that they were added as requirements in the 2011 revisions to the ordinance (*6*).

San Francisco's Reduced-Risk Pesticide List (RRPL) is specific to San Francisco City properties, and not appropriate for adoption by residents or even other agencies. The City includes many specialized facilities, such as a tournament golf course and the Conservatory of Flowers, that are not commonly found elsewhere and have specialized pest management needs. . Pesticide products are listed or removed after much research and deliberation, but they are generally professional-grade products (unavailable to residents) and occasionally higher hazard, Tier I products (too concentrated for residential use by untrained applicators). Other local agencies frequently contact IPM Program staff inquiring about simply adopting the San Francisco RRPL in their localities. The response to those requests is "a list is not a program" which informs the requester that overall concept of IPM is more complex and simply dictating which pesticides may or may be used does not qualify as an IPM program.

However, the tier ranking system has found more universal application. It is administratively simple, and for this reason has been easily adopted by smaller jurisdictions. Most ratings can be done with the use of publicly available information, such as the online Pesticide Action Network databases (URL http://www.pesticideinfo.org). As a result, the US Green Building Council adopted the San Francisco hazard screening system as part of its 2009 LEED for Existing Buildings standard (*7*).

The selective limitation of certain pesticides, and incorporation of regular IPM trainings for San Francisco City staff, have resulted in significant pesticide reductions (Figure 1). Nevertheless, it is likely that the impacts of these reductions on water quality are relatively small when compared to the total volume of pesticides used for commercial and residential pest control activities (*8*). For commercial and residential audiences, other tactics are needed, such as focused outreach/education efforts to encourage use of IPM practices.

Encouraging Use of Alternative Practices

The most widespread method of persuading professionals and home users to become partners to improve the quality of water in urban areas is to provide education through workshops, fact sheets, and other training that will give the users confidence to use IPM, reduce fertilize use, and modify irrigation practices. These programs are designed to reduce both the amounts of pollutants in surface water runoff and to reduce the total amount of runoff. There are two major target audiences: non-professionals and professionals.

Educating Home Gardeners, Landscapers, and Other Non-Professionals

Programs developed to inform and educate home gardeners and other non-professionals throughout the country include the Green-Blue Program for IPM and Water Quality in the Northeast U.S., sustainable landscaping programs such as those in northern California (Bay Friendly) and Maryland (Bay-Wise), and Our Water-Our World and Healthy Garden-Healthy Home programs in northern and southern California, respectively. The programs are generally conducted on a local or regional scale although the funding for such projects may also come from state or federal sources.

An example of such a program is being implemented in Maryland to reduce surface and ground water pollution in the Chesapeake Bay although the latter is not discussed here.

The sixth most densely populated state in the nation, Maryland is undergoing rapid changes in population growth and migration, land cover, community character, ecosystem stability, and economic diversity. State and U.S. Census Bureau estimates predict that Maryland's population will grow from approximately 5.7 million today to 6.6 million by 2030. Maryland's combination of heavily urbanized, densely populated regions, diverse agriculture, and forested areas create complex water quality challenges for the Chesapeake Bay and other natural resources. In many Maryland waters and in the Chesapeake Bay, a challenge is to improve water quality and maintain viable natural resources.

Urban and suburban sprawl has led to the conversion of thousands of acres of our native landscape into developed lands, impervious surfaces, and home lawns or gardens. These lawns and gardens were created using concepts that

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

were developed decades ago and are now outdated. However, most residents, planners and developers do not recognize the urban and suburban landscape as part of the greater ecosystem, and they have generally failed to incorporate environmental and ecological concepts into their landscape plans. This failure has led to the continued degradation of soil and water quality. Also, landscape plantings continue to add exotic and sometimes invasive plant species into the landscape. Because these landscapes generally lack diversity and rely too heavily on mowed turf as a ground cover, they fail to attract desirable wildlife that can add balance to a damaged ecosystem. All told, the area has been left with an unhealthy and unsustainable landscape.

Studies have shown that the region's ground and surface waters contain high levels of the nutrients nitrogen and phosphorus (N and P), sediments, and toxic contaminants, all of which adversely affect water quality, aquatic organisms, fisheries, and human health in and around the Chesapeake Bay (*9*). The 2000 Chesapeake Bay Agreement (URL http://dnrweb.dnr.state.md.us/bay/res_protect/c2k/agreement.asp) committed to fulfilling the 1994 goal of reducing or eliminating the input of chemical contaminants from all controllable sources to levels that result in no toxic or bio-accumulative impact on the living resources that inhabit the Bay or on human health. The agreement mandated a 40 percent reduction in nutrient loading into the Bay by the year 2010. This mandate was not met. In 2010, the Chesapeake Clean Water and Ecosystem Restoration Act, which proposes legally-binding pollution reduction targets on Bay area states, was still on the legislative calendar as of this printing.

Lacking legislative remedies, a new educational strategy was needed to change prevailing views on the urban/suburban landscape and to point towards better management approaches. Maryland Bay-Wise Landscape Management is an environmental education program conducted by University of Maryland Extension that addresses water quality concerns within the Chesapeake Bay. It uses the time and talents of trained Master Gardener volunteers to teach environmentally sound landscape practices to homeowners and youth. The long-term goal is to reduce the amount of nutrients, sediments, and toxic chemicals entering the Chesapeake Bay.

Maryland Master Gardeners receive approximately 40 to 50 hours of basic training in soils, soil testing, fertilizers, composting, and troubleshooting soil problems. They also learn about insects, diseases, fruit and vegetable gardening, lawn care, tree and shrub care, and propagating plants. In addition, some Maryland Master Gardeners in several counties choose to receive 14 hours of advanced training in such topics as the state of the Chesapeake Bay, hydrology, well and septic system care, hazardous household products and environmentally sound landscape maintenance. After completion of this training, they are eligible to have their home landscape certified as Bay-Wise. Master Gardeners then teach their fellow county residents (clients) how to reduce their negative impact on the environment through one-on-one site visits, staffing booths at community fairs and events, garden tours, web pages and classroom teaching.

As of 2010, 385 Master Gardeners have had their home landscapes certified as demonstration sites and 23,066 Maryland residents have been educated (2005-2010). Master Gardeners have certified 646 residential landscapes and 78 public landscapes as Bay-Wise throughout the state and volunteered 89,272 hours (as of 2009). This volunteer service is valued at over $1.9 million by the Governor's Office on Service & Volunteerism. Educational resources developed include the Bay-Wise MD Yardstick (a checklist of homeowner best management practices), HomeWork notebook (Bay-Wise Training Manual), and several Bay-Wise fact sheets available at URL http://www.hgic.umd.edu/content/onlinepublications.cfm.

Maryland Master Gardeners who completed the advanced training were asked to complete a post-class assessment to measure knowledge and behavioral change 7 to 9 months following the training. The following topics related to pest management were assessed:

- Attracting beneficial insects and animals to manage pests
- Mowing grass high to reduce weeds
- Reducing total lawn area
- Conserving water in the landscape

First, participants were asked how much they knew prior to and after receiving their training and then were asked whether they had already or planned to implement any of suggested actions, which directly or indirectly affect pest problems in the landscape, as a result of taking the training. Additional questions not listed above addressed water conservation inside the home, recycling yard waste and testing well water. This survey was given to 202 Master Gardeners from 17 Maryland counties over a three-year period. Sixty-seven surveys were completed (33% response rate).

This training resulted in a strong change in knowledge as only 39.4% of participants rated their knowledge of using beneficial organisms to reduce pests as a 3 or 4 (on a scale of 1 to 4 where 1 = not much activity and 4 = a lot) as compared to 83.3% of those rating their knowledge as high (3 or 4) after training. Likewise, behavior change was also high; 27.3% rating themselves as 3 or 4 before training versus 86.5% after (Figure 2).

Similar results were observed with participants conserving water in the landscape. Originally 60% of participants reported they "knew a lot" about the subject prior to training while after training, 96.9% reported they "knew a lot". Correspondingly, 70.3% of participants scored themselves as practicing water conservation in the landscape at a high level and after training 92.5% were planning to or are already conserving water in the landscape (data not shown).

Another example of outreach and education for the home gardener is the "Healthy Garden-Healthy Home" Program (HGHH), which is a cooperative project between the University of California's Cooperative Extension program in San Diego County, California and the County's Project Clean Water program (http://www.projectcleanwater.org). HGHH was initiated to provide IPM information and training to residents with goal of preventing overuse and runoff of home-use pesticides.

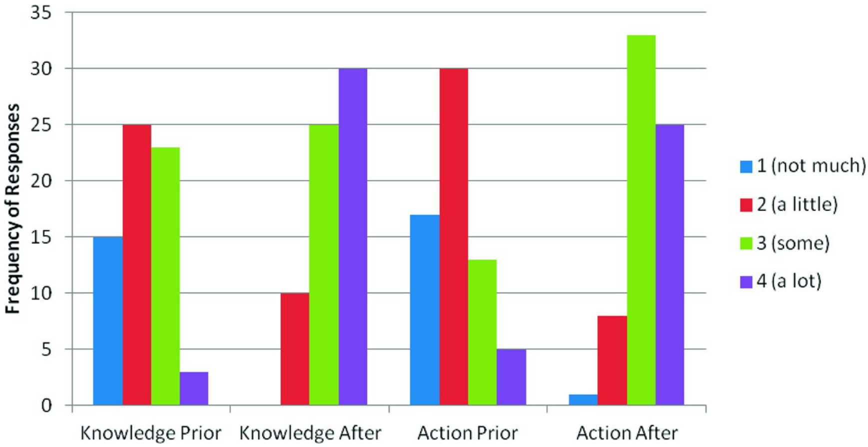


Figure 2. Behavior change of Maryland Bay-Wise Master Gardeners after receiving training on attracting beneficial organisms to control pests

HGHH programs include workshops on least-toxic methods to manage pests on popular garden crops such as tomatoes and citrus, as well as methods to manage specific pests such as ants and garden snails that are responsible for much homeowner pesticide use (*10*). Each workshop includes information about the local watersheds and the impact pesticides have on them. In addition to the lecture and handouts, the participants receive an incentive related to the topic. For example, at the tomato pest workshop the participants received a disease and nematode resistant tomato plant. Handouts include copies of the related Pest Notes and Pest Tip cards (http://www.ipm.ucdavis.edu).

University of California Master Gardeners, who received advanced water quality and IPM training were active at community events and reached an even wider audience for HGHH. They distributed the Pest Tip cards, answered questions about IPM and encouraged visitors to the booths to reduce their use of pesticides and dispose of unused pesticides properly.

One of the more enthusiastically accepted types of outreach are portable touch screen kiosks that allow users to select pests or diagnose problems and learn about least toxic pest management (Figure 3). Videos developed to show the connection between pesticide use and water quality can also be viewed. The kiosks are used by Master Gardeners at public events and are lent to retail nurseries, libraries, and public venues. The information is contained on a solid-state hard drive so there are no moving parts to break and no internet connection needed. The computer and screen are one unit. A small thermal printer is attached to the computer to print more detailed information if the user desires (Figure 3, right).

Figure 3. Diagnosis entry screen of IPM kiosk (L) and kiosk with attractor board and thermal printer (R). Photos by Scott Parker; used by permission of UC Statewide IPM Program.

Currently, over 60 common home and garden pests are included on the kiosks and the information is in both English and Spanish. The kiosks also include modules containing tips for proper watering, fertilizing, and avoiding problems associated with garden chemicals including safe use and disposal. These kiosks were so successful that their use has expanded beyond San Diego County are now used throughout California with 12 units in 2007 and an additional 4 units added in 2008. These kiosks average approximately 1,200 visits each per year.

Three years after the start of the HGHH Program, a survey was conducted to determine the impact of the program. Approximately one third of respondents (n = 744; 34.1%) reported having *"heard or seen something in the media or on posters, brochures, or billboards about pesticide use and water quality in the last year or so"*. Of these 254 respondents, 164 specified what they had heard. Fifty percent had heard messages about IPM but only 17% were aware of how pesticides affected water quality. It appears that residents recognized that there are alternative practices to manage pests but not that there was a relationship between water quality and pesticide use.

Educating Structural Pest Management Professionals

Home users are not the only group contributing to pesticide surface runoff in urban areas. Pesticide applications by professionals, both licensed and unlicensed, are potential contributors to the pesticide load in surface runoff. Licensed applicators are a much easier group to reach as they are registered in states where they operate and generally must obtain a minimum number of continuing education hours or have other training to maintain their licenses. Nevertheless, their main source of pesticide information is often from their pesticide supplier. They are also more hesitant to reduce or modify their applications for fear of losing customers.

Using Successful Companies To Demonstrate IPM Practices

Pest ants are significant problems in urban environments. Homeowners often hire pest management companies to use insecticidal sprays to treat the areas around their homes, sometimes on impermeable surfaces such as driveways and concrete walkways. A growing body of research (*11–14*) documents that these kinds of treatments have resulted in potentially harmful pesticide runoff into urban watersheds.

Structural pest management companies often measure the success of their pest management program by how many times they are contacted by customers to spray for pests between their regularly scheduled visits. Fewer "callbacks" indicate that the customer is satisfied with the level of pest management provided. Structural pest management professionals (PMPs) generally avoid modifying treatments due to fear of losing the customer in case the change results in increased callbacks. One way to allay the fear of losing clients is to demonstrate that customers will accept alternative pest management programs, including the use lower toxicity pesticides that do not affect water quality.

The California Department of Pesticide Regulation funds and manages the Pest Management Alliance Grant Program which encourages creation of a working team of public, private, educational and other stakeholders to demonstrate IPM practices and promote wider adoption and implementation of these practices throughout the industry. The Urban Pest Ant Management Alliance (UPA Alliance) was such a program. The program was funded to demonstrate that pyrethroid pesticide use around homes could be reduced by at least 50% through the use of alternative pesticides, IPM, and training.

The UPA Alliance consisted of researchers and extension academics from the University of California, regulators from the state and counties, allied industries, and PMPs from leading structural pest management companies who donated their time and expertise to the project. PMP Team Members compared service routes receiving traditional services to routes where at least 50% less pyrethroid was applied. Each company developed their own customized IPM program which, for example, could include combinations of increased monitoring, use of alternative pesticides such as plant oil-based products, adjusting spray techniques, and other IPM practices. The industry team members surveyed their clients to determine if ant IPM strategies were perceived as providing good ant management and to determine the level of acceptance of the program by residents and PMPs.

The results of these demonstrations were dramatic. The IPM routes included alternative pesticides such as plant essential oils, exclusion, baiting, and/or reducing the number of treatments per year. Replacing a portion of the pyrethroid with fipronil, plant oil-based products, and the use of gels or scatter baits resulted in at least 50% reduction in pyrethroid use. PMPs reported that there were no negative impacts on the company and in fact, one reported that the number of customers under the IPM routes increased 7% and his income increased 24%.

Alliance PMPs noted that for an IPM program to be successful, training and buy-in from the technicians and good customer communication was essential. Often customers expect the technician to spray every time there is a visit,

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

regardless of pest pressure. Therefore, the technician needs to keep the customer aware of what he or she is doing so that the client remains satisfied.

To disseminate the results of this Alliance to professionals throughout the state, educational meetings were held where the PMPs shared their experiences, successes, and ways for others to implement similar IPM programs. Additionally, a web site was created (http://groups.ucanr.org/UrbanAnt) where PMPs can find copies of the presentations from some of the participating companies, recent research updates, and links to other useful sites.

The participation of the PMP Team Members and the sharing of their experiences with other PMPs were essential to the success of this project. PMP Team Members were trusted messengers who, because of their knowledge of the industry, made them particularly useful for conveying information and results that their peers would accept as valid and useful.

Conclusions

In many cases, pesticide users may not understand or know that there is a connection between pesticide or fertilizer use, runoff, and water quality. Nevertheless, they will adopt IPM or other alternatives if shown that it will benefit them or the environment. More outreach needs to be done to educate non-agricultural users about the relationship between pesticide or fertilizer use and water quality.

Adoption of IPM by the professional sector, including governmental agencies, and home users can be influenced by education and successful demonstrations. It is clear that several methods of outreach, such as fact sheets, electronic sources of information, workshops, and personal interactions, are needed to effectively reach the intended audience.

Budget limitations may affect traditional or formal methods of extending information. University-certified Master Gardener volunteers could be a resource to help reach a wider audience. Using websites, electronic kiosks, or other information delivery systems such as smartphone apps are useful and may be necessary to reach the growing urban population.

References

1. San Francisco Integrated Pest Management Ordinance amended version. http://www.sfenvironment.org/downloads/library/ipmordinance.pdf, 2000.
2. Geiger, C. San Francisco Dept. of the Environment. Integrated Pest Management Program Report 2008-09. http://www.sfenvironment.org/downloads/library/final_ipm_rpt_200809_final_submitted.pdf, 2010.
3. National Coalition for Pesticide-Free Lawns Grassroots Action. Grassroots Action Supplement: Organic land care policies and pesticide-free zones growing: Inspiring stories from across the country. http://www.beyondpesticides.org/pesticidefreelawns/actions/Grassroots%20Action%20Supplement,Dec2006.pdf, 2006.

4. Natural Resources Defense Council. More effective and economical pest control: Integrated Pest Management. http://www.nrdc.org/health/files/ipm.pdf, 2008.
5. Dickey, P.; Geiger, C. Guide to the City of San Francisco's Reduced-Risk Pesticide List. http://www.sfenvironment.org/downloads/library/approved_list_guide_07b.pdf, 2007.
6. San Francisco Environment Code, Chap. 3. http://www.sfbos.org/ftp/uploadedfiles/bdsupvrs/ordinances11/o0007-11.pdf, 2011.
7. U.S. Green Building Council. LEED 2009 for Existing Buildings: Operations & Maintenance Rating System. http://www.usgbc.org/ShowFile.aspx?DocumentID=8876, 2009.
8. Moran, K. Bay area pesticide use: Urban/agricultural use comparison, 2003 (memo). http://www.up3project.org/documents/urban-agmemo051105.pdf, 2005.
9. Boward, D. M.; Kazyak, P. F.; Stranko, S. A.; Hurd, M. K.; Prochaska, T. P. *From the Mountains to the Sea: The State of Maryland's Freshwater Streams*; EPA 903-R-99-023; Maryland Department of Natural Resources, Monitoring and Nontidal Assessment Division: Annapolis, MD, 1999.
10. Wilen, C. Survey of Residential Pesticide Use and Sales in the San Diego Creek Watershed of Orange County, California. http://www.ipm.ucdavis.edu/PDF/PUBS/sdcrk.pdf, 2001.
11. Greenberg, L; Rust, M. K.; Klotz, J. H.; Haver, D.; Kabashima, J. N.; Bondarenko, S.; Gan, J. Impact of ant control technologies on insecticide runoff and efficacy. *Pest Manage. Sci.* **2010**, *66*, 980–987.
12. Oki, L; Haver, D.; Bondarenko, S.; Gan, J. Pesticide pollution in runoff from northern and southern California neighborhoods. *Abstr. Am. Chem. Soc. Conf.* **2010**, 121.
13. Weston, D. P.; Holmes, R. W.; Lydy, M. J. Residential runoff as a source of pyrethroid pesticides to urban creeks. *Environ. Pollut.* **2009**, *157*, 287–294.
14. Weston, D. P.; Holmes, R.W.; You, J.; Lydy, M. J. Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ. Sci. Technol.* **2005**, *39*, 9778–9784.

Resources

- University of California Statewide IPM Program developed resources to support IPM education with the focus on reducing pesticides and pesticide runoff. These include a newsletter (Green Bulletin), IPM Pesticide Tip Cards, and online training modules. http://www.ipm.ucdavis.edu.
- Trends related to pesticide use by both licensed and unlicensed professional pesticide applicators: Kreidich, N.; Flint, M. L.; Wilen, C. A.; Zhang, M. Tracking Non-Residential Pesticide Use in Urban Areas of California. http://www.ipm.ucdavis.edu/PDF/PUBS/ucdavisrep.pdf, 2005.

- The Bay-Friendly Gardening Program provides resources for home gardeners and professional landscapers to help design, construct and maintain gardens and landscapes that promote water conservation and pollution prevention in the San Francisco Bay Watershed. stopwaste.org/home/index.asp?page=8.

Chapter 9

Comparison of Pesticide Runoff from Organic and Conventional Walnut Orchards

Nicole David,*,[1] Fred Thomas,[2] and Debra Denton[3]

[1]San Francisco Estuary Institute, 7770 Pardee Lane, 2nd Floor, Oakland, CA 94621, USA
[2]CERUS Consulting, 2119 Shoshone Avenue, Chico, CA 95926, USA
[3]U.S. Environmental Protection Agency, 1001 I Street, Sacramento, CA 95814, USA
***nicoled@sfei.org, Tel: 1-510-746-7386, Fax: 1-510-746-7300**

Contamination from pesticide and nutrient applications to orchard crops is a major water quality issue in California. The goals of this study were to compare pesticide concentrations in water and sediment in runoff from organic and conventional walnut orchards and to compare the observed concentrations to water quality criteria and aquatic life benchmarks. Water and sediment samples were collected from five orchards over two years. Slightly lower, but not significantly different, pesticide concentrations for several pesticides (chlorpyrifos, diazinon, dimethoate, lambda-cyhalothrin, and esfenvalerate) in runoff from organic orchards were measured compared to the conventional orchards. Average concentrations of bifenthrin in sediment were statistically significantly lower ($p < 0.05$) at the organic sites compared to the conventional sites. This work indicates that BMP implementation and organic farming practices are effective in minimizing concentrations of pesticides in orchard runoff.

Keywords: organophosphate pesticides; pyrethroids; agricultural runoff; organic; walnuts

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Introduction

Intensive use of organophosphate (OP) pesticides, pyrethroids, herbicides, and fungicides in orchards and other agricultural fields is a significant source of pesticide contamination to water bodies in the Central Valley of California (*1*, *2*) (Figure 1). The Sacramento River watershed (Figure 1) is included on the 303(d) List of impaired water bodies and revised Total Maximum Daily Loads (TMDLs) for chlorpyrifos and diazinon were approved by the State Water Resources Control Board in 2008 (*3*). Water and sediment samples were collected from several orchard tail ditches to evaluate improvements in water and sediment quality due to organic growing practices. Pesticides and pesticide groups included in this study were selected based on recommendations by the State Water Board, amounts of active ingredient applied in walnuts according to the pesticide use report, and the capability of the analytical laboratory.

Materials and Methods

Study Area and Sampling Locations

All sampling sites were located in Solano County in the Sacramento Valley (Figure 1). Organic walnuts are grown without using most conventional pesticides, fertilizers made with synthetic ingredients or sewage sludge. Replacing the use of pesticides are Best Management Practices (BMPs), which emphasize the use of renewable resources and the conservation of soil and water. BMPs implemented by certified organic farmers included monitoring of pest pressures and soil fertility, applying organic pesticides and nutrients, using pheromone disruption, cover crops, filter strips, and beneficial insects. In conventional farming, chemical plant protectants, herbicides, and chemical fertilizers are common. Some of the conventional orchards monitored in this study included BMPs, e.g., biological control (bats were successfully used for the control of codling moths).

Walnut orchards were selected with the intention of covering geographical areas with similar crops, site characteristics, and soil types to provide a good comparison between organic and conventional farming. The orchards were between 12 and 32 ha and were located within an 8 km radius of each other; hence, they experienced similar pest problems and rainfall. All monitored orchards were flood irrigated between April and September with no dormant spray applications during the winter months. Average tree density was 95 trees per ha and the average age of the trees was 20 years with no tillage between the trees at both sites.

Approximately 9,000 kg/ha of turkey or chicken manure were applied to the organic orchards in March, while 680 kg/ha of the synthetic fertilizer ammonium sulfate were applied in form of a granular material to the conventional orchards in April and June (Table 1). Approximately 14 kg/ha of copper hydroxide per year were applied by helicopter to the organic orchards as a bacteriocide to control walnut blight, *Xanthomonas campestris* pv. *juglandis*. The conventional orchards used 11 kg/ha of copper hydroxide annually according to the pesticide use report data. Additionally, Spinosad®, derived from a naturally occurring soil

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

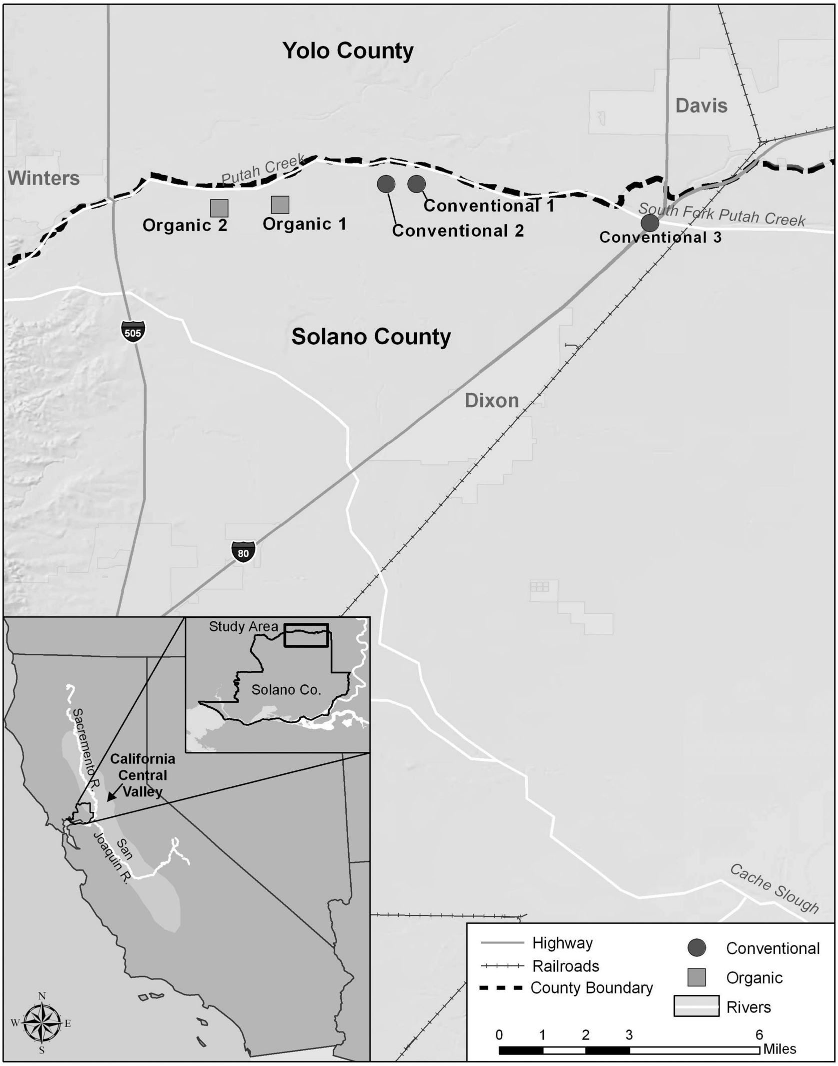


Figure 1. Map of all sampling sites in Solano County, California, USA.

dwelling bacterium called *Saccharopolyspora spinosa,* was applied to the trunks and the main limbs of organic walnut trees by handgun to control walnut husk fly, *Rhagoletis completa*, in August. For the control of a variety of other pests, 120 kg/ha of Surround® WP (95% kaolin clay, a naturally occurring mineral) was used at the organic sites on an annual average. Two applications of chlorpyrifos (annual average of 3.26 kg a.i./ha) were reported by the conventional growers, one in July, one in August, and 0.22 kg a.i./ha of bifenthrin were applied. Less consistent were the use of paraquat (approximately 1.92 kg a.i./ha annually), oxyflurofen (0.66 kg a.i./ha annually), maneb (2.06 kg a.i./ha annually), and 2,4-D (0.59 kg a.i./ha annually) over the study period.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table 1. Annual application of fertilizers and active ingredients of pesticides in organic and conventional walnut orchards

Application	*Organic Orchards*[b]	*Conventional Orchards*[b]	*Time of Application*
Fertilizer:			
turkey or chicken manure	9,000 kg/ha (1)	-	March
ammonium sulfate	-	680 kg/ha (2)	April and June
Pesticides:			
copper hydroxide	10.80 kg a.i./ha (2)	8.50 kg a.i./ha (2)	March and April
Spinosad	0.048 kg a.i./ha (1)	-	August
Surround WP [a]	114 kg a.i./ha (1)	-	August
chlorpyrifos	-	3.26 kg a.i./ha (2)	July and August
bifenthrin	-	0.22 kg a.i./ha (2)	July and August
paraquat	-	1.92 kg a.i./ha (2)	April and July
oxyflurofen	-	0.60 kg a.i./ha (2)	April and July
maneb	-	2.06 kg a.i./ha (2)	March and April
2,4-D	-	0.59 kg a.i./ha (2)	April and July

[a] 95% Kaolin clay [b] (*) number of applications per year

Water and sediment samples were collected from the soft-bottom, tail ditches of five orchards. Tail ditches were at least partially covered with cover crops at the organic sites but not vegetated at conventional sites. Tail ditches were within 3 to 5 m from the last row of trees at all sites. Samples were collected three times during the summer growing season with flood irrigation runoff and once during the first winter storms in 2007, 2008, and 2009. Since no pesticides were applied to walnuts during the dormant season, no further storm water sampling was conducted after the first flush. Sampling times varied from 1 to 8 h after runoff started. A total of 42 water and 39 sediment samples were collected for each of the monitored pesticides over the course of the two monitored seasons, including samples for quality assurance.

Sediment Sampling

Sediment sampling was conducted using a Petite Ponar grab with a surface area of 0.1 m^2. The grab and all scoops, stirrers, and buckets were made of stainless steel and coated with Dykon® to make them chemically inert. Sediment sampling equipment was thoroughly cleaned (sequentially with detergent, acid, methanol, and rinsed with ultrapure water) at each sampling location prior to each sampling event (*4*).

The top 5 cm of sediment were scooped in each of the grabs and placed in a bucket to provide a single composite sample for each site. Between sample grabs, the bucket was covered with aluminum foil to prevent airborne contamination. After all sediment grabs were completed, the bucket was thoroughly mixed to obtain a uniform, homogeneous mixture. Aliquots were subsequently split into 250-mL amber glass containers and kept at 4ºC for sediment and total organic carbon analyses.

Water Sample Collection

Water samples were collected directly from the tail ditch of each orchard. The 1-L amber glass containers were filled completely to eliminate any headspace, and care was taken to minimize exposure of samples to sunlight. Immediately after collection, the containers were closed and placed on ice in a cooler.

Analytical Methods

Sediment and water samples were analyzed for OP and pyrethroid pesticides. Analysis for OP pesticides included chlorpyrifos, diazinon, azinphos-methyl, dimethoate, disulfoton, malathion, methidathion, parathion, phorate, and phosmet. Analysis for pyrethroid pesticide included bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, and permethrin.

OP pesticides in water were analyzed following modified EPA Methods 8140 and 8141AM (*4*). Analysis entailed liquid-liquid extraction and GC with a Flame Photometric Detector (FPD) in phosphorus mode and Thermionic Bead Specific Detector (TSD). OP pesticides in sediment were analyzed using EPA Method 8141AM with FPD on phosphorus mode and/or TSD. The method detection limit (MDL) and reporting limit (RL) for OP pesticides in water samples were 0.005 µg/L and 0.02 µg/L, respectively; and 2.0 ng/g and 5.0 ng/g, respectively, for sediment samples.

Pyrethroids in water were analyzed following modified EPA Method 8081A using liquid-liquid extraction and GC with electron capture detection and GC-MS with an ion trap detector for confirmation. Pyrethroids in sediment were analyzed using a modified EPA Method 8081BM. Dual column GC was used with electron capture. For the majority of pyrethroids in water the MDL and RL were 0.002 µg/L and 0.004 µg/L, respectively. Bifenthrin, esfenvalerate, and lambda-cyhalothrin had a MDL and RL of 0.001 µg/L and 0.002 µg/L, respectively. In sediment samples, the MDLs were between 0.5 ng/g (bifenthrin) and 2.0 ng/g (cyfluthrin, cypermethrin, deltamethrin) and the RLs were between 1.0 ng/g and 4.0 ng/g.

Relative percent differences (RPDs), calculated as the difference in concentration of a pair of analytical duplicates divided by the average of the duplicates, were within the target range of +/-25%, with the only exception of chlorpyrifos in sediment for which one RPD was 36%. Percent recoveries for laboratory control were predominantly within the range of 75-125%. No pesticides were detected in the method blank quality assurance samples. Also, all field blank samples were below the method detection limit for all pesticides. For the calculation of average concentrations non-detectable results were included as zeros.

Results and Discussion

Chlorpyrifos concentrations ranged from below the 0.005 µg/L MDL to 0.840 µg/L at the conventional sites with an average chlorpyrifos concentration of 0.125 µg/L (n = 15) (Figure 2). At the organic sites, concentrations ranged from below the MDL to 0.140 µg/L with an average of 0.020 µg/L (n = 19), even though no chlorpyrifos had been applied for at least 10 years. In comparison to the freshwater acute criterion maximum concentration (CMC) (*5*) for chlorpyrifos of 0.025 µg/L and the chronic criterion continuous concentration (CCC) of 0.015 µg/L the low concentrations at the organic sites may pose a risk to aquatic life.

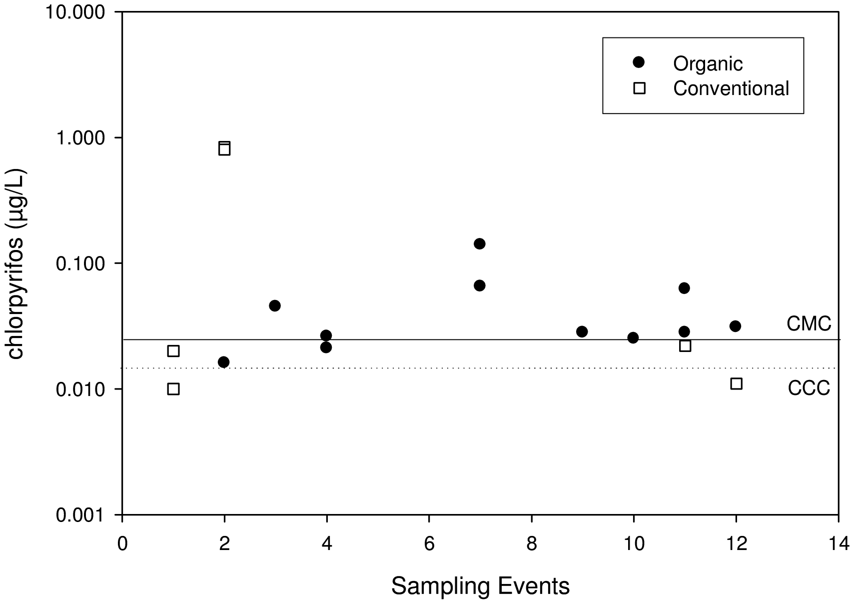


Figure 2. Chlorpyrifos concentrations at organic and conventional sites in µg/L. Average concentrations were not statistically significantly different (p = 0.05, t-test). Sampling dates were Feb 2007 (1), Jun 2007 (2), Aug 2007 (3), Sep 2007 (4), Dec 2007 (5), Apr 2008 (6), Jul 2008 (7), Jul 2008 (8), Aug 2008 (9), Aug 2008 (9), Aug 2008 (10), Nov 2008 (11), Nov 2008 (12).

Even though the monitored organic walnut orchards have been certified organic for approximately 10 years and part of an all-organic operation with no synthetic pesticides being used, results of this study suggest synthetic pesticides are still present. There are several possible explanations for this observation. Pesticides could be entering the orchard with contaminated irrigation water (*6*), spray drift during aerial or ground pesticide applications in neighboring orchards (*7*), or transport of contaminated dust particles.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Diazinon concentrations (Figure 3) with both practices were below the CMC and the CCC of 0.16 and 0.10 µg/L (*5*), respectively. Diazinon ranged from below the 0.005 µg/L MDL to 0.014 µg/L at the conventional sites with an average concentration of 0.002 µg/L. The average concentration at the organic sites was 0.001 µg/L, ranging from below the MDL to 0.01 µg/L. Similar to chlorpyrifos, no statistically significant difference between walnut growing practices was observed ($p > 0.05$).

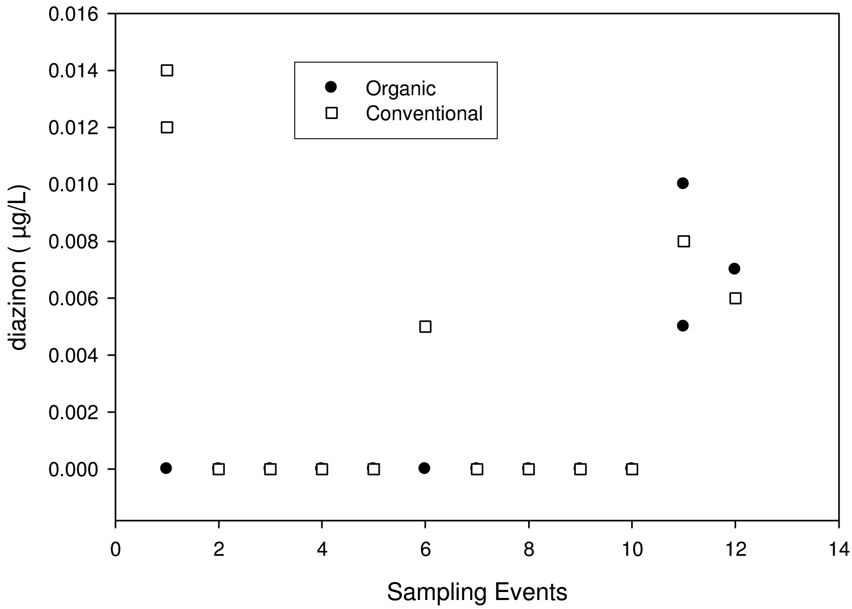


Figure 3. Diazinon concentrations at organic and conventional sites in µg/L. Average concentrations were not statistically significantly different (p = 0.1, t-test). Sampling dates were Feb 2007 (1), Jun 2007 (2), Aug 2007 (3), Sep 2007 (4), Dec 2007 (5), Apr 2008 (6), Jul 2008 (7), Jul 2008 (8), Aug 2008 (9), Aug 2008 (9), Aug 2008 (10), Nov 2008 (11), Nov 2008 (12).

Low concentrations of dimethoate (0.38 to 0.42 µg/L), another OP pesticide, were detected at the conventional sites, while all results at the organic sites were below the 0.03 µg/L MDL. The average concentration at the conventional sites was 0.41 µg/L and far below aquatic life benchmarks for fish (620 µg/L) and for invertebrates (4.3 µg/L) (*8*).

Concentrations of lambda-cyhalothrin in water also showed no significant difference related to growing practices. Surprisingly, the highest concentration found in water during this study was at an organic site (0.02 µg/L). Average concentrations were still slightly higher at the conventional sites (0.002 µg/L) compared to the organic sites (0.001 µg/L). Pyrethroid aerial concentrations decline much faster after applications than those of OP pesticides but they are still transported and re-deposited with dust particles for a long time (half-life of up to 44 days) (*9*, *10*); this may explain the occurrence of lambda-cyhalothrin at the organic site if a neighboring field/orchard was treated with pyrethroids.

The pyrethroid esfenvalerate was detected in some conventional water samples with an average concentration of 0.012 µg/L, while all organic samples were below the 0.001 µg/L MDL. The average conventional concentration was above the benchmark for fish (0.007 µg/L) and for invertebrates (0.005 µg/L).

Pyrethroid concentrations in sediment exhibited the only significant difference between the growing practices. Bifenthrin concentrations in sediment ranged from below the 0.5 ng/g MDL to 24 ng/g at the conventional sites (averaging 5.61 ng/g). The average concentration for the organic sites was 0.44 ng/g, ranging from below the MDL to 8.52 ng/g. The difference between the two site types was significant ($p = 0.002$, t-test).

Since pyrethroid bioavailability is highly dependent on carbon content, pyrethroid sediment concentrations were carbon-normalized (Figure 4) for a more ecologically relevant assessment. The LC50 for *Hyalella* for bifenthrin is 0.52 µg/g OC (*1*). Three out of 16 conventional samples had bifenthrin concentrations above the LC50, indicating a potential risk for sensitive species at the conventional sites. None of the 19 samples at the organic sites were above that toxicity threshold. The LC50 for lambda-cyhalothrin is 0.45 µg/g OC (*1*) and all conventional and organic sediment samples in this study were below this value.

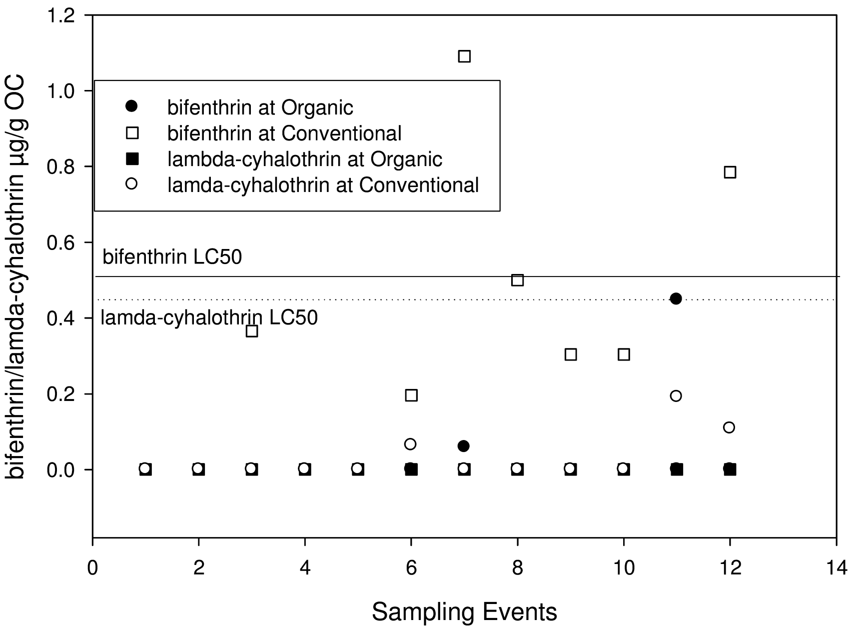


Figure 4. Bifenthrin and lambda-cyhalothrin concentrations in µg/g TOC at organic (black symbols) and conventional (white symbols) sites. The solid line shows the LC50 for Hyalella for bifenthrin of 0.52 µg/g OC published by Amweg et al. (1). The dotted line shows the toxicity threshold for lambda-cyhalothrin of 0.45 µg/g OC with all samples being below the LC50 for Hyalella toxicity (1).

The conventional walnut growers, whose runoff was monitored in this study, were very open to best management practices (e.g., biological control) and pesticide reduction. Ideally, runoff from growers that are more dependent on pesticide usage would have been sampled but those farmers did not agree to participate in this study. The low pesticide usage at the conventional sites examined in this study resulted in few appreciable differences in pesticide concentrations between the different growing practices.

Conclusion

The chemical concentrations detected at the conventional sites, especially for chlorpyrifos and lambda-cyhalothrin in water samples and bifenthrin in sediment samples were above the aquatic life criteria. However, only bifenthrin concentrations were statistically significantly higher at the conventional orchards. Although diazinon, dimethoate, and esfenvalerate concentrations were higher at the conventional sites compared to the organic orchards, the difference was not statistically significant.

In general, this study indicated that the risk of harmful environmental effects is lower with organic than with conventional growing practices. Even though organic growers did not use the synthetic pesticides that were monitored during the study, the water and sediment samples collected from the organic orchards were not pesticide free. Some of the samples at the organic sites even were slightly higher than the aquatic life criteria. The data from this study suggest that additional controls or more careful management practices in neighboring conventional orchards are needed to prevent pesticide contamination of organic orchards.

Acknowledgments

This project was funded by the California State Water Resources Control Board and the authors would like to thank Ahmad Kashkoli leading this Project as Grant Manager. We thank Alicia Gilbreath and Kat Ridolfi for field data collection and Cathy Holden, Cindy Lashbrook, Ben Greenfield, Jay Davis, and Lester McKee for review comments. Dave Crane, Abdou Mekebri, and Patty Brucknell managed the laboratory analysis. The author would also like to thank Craig McNamara, Russ Lester, and Joe Martinez for their knowledge and support with all aspects of the sample collection. This document has been reviewed in accordance with U.S. EPA policy and approved for publication. Approval does not signify that the contents necessarily reflect the views or policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

References

1. Amweg, E. L.; Weston, D. P.; Ureda, N. M. Use and toxicity of pyrethroid pesticides in the Central Valley, California, USA. *Environ. Toxicol. Chem.* **2005**, *24* (4), 966–972.
2. Pereira, W. E.; Domagalski, J. L.; Hostettler, F. D.; Brown, L. R.; Rapp, J. B. Occurrence and accumulation of pesticides and organic contaminants in river sediment, water and clam tissues from the San Joaquin River and tributaries, California. *Environ. Toxicol. Chem.* **1999**, *15* (2), 172–180.
3. SWRCB. *Approving an Amendment to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (Basin Plan) for the Control of Diazinon and Chlorpyrifos Runoff into the Sacramento and Feather Rivers*; Resolution No. 2008-0013; Sacramento, CA, USA, 2008.
4. David, N.; Yee, D. *Quality Assurance and Project Plan for the Going Organic Project*; San Francisco Estuary Institute: Oakland, CA, USA, 2007.
5. CVRWQCB. *Basin Plan Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Diazinon and Chlorpyrifos Runoff into the Sacramento and Feather Rivers*; May 2007 Final Staff Report, 2007.
6. USGS. *Pesticides in Storm Runoff from Agricultural and Urban Areas in the Tuolumne River Basin in the Vicinity of Modesto, California*; Water Resources Investigations Report 98-4017; Sacramento, CA, USA, 1998.
7. Owens, K.; Feldman, J. Getting the Drift on Chemical Trespass. *Pesticides and You* **2004**, *24* (2), 16–21.
8. USEPA. Office of Pesticide Programs' Aquatic Life Benchmarks. http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm, 2011.
9. Berger-Preiess, E.; Preiess, A.; Sielaff, K.; Raabe, M.; Ilgen, B.; Levsen, K. The Behavior of Pyrethroids Indoors: A Model Study. *Indoor Air* **1997**, *7* (4), 248–262.
10. Gassner, B.; Wuethrich, A.; Lis, J.; Scholtyzik, G.; Solioz, M. Topical application of synthetic pyrethroids to cattle as a source of persistent environmental contamination. *J. Environ. Sci. Health, Part B* **1997**, *2* (5), 729–739.

Chapter 10

Introduction of Atrazine Degrader To Enhance Rhizodegradation of Atrazine

Chung-Ho Lin,[1,*] Brian M. Thompson,[2] Hsin-Yeh Hsieh,[2] and Robert N. Lerch[3]

[1]Center for Agroforestry and Department of Forestry, 203 Anheuser-Busch Natural Resources Building, University of Missouri, Columbia, MO 65211
[2]Department of Veterinary Pathobiology, 402 Bond Life Sciences Center, University of Missouri, Columbia, MO 65211
[3]USDA-ARS, Cropping Systems and Water Quality Research Unit
[*]Corresponding author. Linchu@missouri.edu

Atrazine (ATR) runoff from farm fields may negatively impact water quality in agricultural watersheds. Vegetated buffers strips (VBS) are commonly used to mitigate impacts. A growth chamber study was conducted to investigate the effect of introducing the bacterial ATR-degrader *Pseudomonas* sp. ADP into VBS soil on ATR degradation. The introduction of *Pseudomonas* sp. ADP into soil that had been maintained with and without switchgrass (*Panicum virgatum*) enhanced the rate of ATR degradation. More than 99% of applied ^{14}C-ATR was degraded within the first 72 hours post-inoculation with 54.5% of applied ^{14}C ATR mineralized to CO_2. Degradation rates were less than 18% and 26% in un-inoculated control and switchgrass soils, respectively. Hydroxylated metabolites of ATR, including hydroxyatrazine and desethylhydroxyatrazine, were the major degradation products in the inoculated treatments. ATR's N-dealkylated metabolite desethylatrazine was the major degradation product in the un-inoculated soil. Quantitative PCR amplification studies showed that soil from the switchgrass treatment sustained the number of *atzA* gene copies at higher levels early in the treatment when compared to the bulk soil without switchgrass. In the presence of switchgrass, *atzA* copy number was stimulated for the first two weeks postinoculation with levels steadily decreasing to about 10% of the day 0 value

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

in this time period. A continued decrease to about 2% of the time-zero value was observed over days 24-37. The lack of complete ATR mineralization may be attributed to the loss of *atzA* gene copy number over time since this implied a loss of ATR-degrading potential. The addition of *Pseudomonas* sp. strain ADP resulted in a 3-fold or greater increase in *atzA* copy number as compared with *atzA* copy number in soil samples collected from ATR treated field samples. Results indicate that addition of ATR degrading bacteria into VBS soil has the potential to enhance buffer performance by increasing degradation rates of entrapped ATR.

Keywords: atrazine; degraders; rhizodegradation

Introduction

Atrazine (ATR, 2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine) has been one of the most widely applied herbicides in the US and Midwestern states. An estimated 36.3 million kg of ATR were applied annually to more than 69% of all U.S. corn acreage (*1*). A U.S. Geological Survey study found ATR and its metabolites were detected in approximately 75 percent of stream water and about 40 percent of all groundwater samples from agricultural areas tested between 1992 and 2001 (*2*). The contamination of surface and ground water by ATR and its chlorinated metabolites has raised public health and ecological concerns (*3*, *4*).

Vegetated buffer strips (VBS) have been proven to be an effective mitigation practices for removing ATR from surface runoff derived from agronomic operations (*5*, *6*). This remediation mechanism involves physical trapping of the ATR via improved infiltration and enhanced rhizodegradation (*5*, *6*). Recently, the addition of C_4 perennial bioenergy crops, particularly switchgrass, into riparian VBS systems was encouraged since it provided both economic benefits and environmental benefits (*7*). One of the identified environmental benefits is the mitigation of contamination of non-point source pollutants, including ATR. Results from a rainfall simulation study showed that 4-8 m wide switchgrass buffer removed 58% to 72% of dissolved and sediment-bound ATR in the surface runoff (*6*, *8*). In a field lysimeter study, C_4 warm-season switchgrass has shown significantly better capacity to enhance the degradation of ATR than C_3 cool-season species. The dissipation of ATR was increased by 57% in switchgrass as compared with bulk soil control. More than 80% of the ATR in the switchgrass rhizospheres was degraded to less toxic metabolites, with 47% of these residues converted to the less mobile hydroxylated metabolites 25 d after application (*5*). However, the mineralization of ATR and its chlorinated metabolites or complete cleavage of the triazine ring in the rhizosphere was limited to less than 2-10% under both laboratory and field conditions near the riparian VBS regions where the microorganisms had not developed the adaptation to ATR (*9*–*11*).

A few bacteria strains that have the potential rapidly degrade ATR, including *Pseudomonas* sp. ADP, have been isolated in the past decade from heavily contaminated ATR spill sites (*12*, *13*). The catabolic metabolites and the genes encoding for the enzymes responsible for each step of degradation process have been well characterized (Figure 1). *Pseudomonas* sp. strain ADP can utilize ATR and its metabolites as a carbon source and sole nitrogen source (*12*, *14*). This property is due to the presence of the pADP-1 plasmid, an 108-kDa catabolic plasmid which encodes for all the metabolic enzymes necessary to completely degrade ATR into CO_2 and NH_3 (*12*, *15*). The genes that encode for the enzymes, atzABC, are not unique to *Pseudomonas* sp. strain ADP, but are found among soil bacteria isolates across the U.S. and Europe (*16*). The atzA chlorohydrolase metalloenzyme not only has the ability to dechlorinate ATR into the significantly less toxic hydroxyatrazine, but also has activity on the *s*-triazine herbicides simazine and desethylatrazine (*17*, *18*). AtzB metabolizes the hydroxyatrazine to *N*-isopropylammelide, whose hydrolytic deamidation to cyanuric acid and isopropylamine is catalyzed by AtzC (*18*, *19*). *atzD* encodes a cyanuric acid amidohydrolase, which converts cyanuric acid to biuret. The presence of the *atzDEF* operon is unique to *Pseudomonas* sp. strain ADP and allows this bacterium to further catabolize the cyanuric acid (produced by the activities of atzABC) into CO_2 and NH_3 (*12*). AtzE is a biuret hydrolase and AtzF is an allophanate hydrolase, converting biuret to allophanate and allophanate into CO_2 and NH_3, respectively (*12*). This plasmid is highly transmittable between microorganisms and gene expression, particularly *atzD* and *atzF*, are sensitive to alternative N sources in the environment (atz+ → atz-) (*20*).

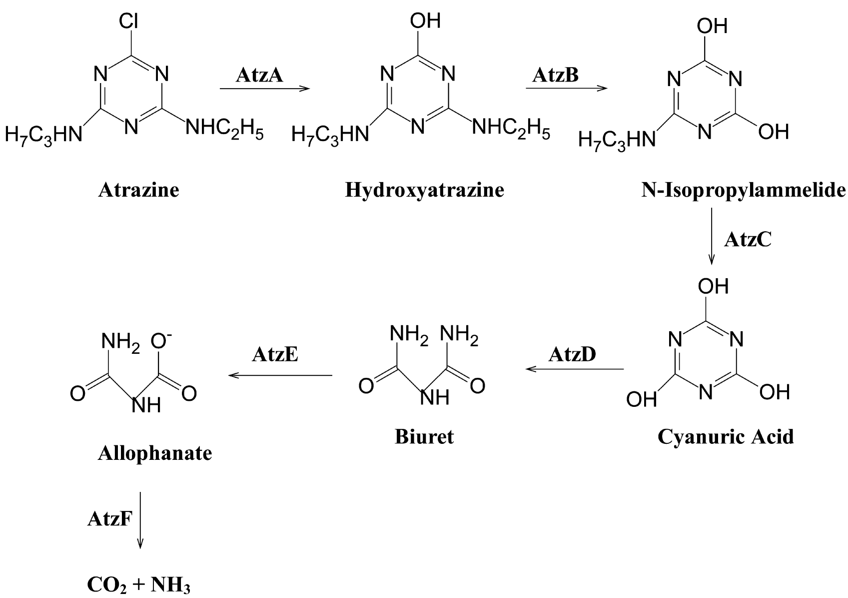


Figure 1. Catabolic degradation of atrazine by P. ADP (12).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Introducing bacterial ATR degraders such as *Pseudomonas* sp. strain ADP into an established switchgrass VBS (*5*) could lead to enhanced ability of the VBS to degrade ATR and its metabolites that have been deposited by surface runoff from cropland. However, previous research suggested the instability of the *atzABC* genes due to transposon insertion sequences flanking each gene resulting in a large (>40 kbp) unstable region in the pADP-1 plasmid (*12*, *15*). These transposase sequences allow for both the loss of these genes and the ATR-degrading phenotype, as well as the passage of these genes to other soil bacteria species (*16*). As the *atzABC* genes are inherently unstable, precise fluctuations in copy numbers of these genes need to be obtained in order to determine their stability and the overall population of potential ATR degraders (*Pseudomonas* sp. strain ADP and others which have obtained the *atzA* gene) in a dynamic soil sample (*17*, *18*). Accurate enumeration of catabolic genes introduced into the grass rhizospheres of a VBS system will help to determine the viability of the introduced bacteria and the potential for sustained degradative capacity. Furthermore, the persistence of the catabolic genes is of greater importance than the viability of the introduced bacteria because the expression of these genes is the critical factor in sustaining a high level of degradative activity for the purpose of bioremediation. Therefore, the objectives of this research were to (1) determine the effects of *Pseudomonas* sp. strain ADP inoculation on ATR degradation in soil, and (2) quantify the effects of the switchgrass on the stability of the highly transmittable ATR degrading gene *atzA* in the rhizospheres.

Materials and Methods

Design of the Experiment

The experiment was conducted in a walk-in growth chamber in triplicate with either switchgrass (*Panicum virgatum* L., **SW**) or a control treatment (bulk soil). Plants were allowed to grow in a 7-L pot with mixture of 60% sand and 40% Mexico Silt Loam soil for 12 months. Before the experiment, the soils were autoclaved for 60 minutes to inactivate residual plant seeds and other organisms (e.g., microorganisms and earthworms) from the field soil samples which can contribute to significant variation in ATR degradation activities and profiles in this study. These samples were then exposed to ambient conditions in a greenhouse for 2 weeks to allow for microbial repopulation of the soil before the experiment (achieved repopulation of 10^8 CFU of bacteria g^{-1} for both soil types after the two week incubation). This procedure allowed us to use the field soils of choice with bacteria and other microorganisms obtained from the greenhouse environment. The soil was 108 g kg^{-1} clay, 338 g kg^{-1} silt and 557 g kg^{-1} sand (sandy loam texture); cation exchange capacity (CEC) was 8.1·cmol kg^{-1}; pH 7.2; and initial organic carbon (OC) content was 6 g kg-1. Environmental conditions were: light intensity of 1400 μEinsteins•m^{-2}•sec^{-1}; light/dark period of 15/9 hours; relative humidity of 50%; and temperature at 25ºC (light)/20ºC (dark). After 12 months of plant growth, rhizosphere soil was separated from each plant and soil moisture

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

content was adjusted to 20%. Atrazine solution prepared with 1 μCi of ^{14}C-ATR with a specific activity of 18.1 mCi/mmol (atrazine-ring-UL-^{14}C, purity > 95%; Sigma-Aldrich, St. Louis) and non-radioactive ATR was then added to 20 g (dry weight equivalent) of soil to achieve a final ATR concentration of 100 μg kg^{-1}.

Pseudomonas sp. strain ADP was cultured in the Modified-R medium as described in Thompson *et al.* (*21*). In brief, a 10 mL aliquot of a 50 mL overnight *Pseudomonas* sp. strain ADP culture was inoculated into 1L of R medium supplemented with ATR and incubated on a 37ºC rotary shaker until the culture reached stationary phase OD_{600} of ~0.8. The ATR suspension consisted of 1 g ATR suspended in 10 mL methanol. Colony forming units (CFUs) were determined by plating replicates of each suspension on R plates and incubation at 30ºC for 48 hours. Colonies of *Pseudomonas* sp. strain ADP were verified by the appearance of ATR-clearing zones around the colonies (*14*). The *Pseudomonas* sp. strain ADP cell suspension were added to the rhizosphere soils to achieve the initial concentrations of 4 x 10^6 *Pseudomonas* cells g^{-1} dry soil. Another duplicate experiment without inoculation of *Pseudomonas* sp. strain ADP was prepared to assess the degradation kinetics of the ATR. The herbicide-treated soil was then incubated in sealed jars for 14 days at 25ºC in the dark.

Analysis of ^{14}C Atrazine and Its Metabolites

Atrazine mineralization was measured using alkali traps (2 M NaOH) placed in the jars. Traps were periodically replaced throughout the incubation period. At the end of the 14-day incubation period, ^{14}C-ATR and its degradation products were extracted with 250 mL of 90% MeOH with 1 hour of sonication. The extract was concentrated to 10 mL using a Savant concentrator (Holbrook, NY). The final extracts were concentrated to 200 μL under flow of N_2 gas. ^{14}C-ATR and its degradation products were separated using a silica-based Columbus C8 column (4.6 mm x 250 mm, 5 μm; Phenomenex, Torrance, CA) on a Shimadzu SCL-10Avp high performance liquid chromatography system (HPLC) (Columbia, MD). The radioactivity was quantified by an in-line IN/US ScinFlow β-Ram Model 3 (Tampa, FL) flow scintillation analyzer (FSA). Injection volume was 10 μL, and mobile phase flow rate was 1 mL min^{-1}. ^{14}C-ATR and its metabolites were eluted with a two-part mobile phase gradient. Mobile phase A consisted of 0.1% H_3PO_4 buffer (pH =2.1), and mobile phase B was 100% ACN. The gradient started at 10% B and ramped linearly to 40% B at 30 min, 75% B at 40 min, 10 % B at 45 min, and held at 10% B for 14 min. Metabolites were identified by comparing the retention times of unlabeled standards based on HPLC-UV detection at 220nm. The standards including ATR, deethylatrazine (DEA), deisopropylatrazine (DIA), hydroxyatrazine (HA), deisopropylhydroxyatrazine (DIHA), deethylhydroxyatrazine (DEHA), didealkylatrazine (DDA), ammeline (AM) and ammelide were purchased from ChemService (West Chester, PA). The mineralization of ^{14}C-atrazine was determined by counting the radio activities of the evolved $^{14}CO_2$ using a Beckman LS600 liquid scintillation counter (Beckman, Fullerton, CA).

Quantification of *atzA* Gene Copies

DNA Extraction

Five hundred milligrams of soil (dry weight equivalent) from each of the inoculated samples was collected at 0, 1, 3, 5, 7, 14, 24, and 37 days and subjected to DNA extraction with a FastDNA SPIN for Soil kit (MP Biomedicals, Solon, Ohio). After 2 hours of gentle agitation in 0.1 M sodium phosphate buffer (pH 8.0) to remove residual humic acids, soil suspensions were processed as per the manufacturer's directions. Extracted DNA was eluted in 100 µL DNase/RNase free water, and separated by electrophoresis on a 0.5% agarose gel to demonstrate the lack of shearing of extracted DNA products, as has been reported for extraction procedures utilizing similar bead-beating methodologies (*22*). We recovered 0.9-551 µg of DNA per extraction depending on the inoculation. DNA concentrations were determined as per the PicoGreen dsDNA Quantitation Kit (Invitrogen, Carlsbad, CA) and manufacturer's specification, and using a Bio-Tek Synergy HTTR-1 plate reader. Optimizations of conditions and reagents for PCR are described in detail in Thompson *et al.* (*21*); they were applied throughout this study. A 1 µl of extracted DNA from inoculated soil samples was utilized as template for PCR amplification combined with Premix Ex Taq 2X PCR Solution (Takara Bio, Shiga, Japan) and ddH_20 for a final volume of 50 µl. PCR primers P. ADP Forward and P. ADP Reverse (Table I) were then added at a final concentration of 0.5 µmol L^{-1}. Primers used in this study were those designed by de Souza *et al.* (*15*) to amplify a 444 bp fragment of *atzA* between nucleotides 472-915 with minimal specificity issues (*15*). One µg mL^{-1} bovine serum albumin (BSA) was also added to PCR mixture for enhancement. Amplification of DNA was performed under the following conditions: 35 cycles of 94ºC for 1 min, 50ºC for 30 sec, and 72ºC for 1 min. Amplicons were separated on 1.5% agarose gels by electrophoresis. Band intensities were obtained via Multi-Gauge analytical software (Fujifilm, Tokyo, Japan). All PCRs were performed in triplicate.

Quantification of atzA Gene Copy Number by Quantitative Real-Time (qPCR)

The optimization of primer concentration and reagents was described in Thompson *et al.* (*21*). The TaqMan probe and the primer pair are listed in Table I. The probe was designed using the Primer Express software (Applied Biosystems Inc., Foster City, CA) to find an optimal probe with a T_m that is 10ºC greater than the primers (60ºC compared to 50ºC). Primer and probe specificity was tested by BLAST analysis (NCBI) to prevent known non-specific binding targets that could be obtained in soil extracts and among *Pseudomonas sp.* strain ADP DNA. Final PCR mixtures consisted of 25 µL Premix Ex Taq (Perfect Real Time) (Takara Bio, Shiga, Japan), 900 nM of each primer, 12.5 pmole of the TaqMan probe (Applied Biosystems), 1.0 µL of soil DNA extract in a 1:100 dilution, 1 µg mL^{-1} BSA, and RNase/DNase-free water to reach a final volume of 50 µL. All real-time *q*PCRs were initiated with activation of DNA polymerase at 95ºC for 10 min, and 40 cycles of 95ºC for 1 min, 50ºC for 1 min, and 72ºC for 1 min.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table I. Designed primers for real-time *q*PCR (*21*)

P. ADP Forward:	GCACGGGCGTCAATTCTA
P. ADP Reverse:	CGCATTCCTTCAACTGTC
***atzA* TaqMan® MGB Probe:**	6FAM -ATCGGATGGACGGGCGCA-MGBNFQ

The *atzA* gene amplified by PCR (Primers P. ADP Forward and P. ADP Reverse) from *Pseudomonas* total DNA was cloned into *E. coli*. The correct plasmids purified from *E. coli, were* quantified, and used as standards for real-time *q*PCR. A standard curve constructed at concentrations of 10^2 through 10^8 gene copies μL^{-1} was utilized to determine the copy number of the target *atzA* gene in the spiked soil samples. All real-time *q*PCR assays were performed in triplicate using a 7500 Fast real-time *q*PCR machine (Applied Biosystems, Carlsbad, CA). The SYBR *Premix Ex Taq* (Takara Bio, Shiga, Japan) plus ROX Reference Dye II were utilized for the PCR mixtures and the primer concentration of 900 nM was applied as described by Thompson *et al.* (*21*).

To compare the copy number of *atzA* between this study and the environmental field samples, 45 to 63 soil samples were collected from each of the following land use treatments: 1) corn-soybean rotation, 2) contour grass buffers, and 3) contour agroforestry buffers established at the University of Missouri-Greenley Memorial Research Center in Knox County, Missouri (40º 01'N, 92º 11'W). The selected sites had a long history of ATR application (>20 years). The detailed experimental design of the established sites was described in Lin *et al.* (*9*). Detection frequency, average *atz*A copy number, and ^{14}C-ATR mineralization rates for soils were determined using the same procedure described above.

Results and Discussions

Degradation of Atrazine

As shown in Figure 2, the introduction of *Pseudomonas* sp. strain ADP into soil enhanced the rate of ATR degradation ($p < 0.05$). More than 99% of applied ATR was degraded within the first 72 hours of inoculation. The average total applied ^{14}C-ATR mineralized to CO_2 was 56.1% for control and 54.5% for switchgrass treatment after 14 days of inoculation (Table II). The dissipation rates of ATR were similar between the control (bulk soil) and switchgrass treatment ($p > 0.05$). In contrast, uninoculated soils degraded only 18% and 26% of applied ^{14}C-ATR for the control and switchgrass treatment, respectively. Only 0.2% to 0.3% of the applied ^{14}C-ATR was mineralized into $^{14}CO_2$ the 14 days. No statistical difference in soil ATR concentrations was found between control (bulk soil) and switchgrass treatments after 14 days of inoculation. The similar ATR degradation rates and profiles between inoculated switchgrass treatment and inoculated bulk soil control suggested that the *Pseudomonas* sp. strain ADP is the predominant factor leading to the rapid ATR degradation. The rhizosphere effects on ATR degradation was not significant during the incubation period.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

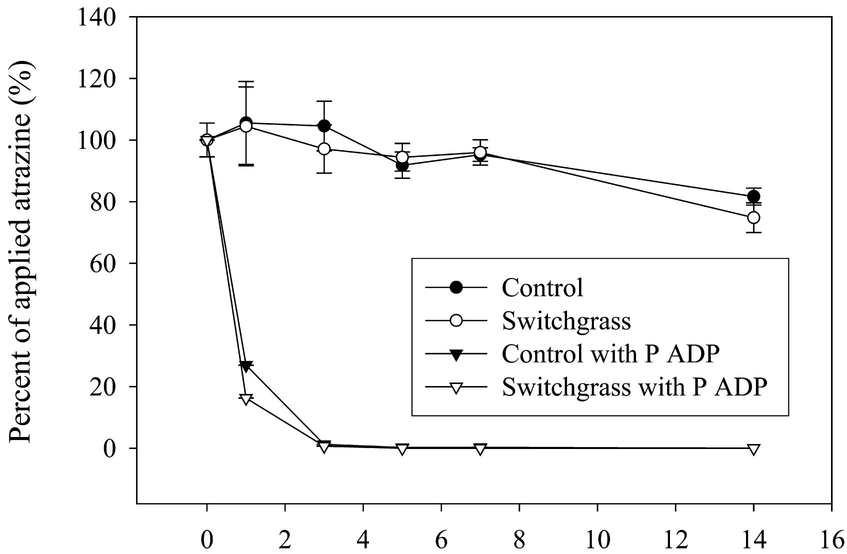


Figure 2. Degradation of atrazine with vs. without inoculation of an atrazine – degrading bacterium Pseudomonas sp. ADP in either switchgrass rhizosphere and control (bulk soil).

When the relative degradation profiles between treatments were compared, the un-inoculated treatments had significantly higher concentrations of DIA, Unk_10.2 (Unk_10.2: unknown degradation product with a retention time of 10.2 minutes; Figures 3A and B), Unk_13.6, DEA, Unk_19.5, Unk_25.6, and Unk_37.9 than inoculated treatments (Table II). The DEA and DIA were the predominant degradation products in the un-inoculated treatments, and the results are consistent with our previous findings (*5*).

In contrast to the metabolite profile in the inoculated treatments, DEHA, DDA, and HA were the major degradation products in inoculated treatments (Table II, Figures 3A and B). The significantly higher concentrations of DEHA in switchgrass rhizosphere than in bulk soil control treatment suggested that the hydrolysis of DEA was enhanced by the switchgrass rhizospheres. In addition, low concentrations of DEA and DIA in the inoculated treatments suggested that the rapid hydrolysis of ATR by *Pseudomonas* sp. ADP had consumed most of the ATR before it had the chance to be transformed through a much slower dealkylation process. We did not observed the accumulation of cyanuric acid as other studies have described (*23*). For inoculated treatments, the total recovery rates of ^{14}C activities were 61.8% and 62.6% in bulk soil and switchgrass treatments, respectively. The non-extractable bound residues in the inoculated treatment account for about 40% of the initial applied ^{14}C-ATR, while only 1.0-7.4% remained as non-extractable bound residues in non-inoculated treatments. These values are similar to the finding reported previously (*23*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table II. The degradation profiles of the atrazine with vs. without inoculation of an atrazine – degrading bacterium *Pseudomonas* sp. ADP in either switchgrass rhizosphere and control (bulk soil).

	Percent of Applied ^{14}C atrazine (%)			
Atrazine and Metabolites	**Control**	**Switchgrass**	**Control with *P.* ADP**	**Switchgrass with *P.* ADP**
AM	0.00A†	0.00A	0.00A	0.00A
DIHA	1.05A	0.00B	0.00B	0.00B
DEHA	0.73B	2.00A	0.60B	1.75A
Unk_3.5*	0.00B	0.00B	0.00B	0.13A
DDA	0.85A	1.63A	0.93A	0.75A
Unk_4.5	1.48A	0.55A	0.20A	0.40A
Unk_7.2	0.78BC	0.28C	0.65BC	1.38A
HA	1.55B	2.00A	1.88A	1.93A
Unk_10.2	1.03A	0.90A	0.85A	0.78A
DIA	1.95A	2.13A	0.05B	0.03B
Unk_13.6	0.30A	0.25A	0.03B	0.03B
DEA	6.40A	7.03A	0.05B	0.15B
Unk_19.5	0.18AB	0.28A	0.08B	0.15B
Unk_25.6	0.35A	0.38A	0.00B	0.00B
ATR	81.65A	74.48A	0.30B	0.35B
Unk_37.9	0.38A	0.50A	0.15B	0.23B
Recovery (%)	98.63	92.40	5.78	8.05
Mineralized ^{14}C	0.33	0.20	56.09	54.50

† Means followed by the same letter within the row did not differ significantly from each other at a significance level of 95% using Fisher's LSD test. *Unknown and its retention.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

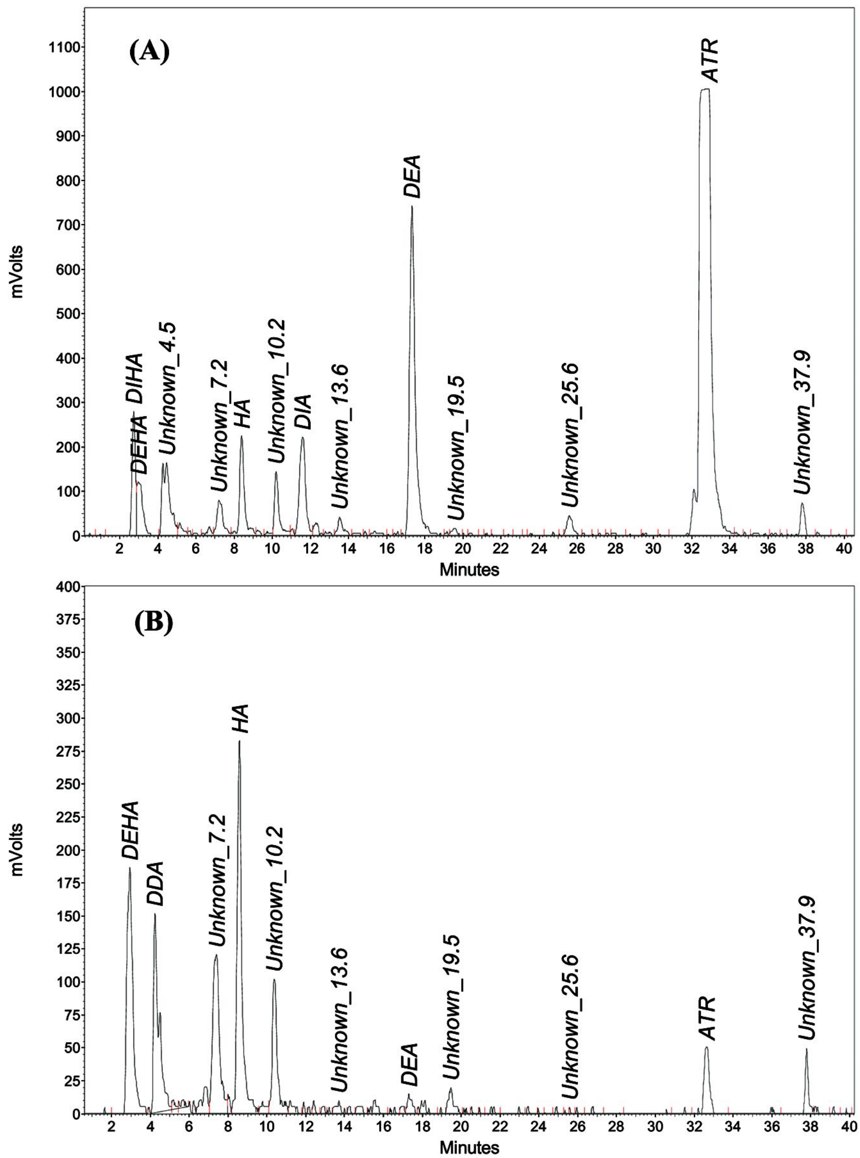


Figure 3. The radio chromatograms of [14]C-atrazine and metabolites extracted from switchgrass rhizosphere without inoculation ***(A)****, and with inoculation* ***(B)****.*

The extent of ATR degradation in the un-inoculated switchgrass rhizospheres reported here was considerably lower than observed under field conditions (*5*, *9*). In a previous field study, we demonstrated that the degradation of ATR and its metabolites in the switchgrass rhizosphere was significantly enhanced (*5*). In that study, the ATR dissipation rate of the switchgrass treatment was 57% greater than

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

a plant-free soil control 25-days after ATR application. More than 80% of the applied ATR was degraded to less toxic metabolites, with 47% of these residues converted to the less mobile hydroxylated metabolites. In current study, the dissipation of ATR in the switchgrass rhizosphere was only 8.7% greater than the bulk soil control. We believe the differences in dissipation rates of ATR between our previous field study and the growth chamber study reported here is mainly attributed to the short incubation time and inability of the microbial community that was reestablished in autoclaved soil to respond to ATR in our system.

The complete degradation of ATR and it metabolites in the *Pseudomonas* augmented rhizosphere soil has demonstrated the potential of this bacterium to enhance ATR degradation in switchgrass rhizosphere soil. As shown in Figure 4, the switchgrass rhizosphere enhanced the rates of the ^{14}C-ATR mineralized by *Pseudomonas* sp. strain ADP during the first 24 hours. When compared with ^{14}C-ATR mineralization in inoculated bulk soil control, the ^{14}C-ATR mineralization in inoculated switchgrass soils was increased by 39.1% at first 24 hours. The difference in ATR mineralization between the treatments were not significant after 24 hours. Previous studies have reported that the increased carbon sources in environments, such as increased organic carbon in the rhizospheres, will stimulate the catabolic activities and growth of *Pseudomonas* sp. strain ADP (*5*, *14*). However, increased sorption of ATR in soils with high organic matter content has been shown to limit the biodegradation of ATR and its metabolites (*24*). Results of this study showed that the addition of *Pseudomonas* sp. strain ADP to soil, with or without plants, will greatly increase ATR degradation and mineralization. We conclude that inocualtion of VBS buffer soil with *Psuedomonas* sp. strain ADP may improve buffer system potential to attenuate ATR in surface runoff.

Monitoring Copy Number of *atzA* in the Rhizospheres

We monitored the *atzA* copy number to quantify the effects of the switchgrass on the stability of the highly transmittable ATR degrading gene *atzA* in the rhizospheres. The *atzA* gene is localized on a 96-kbp self-transmissible plasmid in *Pseudomonas* sp. strain ADP, and this plasmid and genes can be transferred to other soil bacteria (*15*). In order to create an accurate view of the state of ATR degradation over time, we needed the ability to track *atzA*, both from *Pseudomonas* sp. strain ADP and from native bacteria species to which the *atzA* gene had been transferred. To achieve our goal, we developed a TaqMan probe-based real-time *q*PCR to quantify the target *atzA* gene. TaqMan probe-based quantitative real-time PCR is a relatively new method allowing the quantification of the specific target sequence from the DNA samples. The technique is more selective and accurate than Sybr Green based methods of real-time *q*PCR (*21*). Also, the polymerase used in this method was resistant to humic acids, the primary PCR inhibitor commonly found in the soils. The TaqMan probe-based real-time *q*PCR was successfully applied to monitor *atzA* copy number in rhizosphere soil samples in the context of a biodegradative rhizosphere environment.

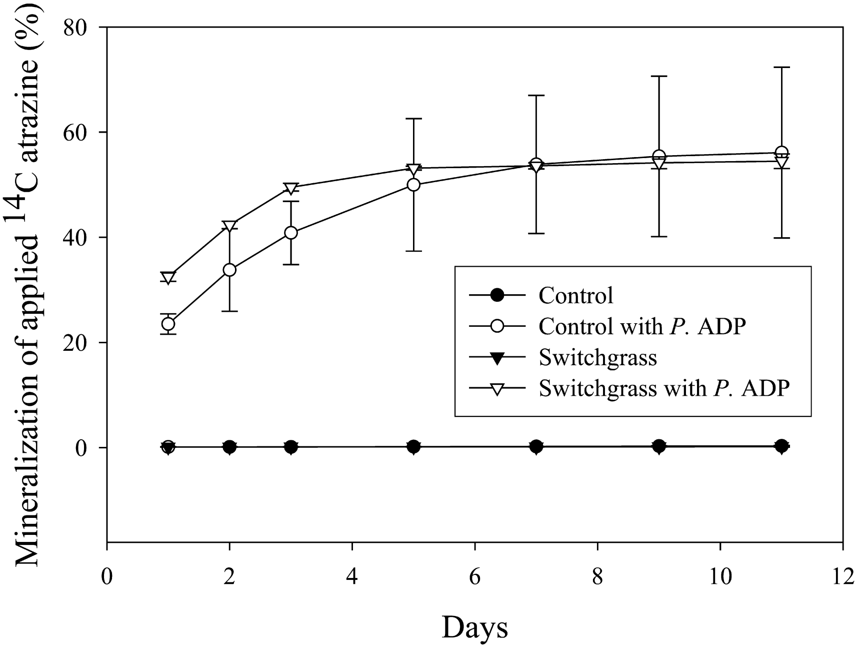


Figure 4. Percentage of applied ^{14}C-atrazine mineralized with inoculation vs. without inoculation of Pseudomonas sp. strain ADP. Error bars represent the standard deviation

As shown in Figure 5, the switchgrass rhizospheres helps to maintained the copy number of *atzA* to a greater extent than the plant-free control early in the incubation period. In the presence of switchgrass, *atzA* copy number was more persistent than the control over the first 24 days, but it returned to similar levels to that of the control soil by the end of the incubation. The *atzA* copy number was stimulated by the presence of the switchgrass for the first two weeks postinoculation with levels steadily decreasing to about 10 % of the day 0 value in this time period. A continued decrease to about 2 % of the time-zero value was observed over days 24-37. Consistent with these results, *atzC* copy number and bacterial biomass have been reported to increase when exposed to nutrients in the rhizosphere (*5*, *25*, *26*). The increased *atzA* levels during the first 24 hours after ATR application presumably resulted from growth of the added bacteria. The increase in ATR-degrading populations of bacteria in response to ATR has been seen in previous studies (*25*, *26*). Devers *et al.* (*27*) has also reported an immediate stimulation of the catabolic activity and *atz* gene expression after adding ATR. They have concluded that *atzA* and *atzB* mRNA levels were both up-regulated (stimulated 8-fold) in response to ATR addition. The return to baseline levels of *atz*A in both soil types is likely due to the lack of atrazine in the environment and lack of necessity for the *atzA* gene. The baseline levels of *atz*A found was approximately 3-fold higher than that found in field samples exposed to repeat treatments of atrazine (Table III).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

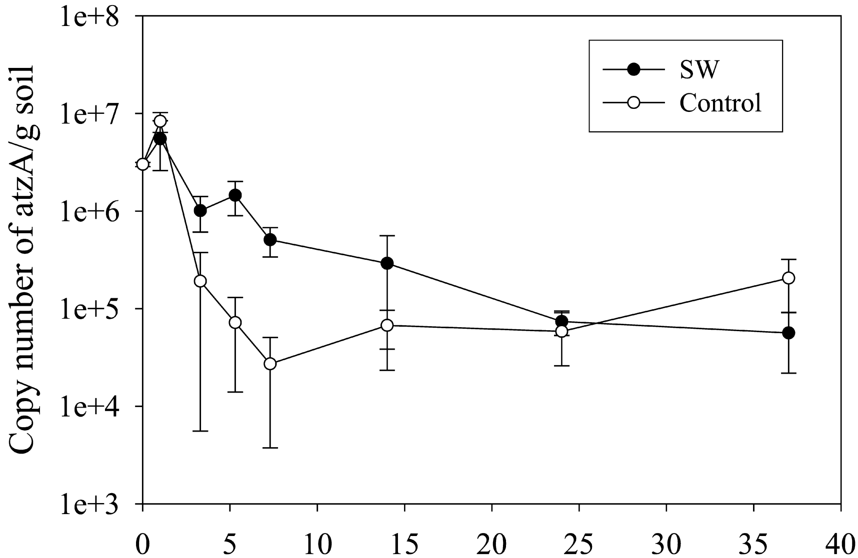


Figure 5. Copy number of atzA in the switchgrass (SW) rhizosphere vs. bulk soil (control) after inoculation with Pseudomonas sp. strain ADP.

Table III. Detection frequency (%), average *atz*A copy number, and ^{14}C-atrazine mineralization rates for soils collected from 1) corn-soybean rotation, 2) contour grass buffers, and 3) contour agroforestry buffers with long-term exposure to atrazine.

	Detection Frequency (%)	*atzA Copy Number/g*	*^{14}C-atrazine Mineralization Rates (%)*
1. Corn-Soybean rotation (n =63)	43%	26,000A[a]	9.9A
2. Grass Buffer (n=63)	44%	30,000A	5.8B
3. Agroforestry Buffer (n= 45)	32%	42,000A	8.9A

[a] Means followed by the same letter within the column did not differ significantly from each other at a significance level of 95% using Fisher's LSD test.

Analysis of soil collected from ATR-exposed fields near Central Missouri demonstrated the presence of atzA in 31.7% to 44.4% of soil samples (Table III, limit of detection is >50 gene copies). The majority of field samples did not contain *atzA* levels detectable by PCR or real-time *q*PCR. This was not expected due to the constant exposure of these fields to ATR over the last 20 years (*9–11*). Of those field samples positive for *atzA*, the average *atzA* copy number ranged from

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

27,000/g to 42,000/g. The inoculation of *Pseudomonas* sp. strain ADP leads to a 300% increase in atz*A* copy number over field samples, and a dramatic increase in ATR mineralization.

In our study, the *Pseudomonas* sp. strain ADP showed an immediate increase in *atz*A copy number following addition to the switchgrass rhizospheres. The lack of complete ATR mineralization under these conditions was attributed to the eventual loss of *atzA* gene copy number over time. *Pseudomonas* sp stain ADP augmentation may not increase the overall atzA levels in the soil dramatically (only increased by 3X), but the augmentation of soil with *Pseudomonas* sp. strain ADP does allow for the complete mineralization of atrazine, not just the conversion of atrazine to hydroxyatrazine.

Conclusions

This study demonstrated that the introduction of an ATR degrader, *Pseudomonas* sp. strain ADP, into VBS rhizospheres is a promising bioremediation approach to accelerate the degradation of ATR and its degradation products deposited into VBS. Switchgrass was able to maintain higher *atz*A levels than bulk soil control during first two weeks post inoculation. However, the ATR degradation rates and profiles were similar between inoculated switchgrass treatment and inoculated bulk soil control, suggesting the *Pseudomonas* sp. strain ADP is the predominant factor over the rhizosphere factor for ATR degradation. The addition of *Pseudomonas* sp. strain ADP only resulted in a 300% increase in atz*A* copy number as compare with atz*A* copy number in field samples, but the ATR mineralization was dramatically increased. From a crop production standpoint, the addition of *Pseudomonas* sp. strain ADP into the soil environment may raise the concerns due to its ability to transfer *atzA* and other catabolic genes to the surrounding areas leading to the loss of ATR efficacy. A more detail field study is required to assess the dispersion of the degrading genes before this strategy can be recommended for large-scale ATR mitigation application.

Acknowledgments

This work was funded through the University of Missouri Center for Agroforestry under cooperative agreement 58-6227-5-029 with the USDA-ARS. Any opinions, findings, conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the view of the U.S. Department of Agriculture or the University of Missouri. We would like to acknowledge Dr. Michael Sadowsky, University of Minnesota, for the gracious gift of the *Pseudomonas* sp. strain ADP. We would also like to acknowledge Madelyn Myers, Sandhya Thondapu, and Matthew Kovacs for their valuable assistance.

References

1. United States Department of Agriculture. *Agricultural Chemical Usage, 2003 Field Crops Summary. Report Ag Ch1 (04) a*; National Agricultural Statistics Service: Washington, DC, 2004; p 158.
2. Gilliom, R. J.; Barbash, J. E.; Crawford, C. G.; Hamilton, P. A.; Martin, J. D.; Nakagaki, N.; Nowell, L. H.; Scott, J. C.; Stackelberg, P. E.; Thelin, G. P.; Wolock, D. M. *The Quality of Our Nation's Waters: Pesticides in the Nation's Streams and Ground Water: Pesticides in the Nation's Streams and Ground Water, 1992–2001*; U.S. Department of the Interior, U.S. Geological Survey: Reston, VA, 2006; p 184.
3. Hayes, T. B.; Case, P.; Chui, S.; Chung, D.; Haeffele, C.; Haston, K.; Mai, M. L. V. P.; Marjuoa, Y.; Parker, J.; Tsui, M. *Environ. Health Perspect.* **2006**, *114*, 40–50.
4. Waller, S. A.; Paul, K.; Peterson, S. E.; Hitti, J. E. *Am. J. Obstet. Gynecol.* **2010**, *202*, 241.e1–241.e6.
5. Lin, C. H.; Lerch, R. N.; Garrett, H. E.; George, M. F. *J. Environ. Qual.* **2008**, *37*, 196–206.
6. Lin, C.-H.; Lerch, R. N.; Goyne, K. W.; Garrett, H. E. *J. Environ. Qual.* **2011**, in press.
7. Turhollow, A. *Cost of Producting Biomass from Riparian Buffer Strips*; Technical Report ORNL/TM-1999/146; Energy Division, Oak Ridge National Laboratory: Oak Ridge, TN, 2000.
8. Lin, C. H.; Lerch, R. N.; Garrett, H. E.; Gantzer, C. J.; Anderson, S. H. *Proceedings of the 10th North American Agroforestry Conference*; 2007, pp 113−121.
9. Lin, C. H.; Lerch, R. N.; Kremer, R. J.; Garrett, H. E.; Udawatta, R. P.; George, M. F. Soil microbiological activities in vegetative buffer strips and their association with herbicides degradation. In *Moving Agroforestry into The Mainstream: Proceedings of the Ninth Conference on Agroforestry in North America*, 12−15 June 2005; Brooks, K. N., Folliott, P. F., Eds.; Department of Forest Resources, University of Minnesota: St. Paul, MN, 2005; p 1−10.
10. Zhao, S.; Arthur, E. L.; Moorman, T. B.; Coats, J. R. *Environ. Toxicol. Chem.* **2005**, *24*, 2428–2434.
11. Zablotowicz, R. M.; Weaver, M. A.; Locke, M. A. *Weed Sci.* **2006**, *54*, 538–547.
12. Martinez, B.; Tomkins, J.; Wackett, L. P.; Wing, R.; Sadowsky, M. J. *J. Bacteriol.* **2001**, *183*, 5684–5697.
13. De Souza, M. L.; Sadowsky, M. J.; Wackett, L. P. *J. Bacteriol.* **1996**, *178*, 4894–4900.
14. Mandelbaum, R. T.; Allan, D. L.; Wackett, L. P. *Appl. Environ. Microbiol.* **1995**, *61*, 1451–1457.
15. De Souza, M. L.; Wackett, L. P.; Sadowsky, M. J. *Appl. Environ. Microbiol.* **1998**, *64*, 2323–2326.
16. De Souza, M. L.; Seffernick, J.; Martinez, B.; Sadowsky, M. J.; Wackett, L. P. *J. Bacteriol.* **1998**, *180*, 1951–1954.

17. De Souza, M. L.; Sadowsky, M. J.; Wackett, L. P. *J. Bacteriol.* **1996**, *178*, 4894–4900.
18. Boundy-Mills, K. L.; De Souza, M. L.; Mandelbaum, R. T.; Wackett, L. P.; Sadowsky, M. J. *Appl. Environ. Microbiol.* **1997**, *63*, 916–23.
19. Sadowsky, M. J.; Tong, Z.; De Souza, M.; Wackett, L. P. *J. Bacteriol.* **1998**, *180*, 152–158.
20. García-González, V.; Govantes, F.; Shaw, L. J.; Burns, R. G.; Santero, E. *Appl. Environ. Microbiol.* **2003**, *69*, 6987–6993.
21. Thompson, B. M.; Lin, C.-H.; Hsieh, H.-Y.; Kremer, R. J.; Lerch, R. N.; Garrett, H. E. *J. Environ. Qual.* **2010**, *39*, 1999–2005.
22. Zhou, J.; Bruns, M. A.; Tiedje, J. M. *Appl. Environ. Microbiol.* **1996**, *62*, 316–322.
23. Shaffer, E.; Sims, G.; Cupples, A.; Smyth, C.; Chee-Sanford, J. *Int. J. Soil, Sediment Water* **2010**, *3*, 1–26.
24. Chiou, C. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. In *Reactions and Movement of Organic Chemicals in Soils*; Sawhney, B.; Brown, K., Eds.; Soil Science Society of America: Madison, WI, 1989; pp 1−29 (SSSA Special Publication).
25. Piutti, S.; Hallet, S.; Rousseaux, S.; Philippot, L.; Soulas, G.; Martin-Laurent, F. *Biol. Fertil. Soils* **2002**, *36*, 434–441.
26. Martin-Laurent, F.; Piutti, S.; Hallet, S.; Wagschal, I.; Philippot, L.; Catroux, G.; Soulas, G. *Pest Manage. Sci.* **2003**.
27. Devers, M.; Soulas, G.; Martin-Laurent, F. *J. Microbiol. Methods* **2004**, *56*, 3–15.

Chapter 11

Free-Enzyme Bioremediation of Pesticides

A Case Study for the Enzymatic Remediation of Organophosphorous Insecticide Residues

Colin Scott,*[,1] Cameron Begley,[1] Matthew J. Taylor,[1] Gunjan Pandey,[1] Vinko Momiroski,[2] Nigel French,[1] Clint Brearley,[2] Steve E. Kotsonis,[2] Michael J. Selleck,[2] Flerida A. Carino,[3] Cristina M. Bajet,[4] Craig Clarke,[2] John G. Oakeshott,[1] and Robyn J. Russell[1]

[1]CSIRO Ecosystem Sciences, GPO Box 1700, Canberra, Australian Capital Territory 2601, Australia
[2]Orica Australia Pty Ltd., 1 Nicholson Street, Melbourne Victoria 3000, Australia
[3]Institute of Chemistry, University of the Philippines, Diliman, Quezon City 1101, Philippines
[4]Pesticide Toxicology and Chemistry Laboratory, National Crop Protection Center, University of the Philippines, Los Banos, Laguna 4031, Philippines
***colin.scott@csiro.au**

Free-enzyme bioremediation is a recently developed technology that allows rapid detoxification of pesticide residues in surface waters, such as irrigation tail water, and potentially from other wettable materials such as soil and the surfaces of commodities. Here we consider the advantages of this technology compared with other pesticide bioremediation strategies, as well as its current limitations and challenges for the future. We exemplify the development of free-enzyme bioremediants with a case study, the Landguard™ OP-A organophosphate bioremediant, highlighting the enzymatic, physical and toxicological properties of the enzyme that predispose it to be an effective and efficient environmental bioremediant and the applications explored for it to date.

Introduction

Over the past five to six decades bioremediation has been promoted as a low cost, effective strategy for reducing the impacts of environmental pesticide residues. Over this period the level of sophistication in bioremediation technologies has advanced significantly. Through the most recent advances in bioremediation, free enzymes can now be used directly, with several major advantages over more established bioremediation technologies, as well as some specific limitations. The advantages and current limitations of enzymatic bioremediation are considered herein, and we exemplify the development of free-enzyme bioremediants with a case study, the Landguard™ OP-A organophosphate bioremediant.

Bioremediation

Whole Organism Bioremediation

Historically, the focus of bioremediation has been on soil contamination, with whole organisms, usually bacteria or plants, being used as the catalysts for the clean up. Microbial bioremediation may take the form of biostimulation or bioaugmentation. Plant-based bioremediation is known as phytoremediation.

Microbial Bioremediation: Biostimulation and Bioaugmentation

Biostimulation is the introduction of otherwise rate-limiting nutrients to a contaminated area to encourage the growth of the endemic microbiota and accelerate the rate of biodegradation of the contaminants (*1*). There are several prerequisites for effective biostimulation: the environmental conditions must be appropriate to accept the added nutrients (e.g. heavy clays sequester nutrients by sorption), conditions must be permissive of bacterial growth and able to support the biochemical requirements of contaminant degradation (temperature, pH, aerobiosis, etc.), and the required catabolic pathways must be present in the local microflora at the outset. If the requisite catabolic pathway is absent, it must be introduced via appropriate non-native organisms in a process termed bioaugmentation.

Bioaugmentation is the introduction of non-native micro-organisms to a polluted area with the intention of augmenting the biochemical potential of the environment (*2*). The strains of microorganism introduced must possess suitable catabolic pathways for the remediation of the target pollutant and also have suitable growth characteristics for the selected environment (tolerance to pH, salts, temperature maxima and minima etc.) (*3*). Much effort has been expended in the engineering of environmentally robust bacteria to remediate synthetic pollutants (*4*–*6*). However, the complexities of genetic modification (GM) have often proven too challenging to produce bacterial strains that can survive and proliferate in the environment. Even where suitable bacteria can be engineered, regulatory policies may still prevent their effective deployment (*7*).

Phytoremediation

Phytoremediation is the introduction of plants that either accumulate or, preferably, catabolise environmental pollutants (*1*, *8*). There is now great interest in enhancing the catabolic abilities of appropriate crop plants with GM technology. Reports are emerging of transgenic plants transformed with certain cytochromes P450 (*9*) and hydrolases (*10*) which show significantly enhanced abilities to degrade particular pesticides. However, establishing a bioremediation "crop" is necessarily a lengthy process, contingent upon the growth characteristics of the species used. Additionally, as with transgenic bacteria, the regulatory environment for open-field use of transgenic plants is complex, albeit there are many more examples of the successful development and use of transgenic crops (*11*).

Biostimulation, bioaugmentation and phytoremediation all require significant periods of time to operate, because they depend upon the growth of the organisms employed. These technologies, then, are best suited to situations where time is not a principle limitation, such as the *in situ* decontamination of soil for land reclamation, rather than the treatment of surface water.

Free-Enzyme Bioremediation

Ultimately bioremediation is underpinned by specific enzymatic processes (*12*, *13*), so it is possible to consider using cell-free enzymes as an alternative to organismal bioremediation (*12*, *14*). There are many advantages of free enzyme bioremediants over the use of whole organisms. The activities of enzymes are independent of growth and therefore do not require the addition of growth enhancing nutrients. Enzymes act relatively quickly (requiring just minutes or hours for adequate remediation; see below), and with predictable behaviour, so it is possible to develop cost-effective dosing regimes for specific applications. Additionally the physiochemical tolerances of enzymes are often greater than those of most organisms, so whilst different bacterial bioremediants may be required for different environments, a single free enzyme bioremediant is likely to suit most (if not all) relevant environmental conditions. Equally, enzymes are readily biodegradable, minimising concerns about their long term effects upon the environment.

Enzymes potentially suitable for use as free enzyme bioremediants can be sourced from a vast array of organisms. They can then be modified by protein engineering or *in vitro* evolution to make them "fit-for-purpose" (*12*, *15*). Importantly, enzymes can be produced at scale in standard fermentation procedures and then treated post-harvest to remove contaminating genetic material, thus avoiding community or regulatory concerns about the release of genetically modified organisms into an open environment.

Although there are many advantages of free-enzyme bioremediants over whole organisms, there are also significant constraints. The catalysis needs to provide detoxification of the pesticide, preferably in a single enzymatic step and without using expensive, diffusible cofactors (e.g. NADH). The enzyme's kinetic properties must be adequate, with a low K_M (µM or ppm) to allow activity at

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

environmentally relevant pesticide concentrations and at least moderate k_{cat} (>100 turnovers/minute), and preferably work across an entire class of pesticides (e.g. triazine herbicides or organophosphate insecticides). The enzyme must also be physically robust (e.g. to extremes in pH, temperature) and have good production economics.

The cofactor issue essentially restricts this technology to the use of hydrolases, lyases and certain oxidases that do not require diffusible cofactors. Notwithstanding this restriction, free-enzyme bioremediation represents a major advance in the treatment of pesticide residues in water. Here, we consider an organophosphate (OP) insecticide-degrading free-enzyme bioremediant as a case study in the development of such technologies. We outline its credentials against a series of biochemical performance criteria for an effective bioremediant and summarise laboratory and field trials showing its safety and efficacy in the clean up of contaminated liquids, soils and commodities.

Landguard™: A Case Study for Free-Enzyme Bioremediation

Bacterial Phosphotriesterase: A Perfect Free Enzyme Bioremediant?

CSIRO and Orica Watercare have developed a free enzyme bioremediant called Landguard™ OP-A that can degrade OP insecticides (*12*). The technology is based on a bacterial phosphotriesterase (PTE; EC 3.1.8.1), OpdA, which is well suited for use as a free-enzyme bioremediant (*12*, *15*). Landguard OP-A is currently produced as a wettable powder, although new formulations may be used in future for specific applications. The studies reported below were conducted with Languard™ OP-A, however a catalytically improved version of the enzyme used has been developed (A900) and Landguard™ A900 is intended to replace Landguard™ OP-A in the future.

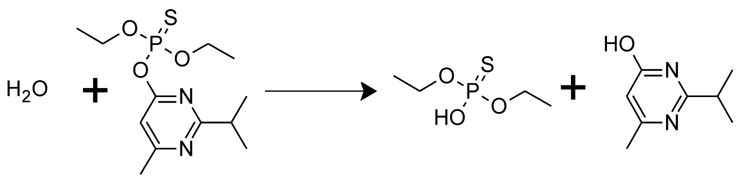


Figure 1. Hydrolysis of an organophosphorous insecticide (diazinon) by the phosphotriesterases OpdA. The products are diethyl thiophosphoric acid and 2-isopropyl-4 methyl-pyrimidin-6-ol.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Physical and Kinetic Properties of PTE

The *opdA* gene was isolated from a soil bacterium and encodes a *ca.* 30 kDa metal-dependent α_8/β_8 hydrolase and (*16*, *17*). OpdA hydrolyses one of the three phosphoester bonds of the phosphotriesters (Fig. 1) by nucleophilic substitution (an S_N2 mechanism) of the phosphoester group (*18*), effectively detoxifying the OP. The rate of this reaction depends upon the OP insecticide (Table 1), but can approach diffusion limited rates of 10^7 $sec^{-1}.M^{-1}$ (*19*). Its broad substrate range, rapid rate of hydrolysis and cofactor-free reaction mechanism make OpdA an ideal candidate as a bioremediant of OP insecticides (*12*, *15*, *20*).

Improving PTEs by Enzyme Evolution and Engineering

Enzyme engineering and *in vitro* evolution have been used extensively with the bacterial phosphotriesterases to produce variant enzymes with significantly improved kinetic properties. This is exemplified by the composition of Landguard™ OP-A. The current Landguard™ formulation is based on the wild-type enzyme. This will be replaced with a rationally improved OpdA (A900), which possesses higher k_{cat}/K_m values than OpdA against the commercially important OP insecticides chlorpyrifos, diazinon and parathion (Table 2).

Toxicity of Landguard™ OP-A and the OP Metabolites

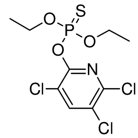
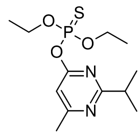
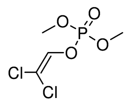
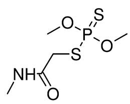
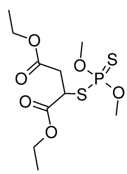
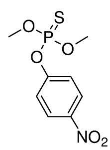
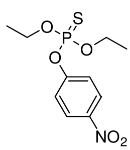
Before using an OpdA-based bioremediant in the field it was essential to establish its toxicity and fate in the environment, and to ensure that it catalysed a reaction that was an effective detoxification of the phosphotriester insecticides.

Toxicity of Landguard ™

The toxicity of Landguard™ to mammals was established in formal toxicity studies with Wistar rats (Table 3). Landguard™ was either fed or applied dermally to the animals (Table 3) at dose rates of 50, 200 and 1000 mg/kg per day for 28 days (oral) or at 4 mL/kg of a 500 mg/mL solution per day for 15 days (dermal). Biopsies revealed no noticeable detrimental effects of oral Landguard™ application in the rats, whilst the dermal application produced a mild skin irritation with no clinical effects.

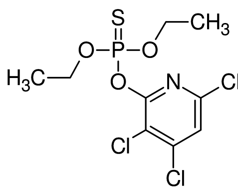
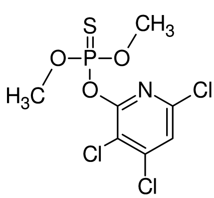
The environmental toxicity of Landguard™ OP-A was tested by applying it at 1g/L to activated sludge, and at 100 mg/L to cultures of the alga *Scenedesmus subspicatus*, the arthropod *Daphnia magna*, and the fish species *Brachydanio rerio*, with no adverse affects found in any of these indicator species (Table 3). The dose rates used in these toxicity and ecotoxicity studies were higher than in many of the successful field trials of the enzyme's efficacy as a bioremediant (see below), demonstrating that it could be used in environmental applications without adverse environmental effects.

Table 1. Examples of OP insecticides degraded by OpdA

Phosphotriester	*Structure*	*k_{cat}/K_M ($sec^{-1}.M^{-1}$)*	*Source*
Chlorpyrifos		2.8×10^5	(*21*)
Diazinon		1.5×10^5	(*22*)
Dichlorvos		8.1×10^5	(*23*)
Dimethoate		9.0×10^3	(*24*)
Malathion		4.8×10^1	(*25*)
Methyl parathion		1.2×10^7	(*18*)
Ethyl parathion		2.7×10^6	(*26*)

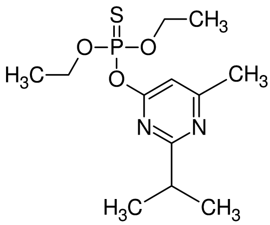
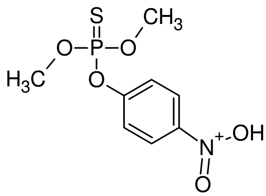
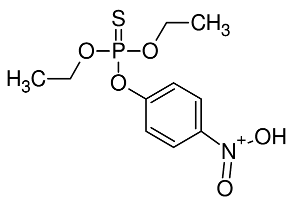
The ecotoxicology studies of Landguard™ OP-A were also complemented with a study of its biodegradability (Figure 2). In this study the rate of digestion of Landguard™ was assessed in a manometric respirometry test, whereby the amount of Landguard™ digested was calculated based on the biological oxygen demand of activated sludge fed with Landguard™ as a carbon source. An equivalent amount of carbon, provided as the readily digestible compound sodium benzoate, was used as a positive control. The result of this test was that > 95% of both the Landguard™ and the sodium benzoate were digested over a 15 day period, showing that Landguard™ is readily degraded. Furthermore, there was no reduction in the biological oxygen demand when sodium benzoate and Landguard™ were added simultaneously, suggesting that Landguard™ has no inhibitory affect upon bacterial growth when it is not the sole carbon source. The stability of Landguard™ in natural water was also monitored, using the hydrolysis of methyl parathion as an indication of the relative amount of Landguard™ remaining in the sample (Table 4). In this experiment the half-life of Landguard™ was seventy nine hours, with less than 1 percent of the original activity remaining after seven days. These data suggest that Landguard™ is biodegradable, and has a relatively short half-life in natural systems.

Table 2. Comparison of the second order rate constants (k_{cat}/K_M)[a] of OpdA and the rationally designed OpdA variant A900 against commercially important OP insecticides

Insecticide	*Structure*	*k_{cat}/K_M ($sec^{-1}.M^{-1}$)*	
		OpdA	*A900*
Ethyl chlorpyrifos		2.8×10^6	2.2×10^6
Methyl chlorpyrifos		1.2×10^4	3.7×10^5

Continued on next page.

Table 2. (Continued). Comparison of the second order rate constants (k_{cat}/K_M)[a] of OpdA and the rationally designed OpdA variant A900 against commercially important OP insecticides

Insecticide	*Structure*	*k_{cat}/K_M (sec^{-1}.M^{-1})*	
		OpdA	*A900*
Diazinon		1.9×10^6	3.9×10^6
Ethyl parathion		1.7×10^7	9.4×10^7
Methyl parathion		5.0×10^6	3.6×10^6

[a] k_{cat}/K_M values were obtained for enzymes purified by the methods described in Jackson *et al*, 2006 (*17*). Hydrolysis rates were determined at 25°C in MOPS buffer (pH8.0) using UV-vis spectroscopy at 250 nm (diazinon), 330 nm (chlorpyrifos ethyl and methyl) and 405 nm (parathion ethyl and methyl).

Metabolite Toxicity

Detoxification of the pesticide was established by exposing an indicator arthropod species, *Ceriodaphnia dubia*, to either untreated diazinon (50 mg/L) or diazinon (50 mg/L) that had been pre-treated with Landguard™ OP-A (Table 5). The survival rate of the *Ceriodaphnia* was monitored after 24 and 48 hours of exposure. At both time points the EC_{50} (effective concentration for 50% survival) for *Ceriodaphnia* exposed to the Landguard™ treated diazinon was nearly 200,000 times greater than for exposure to the untreated pesticide. Similar increases in the LOEC (Lowest concentration at which an effect is observed; Table 5) and NOEC (Highest concentration at with no effect is observed; Table 5) were also observed. The products of diazinon hydrolysis by Landguard™ OP-A were confirmed by mass spectroscopy to be diethyl thiophosphoric acid

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

and 2-isopropyl-4 methyl-pyrimidin-6-ol, consistent with the characterised mechanism of phosphotriesterases (Figure 1). These data demonstrate that Landguard™ OP-A performs in a predictable manner and that its action significantly detoxifies the phosphotriester insecticide.

Extensive ecotoxicological data are also available for another OP insecticide, chlorpyriphos, and its hydrolysis products (diethyl thiophosphoric acid and TCP; 3,5,6 trichloropyridin-2-ol) (*27*). Both products are considerably less toxic than the parent compound in indicator species such as Bluegill (*Lepomis macrochirus*) (*28*) and TCP has also been shown to be of low to moderate toxicity to aquatic and terrestrial biota (*27*). Hydrolysis of insecticidal phosphotriesters by OpdA therefore represents a significant reduction in their mammalian toxicities and ecotoxicities.

Efficacy of Landguard OP-A™

The efficacy of the Languard™ product has been investigated for a number of potential applications, and field trials have been conducted for the treatment of spent animal dip waste water (dip liquor), irrigation tail water, and soil and commodity treatments. The details of these trials (below) indicate that Landguard™ is highly effective in the treatment of aqueous contamination and the treatment of soils and commodities has a great deal of early promise.

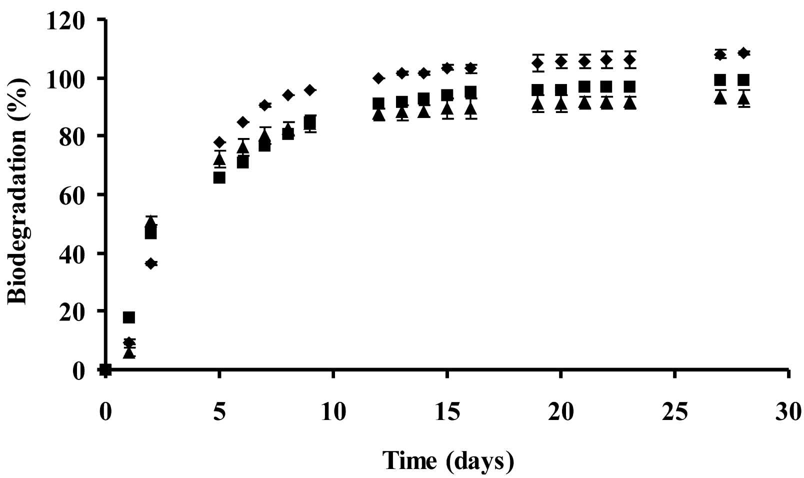


Figure 2. Biodegradability of Landguard™ (diamonds) and sodium benzoate (triangles) assessed by a manometric respirometry test. Inhibition of bacterial respiration by Landguard™ was also assessed by measuring the rate of respiration in the presence of both sodium benzoate and Landguard™ (squares).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table 3. Ecotoxicity and mammalian toxicity of Landguard™ OP-A

Test	*Monitoring time*	*Dose rate*	*Effect of Landguard*
Scenedesmus subspicatus	72 hour	100 mg/L	No growth effects observed
Activated sludge	3 hour	1000 mg/L	No inhibitory effect on bacterial respiration
Brachydanio rerio	96 hour	100 mg/L	No mortality or visible abnormalities observed
Daphnia magna	48 hour	100 mg/L	No mortality (immobilisation of cells) observed
Wistar rat (oral) (n = 30, 15 male and 15 female at each dose rate)	28 day	50, 200 and 1000 mg/kg/day	All test animals survived with no apparent signs of toxicity. No adverse responses were observed.
Rats (Dermal) (n= 10, 5 male and 5 female)	15 days	4 mL/kg of a 0.5 g/mL solution	Slight general erythema observed in test animals. No clinical effects noted.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table 4. Stability of Landguard™ OP-A in natural water

Time (hours)	*Activity (U/L)[a]*	*Activity (% initial)*
0	2133	100%
17	2306	108%
24	2341	110%
48	1894	89%
96	624.4	29%
168	19.55	0.92%

[a] The activity (U/L) of Landguard™ was measured using methyl parathion as substrate. One unit of enzyme activity (U) is equivalent to the amount of enzyme required to hydrolyse 1 µmol of methyl parathion per minute. The values shown are the mean of two relicate that did not differed by less than 5% at each reading.

Table 5. Toxicity of diazinon to *Ceriodaphnia dubia* before and after treatment with Landguard™ OP-A

	Untreated diazinon		*Landguard TM OP-A treated diazinon[a]*		*Fold improved survival*	
	24 hours	*48 hours*	*24 hours*	*48 hours*	*24 hours*	*48 hours*
EC 50 (µg/L)[b]	0.389	0.195	73,000	46,100	1.9×10^5	1.9×10^5
LOEC (µg/L)[b]	0.55	0.275	100,000	100,000		
NOEC (µg/L)[b]	0.275	0.138	30,000	30,000		

[a] Landguard™ dosed at a rate of 0.05 g/L. The values shown are the mean of two relicate that did not differed by less than 10% at each reading. [b] EC50, effective concentration for 50% survival; LOEC, Lowest concentration at which an effect is observed; NOEC: Highest concentration at which no effect is observed.

Dip Liquor Treatment

Parasite control often involves plunge-dipping livestock into concentrated OP insecticide solutions, leaving pesticide-containing spent dip liquor that requires appropriate disposal. Free-enzyme bioremediation provides a solution for the rapid clean up of these liquors, allowing them to be disposed of safely. The OP-degrading Landguard™ was used in five trials in Australia to remediate diazinon from spent liquors. The volumes of the dipping tanks varied from 3,000 – 8,000 litres, with diazinon concentrations ranging from 0.91 – 75 mg/L (Table 6). The diazinon used was formulated by either Coopers (North Ryde, NSW, Australia) or Vibrac Animal Health (Milperra, NSW, Australia). Enzyme amounts added varied between 103 and 5150 U/L (where a unit, U, is defined as the amount of enzyme that is required to degrade 1 µmol of methyl parathion in one minute), and treatment times ranged between 10 and 60 minutes.

Table 6. Australian field trials of Landguard OP-A™ in spent diazinon-based sheep dip liquors

Date	*Location*[a]	*Formulation*	*[Enzyme] (U/L)*[b]	*Time (min)*	*[Diazinon] (mg/L)*	*Percent reduction*[c]
2004	Darlington	Coopers	0	0	0.91±0.09	**0**
			625	10	0.11±0.02	**87.91**
			625	20	0.01±0.01	**99.23**
2004	Lake Bolac	Virbac	0	0	34.7±1.7	**0**
			1030	30	<0.01	**>99.97**
			1030	60	<0.01	**>99.97**
			257	30	<0.01	**>99.97**
			515	30	<0.01	**>99.97**
			1030	30	<0.01	**>99.97**
2005	Gundagai	Coopers	0	0	59.3±6.12	**0**
			515	30	9.6±0.86	**83.81**
			515	60	2.0±0.12	**96.63**
			103	30	47.0±5.27	**20.74**
			257	30	33.0±2.31	**44.35**
			515	30	12.3±0.96	**79.26**
			2060	30	0.76±0.11	**98.72**
2005	Loxton	Coopers	0	0	75±5.31	**0**
			2575	30	0.41±0.01	**99.45**
			2575	60	0.079±0.01	**99.89**
			515	30	5.9±0.34	**92.13**
			1030	30	2.3±0.02	**96.93**
			2060	30	1.6±0.01	**97.87**
			2575	30	0.71±0.01	**99.05**
			3090	30	0.58±0.02	**99.23**
			5150	30	0.21±0.01	**99.72**
2005	Flinders Island	Coopers	0	0	39.4±2.48	**0**
			724	20	<0.05	**>99.87**

Continued on next page.

Table 6. (Continued). Australian field trials of Landguard OP-A™ in spent diazinon-based sheep dip liquors

Date	*Location[a]*	*Formu-lation*	*[Enzyme] (U/L)[b]*	*Time (min)*	*[Diazinon] (mg/L)*	*Percent reduction[c]*
			724	30	<0.05	**>99.87**
			724	30	<0.05	**>99.87**
			0	0	30.5±4.65	**0**
			839	20	<0.05	**>99.84**
			839	30	<0.05	**>99.84**
			839	30	<0.05	**>99.84**

[a] Trials occurred in Victoria (Darlingtion and Lake Bolac), New South Wales (Gundagai), South Australia (Loxton) and Tasmania (Flinders Island). [b] One unit of enzyme activity (U) is equivalent to the amount of enzyme required to hydrolyse 1 µmol of methyl parathion per minute. One gram of Landguard™ OP-A = 20,000 U [c] Calculated from mean values

The degree of diazinon degradation achieved varied in a predictable manner according to the amounts of enzyme and substrate involved and the treatment time. However, there were a range of conditions under which better than 99% degradation was consistently achieved. Notably also, the time periods tested in these field trials was much shorter than a farmer may need (often overnight treatment is employed), so enzyme dose rates can be reduced significantly, whilst still achieving the same levels of decontamination. In fact dose rates of 1 g/100 L (equivalent of 200 U/L) are currently recommended for a three hour treatment in order that a 99.99 % reduction in OP concentration can be achieved.

Tail Water Treatment

OP insecticides are also widely used to reduce pest damage in agricultural and horticultural crops. In the case of irrigated cropping a significant proportion of the OP contaminant is often washed into drainage or interception ditches along with irrigation tail water, from where a variety of secondary contamination scenarios may ensue.

The first field trial treating OP-contaminated tail water with Landguard™ OP-A was reported in 2001, with a >90% reduction in OP concentration achieved in just 10 minutes (*29*). In this early trial, and also in subsequent ones (Table 7), a concentrated solution of Landguard™ OP-A was 'bled' into the flowing tail water as it entered the drainage ditch at a rate that determined the final U/L dose rate. In the field trial conducted at Coleambally, NSW (2007), tail water contaminated with 55 mg/L chlropyrifos was treated with 7, 35 or 70 U/L Landguard™. All three dosing regimes achieved >99% degradation of the OP, in 2 hours at the lowest dose rate and in less than 15 minutes at the highest dose rate.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table 7. Field trials of Landguard™ OP-A in chlorpyrifos-contaminated tailwater from broad acre cropping

Date	*Location*[a]	*Formulation*	*[Enzyme] (U/L)*[b]	*Time*	*[Chlorpyrifos] (mg/L)*	*Percent reduction*[c]
2007	Coleambally	Lorsban	0	8 hrs	55.00±6.03	**0**
			7.00	15 min	1.30±0.21	**98.00**
				30 min	0.62±0.01	**99.00**
				1 hr	0.87±0.02	**98.00**
				2 hrs	0.74±0.02	**99.00**
				4 hrs	0.55±0.01	**99.00**
				8 hrs	0.68±0.01	**99.00**
			35.00	15 min	1.10±0.13	**98.00**
				30 min	0.13±0.01	**99.80**
				1 hr	0.08±0.01	**99.90**
				2 hrs	0.04±0.01	**99.90**
				4 hrs	0.03±0.01	**99.90**
				8 hrs	0.02±0.01	**99.96**
			70.00	15 min	0.19±0.02	**99.70**
				30 min	0.24±0.02	**99.60**
				1 hr	0.15±0.01	**99.70**
				2 hrs	0.04±0.01	**99.90**
				4 hrs	<0.01	**>99.98**
				8 hrs	<0.01	**>99.98**
2007	Gustine	Lorsban	0	0	2.68±0.31	**0**
			0.59	15 min	2.24±0.38	**16.00**
				30 min	1.65±0.12	**38.00**
				1 hr	1.10±0.16	**59.00**
				2 hrs	0.61±0.08	**77.00**
				3 hrs	0.18±0.03	**93.00**

[a] Trials were conducted on runoff from a rice paddy (Coleambally, NSW) and an alfalfa field (Gustine, Central California). [b] One unit of enzyme activity (U) is equivalent to the amount of enzyme required to hydrolyse 1 µmol of methyl parathion per minute. One gram of Landguard™ OP-A = 20,000 U. [c] Calculated from mean values.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

In Gustine (California), a lower dose rate (0.59 U/L) was used to treat low level chlorpyrifos contamination (2.24 mg/L) in tail water from an alfalfa crop. Even with this low dose rate, 93% degradation of the chlorpyrifos was achieved in just 3 hours. Unlike the spent dip liquor treatment above, the treatment of tail water is tightly time-bound (because it is generally necessary in these circumstances to achieve substantive detoxification before the water in question leaves the farm and joins public waterways) and the dose rate of Landguard™ cannot be reduced by allowing a longer reaction time. From the field trial data reported herein, a dose rate of between 0.59 and 7 U/L appears to be required to achieve greater than 99% degradation of chlorpyrifos in less than two hours.

Although these field trials demonstrate that significant tail water decontamination can be achieved using Landguard™ OP-A, the dosing system used to bleed the enzyme into the tail water is probably too cumbersome for general application. An alternative slow-release carrier system is currently under investigation.

Soil Treatment

The treatment of crops with OPs can also contaminate soil, which can lead to the contamination of ground water. Therefore, a potential application of free enzyme bioremediation is in treating contaminated soils.

Early trials with Landguard™ OP-A in soil treatment have been conducted in Australia (Nagambie, Victoria). Almond trees were treated with diazinon (Country Diazinon; 500 g/L) at a rate of 2L/ha, resulting in an average diazinon concentration of 6.4 mg/kg in the first 1 cm depth of top soil. Landguard™ OP-A was applied at 250, 500, or 1000 g/ha (in a water volume of 1000 L/ha) 1 hour after pesticide application. In samples taken at 1 hour after Landguard™ OP-A application a 39% (250 g/ha), 61% (500 g/ha) and 77% (1000 g/ha) reduction in diazinon was observed (data not shown). However, there was no further degradation after 7 days: this is unlikely a result of degradation of the enzyme, as subsequent treatments did not improve the levels of OP hydrolysis. It is possible, however, that irreversible sorption of the OP to the soil could make the some of the diazinon inaccessible to the enzyme. Some reports show that up to 40 % of sorbed diazinon cannot subsequently be desorbed by water (*30*). The inclusion of surfactants in the Landguard™ formulation may permit greater OP degradation in soils.

Commodity Treatment

Post-harvest contamination of commodities is also a concern. Many governments impose strict Maximum Residue Limits (MRLs) on both domestic and imported commodities. These restrictions can constitute significant constraints on commodity trading, with serious economic impacts on growers. Post-harvest treatment of commodities with a bioremediatnt could help reduce contamination.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Early trials of Landguard™ OP-A have been conducted with eggplant, tomato and mango treated with fenitrothion, diazinon, chlorpyrifos and phenthoate. Reductions of up to 40% in chlorpyrifos levels and 35% in diazinon concentrations were obtained in eggplant after 5 minutes treatment (data not shown). Residues of fenitrothion on eggplant and tomato were reduced by 53% and 12%, respectively, and phenthoate residues on eggplant and tomato were reduced by 66% and 53%, respectively, after 15 minutes treatment. Phenthoate and diazinon residues were reduced by 21% and 24% respectively in mango peel.

Although these early data are promising, they do not yet constitute substantive decontamination. More research is warranted to more fully explore this potential application.

Prospects

Free-Enzyme Bioremediation of Other Pesticides

Trials with Landguard™ OP-A have demonstrated that free-enzyme bioremediation can provide a fast, efficient solution for reducing pesticide contamination. This raises the possibility that other pesticide chemistries could be targets for this technology.

The triazine herbicides, including atrazine, are candidates for bioremediation. Organisms and enzymes that degrade atrazine and other s-triazine herbicides have been described (*31*, *32*), and there has been significant effort in whole organism bioremediation of atrazine contaminated soils (*33–36*). Recent work to adapt and improve the enzymes involved for use as free-enzyme bioremediants (*37*) have resulted in at least one successful field trial (*38*).

Synthetic pyrethroid insecticides are another potential target for free enzyme bioremediation, and enzymes that detoxify them have been identified from bacteria and insecticide-resistant Australian blowflies (*Lucilia cuprina*) (*39*). The blowfly enzyme has been the focus of development for a bioremediant, with promising results from an ecotoxicological study published in 2009 (*40*).

Another well studied enzyme system that has immediate potential as a free-enzyme bioremediant is the hexachlorocyclohexane (HCH) degrading *lin* systems (*41*). Two cofactor *lin* independent enzymes are responsible for detoxifying HCH by removing between two and four chlorides from the hexane ring (*41*). These two enzymes may constitute a potential free-enzyme bioremediant.

Enzymes capable of co-factor free detoxification have also been characterised for other pesticides, fungicides and herbicides, including fungicidal carbamates (*42*), insecticidal carbamates (*43*, *44*) and phenyl urea herbicides (*45*). These could also be developed into bioremediants.

Limitations and Challenges for Free-Enzyme Bioremediation

Sorption of pesticide residues to soil or sediment may be a limitation to the effectiveness of enzyme bioremediants, particularly for hydrophobic chemistries (e.g. HCH and synthetic pyrthroids). The extent of limitation is dependent upon the pesticide chemistry, and the composition of the soil. Where pesticdes are reversibly bound to solid particles, there will be competition between the soil and enzyme for the pesticide. Enzymes with low K_M values are better able to compete with the soil for the pesticide. A low K_M is therefore essential for enzymatic bioremediatts, noting that reductions in K_M values can be achieved through *in vitro* enzyme improvement (*37*). Enzymes may be unable to access irreversibly bound pesticides, although these residues may be of reduced biological significance anyway.

Not all detoxifying enzymes can currently be developed into free-enzyme bioremediants, a major limitation being the need many have for diffusible cofactors. Detoxifying enzymes that catalyse cofactor-dependent redox reactions include various insect and mammalian cytochromes P450 that detoxify insecticides (*46*, *47*) and bacterial enzymes that degrade herbicides (*48*) and insecticides (e.g. endosulfan) (*49*, *50*). If free-enzyme bioremediation is to extend to these enzymes, then mechanisms by which cofactors are retained in proximity to the enzyme and recycled to the appropriate redox state must be developed. Several innovative solutions to cofactor recycling have been investigated in recent years, generally involving the co-immobilisation or co-encapsulation of the desired enzyme and cofactor with a second enzyme for regenerating the cofactor (*51*, *52*). Such technologies could expand the scope of free-enzyme bioremediation considerably.

Immobilization and encapsulation technologies also allow the use of free-enzyme technology to address point of use contamination, in addition to point of source contamination. For example, "enzyme activated" filters could be used to treat potable water known, or suspected, to be contaminated with pesticide residues. The time frames of minutes to hours observed in the field trials would be appropriate for the decontamination of drinking water. Other enzyme-activated materials could be used in cleaning spray tanks and other pesticide delivery tools, or in absorbent materials to contain and decontaminate pesticide spills.

Acknowledgments

We thank Time Animal Health (Australia) for providing training in the handling of sheep dipping chemical and equipment. The biodegradability studies were conducted by RCC Ltd (Switzerland). Field trial samples were analysed by Gribbles Analytic Laboratory (Australia). Ecotoxicology and metabolite data for Landguard™ , diazinon and the diazinon metabolites were provided by the National Research Centre for Environmental Toxicology (EnTox) (Australia). Tail water field trials in California (USA) were conducted by the Coalition for Urban/Rural Environmental Stewardship (CURES; Dinuba, California).

References

1. Alcalde, M.; Ferrer, M.; Plou, F. J.; Ballesteros, A. *Trends Biotechnol.* **2006**, *24*, 281–287.
2. Gentry, T. J.; Rensing, C.; Pepper, I. L. *Crit. Rev. Environ. Sci. Technol.* **2004**, *34*, 447–494.

3. Thompson, I. P.; van der Gast, C. J.; Ciric, L.; Singer, A. C. *Environ. Microbiol.* **2005**, *7*, 909–915.
4. Singh, S.; Kang, S. H.; Mulchandani, A.; Chen, W. *Curr. Opin. Biotechnol.* **2008**, *19*, 437–444.
5. de Lorenzo, V. *Clin. Microbiol. Infect.* **2009**, *15*, 63–65.
6. Chauhan, A.; Fazlurrahman; Oakeshott, J. G.; Jain, R. K. *Indian J. Microbiol.* **2008**, *48*, 95–113.
7. Snow, A. A.; Andow, D. A.; Gepts, P.; Hallerman, E. M.; Power, A.; Tiedje, J. M.; Wolfenbarger, L. L. *Ecol. Appl.* **2005**, *15*, 377–404.
8. Jorgensen, K. S. In situ bioremediation. *Adv. Appl. Microbiol.* **2007**, *61*, 285–305.
9. Eapen, S.; Singh, S.; D'Souza, S. F. *Biotechnol. Adv.* **2007**, *25*, 442–451.
10. Cherian, S.; Oliveira, M. M. *Environ. Sci. Technol.* **2005**, *39*, 9377–9390.
11. Akhond, M. A. Y.; Machray, G. C. *Euphytica* **2009**, *166*, 47–59.
12. Scott, C.; Pandey, G.; Hartley, C. J.; Jackson, C. J.; Cheesman, M. J.; Taylor, M. C.; Pandey, R.; Khurana, J. L.; Teese, M.; Coppin, C. W.; Weir, K. M.; Jain, R. K.; Lal, R.; Russell, R. J.; Oakeshott, J. G. *Indian J. Microbiol.* **2008**, *48*, 65–79.
13. Russell, R. J.; Scott, C.; Jackson, C. J.; Pandey, R.; Pandey, G.; Taylor, M. C.; Coppin, C. W.; Liu, J. W.; Oakeshott, J. G. *Evol. Appl.* **2011**, *4*, 225–248.
14. Russell, R. J.; Scott, C.; Jackson, C. J.; Pandey, R.; Pandey, G.; Taylor, M. C.; Coppin, C. W.; Liu, J. W.; Oakeshott, J. G. *Evol. Appl.*, in press.
15. Sutherland, T. D.; Horne, I.; Weir, K. M.; Coppin, C. W.; Williams, M. R.; Selleck, M.; Russell, R. J.; Oakeshott, J. G. *Clin. Exp. Pharmacol. Physiol.* **2004**, *31*, 817–821.
16. Horne, I.; Sutherland, T. D.; Harcourt, R. L.; Russell, R. J.; Oakeshott, J. G. *Appl. Environ. Microbiol.* **2002**, *68*, 3371–3376.
17. Jackson, C. J.; Carr, P. D.; Kim, H. K.; Liu, J. W.; Herrald, P.; Mitic, N.; Schenk, G.; Smith, C. A.; Ollis, D. L. *Biochem. J.* **2006**, *397*, 501–508.
18. Jackson, C. J.; Foo, J. L.; Kim, H. K.; Carr, P. D.; Liu, J. W.; Salem, G.; Ollis, D. L. *J. Mol. Biol.* **2008**, *375*, 1189–1196.
19. Caldwell, S. R.; Newcomb, J. R.; Schlecht, K. A.; Raushel, F. M. *Biochemistry* **1991**, *30*, 7438–7444.
20. Russell, R. J.; Harcourt, R. L.; Oakeshott, J. G. Bioremediation of pesticides using enzymes. In *Seeking Agricultural Produce Free of Pesticide Residues*; Kennedy, I. R., Skerritt, J. H., Johnson, G. I., Highley, E., Eds.; 1998; pp 341−348.
21. Cho, C. M. H.; Mulchandani, A.; Chen, W. *Appl. Environ. Microbiol.* **2004**, *70*, 4681–4685.
22. Lai, K.; Stolowich, N. J.; Wild, J. R. *Arch. Biochem. Biophys.* **1995**, *318*, 59–64.
23. Jackson, C. J.; Weir, K.; Herlt, A.; Khurana, J.; Sutherland, T. D.; Horne, I.; Easton, C.; Russell, R. J.; Scott, C.; Oakeshott, J. G. *Appl. Environ. Microbiol.* **2009**, *75*, 5153–5156.
24. Jackson, C. J.; Liu, J. W.; Coote, M. L.; Ollis, D. L. *Org. Biomol. Chem.* **2005**, *3*, 4343–4350.
25. Efremenko, E. N.; Sergeeva, V. S. *Russ. Chem. Bull.* **2001**, *50*, 1826–1832.

26. Briseno-Roa, L.; Hill, J.; Notman, S.; Sellers, D.; Smith, A. P.; Timperley, C. M.; Wetherell, J.; Williams, N. H.; Williams, G. R.; Fersht, A. R.; Griffiths, A. D. *J. Med. Chem.* **2006**, *49*, 246–255.
27. Barron, M. G.; Woodburn, K. B. Ecotoxicology of chlorpyrifos. *Reviews of Environmental Contamination and Toxicology*; Springer-Verlag: New York, 1995; Vol. 144, pp 1−93.
28. Mayer, F. L.; Ellersieck, M. R. *Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals*; U.S. Department of Interior: Washington, DC, 1986.
29. Russell, R. J.; Sutherland, T. D.; Horne, I.; Oakeshott, J. G. *Australas. Biotechnol.* **2001**, *11*, 24–26.
30. Nemeth-Konda, L.; Fuleky, G.; Morovjan, G.; Csokan, P. *Chemosphere* **2002**, *48*, 545–552.
31. Desouza, M. L.; Wackett, L. P.; Boundymills, K. L.; Mandelbaum, R. T.; Sadowsky, M. J. *Appl. Environ. Microbiol.* **1995**, *61*, 3373–3378.
32. Topp, E. *Biol. Fertil. Soils* **2001**, *33*, 529–534.
33. Topp, E.; Martin-Laurent, F.; Hartmann, A.; Soulas, G. Bioremediation of atrazine-contaminated soil. In *Pesticide Decontamination and Detoxification*; Gan, J. J., Zhu, P. C., Aust, S. D., Lemley, A. T., Eds.; American Chemical Society: Washington, DC, 2004; Vol. 863, pp 141−154.
34. Wackett, L. P.; Sadowsky, M. J.; Martinez, B.; Shapir, N. *Appl. Microbiol. Biotechnol.* **2002**, *58*, 39–45.
35. Strong, L. C.; McTavish, H.; Sadowsky, M. J.; Wackett, L. P. *Environ. Microbiol.* **2000**, *2*, 91–98.
36. Wang, L.; Samac, D. A.; Shapir, N.; Wackett, L. P.; Vance, C. P.; Olszewski, N. E.; Sadowsky, M. J. *Plant Biotechnol. J.* **2005**, *3*, 475–486.
37. Scott, C.; Jackson, C. J.; Coppin, C. W.; Mourant, R. G.; Hilton, M. E.; Sutherland, T. D.; Russell, R. J.; Oakeshott, J. G. *Appl. Environ. Microbiol.* **2009**, *75*, 2184–2191.
38. Scott, C.; Lewis, S. E.; Milla, R.; Taylor, M. C.; Rodgers, A. J. W.; Dumsday, G.; Brodie, J. E.; Oakeshott, J. G.; Russel, R. J. *J. Environ. Manage.* **2010**, *91*, 2075–2078.
39. Heidari, R.; Devonshire, A. L.; Campbell, B. E.; Dorrian, S. J.; Oakeshott, J. G.; Russell, R. J. *Insect Biochem. Mol. Biol.* **2005**, *35*, 597–609.
40. Weston, D. P.; Jackson, C. J. *Environ. Sci. Technol.* **2009**, *43*, 5514–5520.
41. Lal, R.; Pandey, G.; Sharma, P.; Kumari, K.; Malhotra, S.; Pandey, R.; Raina, V.; Kohler, H. P. E.; Holliger, C.; Jackson, C.; Oakeshott, J. G. *Microbiol. Mol. Biol. Rev.* **2010**, *74*, 58–68.
42. Pandey, G.; Dorrian, S. J.; Russell, R. J.; Brearley, C.; Kotsonis, S.; Oakeshott, J. G. *Appl. Environ. Microbiol.* **2010**, *76*, 2940–2945.
43. Cheesman, M. J.; Horne, I.; Weir, K. M.; Pandey, G.; Williams, M. R.; Scott, C.; Russell, R. J.; Oakeshott, J. G. Carbamate Pesticides and Their Biological Degradation: Prospects for Enzymatic Bioremediation. In *Rational Environmental Management of Agrochemicals: Risk Assessment, Monitoring, and Remedial Action*; Kennedy, I. R., Ed.; 2007; Vol. 966, pp 288−305.

44. Naqvi, T.; Cheesman, M. J.; Williams, M. R.; Campbell, P. M.; Ahmed, S.; Russell, R. J.; Scott, C.; Oakeshott, J. G. *J. Biotechnol.* **2009**, *144*, 89–95.
45. Khurana, J. L.; Jackson, C. J.; Scott, C.; Pandey, G.; Horne, I.; Russell, R. J.; Herlt, A.; Easton, C. J.; Oakeshott, J. G. *Biochem. J.* **2009**, *418*, 431–441.
46. Kawahigashi, H.; Hirose, S.; Ohkawa, H.; Ohkawa, Y. *J. Mol. Microbiol. Biotechnol.* **2008**, *15*, 212–219.
47. Scott, J. G. *Insect Biochem. Mol. Biol.* **1999**, *29*, 757–777.
48. Chakraborty, S.; Behrens, M.; Herman, P. L.; Arendsen, A. F.; Hagen, W. R.; Carlson, D. L.; Wang, X. Z.; Weeks, D. P. *Arch. Biochem. Biophys.* **2005**, *437*, 20–28.
49. Sutherland, T. D.; Horne, I.; Russell, R. J.; Oakeshott, J. G. *Appl. Environ. Microbiol.* **2002**, *68*, 6237–6245.
50. Weir, K. M.; Sutherland, T. D.; Horne, I.; Russell, R. J.; Oakeshott, J. G. *Appl. Environ. Microbiol.* **2006**, *72*, 3524–3530.
51. Betancor, L.; Berne, C.; Luckarift, H. R.; Spain, J. C. *Chem. Commun.* **2006**, 3640–3642.
52. Berenguer-Murcia, A.; Fernandez-Lafuente, R. *Curr. Org. Chem.* **2010**, *14*, 1000–1021.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Chapter 12

Efficacy of a Vegetative Buffer for Reducing the Potential Runoff of the Insect Growth Regulator Novaluron

Robert Everich,[1,*] Andrew Newcombe,[2] Mary Nett,[3] and Janet Olinger[4]
[*]Corresponding Author: rce@manainc.com, (919) 276 9300

Novaluron, an insect growth regulator, is a broad spectrum insecticide used on vegetables, fruit, and field crops. There is a potential for runoff of the insecticide into bodies of water following applications to a target crop. The objectives of this study were to determine the effectiveness of a vegetative filter strip buffer in reducing the transport of novaluron and its chlorophenyl urea (CPU) metabolite into water, and to determine the edge of field concentration of novaluron. Using intense simulated rainfall in replicated non-buffered and buffered test plots, the presence of a common Bermuda grass buffer reduced the down-slope transport of novaluron and its CPU metabolite by approximately 65 percent following a rainfall event that occurred two days after the novaluron application.

Introduction

As part of the pesticide registration process, the United States Environmental Protection Agency (EPA) assesses whether exposure to residues resulting from the application of a pesticide results in acceptable risks to the environment. The assessment includes evaluating risks to aquatic and avian organisms and is typically based on the results of predictive modeling. If the modeling data demonstrate that it is necessary to mitigate the potential for a pesticide to impact an aquatic environment, restrictions can be added to the pesticide label. Restrictions may include, for example, lengthening the interval between applications, reducing the application rate, or adding setbacks between the edge of a treated field and water bodies (*1*). Restrictions may also include the requirement to establish a

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

well-maintained vegetative buffer when the treated field is located adjacent to a body of water.

Studies have shown that vegetative filter strips and vegetative buffers are effective in reducing the levels of herbicides, insecticides, and fungicides (*2*, *3*). The degree of vegetative buffer effectiveness varies depending on a number of factors such as the characteristics of the specific chemical (*4*), the intensity of rainfall (*4*), and the flow rate of the runoff water (*3*, *5*). The major physical mitigation process contributing to the reduction of transport within a vegetative filter strip or vegetative buffer is infiltration (*2*, *6–11*). The trapping of sediment by the vegetative buffer is also a major factor leading to retention (*8*, *12–15*). Additionally, the adsorption of the chemical onto the vegetation or organic matter within the vegetative buffer can lead to a reduction in the pesticide concentration (*5*, *8*, *12*, *15–18*).

An important factor regarding the exposure to a chemical in surface runoff from rainfall events is the percent of the chemical at the edge of the field that results from an application to a crop. Edge-of-field pesticide losses typically range from less than 1 percent to greater than 10 percent of the amount of pesticide applied (*4*, *19*, *20*). Studies have shown that a vegetative buffer reduces the concentration of applied material in runoff water. For example, the levels of two herbicides, fluometuron and norflurazuon in runoff water, were reduced from 12 and 5 percent of the applied amount without a filter strip to 5 and 3 percent of the applied amount, respectively, with a filter strip (*19*). In soybeans, the concentrations of the herbicides metolochlor and metribuzin in runoff water were reduced from 4 and 11 percent, to 0.5 and 1.2 percent, respectively, of the applied material by incorporating a vegetative filter strip (*20*).

The greatest potential for runoff is when a severe rainfall event occurs shortly after the pesticide application (*4*). Therefore, a study with a chemical applied at the maximum allowable application rate and a rainfall event occurring shortly after application would provide a worst case estimate of potential exposure via runoff water.

The objective of this study was to evaluate the efficacy of a vegetative buffer in reducing the potential flow of novaluron, an insecticide, and its metabolite chlorophenyl urea (CPU) into water bodies from a single field application of novaluron at the maximum allowable rate using simulated rainfall of known intensity and duration. To demonstrate a worst case scenario, two high-intensity rainfall events were simulated. The first rainfall event occurred approximately forty-eight hours (hr) after test substance application and the second event occurred four days later, or six days after application.

Novaluron is a pesticide used in the production of vegetables, fruit, and field crops. It is an insect growth regulator in the benzoylphenyl urea family, and acts at the pest larval stage by inhibiting chitin biosynthesis and blocking cuticle formation. The physical chemical properties of novaluron predict that it would be associated with the soil component of runoff, with a reported soil adsorption coefficient (K_{oc}) of 9598 (6680 to 11813 range), indicating that it is strongly adsorbed. Novaluron has very low water solubility, 3 µg liter^{-1}, and is lipophilic, with an octanol-water partition coefficient (log K_{ow}) of 4.3 (*21*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Experimental Methods

Test Site Design and Development

Site Delineation, Buffer Installation, and Crop Planting

The study was conducted on an approximately 1.6 hectare plot area with a slope of 2.5 to 3.0 percent that was located in a high-density cotton growing region of Washington County, Mississippi. The soil was classified by the Natural Research Conservation Service (NRCS) as Tunica, clay loam.

Two hydrologically similar replicate test plots of approximately 0.06 hectare each (49 meters long by 12 meters wide), Test Plot 1 and Test Plot 2, were defined within the study field based on a topographic survey and a visual inspection of the field and erosion patterns evident from previous rainfall events. The long dimension of each test plot extended down the natural slope of the field. A buffer width of approximately 6 meters was left between the replicate test areas to prevent inadvertent watering of the adjacent test plot during simulated rainfall events. An approximately 7.6 meter long vegetative buffer strip of common Bermuda grass sod was installed at the bottom of one half of each replicate test plot, resulting in creation of one 6 meter by 56 meter buffered subplot adjacent to one 6 meter by 49 meter non-buffered subplot (Figure 1). The top of the sod was flush with the soil surface and the grade was consistent with the overall slope of the cropped test field. The vegetative buffer strips were maintained by irrigation from a nurse tank (3,785 liter) available at the test site, treatment with maintenance chemicals, and mowing to ensure maximum biomass at the time of runoff generation. The buffered and non-buffered subplots were hydrologically isolated by metal flashing inserted into the soil to a depth of 8 to 10 centimeters prior to novaluron application (Figure 1).

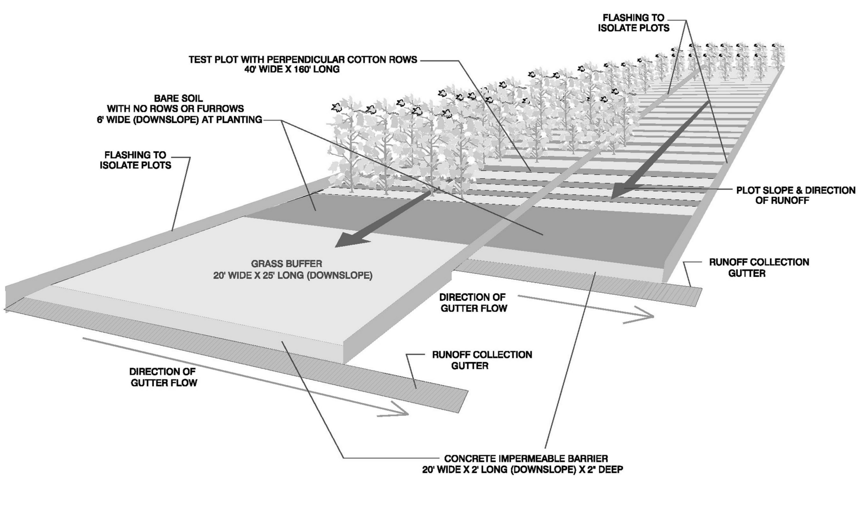


Figure 1. Replicate test plot layout and design.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

The test site was tilled and forty-eight rows of dryland cotton (variety DPL 117) were planted on the contour (approximately 91 cm row spacing, using a conventional four-row planter) of Test Plot 1 and Test Plot 2. The cotton subsequently received an injection of nitrogen fertilizer (112 kg per hectare). The cotton crop was irrigated as needed and treated with maintenance chemicals to control weeds and assist growth.

Runoff Collection Apparatus and Sample Collection Equipment

Runoff water was guided to the runoff sample collection equipment by an impermeable sloping concrete interface and galvanized steel gutter, with approximately 2 percent grade, at the ends of the buffered and non-buffered plots. The gutter guided runoff to a level fiberglass 60-degree trapezoidal flume in a bottom corner of each subplot. A custom-made steel flange sealed the gutter against the flume.

Isco® Model 730 Bubbler Module flow meters were installed at the bottom of each subplot to measure runoff flow at one-minute (min) intervals. Runoff water was withdrawn through Teflon®-lined tubing (9.5 mm inch inside diameter) from "splash pans" located directly below each flume using two calibrated Isco® Model 6712 samplers (C.C. Lynch & Associates, Inc.) Using this equipment, runoff water was collected on a flow-proportional and time-sequenced basis.

Rainfall Simulator

The rainfall simulator employed in this study was a bilateral system. Extensive modifications were made to prototypes designed by the United States Department of Agriculture (USDA) Agricultural Service and the University of Maryland (*22*, *23*). The rainfall simulator was designed to simulate intense natural rainfall with respect to droplet size distribution for a fixed period of time, at a uniform rate. Each replicate test plot (including buffer) was sequentially centered between two polyvinyl chloride (PVC) laterals (102-mm inner diameter) extending down the outer test plot perimeter. Irrigation risers were uniformly positioned in a staggered array approximately every 3.7 meters along the lateral lengths, and extended vertically to a height of 3 meters above the soil surface.

Each individual riser consisted of a 103 kilopascal pressure regulator and a Nelson S3000 part circle (190 degree) head (Nelson Irrigation Company, Walla Walla, Washington). Each head was fitted with a R3000 U-4 + 8 degree rotor plate and a model 25, 3TN nozzle to deliver a controlled simulated rain over both subplots within a given replicate test plot. Water for the simulated rainfall events was supplied by a 75,700 liter Frac® tank (Wade Services, Laurel, Mississippi) positioned at the top of the test site which was supplied with water from an adjacent irrigation well. To initiate a simulated rainfall event, water was pumped from the Frac® tank reservoir to the simulator through PVC aboveground pipe (102 mm) using a centrifugal pump capable of providing a constant pressure (approximately 276 kilo Pascal).

Soil Moisture Characterization and Regulation

Soil core samples (30 cm) were collected from the top, middle, and bottom of each plot for measurement of the soil antecedent moisture and bulk density. Because little rainfall occurred during the three-month period between planting and the week prior to the first simulated rainfall event, each of the replicate plots received approximately 76 mm of water over two days using the rainfall simulator three to four days before the test chemical application. This water input was sufficient to wet the soil (close to estimated field capacity) to enable a 30 to 60 min time to runoff during the study, but not to generate runoff immediately. During the same time period, a total of 41 mm of natural rainfall was also recorded by the manual rain gauge installed at the test site, resulting in a total delivery of approximately 117 mm of water to the test plots in the week immediately prior to the test chemical application. No on-site rainfall was recorded between novaluron application and conclusion of the second simulated rainfall event.

Runoff Sample Generation and Collection

Test Substance Application

A single application of novaluron formulated as Rimon® 0.83 EC (Makhteshim Agan North America, Inc., Raleigh, North Carolina) was made as a broadcast spray to the cotton prior to boll opening on both replicate test plots at the maximum label rate (363 g active ingredient hectare^{-1}) using a handheld boom and backpack spray apparatus. Runoff collection gutters, flumes, automated sampling equipment, and the grass buffers were covered with thick polyethylene sheeting during the test substance application to protect them from accidental contamination. At the time of test substance application, crop height ranged from 91 to124 cm; canopy coverage was estimated at 80 percent.

Generation of Simulated Rainfall

Test Plot 1 and Test Plot 2 were subjected (in sequence) to simulated rainstorms two and six days after test chemical treatment. Each plot received rainfall on the same day at the nominal rate of 25 mm per hr until a minimum of 90 min of runoff had been generated. The rainfall simulator was moved to the second replicate plot subsequent to completion of the runoff event in the first replicate plot. To determine the volume and uniformity of the simulated rainfall application, rainfall was collected in 20 wide-mouthed (114 mm diameter) calibrated cups positioned randomly within each replicate test plot (including buffer) area above the crop.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Runoff Sample Collection

Two types of samples, specifically time-sequenced and flow-proportional samples, were collected for measurement of novaluron, CPU, and total suspended solids (TSS) for the first rainfall event. Flow-proportional samples were not collected following the second simulated rainfall event. For the time-sequenced samples, one of the two Isco® Model 6712 electronic samplers positioned at the bottom of each non-buffered subplot and buffered subplot was programmed to withdraw 90 mL of runoff every three mins. Three consecutive aliquots were combined to provide a single analytical sample representing nine mins of flow. For flow proportional samples, aliquots of one liter per 0.2 cubic meters of flow were collected using a second Isco® Model 6712 pump sampler.

Grab samples to determine TSS were manually collected directly from the flume outflow into wide-mouthed one-liter glass jars on nine min intervals that coincided with the collection of the third 90-mL aliquot of each time-sequenced sample.

Analytical Procedures

The runoff samples were analyzed at PTRL-West Laboratories (Hercules, CA) for novaluron, CPU, and TSS. For novaluron and CPU, frozen runoff samples were brought to room temperature and the entrained sediment was allowed to settle for at least 1 hr. The water fraction was decanted from the residual soil and then partitioned with dichloromethane and sodium chloride. The sediment was extracted with methanol:water (1:1 by volume) followed by acetone:hexane (1:1 by volume). The methanol:water extract was combined with the remaining water fraction and partitioned again with dichloromethane. All acetone:hexane extracts and dichloromethane fractions were dried through sodium sulfate and combined to provide a total concentration of novaluron and CPU in the combined soil and water fractions. The organic solvent was concentrated to dryness and reconstituted in acetonitrile. The novaluron and CPU residues were determined by liquid chromatography/mass spectrometry/mass spectrometry (LC/MS-MS), observing two transitions for each analyte – the transitions of m/z ion 491 to 471 plus 491 to 305 for parent novaluron and m/z 351 to 308 plus 351 to 141 for CPU. The limit of quantitation (LOQ) of the analytical method was 0.1 μg $liter^{-1}$ and the limit of detection (LOD) was 0.004 μg $liter^{-1}$. The method was validated prior to sample analysis. Validation recoveries for novaluron and CPU were determined from samples containing up to 1.1 percent soil fortified with each analyte at 0.1 μg $liter^{-1}$ (LOQ) and 5X, 10X, 100X, 400X, and 1500X LOQ. The average overall novaluron recovery was 85 percent (n = 28) with 12 percent relative standard deviation (RSD). CPU average overall recovery was 96 percent (n = 28) with 8.4 percent RSD. The percent TSS residues were determined using standard methodology (*24*). In summary, each sample was thoroughly mixed before filtering through glass-fiber filter paper. The residue retained on the filter was then dried to a constant weight at a temperature of approximately 104°C. The increase in weight of the filter paper (of known weight) represented the TSS weight of a given sample.

Results and Discussion

Water and Sediment Transport

The percent of the applied rainfall determined in runoff water is shown in Table I. A mean of 51 percent (n = 4) and 67 percent (n = 4) of the applied rainfall was determined in the runoff for the first and second simulated rainfall events, respectively. The higher water yield from the second runoff event was likely due to the presence of established rills and visible sealing of the fine-textured soil surface following the initial simulated rainfall event. Some of the difference may be also attributed to higher antecedent moisture in Test Plot 2 at the top of the plot prior to both the first and second simulated rainfall events and in mid-plot for the first rainfall event. The antecedent moisture of both replicated Test Plots is shown in Table II.

Planting and tilling the crops on the contour was considered to have an impact on runoff during the initial simulated rainfall event. The wheel tracks and slightly depressed areas running alongside each seed furrow were oriented at a 90 degree angle to the fall line (the anticipated direction of flow). In effect, this resulted in the creation of multiple shallow reservoirs of rainwater behind each furrow as water was applied to the plots during the initial simulated rainfall event.

The percent of total sediment and TSS were obtained from two sources - triplicate samples collected during the homogeneous mixing of each flow-proportionally collected sample and from a calculation based on the measured flow volume and percent of TSS determined for the "grab" samples collected at 9 min intervals. The concentration of TSS in individual samples collected on a time-sequenced basis was less than 1 percent. The concentrations ranged from 0.23 to 0.96 g liter^{-1} and from 0.25 to 0.96 g liter^{-1} for the first and second simulated rainfall events, respectively. For the flow-proportional runoff samples collected during the first simulated rainfall event , the TSS concentrations from Test Plots 1 and 2 ranged from 0.27 to 0.75 g liter^{-1}. Thus, the results from the two different measurement approaches were in good agreement.

The total sediment yield from the buffered plots was reduced compared to the non-buffered plots following the first simulated rainfall event (Table III). The sediment yields in the buffered subplots were 57.3 and 34.3 percent less than the non-buffered subplots for Test Plots 1 and 2, respectively. For the second rainfall event, sediment data were only available for Test Plot 2 due to an instrument malfunction for Test Plot 1 and these results showed similar yields for both the buffered and non-buffered subplots. This decrease compared to the first rainfall event could be due to the soil sealing and development of erosion channels in Test Plot 2 that occurred after the first rainfall event.

Sediment load reduction with vegetative filter strips and buffers has been widely reported in the literature (*2*, *8*, *12–15*, *30*) and the sediment load reduction observed in this study is within the range reported. For example, there was a 62 percent sediment load reduction observed with thee use vegetative buffers (*15*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table I. Simulated rainfall application and runoff volumes

	Test Plot 1		*Test Plot 2*	
	Non-Buffered	*Buffered*	*Non-Buffered*	*Buffered*
Runoff event 1				
Total applied rainfall (L)	15,832	20,129	13,686	17,962
Total runoff (L)	8,471	8,327	6,923	10,409
Total runoff (%)	54	41	51	58
Runoff event 2				
Total applied rainfall (L)	15,187	19,675	13,457	16,353
Total runoff (L)	8,883	NA[a]	9,160	12,449
Total runoff (%)	58	NA[a]	68	76

[a] Flow data were not collected due to a malfunction of the electronic Isco® sampler

Table II. Antecedent soil moisture (0-2.5 cm)

Subplot type	*Rainfall event*	*Plot top (%)*	*Mid-Plot (%)*	*Plot bottom (%)*
Test Plot 1				
Buffered	1	9.3	16.4	20.6
Non-Buffered	1	13.5		18.5
Test Plot 2				
Buffered	1	16.3	24.6	19.9
Non-Buffered	1	11.1		20.7
Test Plot 1				
Buffered	2	10.6	20.5	21.5
Non-Buffered	2	12.9		21.3
Test Plot 2				
Buffered	2	14.9	22.3	25.0
Non-Buffered	2	12.7		22.2

Runoff Data, Chemical Transport, and Buffer Efficacy

The study was designed to provide data within a potentially "worst case" runoff scenario, utilizing the maximum application rate and intense simulated rainfall events generated shortly after the test chemical application. The rain patterns of 25 mm per hr, generating a minimum of 90 mins of runoff, with two

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

storms separated by four days, matched natural patterns of significant rainfall in the Mississippi test area (*25*).

The actual simulated rainfall output ranged from 22 to 24 mm per hr, and was in close agreement with the target of 25 mm per hr. Specifically, during the first rainfall event, 24 and 22 mm per hr were delivered to Test Plot 1 and Test Plot 2, respectively. For the second rainfall event, a rainfall intensity of 23 and 22 mm per hr, was delivered to Test Plots 1 and 2, respectively. The coefficients of variation ranged from 18 to 36 percent (n = 78) across the four simulated rainfall events, suggesting that simulated rainfall distribution was fairly uniform across the test plots. A visual inspection of each test plot soil surface during the simulated rainfall events confirmed thorough wetting of the entire soil surface within each subplot as well as the presence of rill networks. The simulated rainfall duration ranged from 91 to 101 mins, was in close with the target of 90 mins.

The results of the chemical transport are summarized in Table III. For the first runoff event, there was very good agreement between the flow-proportional and time-sequenced sampling (Table III) demonstrating the validity of the sampling approach. For the time-sequenced samples collected after the first runoff event, 2.1 to 4.3 percent of the applied novaluron was determined in runoff water from the non-buffered plot and 0.83 to 1.4 percent of the applied novaluron was determined in the buffered plots. The loss resulting in 2.1 to 4.3 percent of the amount applied (edge-of-field concentration) for the non-buffered plots are within the range reported for other agrochemicals (*19*, *20*, *26*). The amount of novaluron determined in the runoff from the second event decreased considerably in both the buffered and the non-buffered plots, with a maximum yield of 1.3 percent observed in the non-buffered subplot of Test Plot 1. However, the amount of CPU degradation product increased in the second event, from a maximum of 1.8 mg per subplot after the first runoff event to a maximum of 6.8 mg per subplot after the second runoff event.

The reduction in novaluron concentration in the buffered subplots compared to the non-buffered subplots ranged from 60.4 to 68.0 percent in the first runoff event and 47.6 percent in the second runoff event. The reduction of CPU residues in the buffered subplot ranged from 61.1 to 69.2 percent in the first runoff event, but the presence of the buffer did not reduce the CPU residues the second runoff event.

Although there were some differences in the quantities of novaluron in the runoff between Test Plots 1 and 2 for both the first and second runoff events, these differences were judged to have little impact on the ability to quantify and compare "field-scale" chemical losses. Differences in runoff yields between Test Plots 1 and 2 are likely due to minor spatial variations in soil texture, initial soil moisture, and differences in channel formation between the test plots following the first simulated rainfall event.

The level of buffer mitigation observed in this study is in line with other published data investigating the efficacy of vegetative buffers or vegetative filter strips. For example, a 44-50 percent reduction in atrazine was observed using a 9-m filter strip (*27*). Use of vegetative buffer strips was found to reduce the concentrations of glyphosate, propiconazole, and fenpropimorph by 39, 63, and 71 percent, respectively (*15*). Reductions of atrazine, metolachlor,

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

and chlorpyrifos were 52.5, 46.8, 54.4 percent and 48.1, 83.1 to 79.9 percent, respectively, were observed in studies conducted with multiple vegetated buffer strips (*28*). A review of studies examining nitrogen removal in riparian buffers concluded that the overall mean removal effectiveness was 67.5 percent ± 4.0, with results varying depending on a number of factors such as buffer width, soil type, and subsurface hydrology (*29*).

The decline in the mass of novaluron residues observed from both replicated test plots during the second simulated event is consistent with the behavior indicated by its physicochemical properties (low aqueous solubility, moderate Koc); and decline in the mass of available parent residue available for transport (due to removal in the first simulated rainfall event; field dissipation/degradation, and the hydrologic effects of a significant first rainfall event). Similarly, the increase in the levels of CPU in the runoff collected during the second simulated rainfall event can be directly related to greater availability due to degradation/metabolism of novaluron to CPU prior to the second rainfall event and to CPU's higher solubility (33 mg liter^{-1} compared to the novaluron water solubility of 3 μg liter^{-1}.)

Table III. Test chemical and sediment transport in runoff water and buffer mitigation

	Test Plot 1		*Test Plot 2*	
	Non-Buffered	*Buffered*	*Non-Buffered*	*Buffered*
Runoff event 1				
Sediment yield (kg)	5.34	2.28	5.63	3.70
Novaluron applied (g)	10.8	10.8	10.6	10.6
Novaluron yield (mg)				
Time sequenced	465.7	149.1	222.0	87.9
Flow proportional	400.7	139.1	242.3	104.9
Novaluron yield as % applied				
Time sequenced	4.3	1.4	2.1	0.83
Flow proportional	3.7	1.3	2.3	0.99
CPU yield (mg)				
Time sequenced	1.8	0.7	1.3	0.40
Flow proportional	1.7	0.8	1.5	1.1
Sediment reduction (%)		**57.3**		**34.3**
Novaluron mitigation (%)		**68.0**		**60.4**
CPU mitigation (%)		**61.1**		**69.2**

Continued on next page.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table III. (Continued). Test chemical and sediment transport in runoff water and buffer mitigation

	Test Plot 1		*Test Plot 2*	
	Non-Buffered	*Buffered*	*Non-Buffered*	*Buffered*
Runoff event 2				
Sediment yield (kg)	5.23	NA[a]	4.47	5.04
Novaluron yield, mg				
Time sequenced	137.8	NA[a]	94.7	49.6
Novaluron yield as % applied				
Time sequenced	1.3	NA[a]	0.90	0.47
CPU yield (mg)				
Time sequenced	6.8	NA[a]	6.0	6.8
Sediment reduction (%)		NA[a]		**-0-**
Novaluron mitigation (%)		NA[a]		**47.6**
CPU mitigation (%)		NA[a]		**-0-**
Cumulative yields				
Sediment yield (kg)	10.57	2.28[a]	10.10	8.74
Total novaluron (mg)	603.5	149.1[b]	316.7	137.5
Total CPU (mg)	8.6	0.7[b]	7.3	7.2
Total novaluron yield as % applied	5.6	1.4[b]	3.0	1.3

[a] Data were not collected due to a malfunction of the ISCO® sampler [b] Data reported are for runoff event 1 only

The data generated in this study demonstrated that the highest residue concentration in water from the non-buffered plots occurred near the beginning of the sampling profile, with a decrease in residue concentration throughout the remainder of the sample collection period. In the buffered plots, the novaluron runoff water concentrations were lower than those in the non-buffered plots at every sampling time and there was less variation in the concentrations with time when compared to the non-buffered plots. The greater consistency in the buffered plot sample concentrations is likely due to infiltration of novaluron and the sediment trapment in the grassed buffers.

Conclusion

The results of the study show that use of simulated rainfall applied to replicated cropped plots is an effective field study design to generate runoff to measure the efficacy of vegetative buffers. Rainfall simulator technology can generate intense rainfall under controlled conditions resulting in the generation of data to measure both water and sediment runoff. The data generated during the conduct of this study, provided more realistic information on the edge-of-field concentrations of novaluron, with a maximum of 4.3 percent of the applied material present at the field edge for the non-buffered plots and a maximum of 1.4 percent for the buffered plots. The study demonstrated the efficacy of a vegetative buffer in reducing the amount of both the applied chemical and sediment in the runoff, within approximately 65 and 50 percent novaluron reduction observed in the buffered subplots compared to the non-buffered subplots following the first and second simulated rainfall events, respectively. CPU concentrations were also reduced 65 percent following the first runoff event.

References

1. Risk Assessment Forum, Guidelines for Ecological Risk Assessment. *Fed. Regist.* **1998**, *93*, 26846.
2. Arora, K.; Mickelson, K. S.; Baker, J. L.; Tierney, D. P.; Peters, C. J. Herbicide retention by vegetative buffer strips from runoff under natural rainfall. *Trans. ASAE* **1996**, *39*, 2155–2162.
3. Wu, J.; Mersie, W.; Atalay, A.; Seybold, C. A. Copper retention from runoff by switchgrass and tall fescue filter strips. *J. Soil Water Conserv.* **2003**, *58*, 67.
4. Schulz, R. Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution. *J. Environ. Qual.* **2004**, *33*, 419.
5. Mersie, W.; Seybold, C. A.; McNamee, C.; Lawson, M. A. Abating endosulfan from runoff using vegetative filter strips: the importance of plant species and flow rate. *Agric., Ecosyst. Environ.* **2003**, *97*, 215.
6. Misra, A. K.; Baker, J. L.; Mickelson, S. K.; Shang, H. Contributing area and concentration effects on herbicide removal by vegetative buffer strips. *Trans. ASAE* **1996**, *39*, 2105.
7. Mickelson, S. K.; Baker, J. L.; Ahmed, S. I. Vegetative filter strips for reducing atrazine and sediment runoff transport. *J. Soil Water Conserv.* **2003**, *58*, 359.
8. Asmussen, L. E.; White, A. W.; Hauser, E. W.; Sheridan, J. M. Reduction of 2,4-D load in surface runoff down a grassed waterway. *J. Environ. Qual.* **1977**, *6*, 159.
9. Kloppel, H.; Kordal, W.; Stein, B. Herbicide transport by surface runoff and herbicide retention in a filter strip – rainfall and runoff simulation studies. *Chemosphere* **1997**, *35*, 129.
10. Zins, A. B.; Wyse, D. L.; Koskinen, W. C. Effect of alfalfa (*Medicago sativa*) roots on movement of atrazine and alachlor through soil. *Weed Sci.* **1991**, *39*, 262.

11. Schmitt, T. J.; Dosskey, M. G.; Hoagland, D. K. Filter strip performance and processes for different vegetation, widths, and contaminants. *J. Environ. Qual.* **1999**, *28*, 1479.
12. Popov, V. H.; Cornish, P. S.; Sun, H. Vegetated biofilters: the relative importance of infiltration and adsorption in reducing loads of water-soluble herbicides in agricultural runoff. *Agric., Ecosyst. Environ.* **2006**, *114*, 351.
13. Tingle, C. H.; Shaw, D. R.; Boyette, M.; Murphy, G. P. Metolachlor and metribuzin losses in runoff as affected by width of vegetative filter strips. *Weed Sci.* **1998**, *46*, 475.
14. Boyd, P. M.; Baker, J. L.; Mickelson, K.; Ahmed, S. Pesticide transport with surface runoff and subsurface drainage through a vegetative filter strip. *Trans. ASAE* **2003**, *46*, 675.
15. Syverson, N.; Bechman, M. Vegetative buffer zones as pesticide filters for simulated surface runoff. *Ecol. Eng.* **2004**, *22*, 175.
16. Krutz, L. J.; Senseman, S. A.; Dozier, M. C.; Hoffman, D. W.; Tierney, D. P. Infiltration and adsorption of dissolved atrazine and atrazine metabolites in buffalograss filter strips. *J. Environ. Qual.* **2003**, *32*, 2319.
17. Baker, J. L.; Mickelson, S. K. Application technology and best management practices for minimizing herbicide runoff. *Weed Science Society of America, Symposium, Denver CO* **1994**, *8*, 862.
18. Krutz, L. J.; Senseman, S. A.; McInnes, K. J.; Zuberer, D. A.; Tierney, D. P. Adsorption and desorption of atrazine, desethylatrazine, deisopropylatrazine, and hydroxyatrazine in vegetated filter strip and cultivated soil. *J. Agric. Food Chem.* **2003**, *51*, 7379.
19. Rankins, A.; Shaw, D. R.; Boyette, M. Perennial grass filter strips for reducing herbicide loses in runoff. *Weed Sci.* **2001**, *49*, 647.
20. Webster, E. P.; Shaw, D. R. Impact of vegetative filter strips on herbicide loss in runoff from soybean (Glycine max). *Weed Sci.* **1996**, *44*, 662.
21. PPDB: Pesticide Properties DataBase, University of Hertfordshire, 2011. http://sitem.herts.ac.uk/aeru/footprint/en/.
22. Meyer, L. D.; Harmon, W. D. Multiple intensity rain-fall simulator for erosion research on row side slopes. *Trans. ASAE* **1979**, *22*, 100.
23. Coody P. N.; Lawrence L. J. Method and system for collecting meso-scale rainfall simulations and collecting runoff. US Patent 5279151, 1994.
24. Eaton A. D.; Clesceri L. S.; Greenberg A. E. *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; American Public Health Association, Part 2540D, United States, 1995; pp 2−56.
25. US Department of Commerce, Weather Bureau, Technical Paper No. 40, Rainfall Frequency Atlas of the United States, 1963.
26. Reichenberger, S.; Bach, M.; Skitschak, A.; Frede, H. Mitigation strategies to reduce pesticide inputs into ground-and surface water and their effectiveness; a review. *Sci. Total Environ.* **2007**, *384*, 1.
27. Hoffman, D. W.; Gerik, T. J.; Richardson, C. W. Use of contour strip cropping as a best management practice to reduce atrazine contamination of surface water. *Proceedings of the Second International Conference IAWP Specialized Conference on Diffuse Pollution*, International Association on Water Quality, Brno and Prague, Czech Republic, 1995; pp 595−596.

28. Arora, K.; Mickelson, S. K.; Baker, J. L. Effectiveness of vegetated buffer strips in reducing pesticide transport in simulated runoff. *Trans. ASAE* **2003**, *46*, 635.
29. Mayer, P. M.; Reynolds, S. K.; McCutchen, M. D.; Canfield, T. J. Meta-analysis of nitrogen removal in riparian buffers. *J. Environ. Qual.* **2007**, *36*, 1172.
30. Daniels, R. B.; Gilliam, J. W. Sediment and chemical load reduction by grass and riparian filters. *Soil Sci. Soc. Am. J.* **1996**, *60*, 246.

Chapter 13

Application Methods in Orchards To Reduce Off-Site Deposition of Pesticides

Robert C. Ehn,[*,1] Dennis M. Dunbar,[1] and Tim Ksander[2]

[1]R3 Ag Consulting, LLC, 1629 Pollasky, Suite 111, Clovis, CA
[2]Ag Advisors, Inc., 1695 Greenwood Way, Yuba City, CA 95993
[*]robertehn@sbcglobal.net

Two experiments were conducted during January and February 2006 in a dormant prune orchard near Live Oak, California, to evaluate off-site movement of Diazinon AG 500 Insecticide sprays using inward only spraying compared to spraying in two directions (inward and outward). Diazinon AG 500 Insecticide was applied at the labeled rate of 4.7 liters/ha. Applications were made on 25 January 2006, under a south wind blowing at 4.8 – 9.6 km/hr and on 3 February 2006, with southwest wind at 3.2 – 6.4 km/hr.

Versi-Dry Lab Soakers (Kimbies) were used to collect the diazinon spray particles within the orchard and outside the orchard. Within the orchard, Kimbies were hung vertically in trees as well as placed horizontally under trees of the first tree row adjacent to the open field sampling area. Outside the orchard, Kimbies were placed horizontally on the ground at 7.6, 15.2, 30.5, 91.4, and 182.9 meters perpendicular to the first tree row. Samples were collected about 20 minutes after the applications in each experiment.

There was 71.2% (Experiment 1) and 92.5 % (Experiment 2) less diazinon spray collected at all sampling stations from the inward only spray treatment compared to the two directional spraying. These results clearly show that inward only spraying of the outside three tree rows reduces the potential amount of total diazinon spray available (average of 81.9% from both experiments) for off-site movement when compared to the standard two-directional spraying.

The amount of the total diazinon spray that moved off-site, however, for both the inward only and inward and outward spray treatments occurred in similar proportions. Considering both experiments, 25.6 to 28.7% of the total diazinon spray collected from the inward only and inward and outward treatments was collected off-site or outside the orchard. For both treatments, 99% of that spray that moved off-site was collected within 30.5 meters from the orchard. For the inward only treatment, the equivalent of 0.25 $\mu g/dm^2$ was collected at 91.4 meters and 0.07 $\mu g/dm^2$ was collected at 182.9 meters. For the inward and outward treatment, the equivalent of 3.4 $\mu g/dm^2$ was collected at 91.4 meters and 0.8 $\mu g/dm^2$ was collected at 182.9 meters. Far less diazinon spray was collected off-site at 91.4 meters and 182.9 meters from the inward only spray treatment when compared to the two-directional spray treatment. Spraying the last three rows of an orchard using inward only spraying results in >80% reduction in diazinon spray that potentially could move off-site.

Introduction

Spray drift from orchards that are dormant and sprayed with organophosphate (OP) pesticides is considered to be one means for pesticide movement off-site and a potential source for contaminating surface waters. In a typical orchard spraying situation, air-blast sprayers are towed between rows of trees and spray is directed in two directions. When the sprayer approaches the edge rows of the orchard (those rows adjacent to the end of the planted orchard), drift can sometimes be observed to "overspray" the trees and drift past the edge of the orchard. Because the spray plume from air-blast sprayers is often very visible, the perception exists that there is a high level of drift from most orchard air-blast sprayer applications.

The objective of this orchard air-blast sprayer study utilizing inward only spraying compared to conventional two-directional spraying is to quantify off-target movement from orchards sprayed during the dormant period with an OP pesticide. This study is designed to test the Best Management Practice as outlined in the Supplemental Label for Diazinon AG 500 Insecticide (EPA Reg. No. 66222-9) from Makhteshim-Agan of North America. The Supplemental Label for Diazinon AG 500 has directions to mitigate off-target movement of sprays such as:

> Do not apply within 30.5 meters upslope of sensitive aquatic sites such as any irrigation ditch, drainage canal or body of water that may drain into a river or tributary unless a suitable method is used to contain or divert runoff waters.

> Apply only when wind speed is 4.8 – 16 km/hr at the application site as measured by an anemometer outside of the orchard on the side nearest and upwind from a sensitive site.
>
> When sensitive aquatic sites are downwind from orchards, spray the first three rows nearest the sensitive aquatic sites only when the wind is blowing away from the sites. The row at the edge of the field next to sensitive aquatic sites must be sprayed with the outside nozzles turned off. Spray must not be directed higher than the tree canopy and spray must be directed away from sensitive aquatic sites.

In this study, off-site spray drift was measured after the first three tree rows on the edge of a commercial prune orchard were sprayed with nozzles operating in two directions (inward and outward) compared to when the spray was directed inward only (outside nozzles were shut-off). An open area downwind to the edge row of trees was designated as the sensitive aquatic site and used for sample collection.

Methods and Materials

Prior to study initiation, the protocol for this study was submitted for review by the California Department of Pesticide Regulation.

Orchard

Two experiments were conducted about one week apart in a mature French prune orchard that was dormant near Live Oak, CA. The orchard was at Lomo Station about 8 km north of Yuba City on State Highway 99.

Trees were 3.7 to 4.6 meters tall and approximately 14 years old. Tree spacing was 6.1 x 6.1 meters in a square configuration with the tree rows running east to west. The sample stations were north of the treated rows perpendicular to the direction of the tree rows.

Diazinon AG 500 Insecticide was applied one time in each experiment at a rate of 4.7 liters/ha (1.12 kg/ha). An OMC air-blast orchard sprayer pulled by a John Deere 1010 tractor was used in each experiment. The OMC sprayer had 10 Teejet nozzles per side configured with 3,4,4,5,5,4,4,3,3,3 disks and 25 cores. (Note: Airblast sprayers use a combination of disc and swirl sizes to determining the output of the sprayer. Different combinations produce droplets of varying size. The higher the disc number, the greater the spray output) The sprayer was pulled at a speed of 3.2 km/hr with 120 psi delivering 935.3 liters of finished spray per hectare. Droplet sizes ranged from fine to coarse with most in the medium range.

Experiment 1

The application was made on 25 January, 2006 at approximately 2:00 pm PST. The inward only treatment was applied first followed immediately by spraying in both directions (inward and outward). The two treatments were separated by

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

about 219.5 meters with the inward only plot located on the west side of the prune orchard. At the time of spraying, there was a 4.8 – 9.6 km/hr south wind with an air temperature of 11.7º C. A diagram of the orchard, direction of spraying and sampling stations is provided in Figure 1.

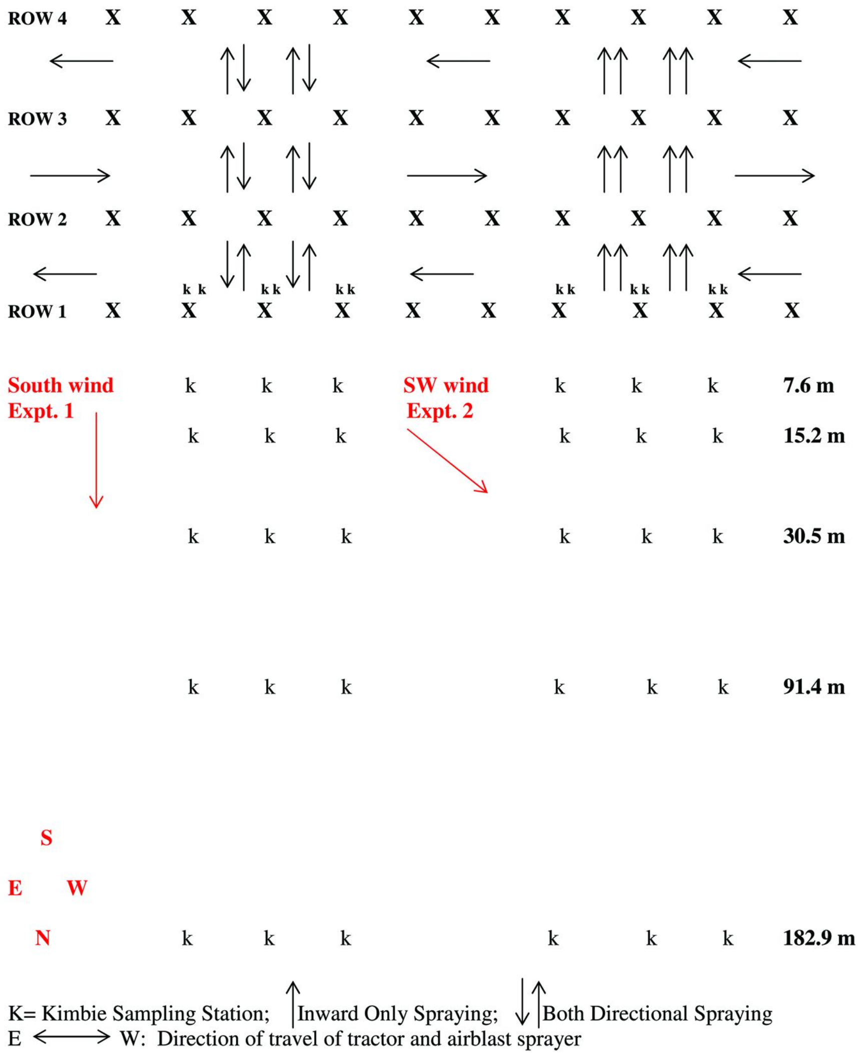


Figure 1. View of Test Site Orchard – Aerial View

Experiment 2

This experiment was conducted in the same mature French prune orchard as Experiment 1, however on trees in the same rows, but about 18.3 meters further down in the orchard than in Experiment 1. The application was made on 3 February 2006 at approximately 10:00 am PST. The inward and outward treatment was applied first, followed by the inward only treatment. Wind speed was 3.2 – 6.4 km/hr from the southwest with an air temperature of 9.4º C.

Sampling

As specified in the protocol, prior to each application, the Versi-Dry Lab Soakers (Kimbies) were placed in an open field at the pre-determined distances of 0, 7.6, 15.2, 30.5, 91.4 and 182.9 meters downwind of the application. Each Kimbie was 50.8 cm x 46.4 cm (2,357 cm^2) in size and laid out horizontally on the ground on a piece of hard plastic (Figure 2). The Kimbies were held onto the plastic with paper clips. The hard plastic pieces were held in place with garden pins.

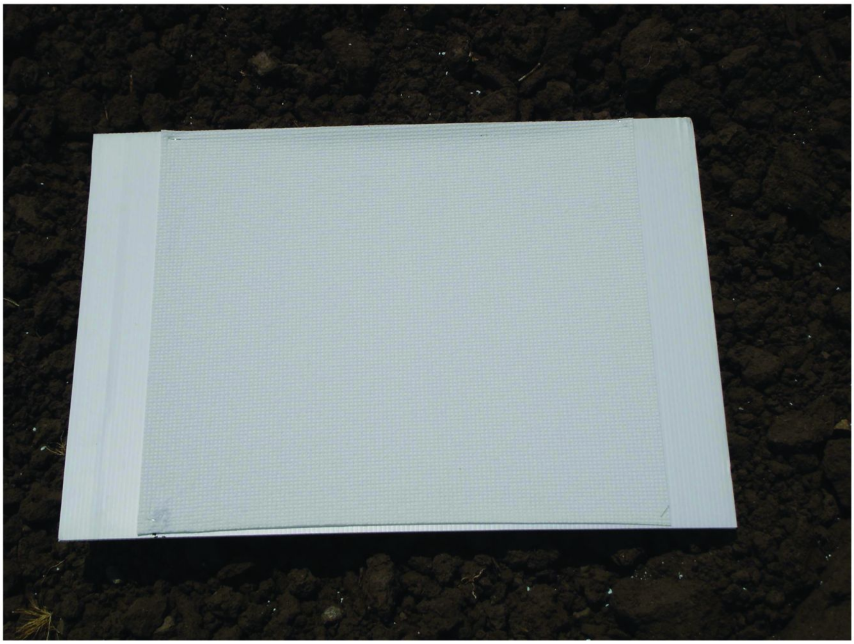


Figure 2. Sampling Sheet (Kimbie) on Hard Plastic Laid Horizontal on Ground

In-tree sampling was accomplished by hanging two Kimbies in each of three trees in each treatment. The Kimbies were 20 cm x 30 cm (600 cm^2) in size and wrapped around a hard surface (PVC pipe) (Figure 3). In each tree, one Kimbie was hung in the upper 1/3 of the canopy and the second Kimbie was hung in the same tree in the lower 1/3 of the canopy.

Figure 3. Sampling Sheet (Kimbie) Wrapped Around PVC Pipe and Suspended in Tree

Approximately 20 minutes after completion of the applications for each experiment, the Kimbies were picked up and placed into pre-labeled Zip-Lock bags. Each Kimbie was folded inward to prevent chemical treated surfaces from contacting the Zip-Lock bags. These samples were placed into coolers with Blue Ice and then transferred to a freezer, where they were held until delivery to the analytical laboratory. Samples from Experiment 1 were transferred to the laboratory on 31 January, 2006 whereas samples from Experiment 2 were transferred to the laboratory on 7 February, 2006. Samples were kept frozen with dry ice during transport to the laboratory.

Analytical

Samples were analyzed by Environmental Micro Analysis, Inc. (E.M.A.) in Woodland, CA. E.M.A. Inc. used EPA Method 8141 for analysis of the samples and detection of diazinon. Each Kimbie sample was cut into small pieces to fit into a wide mouth jar where 500 mls of petroleum ether/ methyl t. butyl ether at 1:1 were added to cover the sample. The jar was shaken and a vial of the solution was loaded for GC analysis. Sample results are reported by the laboratory as micrograms diazinon per Kimbie (µg/Kimbie). Kimbies from Experiment 1 were extracted on 2 and 8 February, 2006 and analyzed on 9 and 10 February, 2006. Kimbies from Experiment 2 were extracted on 15 February, 2006 and analyzed on 11 and 14 March, 2006.

Results

Raw data obtained from E.M.A. Labs for Experiments 1 and 2 are summarized in Tables 1 and 2, respectively. There were three replicates for each sampling station in each experiment. All replicate data along with means and standard deviation of the mean are provided in the tables. Under tree for A and B data have been combined in this table to represent one "under tree" value for statistical purposes.

As reported above, the Kimbies hung in the trees had less surface area than the Kimbies laid out horizontally on the ground. Therefore, the raw data were converted from micrograms per Kimbie (µg/Kimbie) to micrograms per square decimeter (µg/dm^2) in order to present the data from all sample stations in the same units. A square decimeter (dm^2) is equal to 100 square centimeters (100 cm^2) and was a convenient conversion for data from these experiments. Results converted to µg/dm^2 are shown graphically in Figures 4 and 5.

In Experiment 1, there was a 4.8 – 9.6 km/hr south wind that blew out over the orchard and sampling area. This provided an excellent opportunity to collect in-orchard and off-site movement of the diazinon spray. Using mean collections from each sampling station, the total diazinon spray collected from all sampling stations was 581.9 µg/dm^2 in the inward only treatment and 2,019.9 µg/dm^2 in the inward and outward spray treatment. This represents 3.5 times less diazinon spray deposit collected from the inward only spray treatment than the inward and outward spray treatment. With the exception of the 15.2 and 30.5 meter collection stations, there was significantly more diazinon collected at each sampling station in the inward and outward spray treatment than in the inward only spray treatment.

In Experiment 2, there was only a 3.2 – 6.4 km/hr wind and it was blowing from the southwest. This blew spray deposit out over the sampling area at an angle and not exactly perpendicular to the sampling stations as in Experiment 1. Using the mean total diazinon spray collected per station as demonstrated above for Experiment 1, there was far less diazinon collected from the sampling stations in each treatment than in Experiment 1. The results, however, were similar to Experiment 1 in that far more diazinon spray (13 times) was collected from the inward and outward spray treatment (998.4 µg/dm^2) compared to the inward only spray treatment (75.1 µg/dm^2). There was a significant difference between diazinon spray deposits collected at each sampling station through 30.5 meters. Collections of diazinon spray at stations located at 91.4 and 182.9 meters were not significantly different.

Table 1. Converted Data – Off-Site Movement of Diazinon Spray from an Application Made to Dormant Prune Trees Utilizing Inward Only Spraying Compared to Spraying in Two Directions (Inward and Outward) (Experimnet 1: Live Oak, CA 2006)[1– 5]

	Rep. 1	Rep. 2	Rep. 3	Mean		Rep. 1	Rep. 2	Rep. 3	Mean	LSD
Inward Only (I)	µg/ dm^2	µg/ dm^2	µg/ dm^2	µg/ dm^2	**Both Directions (B)**	µg/ dm^2	µg/ dm^2	µg/ dm^2	µg/ dm^2	
Tree Top	65.2	80.5	88.0	**77.9 b**	**Tree Top**	558.3	388.3	611.7	**519.4 a**	290.2
Tree Bottom	104.5	82.7	380.0	**189.1 b**	**Tree Bottom**	541.7	578.3	865.0	**661.7 a**	77.3
Under Tree-A	180.7	251.2	162.9		**Under Tree-A**	381.8	470.9	500.6		
B	160.8	228.7	148.9	**188.9 b**	**B**	521.8	396.7	441.2	**452.2 a**	79.1
7.6 m	56.4	70.9	66.2	**64.5 b**	**7.6 m**	401.8	287.7	263.5	**317.7 a**	199.9
15.2 m	41.7	49.6	47.5	**46.3 a**	**15.2 m**	53.0	81.9	13.9	**49.6 a**	83.6
30.5 m	13.8	16.0	15.2	**15.0 a**	**30.5 m**	20.0	19.3	6.6	**15.3 a**	19.5
91.4 m	0.2	0.3	0.1	**0.2 b**	**91.4 m**	2.6	2.9	3.1	**2.9 a**	0.8
182.9 m	0.06	0.04	0.02	**0.04 b**	**182.9 m**	1.2	1.0	1.0	**1.1 a**	0.3
Total				**581.9**	**Total**				**2,019.9**	

1. **Date Treated & Sampled:** **1/25/06**
2. **Date Extracted:** **2/2/06 and 2/8/06**
3. **Date Analyzed:** **2/9/06 and 2/10/06**
4. **Units:** **Micrograms/dm^2 (Square decimeter = 100 cm^2) - Kimbies hanging in trees were 20 x 30 cm (600 cm^2); Kimbies on the ground were 50.8 x 46.4 cm (2357 cm^2)**
5. **Statistics:** **Means within a row with the same letter are not statistically different (ANOVA: p=0.05; mean separation by Student-Newman-Keuls Test)**

Note: Tree A and tree B data were combined for statistical analysis purposes.

Table 2. Converted Data – Off-Site Movement of Diazinon Spray from an Application Made to Dormant Prune Trees Utilizing Inward Only Spraying Compared to Spraying in Two Directions (Inward and Outward) (Experiment 2: Live Oak, CA 2006)[1–5]

	Rep. 1	Rep. 2	Rep. 3	Mean		Rep. 1	Rep. 2	Rep. 3	Mean	LSD
Inward Only (I)	µg/ dm^2	µg/ dm^2	µg/ dm^2	µg/ dm^2	**Both Directions (B)**	µg/ dm^2	µg/ dm^2	µg/ dm^2	µg/ dm^2	
Tree Top	11.7	14.6	31.3	**19.2 b**	**Tree Top**	193.3	213.3	256.7	**221.1 a**	54.8
Tree Bottom	4.8	7.6	11.5	**8.0 b**	**Tree Bottom**	115.8	245.0	256.7	**205.8 a**	187.1
Under Tree-A	5.8	23.2	39.7		**Under Tree-A**	191.3	178.3	170.6		
B	4.9	16.0	65.3	**25.8 b**	**B**	203.2	141.7	253.7	**189.8 a**	31.9
7.6 m	4.4	8.4	18.2	**10.3 b**	**7.6 m**	200.3	223.2	157.8	**193.8 a**	97.2
15.2 m	2.1	7.4	12.3	**7.3 b**	**15.2 m**	95.9	159.9	101.0	**118.9 a**	88.1
30.5 m	1.7	5.1	5.5	**4.1 b**	**30.5 m**	25.9	62.4	106.3	**64.8 a**	95.4
91.4 m	0.2	0.3	0.4	**0.3 a**	**91.4 m**	4.6	5.0	1.9	**3.8 a**	4.4
182.9 m	0.04	0.1	0.09	**0.1 a**	**182.9 m**	0.8	0.2	0.1	**0.4 a**	1.0
Total				**75.1**	**Total**				**998.4**	

1. **Date Treated & Sampled:** **2/3/06**
2. **Date Extracted:** **2/15/06**
3. **Date Analyzed:** **3/11/06 and 3/14/06**
4. **Units:** **Micrograms/dm^2 (Square decimeter = 100 cm^2) -kimbies hanging in trees were 20 x 30 cm (600 cm^2); kimbies on the ground were 50.8 x 46.4 cm (2357 cm^2)**
5. **Statistics:** **Means within a row with the same letter are not statistically different (ANOVA: p=0.05; mean separation by Student-Newman-Keuls Test)**

Note: Tree A and tree B data were combined for statistical analysis purposes.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

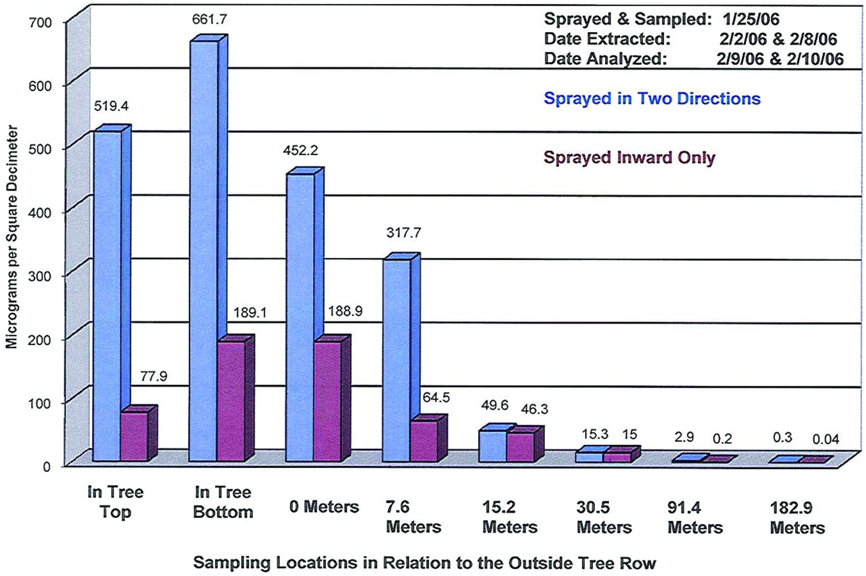


Figure 4. Off-Site Movement of Diazinon Spray From an Application Made to Dormant Prune Trees Utilizing Inward Only Spraying Compared to Spraying in Two Directions (Inward and Outward) (Experiment 1: Live Oak, CA 2006)

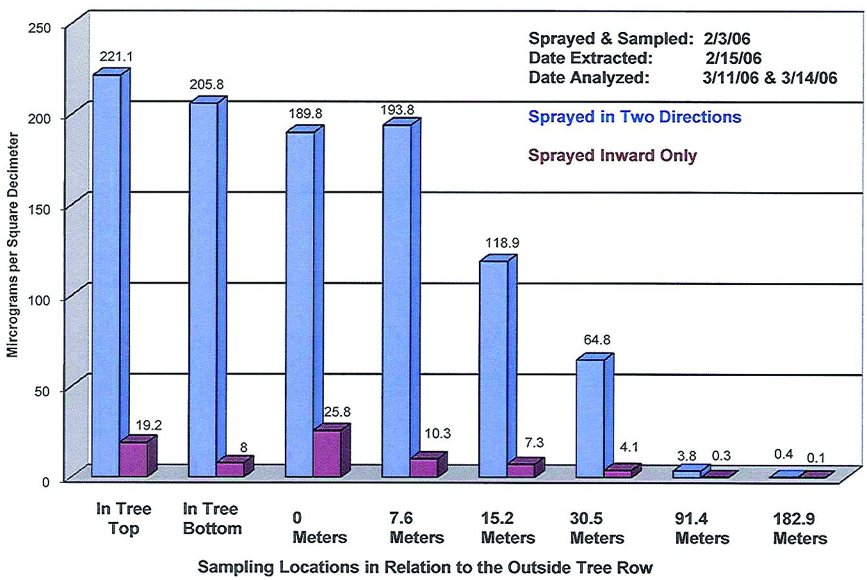


Figure 5. Off-Site Movement of Diazinon Spray From an Application Made to Dormant Prune Trees Utilizing Inward Only Spraying Compared to Spraying in Two Directions (Inward and Outward) (Experiment 2: Live Oak, CA 2006)

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

The fact that less spray deposit was collected in Experiment 2 than Experiment 1 was likely a direct result of less wind and the fact that the wind was blowing to the southwest which may have taken some spray off the direct line of the sampling stations.

As shown in Figure 6, the total diazinon spray deposit collected from the inward only spray treatment was reduced dramatically when compared to the inward and outward spray treatment (71.2% reduction in Experiment 1 and 92.5% reduction in Experiment 2). These results clearly show that spraying the last three rows of an orchard using inward only spraying as described in the BMP for Diazinon AG 500 Insecticide results in far less spray that could potentially drift off-site from an application to trees during the dormant period. This was demonstrated in both experiments.

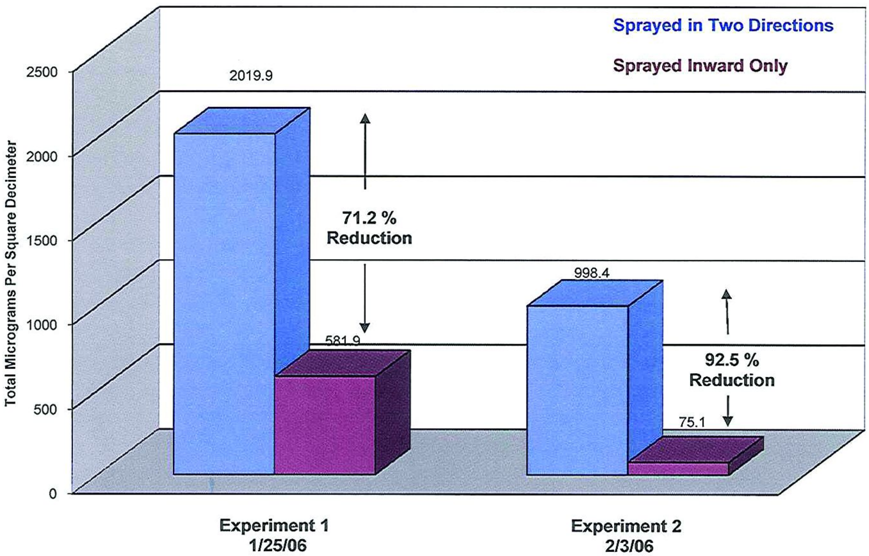


Figure 6. Off-Site Movement of Diazinon Spray From an Application Made to Dormant Prune Trees Utilizing Inward Only Spraying Compared to Spraying in Two Directions (Inward and Outward) (Experiments 1 and 2: Live Oak, CA 2006)

In terms of where the diazinon spray deposits were collected, the majority of the spray collected from both experiments was in the orchard itself (tree top, tree bottom, and under the trees). For the inward only spray treatments, 78.3 and 70.6% of the total diazinon spray collected from Experiment 1 and Experiment 2, respectively, came from sampling stations within the orchard. For the inward and outward spray treatment, 80.9 and 61.7% of the total diazinon spray collected from Experiment 1 and Experiment 2, respectively, came from sampling stations within the orchard.

The percentage of total spray collected outside the orchard (off-site) was similar for the inward only treatment (mean 25.6% for both experiments) and

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

inward and outward treatment (mean 28.7% for both experiments). The key difference, however, is that there was far less spray moving off-site from the inward only treatment when compared to the inward and outward spray treatment (42 µg/dm^2 vs. 384.2 µg/dm^2).

Considering that 25-29% of the total diazinon spray collected from both treatments was outside the orchard (off-site), where was it collected? As shown in Figure 7, over 80% of the spray deposit that moved off-site was collected within 15.2 meters of the orchard for both treatments and 99% was collected within 30.5 meters. Very small amounts were collected at 91.4 and 182.9 meters off-site. For the inward only treatment, the equivalent of 0.25 µg/dm^2 was collected at 91.4 meters and 0.07 µg/dm^2 was collected at 182.9 meters. For the inward and outward treatment, the equivalent of 3.4 µg/dm^2 was collected at 91.4 meters and 0.8 µg/dm^2 was collected at 182.9 meters.

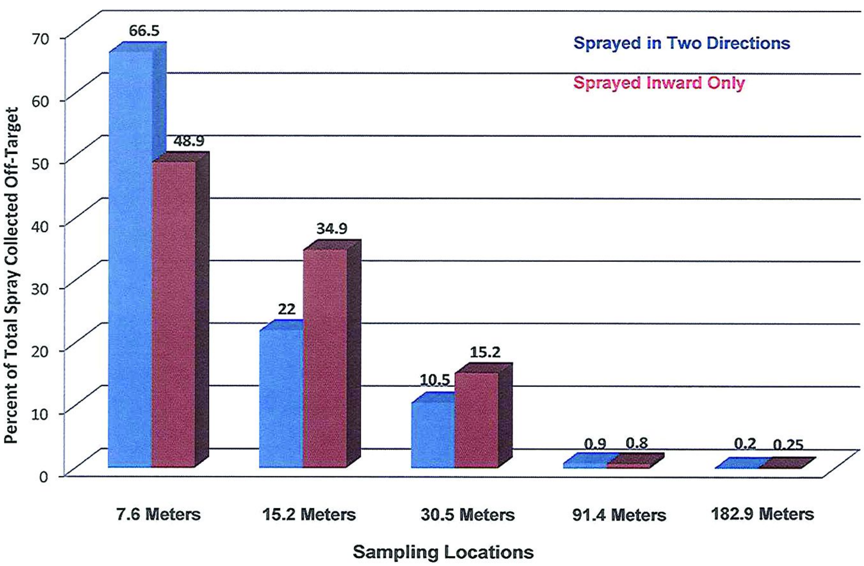


Figure 7. Off-Site Movement of Diazinon Spray After an Application Made to Dormant Prune Trees Utilizing Inward Only Spraying Compared to Spraying in Two Directions (Inward and Outward) (Experiments 1 and 2: Live Oak, CA 2006)

Conclusions

Spraying the outside three rows of a dormant prune orchard with sprays directed only inward resulted in 81.9% less diazinon spray collected at all sampling stations compared to the two directional spray (inward and outward) spray treatment. The percentage of the diazinon spray collected outside the orchard (mean of both experiments) was similar for the inward only (25.6%) and inward and outward (28.7%) spray treatments. However, the total amount of

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

spray collected in micrograms per square decimeter was significantly less in the inward only program versus the inward/outward trial. For each treatment, 99% of the diazinon spray that moved off-site was collected within 30.5 meters of the outside tree row. The results of this study support the BMP for Diazinon AG 500 Insecticide and show that off-site movement of spray can be reduced dramatically by utilizing inward only spraying of the last three orchard tree rows. The results of this study suggest that the use of inward only spray practices near sensitive areas where buffer zones less than 30.5 meters are in place significantly reduces the amount of pesticide deposited within the buffer zone. The benefit of inward only applications increases for products with reduced buffer zones.

Further, the BMP states that the first three rows nearest a sensitive aquatic area should be sprayed inward only when the wind is blowing away from the sensitive area. In these experiments, the spray was blowing toward the sensitive area (sampling stations) in order to measure a “worst case” scenario for each treatment. If the BMP had been followed and the wind had been blowing away from the sampling stations, even less spray would have been collected from each treatment, providing even further support for the BMP for Diazinon AG 500 Insecticide.

Inward only applications also provide a benefit to reduce surface runoff of pesticides as the transport mechanisms to surface water are a combination of drift and surface water runoff. This is especially important during the dormant spray season when storm water runoff is most problematic. Any application BMP that reduces total load on soil surface will also reduce amount of pesticide available to storm water or irrigation runoff.

Chapter 14

Modeling Approaches for Pesticide Exposure Assessment in Rice Paddies

Yuzhou Luo,[1,*] W. Martin Williams,[2] Dirk F. Young,[3] Hirozumi Watanabe,[4] Julien Boulange,[4] Amy M. Ritter,[2] and Thai Khanh Phong[5]

[1]Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA 95812, USA
[2]Waterborne Environmental, Inc., Leesburg, VA 20175, USA
[3]Office of Pesticides, US Environmental Protection Agency, Washington, DC 20460, USA
[4]Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan
[5]National Research Center for Environmental Toxicology, the University of Queensland, Brisbane QLD 4108, Australia
[*]yluo@cdpr.ca.gov

Pesticide use in paddy rice production may contribute to adverse ecological effects in surface waters. Risk assessments conducted for regulatory purposes depend on the use of simulation models to determine predicted environment concentrations (PEC) of pesticides. Often tiered approaches are used, in which assessments at lower tiers are based on relatively simple models with conservative scenarios, while those at higher tiers have more realistic representations of physical and biochemical processes. This chapter reviews models commonly used for predicting the environmental fate of pesticides in rice paddies. Theoretical considerations, unique features, and applications are discussed. This review is expected to provide information to guide model selection for pesticide registration, regulation, and mitigation in rice production areas.

Introduction

Rice, one of the world's most important crops, is commonly produced in paddies that are flooded soon after planting. Pesticides are usually applied directly onto paddy water. Residues may be released to downstream waters via controlled drainage and overflow, or to groundwater via leaching. Reported pesticide losses from rice paddies range from a few to 60% of applied amounts (*1*, *2*). Rice pesticides have been often detected in river systems adjacent to rice cultivated regions worldwide (*3–6*). Herbicides constitute the major group of active ingredients detected.

Threshold concentrations or water quality standards are commonly established for drained water from rice paddies and in downstream receiving waters. For example, the State of California (USA) set performance goals for major pesticides used in rice production, not to be exceeded in agricultural drains and in drinking water sources (*7*). Management practices designed to meet the water quality standards include use restrictions for certain areas and seasons, water-holding requirements, excess water storage, recirculation systems, drift control, improved irrigation, and seepage prevention (*8–10*).

As is the case with other crops, mathematical models are used to evaluate fate and transport of pesticides applied to rice paddies. Models provide PECs of pesticides that are used to assess potential exposures and human and ecological risks. Computed PECs also provide guidance in selection and evaluation of mitigation measures. Tiered modeling approaches are generally accepted for risk and exposure assessments in rice paddies in the U.S., Japan, and Europe (*11–13*). Assessments at lower tiers are based on relatively simple models with conservative scenarios, while those at higher tiers may have more realistic (and therefore more complex) representation of physical and biochemical processes.

This chapter provides an overview of modeling approaches and describes representative models used to assess water quality impacts of pesticide use in paddy rice production.

Environmental Modeling for Rice Pesticides

Environmental Characterization of Rice Paddies

Schematically, a rice paddy consists of paddy water (with sub-compartments of bulk water, suspended solids, DOC, etc.), sediment (pore water and sediment particles), and rice plants (Figure 1). Within this system pesticides undergo processes of interfacial and convective transport, partitioning between phases, and degradation. Paddy water depth is determined by precipitation, evapotranspiration, infiltration, irrigation, drainage and other water management activities. The sediment compartment consists of that part of the sediment which is in active exchange with overlying paddy water. Rice plants are simulated mainly to estimate canopy coverage of the paddy water surface, which is a key determinant for determining canopy interception of applied pesticides and shading effects for aqueous photolysis. Some models also account for plant uptake of pesticides and interactions with the lower layer of troposphere (*14*, *15*).

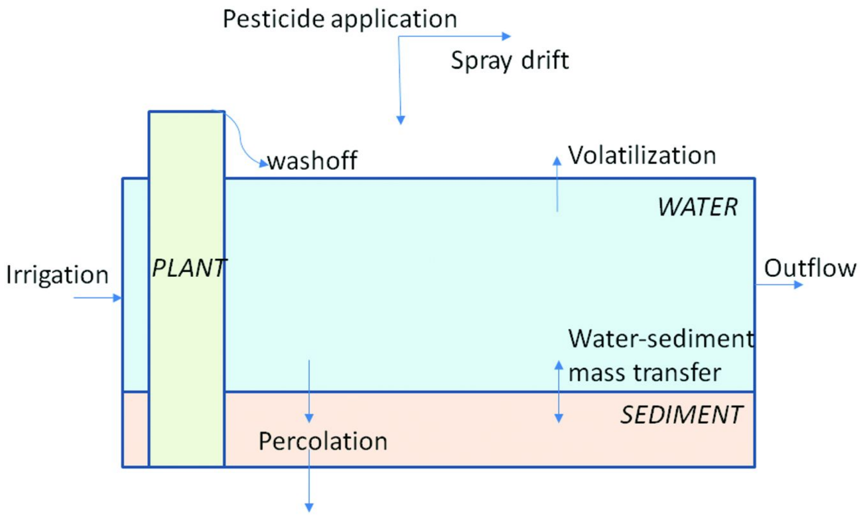


Figure 1. Environmental description and primary processes of pesticide transport in a rice paddy

Lower-Tier Models Overview

Lower-tier models provide rapid PEC evaluations. Those models are generally based on the assumption of instantaneous chemical equilibrium controlling pesticide distribution between paddy water and sediment. Under this assumption, pesticide concentrations and masses in water and in sediment are related directly by simple partition coefficients. Individual mass exchange processes between water and sediment, such as settling, resuspension, and diffusion, are not considered in simulations. In addition, pesticide dissipation processes are generally represented as first-order in concentration or mass with invariant rate constants during the simulation period. Similarly, fixed water flows and weather conditions are used in dynamic simulations. Core equations include:

[1] Initial mass balance:

$$M_T = M_W(0) + M_S(0) \tag{1}$$

where M_T (kg) is the effective amount of pesticide application into the rice paddy. M (kg) is pesticide mass with subscripts W and S for compartments of water and sediment, respectively.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

[2] Chemical partitioning between water and sediment:

$$C_S(t) = K_d \cdot C_W(t), \text{or}$$
$$M_S(t) = K_2 \cdot M_W(t) \tag{2}$$

where C is the pesticide concentration (kg m^{-3} in water and kg kg^{-1} in sediment), K_d (m^3 kg^{-1}) is the distribution coefficient of the pesticide, and K_2 (dimensionless) is the ratio of the pesticide masses in paddy water and in sediment.

[3] Dynamic mass balance:

$$\frac{d}{dt}[M_W(t) + M_S(t)] = -k_W M_W(t) - k_S M_S(t) \tag{3}$$

where k is the overall dissipation rate constant of the pesticide. In addition to pesticide degradation, other dissipation processes such as those related to drainage and leaching could be also represented by k.

Higher-Tier Models Overview

Higher-tier models simulate pesticide fluxes between paddy water and sediment, including settling, resuspension, and diffusion. These models are used to refine PECs derived by lower-tier models when unacceptable risks are indicated. Often applied amounts are adjusted by drift loss and possibly formulation active ingredient release effects to get the effective amount of pesticides in the water-sediment-plant system. Pesticides may also interact with rice canopy by interception and washoff before becoming incorporated with the water or the sediment. Pesticide transport is assessed by considering water-sediment interfacial processes; and convective transport processes associated with drainage, seepage, and leaching (Figure 1).

Management practices for the rice crop, water, and pesticides differentiate higher-tier models. Management events are usually defined by a calendar of operations (*22*, *25*). Plant growth is mainly simulated to estimate canopy coverage and evaluate the pesticide spray interception and the shading effects for aqueous photolysis. Timing of pesticide applications are determined by the growth stages. Water managements of irrigation and drainage are usually associated with two prescribed water depths: the depth to initiate the event and the one to terminate. Based on different model assumptions, target water depths may be reached immediately or as time-dependent processes according to user-defined flow rates. Water holding is simulated by disabling water discharge from the paddy during a given period.

The following differential equation describes the general unsteady-state mass balance in a rice paddy:

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

$$\frac{dM_i}{dt} = S_i + \sum_j (Q_{ji} - Q_{ij}) \tag{4}$$

where M_i (kg or mol) is the pesticide mass in the compartment i during a given time-step, and j a running index for all compartments with inter-compartment transport processes (Figure 1), S_i (kg day^{-1}) is the effective pesticide application by considering all source and dissipation processes, Q_{ij} and Q_{ji} (kg day^{-1}) are the unidirectional chemical fluxes from i to j and vice versa. A daily time step is commonly applied for implementing management practices. Sub-daily intervals may be applied for processes of hydrology, transport, and transformation.

Description of Selected Lower-Tier Models

Adsorption/Dilution Model

The model was developed by California Department of Food and Agriculture to evaluate herbicide behavior in rice paddies (*16*). Degradation, volatilization, and plant uptake were omitted to simplify the need for input parameters. This model considers pesticide distribution in bulk water, pore water, and sediment. Initial mass inventory in the paddy water and in sediment is expressed as:

$$\begin{aligned} M_W(0) &= C_W(0)(V_W + V_{pore}) = C_W(0)A(d_W + d_S\theta_{sed}) \\ M_S(0) &= C_S(0)m_{sed} = C_S(0)Ad_S\rho_b \end{aligned} \tag{5}$$

where d_W (m) is the water depth, d_S (m) is the depth of active sediment, θ_{sed} (dimensionless) is the porosity of sediment, ρ_b (kg m^{-3}) is the bulk density of sediment (kg m^{-3}), V_W and V_{pore} (m^3), volume of the bulk water and the pore water, respectively, and m_{sed} (kg) is the dry weight of sediment. By assuming instantaneous equilibrium controls pesticide distribution between water and sediment (Eq. (2), the initial concentration is calculated as:

$$C_W(0) = \frac{M_T / A}{d_W + d_S(\theta_{sed} + \rho_b K_d)} \tag{6}$$

This model considers a time-dependent penetration depth into the paddy sediment based on an infiltration rate (IR, m day^{-1}):

$$d_S(t) = \frac{IR \cdot t}{\theta_{sed}} \tag{7}$$

The model suggests an infiltration rate of 2.56 cm day^{-1}, sediment bulk density of 1250 kg m^{-3} and sediment porosity of 0.41 in a case study in California (*16*).

USEPA Tier I Rice Model

Developed by USEPA (*17*), this model is similar to the adsorption/dilution model (*16*) with initial pesticide concentration in the paddy water is estimated from Eq. (6). K_d is estimated from the K_{OC} value of the pesticide and the organic carbon (OC) content in the sediment particle (f_{oc}, dimensionless):

$$K_d = f_{oc} \cdot K_{OC} \tag{8}$$

Parameterized using conservative values that represent rice paddies in the United States (*17*), e.g., $d_S = 1$ cm, the model is finalized as:

$$C_W(0) = \frac{M_T / A}{1.32 \times 10^{-3} + 1.3 \times 10^{-6} K_{OC}} \tag{9}$$

with C_W in μg L^{-1} and (M_T/A) in kg ha^{-1}.

PEC Calculation in MED-Rice Scenarios

The European Commission working group of Mediterranean Rice (MED-Rice) developed a simple model and two standard scenarios for PEC calculation (*13*). The model does not consider pesticide distribution in pore water; therefore, initial pesticide distributions in the paddy water and sediment are given by:

$$\begin{aligned} M_W(0) &= C_W(0)V_W = C_W(0)Ad_W \\ M_S(0) &= C_S(0)m_{sed} = C_S(0)Ad_S\rho_b \end{aligned} \tag{10}$$

Similar to the derivation of the adsorption/diffusion model, the initial pesticide concentration in the paddy water is expressed as:

$$C_W(0) = \frac{M_T / A}{d_W + d_S \rho_b K_d} \tag{11}$$

The model also calculates pesticide dissipation during the water-holding period based on first-order kinetics. In addition to paddy-scale simulations, the MED-Rice scenarios consider a template receiving canal for water discharge from the rice paddy, with 1.0 m depth for water and 0.05 m depth for sediment.

An improved mechanistic model, called the surface water and groundwater model (SWAGW), was developed based on the MED-Rice model and scenarios (*18*). In SWAGW, all applied pesticide is initially incorporated into the paddy water, while pesticide mass in the sediment is given by:

$$M_S = K_2(t)M_W = K_{2,\infty}(1 - e^{-\alpha t})M_W \tag{12}$$

where $K_{2,\infty}$ is the ratio of pesticide masses in paddy water and in sediment at equilibrium, and α is a chemical-specific constant reflecting the time dependence of K_2. Analytical solutions of *M*'s are based on Eq. (3) and (12).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Aquatic PEC Model in Japan

The Japanese Ministry of Agriculture, Forestry and Fisheries developed spreadsheet models for PEC calculations (Aquatic PEC Model) in rice paddies (*5*, *12*). Models are designed to estimate the average PEC of a rice pesticide during the corresponding toxicity-test duration (T_e, day) at a watershed outlet. The model watershed of 100 km^2 includes paddy fields of 500 ha and upland fields of 750 ha. River streamflow at the watershed outlet is set as the median value of 3.0 m^3 s^{-1}. Surface runoff, spray drift, and drainage are considered in the Aquatic PEC Model (*5*):

$$C_W = \frac{M_{runoff} + M_{Dr} + M_{Dd}}{3 \times 86400 \times T_e} \tag{13}$$

where C_W (g m^{-3}) is the average concentration of the pesticide in the river at the watershed outlet, and M_{runoff}, M_{Dr} and M_{Dd} (g) are the pesticide amounts contributed by overflow, spray drift and drainage, respectively. A refined model considers pesticide transport fluxes by seepage to the river ($M_{seepage}$, g) and by adsorption onto tributary sediment (M_{se}, g) based on lysimeter tests:

$$C_W = \frac{M_{runoff} + M_{seepage} + M_{Dr} + M_{Dd} - M_{se}}{3 \times 86400 \times T_e} \tag{14}$$

The *M* terms are generally estimated as fractions of total applied pesticide based on empirical ratios. For example, the maximum runoff ratio for calculating 4-day averages of pesticide concentration is suggested as 29.1% for ground application, and 34.4% for aerial application.

Description of Selected Higher-Tier Models

RICEWQ: Rice Water Quality Model

Introduction

The Rice Water Quality Model, RICEWQ (*19*), was developed in 1991 to extrapolate the results of field monitoring studies conducted in Arkansas and Louisiana for the fungicide benomyl. Prior to 2003, the model was used almost exclusively to support risk assessments for pesticide registration in the U.S. (*2*, *20*). In 2003, the MED-Rice working group proposed the use of the model for higher-tier pesticide exposure scenarios in Europe (*13*). In the past several years, the model has received considerable peer review and use. The model has been also used for pesticide leaching assessments by linking it to the Vadose Zone Flow and Transport model (VADOFT) contained within USEPA's Pesticide Root Zone Model (PRZM) (*21*) and the HYDRUS-1D model (*22*). Assessments of pesticide transport to receiving waters have been conducted by coupling RICEWQ with the USEPA's Exposure Analysis Modeling System (EXAMS) (*23*) and the River Water Quality model (RIVWQ) (*24*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

RICEWQ is developed and compiled with FORTRAN 95 to run under MS-DOS. A Windows modeling platform was developed to facilitate the simulation of standardized scenarios representing predominant rice production practices in California, the Mississippi Delta, and the Gulf Coastal Plain of the U.S. (*25*).

Governing Equations

RICEWQ simulates the unique flooding conditions, overflow, and controlled releases of water that are typical under rice production. Water quality algorithms were derived in part from the lake water-quality model contained within the Simulator for Water Resources in Rural Basins - Water Quality (SWRRBWQ) (*26*) and enhanced over time to simulate important fate and transport problems relevant to specific study needs (e.g., crop interception, degradation products, continued irrigation after drainage, and seed treatment with slow release active ingredients).

The mass balance equation of pesticide residues in the paddy is expressed as:

$$V\frac{dC}{dt} = \sum M_{\text{influx}} - \sum M_{\text{outflux}} - \sum M_{\text{react}} \tag{15}$$

where ΔC is the concentration change over time Δt, ΣM_{influx} and ΣM_{influx} are cumulative influx and outflow of pesticide mass from the control volume V, and ΣM_{react} is mass transformation from all processes.

Water balance algorithms in RICEWQ account for precipitation, evaporation, seepage, irrigation, releases and overflow from various paddy outlet configurations, and controlled drainage prior to harvest (Figure 1). RICEWQ uses a storage accounting model to calculate the water balance in the paddy. Inflow sources include precipitation, which is read from an external file, and irrigation, which can either be regulated automatically or applied at a fixed volume by the user. The automated option requires the depth of water in the paddy at which irrigation will commence (e.g., minimum water level during periods without rainfall) and the depth at which irrigation will cease once it is initiated. Both options require the pumping rate (cm day^{-1}) of the irrigation system.

Outflow is the result of evapotranspiration, seepage, overflow, and controlled drainage. Seepage occurs at a constant rate that is specified by the user. Daily pan evaporation is either read from the external meteorological file or calculated from monthly pan-evaporation rates specified in the master input data file. Evapotranspiration is assumed equal to pan evaporation, which is a valid assumption for an aquatic environment (*27*). Overflow occurs when irrigation and precipitation cause water levels to exceed the depth of the outlet in the paddy (e.g., weir or riser). Paddy drainage occurs by regulating the height of the drainage outlet. Evaporation will continue after the paddy is drained until the moisture content in the sediment reaches the wilting point. The model allows for irrigation and drainage at the same time, which is a common practice in some countries.

Chemical mass balance accounts for chemical residues in rice foliage, the water column, and sediment. Simulated pathways for pesticide fate in rice paddy environments include foliar interception during application, dilution, partitioning between water and sediment, and degradation in foliage, water, and sediment. First order decay relationships are used to simulate degradation processes. Chemical loss to drift can be also represented in the model. The user may specify up to two rate constants and yields each for foliar, aquatic and benthic formation of each degradate to simulate each phase of a bi-phase transformation of parent to degradate. Bi-phase transformations use the "hockey-stick" model, in which the second rate constant and yield are used in the model on a user-specified date.

Input and Output

Input parameters are required to describe the system geometry, rice crop, water management, paddy soil, pesticide application, pesticide environmental fate properties, and meteorological conditions (Table 1). Output produced by the model includes an echo of input data daily mass balance of water and pesticide in addition to a daily time series discharge of water and pesticide mass. The latter file is used to provide time series loadings in other models (e.g., EXAMS, RIVWQ).

Model Performance

RICEWQ was parameterized to represent field monitoring studies in Australia, Greece, Italy, Japan, and the U.S. (*18*, *28–40*). Studies included surface water and leaching assessments and represented a range of chemicals, environmental conditions, and scale. Differences between predicted and observed water volumes and chemical concentrations were considered to be within acceptable ranges, as indicated by statistics such as root mean square error and model efficiency. Sensitive input parameters reported by the users included the sediment/water partition coefficient and mixing depth to allow direct bed sediment portioning, application timing and rate, and weather conditions.

PCPF: Simulation Model for Pesticide Concentrations in Paddy Field

Model Description

The PCPF model series were developed by the Tokyo University of Agriculture and Technology. PCPF-1 was initially developed for paddy plot scale and used to estimate the dissipation of popular rice herbicides in Japan (*41–44*). Current model improvements focused on representations of pesticide application scenarios for spray application and incorporated pesticide washoff phenomena from rice plants (*45*, *46*); and for nursery box application (*47*), a common practice in Japan and Taiwan.

Table 1. List of input parameters for RICEWQ

Simulation controls • Simulation dates (beginning and ending date) • Number of simulation time steps in a day
Hydrologic parameters • Surface area of paddy (ha) • Depth of paddy outlet (cm) • Paddy berm height (cm) • Dates to initiate, change, or terminate irrigation • Depths at which irrigation will initiate and cease • Flow rates of irrigation, maximum drainage, and seepage (cm day^{-1}) • Dates to initiate drainage or fill paddy • Initial water depth of paddy (cm)
Paddy soil parameters • Depth of active soil layer (cm) • Soil properties: bulk density (g cm^{-3}), OC content (%), field capacity (cm cm^{-1}), wilting point (cm cm^{-1}), and soil moisture (cm cm^{-1}) • Mixing velocity (diffusion) (m day^{-1}) • Mixing depth for direct partitioning (cm) • Suspended sediment concentration (mg L^{-1}) • Suspended sediment settling velocity (m day^{-1})
Crop parameters • Dates of crop emergence, maturation, and harvest • Aerial coverage of crop at full canopy • Removal options of residues on foliar after harvest
Pesticide parameters (* for parent compound and metabolites) • Water solubility • Water/sediment partition coefficient (K_d) * • Application date, rate, and depth of incorporation • Rates of biotic degradation, hydrolysis, photolysis, and volatilization in water* • Biotic degradation rates in saturated and unsaturated sediment * • Degradation rate and washoff rate in foliage * • Mixing depth for direct partitioning to bed sediment • Fraction (yield) of degraded mass transforming to degradate(s) in foliage, water, and sediment for a given degradation process * • Flag for bi-phase transformation of parent to metabolite • Date to initiate 2nd phase of bi-phase reaction
Meteorological parameters • Daily rainfall, and daily or monthly pan evaporation

PCPF-1 is a lumped parameter model calculating the water and pesticide mass balance in two compartments, paddy water and 1cm paddy surface soil layer (PSL) (Figure 2). Both compartments are assumed to be completely mixed with an aerobic state with pesticide degradation occurring under oxidative conditions (*48*). Pesticide mass balance in the paddy-water compartment is expressed as:

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

$$\frac{dM_{PW}}{dt} = Q_{PW-DISS} + Q_{PW-DES} + Q_{IRR} - Q_{OF} - Q_{PW-PERC} - Q_{VOL} - Q_{PW-DEG} \tag{16}$$

where M_{PW} (mg) is the total pesticide mass in paddy water, $Q_{PW\text{-}DISS}$ (mg day^{-1}) is the pesticide dissolution rate of applied granule pesticide in the paddy water, $Q_{PW\text{-}DES}$ is the pesticide desorption rate from the PSL into paddy water, Q_{IRR} is the pesticide inflow rate with irrigation, Q_{OF} is the pesticide outflow rate by drainage, overflow and lateral seepage, $Q_{PW\text{-}PERC}$ is the pesticide loss rate by percolation, Q_{VOL} is the pesticide loss rate via volatilization, and $Q_{PW\text{-}DEG}$ is the pesticide dissipations rate by biochemical degradation, hydrolysis, and photolysis.

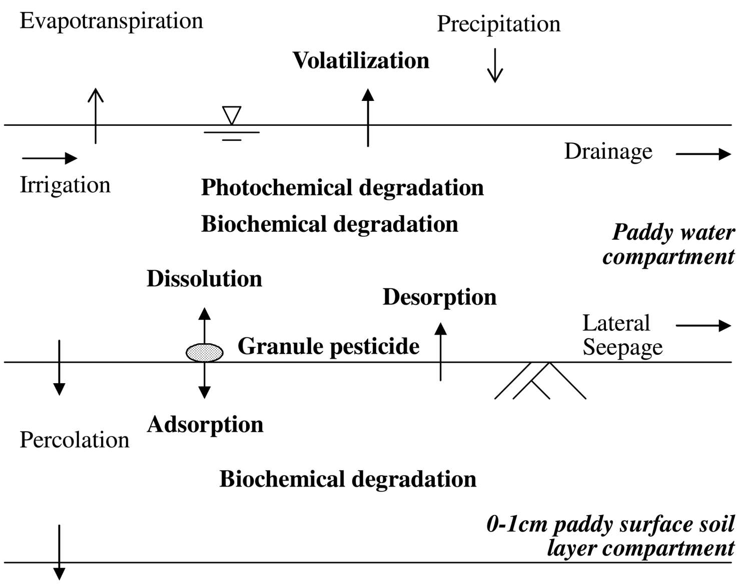


Figure 2. Conceptual pesticide fate in a paddy-rice field. Adapted with permission from reference (43). Copyright 2006 John Wiley & Sons.

Similarly, the pesticide mass balance in the PSL is given as following:

$$\frac{dM_{PSL}}{dt} = Q_{PSL-DISS} - Q_{PSL-DES} + Q_{PSL-PERC} - Q_{PSL-DEG} \tag{17}$$

where M_{PSL} (mg) is the total pesticide mass in the PSL, $Q_{PSL\text{-}DISS}$ (mg day^{-1}) is the pesticide mass gain in PSL upon dissolution process, $Q_{PSL\text{-}DES}$ is the pesticide desorption rate from the PSL into paddy water, $Q_{PSL\text{-}PERC}$ is the net rate of pesticide transport into the PSL through percolation, and $Q_{PSL\text{-}DEG}$ is the pesticide dissipation rate via biochemical degradation process in PSL. Eq. (16) and (17) are iteratively solved for the pesticide concentrations by the 4th order Runge-Kutta

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

scheme (*41*). The model was programmed by Visual Basic® for Applications in Microsoft Excel.

Model Validation

The PCPF-1 model was validated for predicting concentrations of bensulfuron-methyl, imazosulfuron, mefenacet, and pretilachlor in Japanese rice paddies (*42–44*). Predicted concentrations of these herbicides as well as water balance were compared with monitored data for 63 days after the herbicide treatment (DAT) (Figure 3).

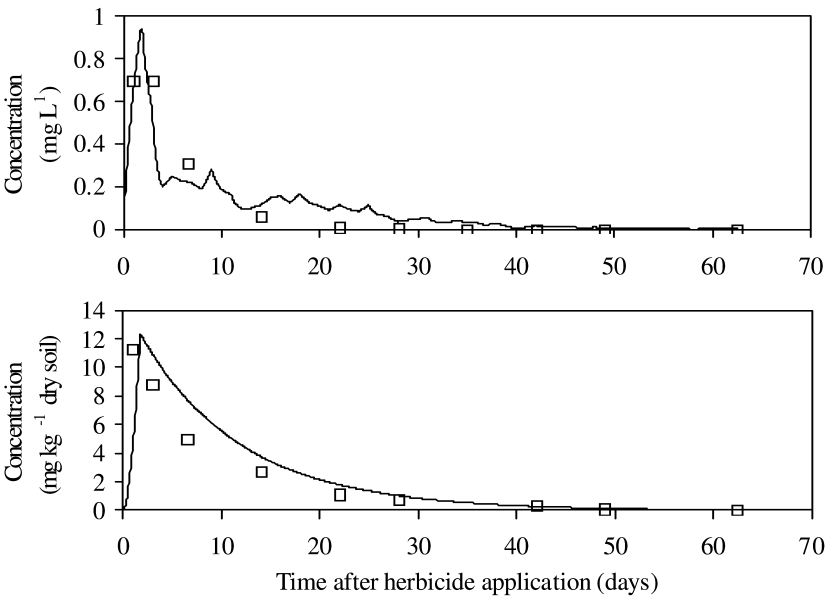


Figure 3. Simulated (line) and observed (square) mefenacet concentrations in paddy water (above) and 1cm surface paddy soil (below). Adapted with permission from reference (42). Copyright 2000 Taylor & Francis.

Modeling results generally captured the dynamics of herbicide concentrations in the paddy water. The sharp decline during the first week due to major rainfall events (2.7 cm and 1.9 cm of rain on 4 DAT and 6 DAT, respectively) was accurately described. The model was able to express the dilution effect by increased paddy water depth; as well as the effect of herbicide desorption from paddy surface soils after appreciable dilution. Similarly, the herbicide concentrations were in close agreement with measured values.

Model Applications

PCPF applications have mainly focused on evaluating best water management practices for reducing pesticide runoff/discharges from paddy fields. In initial application in Japan (*43*), model results identified relatively high water quality risks of rice pesticides to open water bodies associated with traditional water management practices such as spill-over irrigation and continuous drainage. For the monsoon region of Asia where appreciable rainfall is expected during the pesticide application period, maintaining appropriate excess water storage depth (EWSD, a depth between the top of the drainage gate and paddy water level) to store excess rainfall can be a potential management practice for controlling pesticide runoff (*5*, *49*, *50*). A EWSD of 2 cm can control pesticide runoff except for very large rainfall events (*51*, *52*). The PCPF-1 model has been also used to calculate the dissipation and exposure of pretilachlor and cinosulfuron in rice paddies in Europe (*18*).

For pesticide risk assessment in receiving water bodies, PCPF-1 was expanded for use at paddy block and watershed scales. Model modifications were started with PCPF-C model (*5*) and later modified as PCPF-B, which has been validated with data obtained from pesticide monitoring in a paddy watershed (*52*, *53*). For the prediction of pesticide fate in subsoil, PCPF-SWMS was developed by coupling PCPF-1 model with SWMS-2D, a set of two dimensional finite element codes for water flow and solute transport in variably saturated porous media (*54*). The model was successfully validated with field measurements for an inert tracer. PCPF models also utilized Monte Carlo technique to assess the effect of local weather and specific field management on the extent of pesticide discharge from paddy fields (*55*). Results showed that there is greater pesticide runoff potential in southern Japan associated with intensive rain events, and vigorous mitigation measures may be required in order to reduce the pesticide exposure risk in the region.

PFAM: Pesticide in Flooded Agriculture Model

Development of PFAM

The Pesticides in Flooded Agriculture Model (PFAM) was developed by USEPA. The model takes into consideration that there is a limited amount of input data available, that pesticide assessment is a large-scale generic assessment rather than site-specific evaluations, that a regulatory model should be non-proprietary in the sense that it is freely available and open to the public for scrutiny, and that the model must meet basic guidance regarding verification, data corroboration, and validation (*56*) and quality assurance program (*57*).

PFAM is a two-compartment model comprising a water column and a benthic compartment (Figure 4). PFAM can simulate a wide range of management practices, including alternating between flood and unflooded conditions, continuous flow through systems, naturally or man-made variations in flood level, or any combination of these practices.

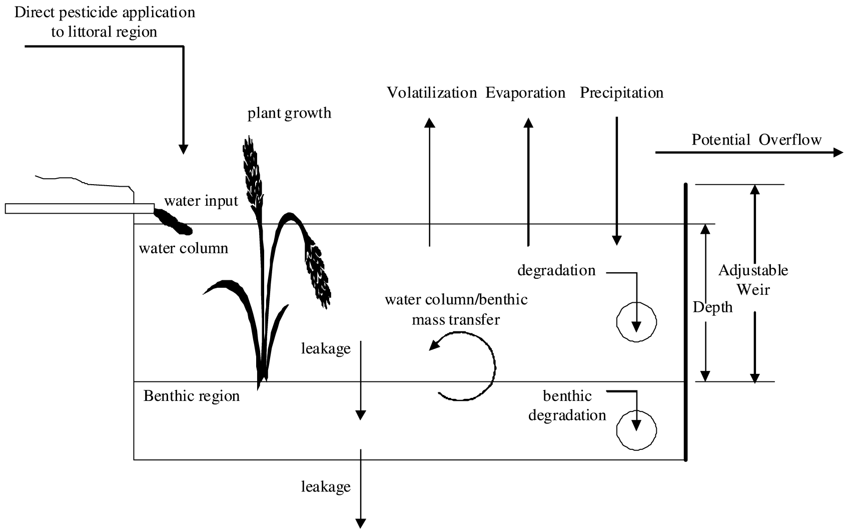


Figure 4. A schematic of the PFAM model

For chemical accounting, PFAM uses two linear differential equations, one for the water column and one for the benthic region:

$$\left(m_{sed1}K_d + v_1\right)\frac{dc_1}{dt} = -\left[Q + QC_{sed}K_d + v_1\mu_{photo} + v_1\mu_{hydr} + v_1\mu_{vol} + Q_L + \left(v_1 + m_{sed}K_d\right)\mu_{bio1}\right]c_1 - \omega\left(c_1 - c_2\right) \quad (18)$$

$$\left(m_{sed2}K_d + v_2\right)\frac{dc_2}{dt} = -\left[\left(v_2 + m_{sed}K_d\right)\mu_{bio2} + v_2\mu_{hydr}\right]c_2 + \left(\omega + Q_L\right)\left(c_1 - c_2\right) \quad (19)$$

where subscripts 1 and 2 are for the water column and benthic region, respectively, c (kg m^{-3}) is the aqueous concentration, m_{sed} (kg) is the mass of sediment, v (m^3) is the volume of water, C_{sed} (kg m^{-3}) is the suspended solid concentration in water column ($=m_{sed1}/v_1$), Q (m^3 s^{-1}) is the discharge flow rate, Q_L (m^3 s^{-1}) is leakage flow rate, ω (m^3 s^{-1}) is the water-column-to-benthic mass transfer coefficient, μ_{hydr}, μ_{photo}, μ_{vol}, and μ_{bio1} (s^{-1}) are the first-order rate constants for hydrolysis, photolysis, volatilization, and overall metabolic degradation, respectively.

In PFAM, assumptions are: (1) suspended matter in the water column occupies negligible volume, (2) hydrolysis, photolysis, and volatilization act only on dissolved species, (3) within a single region (water column or benthic), the rate coefficient for biological metabolism is the same for both dissolved and sorbed forms of pesticide, (4) the hydrolysis rate coefficient in the benthic region is the

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

same as that in the water column, and (5) linear equilibrium partitioning exists within each region among all sorbed species.

Chemical property inputs are supplied by the pesticide registrants. Meteorological inputs are available from the USEPA (*58*). Management practices follow the pesticide label and or practices that occur in the specific area that is being assessed. Input parameters are set to default conservative values if there is no data to support an alternative value. Chemical transformation process algorithms were largely taken from the USEPA standard water body model EXAMS (*23*). Reaction rate constants for hydrolysis, metabolism, photolysis, and volatilization are internally adjusted by PFAM with respect to environmental conditions (temperature). PFAM also performs calculations for up to two degradates in series. Required inputs for degradates are similar to those for the parent in addition to the molar yield of production of each degradate from each parent.

Mathematics and Computer Implementation

Hydrologic and chemical processes were implemented in PFAM in a way that retains an analytical solution for the pesticide concentrations in a daily time interval. This is achieved by making changes in water column volume at the beginning of each day and keeping it constant for the rest of the day. The mathematics for this model is coded with standard FORTRAN 95/2003. The current user interface supplied with the software package is written in Visual Basic.

The program produces an intermediate output file that is routed to post processors. Currently one of the post processors delivers daily water and soil concentrations, daily released pesticide mass, and daily released water. Another available post processor routes the PFAM effluent into the USEPA standard pond and reservoir and determines the subsequent fate of the pesticide in those environments.

Model Evaluation

PFAM performance was evaluated by comparing model estimates to measured concentrations in several field sites and to that of the USEPA Tier I Rice Model (described previously). As one of example, Figure 5 shows the water column concentrations at a field site with a continuous flow-through system along with the PFAM simulation. The PFAM simulation was performed in a manner reflected the available data for a typical risk assessment. The model was not calibrated. PFAM results tracked the measured concentration trends with predicted somewhat higher than measured concentrations. The Tier 1 model estimates were also higher than both the PFAM simulated and measured values. This is an expected trend lower and higher tier model results are compared.

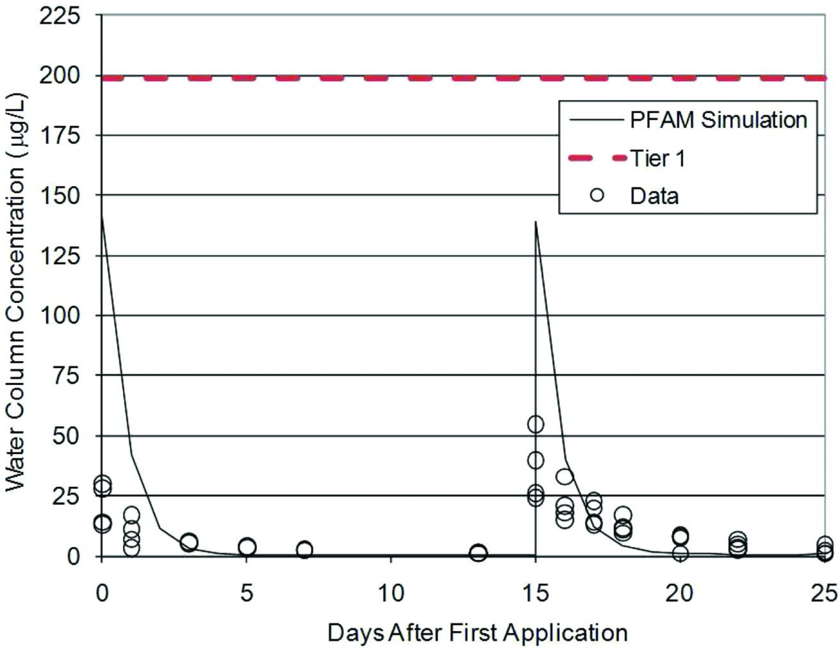


Figure 5. Comparisons of water column concentrations of a field site with estimates from PFAM and the USEPA Tier 1 Rice Model.

Fugacity-Based Models for Rice Pesticides

Fugacity-based modeling is increasingly recognized as a useful tool to simultaneously predict chemical distribution in multiple environmental media (*59*). Fugacity (*f*, Pa) was introduced by Lewis (*60*) as a measure of chemical potential in the form of adjusted pressure. When two phases of a substance are in equilibrium, they share the same value of fugacity. The concept of fugacity was applied in the water quality simulation of pesticides in rice paddy (*14*, *15*, *61*, *62*).

In these models, pesticide transport and transformation processes are simulated based on lumped mass transfer coefficients (MTCs). Therefore, a relatively small set of input data are required for simulations. For example, the mass flux of a pesticide in the general mass balance in Eq. (4) can be formulated as:

$$Q_{ij} = D_{ij}(f_i - f_j) \tag{20}$$

where D_{ij} (mol Pa^{-1} s^{-1}) is the overall MTC (Mackay-type *D* value) from compartment *i* to *j*. MTCs for inter-compartment transport processes are usually estimated as representative values or from empirical equations. For example, the rain-scavenging ratio in wet deposition calculation was set as 200 000 for most organic compounds as suggested by Mackay (*63*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

The Dynamic Aquatic Model (DynA) was developed from the fugacity-based QWASI Lake Model (*63*) for dynamic simulations of pesticide concentration and discharge. Temporal variations in temperature, water flows, and water volume were considered in pesticide fate simulations. Pesticide inputs from application, inflow, and atmospheric depositions (in both dry and wet forms) were considered to be instantaneously incorporated with the water column. Mass balance equations were established in the water and sediment compartments:

$$\frac{df_W}{dt} = D_1 + D_2 \cdot f_S - D_3 \cdot f_W \qquad (21)$$

$$\frac{df_S}{dt} = D_4 f_W - D_5 \cdot f_S$$

where f_W and f_S (Pa) are the pesticide fugacity in the paddy water and in the sediment, respectively, and *D*'s (mol Pa^{-1} s^{-1}) are corresponding overall MTCs. The above equations were solved using the second order Eular modified numerical method of Runge-Kutta numerical integration procedure. Numerical simulation was conducted at an hourly time step, while the dynamic input parameters, such as temperature, water flow, and chemical application, were updated daily. DynA was evaluated with rice pesticides cinosulfuron and pretilachlor and showed a good agreement between measured and predicted concentrations, indicated by model efficiencies ranging from 0.51 to 0.98 (*32*).

The Level-IV fugacity model (FUGIV) was developed for simulating environmental fate of pesticides in the cultivation of irrigated rice (*15*). The model considers four compartments: atmosphere, rice plants, paddy water, and sediment. Pesticide distribution is determined by four ordinary differential equations, for the four simulated compartments, in the same form of Eq. (21). Results of a case study suggested that the model reasonably estimated PECs of carbofuran in the rice growing environment (*15*). The FUGIV model does not support the simulation of actual water management practices of irrigation and drainage. Water depth and water flows are assumed with fixed values in the model simulation. For instance, overall water flux of 1.89×10^{-5} m^3 h^{-1} was assumed in the case study by considering rainfall, evaporation, evapotranspiration, and water recharge of the simulated rice paddy (*14*).

Summary and Conclusions

Assessments at Lower Tiers

Models at lower tiers are developed based on conservative assumptions, and involve initial screening and preliminary risk characterization with readily available data. Those models are usually associated with prescribed scenarios of rice paddy management developed for specific regions (Table 2). Spatially, lower-tier models can perform exposure assessments of rice pesticides at both the paddy field scale (e.g., USEPA Tier I Rice Model, MED-Rice models, and the

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

adsorption/dilution model) and the catchment/watershed scale (e.g., MED-Rice models and Aquatic PEC Model). Model predictions can be greatly dependent on the environmental configurations, especially the depths of paddy water and active sediment layer. Therefore, careful investigations of local field conditions are suggested before applying models for the evaluation and registration of rice pesticides.

Table 2. Parameter values for lower-tier models for pesticide PEC calculation in rice paddy

Parameter	*Adsorption/ dilution model*	*USEPA Tier I Rice Model*	*MED-Rice models*
Water column depth (m)	Field study	0.1	0.1
Sediment depth (m)	Calculated	0.01	0.05
Sediment organic content (%)	Not required	1	1.8 (clay) 0.9 (sand)
Sediment bulk density (kg/m^3)	1250	1300	1500
Sediment porosity (-)	0.41	0.509	Not required
Infiltration rate (cm/day)	2.56	Not required	0.1 (clay) 1.0 (sand)

Assessments at Higher Tiers

For pesticides that do not pass lower-tier screening, additional evaluations are required at higher tiers. Higher-tier models incorporate the effects of actual environmental conditions and management practices, especially their temporal variations, on pesticide fate and behavior in a rice paddy. The models described have been successfully applied and evaluated with various rice production scenarios. The fact that user-defined or empirical parameters are intensively used in rice pesticide modeling indicates that models should be carefully calibrated and validated with site-specific conditions. Assumptions, simplifications, and unique features of the models are compared in Table 3.

RICEWQ is one of the few models which simulate pesticide fate and behavior on plant canopies, including interception, washoff, degradation, and transformation. In PCPF, modeling efforts are incorporated for impacts of rice growth and weather conditions on the water balance and pesticide transport, by accounting for ultraviolet B radiation and evapotranspiration. Compared to other models, PFAM provides the most comprehensive environmental descriptions for the water-sediment system of a rice paddy, simulating pesticide distributions in water, sediment, DOC, and biomass. Functions in PFAM are specifically designed based on parameters typically available from registrant submitted data.

Table 3. Settings of the environment, chemical, and management practices in higher-tier rice pesticide models of RICEWQ, PCPF, and PFAM

Functions	*RICEWQ*	*PCPF*	*PFAM*
Compartments	Water (bulk water, SS); sediment (pore water, particle); rice canopy	Water (bulk water); sediment (pore water, particle)	Water (bulk water, SS, DOC, biomass); sediment (pore water, particle, DOC, biomass)
Crop growth	Linear growth, for interception and washoff	Season-based crop coefficients, for ETc calculation	Linear growth, for photolysis rate adjustment
Water management	Based on target water depth and maximum water flow rates	Based on daily water flow rates	Instantaneous change to target water depths; support continuous irrigation
Crop ET	= ETo, daily data or monthly averages from input file	Daily ETo from Penman-Monteith method, adjusted by crop growth	= ETo, daily data from input file
Pesticide application	Incorporated into water or soil	Incorporated into water	Incorporated into water or soil
Chemical processes on foliage	Interception, washoff, and transformation	No	No
Percolation	Yes	Yes	Yes
Seepage	Yes	Yes	No
Multiple applications	Yes	No	Yes
Slow release	Yes, with a release rate	Yes, with a dissolution rate	No[a]
Volatilization rate	User-defined	Calculated from chemical properties	Calculated from chemical properties and weather data
Aqueous photolysis	May be represented as biphasic	Adjusted by UV-B radiation	Adjusted by plant coverage, latitude, and light attenuation
Hydrolysis	May be represented as biphasic	No[b]	Yes
Degradation in water	May be represented as biphasic	Yes	Adjusted by temperature
Degradation in sediment	May be represented as biphasic	Bi-phasic process	Adjusted by temperature

Continued on next page.

Table 3. (Continued). Settings of the environment, chemical, and management practices in higher-tier rice pesticide models of RICEWQ, PCPF, and PFAM

Functions	*RICEWQ*	*PCPF*	*PFAM*
Degradation on foliage	May be represented as biphasic	No	No
Water-sediment mass transfer	Diffusion, settling, resuspension	Percolation and bi-phasic desorption	Lumped water-sediment transfer
Transformation	Yes	No	Yes

[a] slow release is not explicitly simulated in PFAM, but may be implemented by manually distributing the applied pesticide amount into multiple days. [b] PCPF simulates aquatic dissipation based on a lumped degradation rate.

RICEWQ is able to simulate transformation processes for the parent chemical and up to 4 degradation products in series or in parallel. Similarly, PFAM can simulate up to two degradates in series with first order production. RICEWQ and PCPF have the modeling capability for bi-phasic processes for pesticide transformation and/or desorption. In PCPF and PFAM, empirical equations are integrated for estimating mass transfer coefficients and their temporal variations. These functions minimize the need for input data, and reflect the effects of environmental conditions on pesticide fate processes.

Disclaimer

The information for the PFAM model in this document are those of the authors and do not necessarily reflect the views of the U.S. Environmental Protection Agency.

Acknowledgments

The authors acknowledge Dr. John Sanders of California Department of Pesticide Regulation, the book editors, and three anonymous reviewers for valuable discussions and critical reviews.

References

1. Sudo, M.; Okubo, T.; Kunimatsu, T.; Ebise, S.; Nakamura, M.; Kaneki, R. *Lakes Reservoirs* **2002**, *7*, 301–308.
2. USEPA. *Amendment to reregistration eligibility decision (RED) for propanil (March 2006) and the propanil RED (September 2003)*; U.S. Environmental Protection Agency: Washington, DC, 2006. http://www.epa.gov/oppsrrd1/REDs/propanil_red_combined.pdf (accessed March 2011).

3. Orlando, J. L.; Kuivila, K. M. *Changes in Rice Pesticide Use and Surface Water Concentrations in the Sacramento River Watershed, California*; U.S. Geological Survey: Sacramento, CA, 2004.
4. Schulz, R. *J. Environ. Qual.* **2004**, *33*, 419–448.
5. Watanabe, H.; Inao, K.; Vu, S. H.; Phong, T. K.; Ishihara, S.; Takagi, K.; Tournebize, J. In *Pesticide risk assessment in rice paddies: theory and practice*; Capri, E., Karpouzas, D., Eds; Elsevier: 2008; pp 168−214.
6. Capri, E. In *Pesticide risk assessment in rice paddies: theory and practice*; Capri, E., Karpouzas, D., Eds; Elsevier: 2008; pp 168−214.
7. CDFA. *Information on rice pesticides*; California Department of Food and Agriculture: Sacramento, CA, 1991. http://www.cdpr.ca.gov/docs/emon/surfwtr/1990.pdf (accessed June /2011).
8. Segawa, R. *Review of literature regarding effects of water holding times on rice and pesticide dissipation*; California Department of Pesticide Regulation: Sacramento, CA, 2002. http://www.cdpr.ca.gov/docs/emon/surfwtr/whold02.pdf (accessed June 2011.
9. Watanabe, H.; Nguyen, M. H. T.; Souphasay, K.; Vu, S. H.; Phong, T. K.; Tournebize, J.; Ishihara, S. *Agric. Water Manage.* **2007**, *88*, 132–140.
10. CRC. *Environmental & conservation balance sheet for the California rice industry*; California Rice Commission: Sacramento, CA, 2011. http://www.calrice.org (accessed June 2011).
11. USEPA. *Technical progress report of the implementation plan for probabilistic ecological assessments: Aquatic systems*; U.S. Environmental Protection Agency: Washington, DC, 2000. http://www.epa.gov/scipoly/sap/meetings/2000/april/probaq.pdf (accessed June 2011).
12. MAFF. *Method for short-term PEC Derivation*; Ministry of Agriculture, Forestry and Fisheries of Japan: Tokyo, Japan, 2002. http://www.acis.famic.go.jp/eng/shinsei/13-3987.pdf (accessed June 2011).
13. MED-Rice. *Guidance document for environmental risk assessments of active substances used on rice in the EU for annex I inclusion*; EU Document Reference SANCO/1090/2000 - rev.1, Brussels, 2003. http://ec.europa.eu/food/plant/protection/resources/med_rice_2003_en.pdf (accessed February 2011).
14. Contreras, W. A.; Ginestar, D.; Paraíba, L. C.; Bru, R. *Comput. Math. Appl.* **2008**, *56*, 657–669.
15. Paraíba, L. C.; Plese, L. P. d. M.; Foloni, L. L.; Carrasco, J. M. *Span. J. Agric. Res.* **2007**, *5*, 43–50.
16. Johnson, B. R. *Bull. Environ. Contam. Toxicol.* **1991**, *47*, 244–250.
17. USEPA. *Tier I Rice Model v1.0 for estimating pesticide concentrations in rice paddies*; U.S. Environmental Protection Agency: Washington, DC, 2007.
18. Karpouzas, D. G.; Cervelli, S.; Watanabe, H.; Capri, E.; Ferrero, A. *Pest Manage. Sci.* **2006**, *62*, 624–636.
19. Williams, W. M.; Ritter, A. M.; Zdinak, C. E.; Cheplick, J. M. *RICEWQ: Pesticide runoff model for rice crops: User's manual and program documenation*, version 1.7.3; Waterborne Environmental, Inc.: Leesburg, VA, 2011.

20. USEPA. *Fipronil - Report of the FQPA Safety Factor Committee*; U.S. Environmental Protection Agency: Washington, DC, 1998. http://www.regulations.gov/, accessed June 2011.
21. USEPA. *PRZM users manual for release 3.12.2*; U.S. Environmental Protection Agency: Washington, DC, 2006.
22. Šimůnek, J.; Šejna, M.; Saito, H.; Sakai, M.; van Genuchten, M. T. *The HYDRUS-1D software package*; Department of Environmental Sciences, University of California Riverside: Riverside, CA, 2009.
23. Burns, L. A. *Exposure Analysis Modeling System (EXAMS): User manual and system documentation*; EPA/600/R-00/81-023; U.S. Environmental Protection Agency: Washington, DC, 2000.
24. Williams, W. M.; Cheplick, J. M.; Ritter, A. M.; O'Flaherty, C. E.; Singh, P. S. *RIVWQ chemical transport model for riverine environments - user's manual and program documentation*, Version 2.02; Waterborne Environmental, Inc.: Leesburg, VA, 2004.
25. Williams, W. M.; Ritter, A. M.; Vamshi, R. *Tier 2 ecological risk assessment for rice. Exposure Modeling Public Meeting*; U.S. Environmental Protection Agency: Crystal City, VA, 2007.
26. Arnold, J. G.; Williams, J. R.; Griggs, R. H.; Sammons, N. B. *SWRRBWQ: A basin-scale model for assessing management impacts on water quality*; U.S. Department of Agriculture, Agricultural Research Service: Temple, Texas, 1991.
27. Linsley, R. K.; Franzini, J. B. *Water-Resources Engineering*, 3rd ed.; McGraw-Hill Book Company: New York, NY, 1979.
28. Capri, E.; Miao, Z. *Agronomie* **2002**, *22*, 363–371.
29. Christen, E. W.; Chung, S.-O.; Quayle, W. *Agric. Water Manage.* **2006**, *85*, 38–46.
30. Chung, S. O.; Park, K. J.; Son, S. H. *J. Korean Soc. Agric. Eng.* **2008**, *50*, 3–10.
31. Ferrari, F.; Karpouzas, D. G.; Trevisan, M.; Capri, E. *Environ. Sci. Technol.* **2005**, *39*, 2968–2975.
32. Infantino, A.; Pereira, T.; Ferrari, C.; Cerejeira, M. J.; Di Guardo, A. *Chemosphere* **2008**, *70*, 1298–1308.
33. Karpouzas, D. G.; Capri, E. *Paddy Water Environ.* **2006**, *4*, 29–38.
34. Karpouzas, D. G.; Capri, E.; Papadopoulou-Mourkidou, E. *Agron. Sustain. Dev.* **2005**, *25*, 35–44.
35. Karpouzas, D. G.; Capri, E.; Papadopoulou-Mourkidou, E. *Vadose Zone J.* **2006**, *5*, 273–282.
36. Karpouzas, D. G.; Ferrero, A.; Vidotto, F.; Capri, E. *Environ. Toxicol. Chem.* **2005**, *24*, 1007–1017.
37. Miao, Z.; Cheplick, M. J.; Williams, M. W.; Trevisan, M.; Padovani, L.; Gennari, M.; Ferrero, A.; Vidotto, F.; Capri, E. *J. Environ. Qual.* **2003**, *32*, 2189–2199.
38. Miao, Z.; Padovani, L.; Riparbelli, C.; Ritter, A.; Trevisan, M.; Capri, E. *Paddy Water Environ.* **2003**, *1*, 121–132.
39. Miao, Z.; Trevisan, M.; Capri, E.; Padovani, L.; Del Re, A. A. M. *J. Environ. Qual.* **2004**, *33*, 2217–2228.

40. Ngoc, N. M.; Dultz, S.; Kasbohm, J. *Agric., Ecosyst. Environ.* **2009**, *129*, 8–16.
41. Watanabe, H.; Takagi, K. *Environ. Technol.* **2000**, *21*, 1379–1391.
42. Watanabe, H.; Takagi, K. *Environ. Technol.* **2000**, *21*, 1393–1404.
43. Watanabe, H.; Takagi, K.; Vu, S. H. *Pest Manage. Sci.* **2006**, *62*, 20–29.
44. Takagi, K.; Fajardo, F. F.; Ishizaka, M.; Phong, T. K.; Watanabe, H.; Boulange, J. *Paddy Water Environ.* **2011**, in press, DOI: 10.1007/s10333-10011-10276-10330.
45. Phong, T.; Nhung, D.; Yamazaki, K.; Takagi, K.; Watanabe, H. *Bull. Environ. Contam. Toxicol.* **2008**, *80*, 438–442.
46. Phong, T. K.; Nhung, D. T. T.; Yamazaki, K.; Takagi, K.; Watanabe, H. *Chemosphere* **2009**, *74*, 1085–1089.
47. Thuyet, D. Q.; Watanabe, H.; Motobayashi, T. *J. Pestic. Sci.* **2011**, *36*, in press, DOI: 10.1584/jpestics.G1510-1549.
48. Takagi, K.; Fajardo, F. F.; Inao, K.; Kitamura, Y. *Rev. Toxicol.* **1998**, *2*, 269–286.
49. Phong, T. K.; Watanabe, H.; Thai, Q. H.; Vu, H. S.; Tanaka, T.; Dang, T. T. N.; Motobayashi, T. *J. Pestic. Sci.* **2008**, *33*, 159–165.
50. Inao, K.; Watanabe, H.; Karpouzas, D.; Capri, E. *Jpn. Agric. Res. Q.* **2008**, *42*, 13–21.
51. Vu, S. H.; Ishihara, S.; Watanabe, H. *Pest Manage. Sci.* **2006**, *62*, 1193–1206.
52. Phong, T. K.; Vu, S. H.; Ishihara, S.; Hiramatsu, K.; Watanabe, H. *Pest Manage. Sci.* **2011**, *67*, 70–76.
53. Phong, T. K.; Hiramatsu, K.; Watanabe, H. *Environ. Technol.* **2011**, *32*, 69–81.
54. Tournebize, J.; Watanabe, H.; Takagi, K.; Nishimura, T. *Paddy Water Environ.* **2006**, *4*, 39–51.
55. Watanabe, H.; Kondo, K.; Boulange, J.; Phong, T. K.; Hiramatsu, K.; Inao, K. Presented at the 12th IUPAC International Congress of Pesticide Chemistry, July 4−8, Melbourne, Australia, 2010.
56. USEPA. *Guidance on the Development, Evaluation, and Application of Environmental Models. EPA/100/K-09/003*; U.S. Environmental Protection Agency: Washington, DC, 2009.
57. USEPA. *Guidance for Quality Assurance Project Plans for Modeling, EPA QA/G-5M, EPA/240/R-02/007*; U.S. Environmental Protection Agency, Washington, DC, 2002.
58. USEPA *United States meteorological data: daily and hourly files to support predictive exposure modeling. EPA/600/R-07/053*; U.S. Environmental Protection Agency, Washington, DC, 2007.
59. Mackay, D.; Arnot, J. A.; Webster, E.; Reid, L. In *Ecotoxicology Modeling, Emerging Topics in Ecotoxicology: Principles, Approaches and Perspectives*; Devillers, J., Ed.; 2009; pp 355−375.
60. Lewis, G. N. *J. Am. Chem. Soc.* **1908**, *30*, 668–683.
61. Plese, L. P. M.; Foloni, L. L. *Congr. Proc. - BCPC Int. Congr.: Crop Sci. Technol.* **2005**, *2*, 803–808 (Glasgow, United Kingdom, Oct. 31−Nov. 2, 2005).

62. Vasquez, M. E.; Gunasekara, A. S.; Cahill, T. M.; Tjeerdema, R. S. *Pest Manage. Sci.* **2010**, *66*, 28–34.
63. Mackay, D. *Multimedia environmental models, the fugacity approch*; CRC Press: Boca Raton, FL, 2001.

Chapter 15

Modeling the Effectiveness of Mitigation Measures on the Diazinon Label

Nathan J. Snyder,[1,*] W. Martin Williams,[1] Debra L. Denton,[2] and Christian Bongard[1]

[1]Waterborne Environmental Inc., Leesburg, VA 20175
[2]U.S. Environmental Protection Agency, Region IX, Sacramento, CA 95814
[*]snydern@waterborne-env.com

Publication Date (Web): December 21, 2011 | doi: 10.1021/bk-2011-1075.ch015

The Pesticide Root Zone Model (PRZM) and the water quality model for riverine environments (RIVWQ) were used in combination to evaluate diazinon sources, fate, and transport in the Main Drainage Canal within the Sacramento River Basin in Butte County, California. The modeling system was calibrated using historical stream flows and measured diazinon concentrations, and then applied in conjunction with monitoring data and GIS analysis to identify locations and timeframes of source loadings of agricultural uses of diazinon. Models were also used to evaluate effectiveness of implementing management practices, such as limiting application during dormant periods, implementing filter strips and setbacks, limiting applications if soils are saturated or if rainfall is forecast within a 48-hour period, and using larvae count to optimize applications. The predicted reduction in diazinon loadings to water was 53 percent with a similar reduction in concentration for high exposure events. Monitoring data collected since label changes were implemented in 2004, have shown significant reduction in diazinon concentrations in surface waters in California's Central Valley, presumably due to label changes, education and outreach, cancellation of non-agricultural uses of diazinon, and an overall decrease of use of the product. The models proved to be effective tools in evaluating the relative efficacy of these practices.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Introduction

Diazinon (O,O-Diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate) is a broad spectrum organophosphate insecticide registered for use on a variety of terrestrial food, feed, and nonfood crops. Diazinon detection in the Sacramento and San Joaquin Rivers and their tributaries (*1–7*) resulted in the determination of water quality impairment and the establishment of Total Maximum Daily Loads (TMDLs) in segments of these water bodies. During this period, the U.S. Environmental Protection Agency (USEPA) sponsored several studies under the EPA Clean Water Act §319(h) Nonpoint Source Program to provide a better understanding of diazinon transport in the Sacramento River watershed, including the exposure assessment model discussed herein.

The work was conducted under the Sacramento River Toxic Pollutant Control Program (SRTPCP) to evaluate diazinon sources in the Sacramento River watershed. Activities were directed toward a 38,000-acre area of the Main Drainage Canal (Figure 1). Models were used to assist in identifying sources of diazinon in the basin and to evaluate the relative benefits achieved by implementing the changes to the diazinon labels and other management practices. The Main Drainage Canal was selected for evaluation to complement and expand the utility of other 319(h) initiatives in the sub-watershed that included water quality monitoring in fields and storm monitoring of lateral drainage ways where specific management practices were implemented. The modeling work was completed in 2004.

Several years of monitoring are now (2010) available to determine whether the label changes have been effective in reducing the transport of diazinon to aquatic systems. This paper documents the modeling development and results of the model and reviews monitoring before and after the implementation of the label modifications.

Model Selection

The environmental fate of a pesticide resulting from agricultural uses is governed by the complex interaction of numerous factors, including the physicochemical characteristics of the pesticide, the agronomic practices related to the production of the crop and the use of the pesticide, the soil and hydrogeological conditions where the pesticide is utilized, and climatological conditions at the time of and following its application. Under label uses, diazinon has the potential to appear in aquatic environments as the result of runoff, erosion, and spray drift sources. To estimate environmental concentrations of diazinon in aquatic ecosystems, models were required that account for as many of these governing processes as possible.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

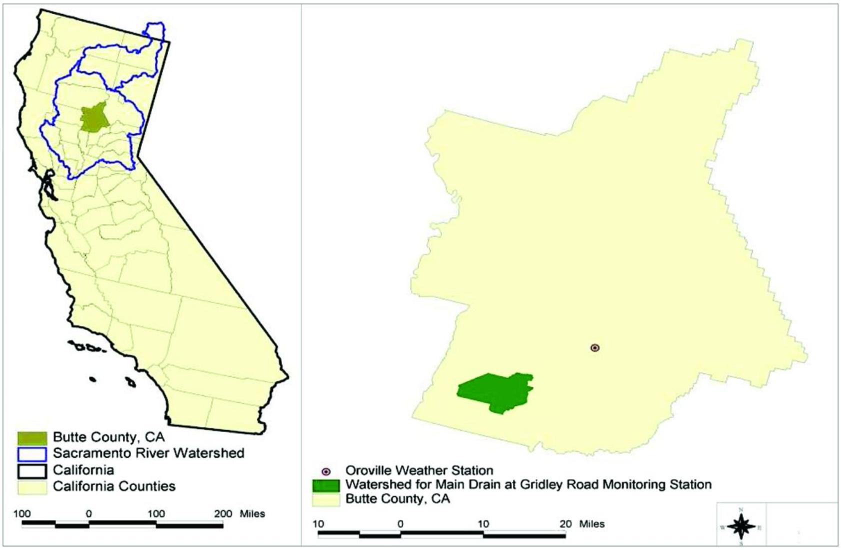


Figure 1. Map of California, Sacramento River Watershed, and the Main Drainage Canal Watershed within Butte County, California (see color insert)

The Pesticide Root Zone Model (PRZM) was selected to evaluate the potential movement of diazinon residues in the terrestrial system based on the model's ability to account for pertinent environmental processes and because of the preference for its use by USEPA's Office of Pesticide Programs (*8*). PRZM is a dynamic, compartmental model for use in simulating water and chemical movement in unsaturated soil systems within and below the plant root zone (*9*). The model simulates time-varying hydrologic behavior on a daily time step, including physical processes of runoff, infiltration, erosion, and evapotranspiration. The chemical transport component of PRZM calculates pesticide uptake by plants, surface runoff, sediment transport, decay, vertical movement, foliar loss, dispersion and retardation. The model includes the ability to simulate metabolites, irrigation, and hydraulic transport below the root zone. PRZM predicted chemical movement in runoff, sediment, and subsurface were used as boundary condition loadings along the channel system in the River Water Quality Model (RIVWQ).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

RIVWQ was selected based on its ability to simulate time-varying flow, represent multiple chemical dissipation pathways, and because of previous applications of its integration with PRZM (*10*). Model geometry is based on the link-node approach in which the simulated system is divided into a number of discrete volumes (nodes or junctions), which are connected by flow channels (links). The model assumes steady state hydraulics that can change from time period to time period (i.e., any change in the hydraulic regime is assumed to be instantaneous throughout the system). Dynamic constituent transport is a combination of advective flows and dispersion processes. Dispersion processes, including constituent mixing as a result of backwater and flow reversals, are lumped together into a single dispersion coefficient. Chemical constituent mass balance is calculated at each node and can accommodate dilution, advection, volatilization, partitioning between water and sediment, degradation in water and sediment, burial in sediment, and re-suspension from sediment. The RIVWQ model includes transformation of parent chemical to metabolites and the degradation of the metabolites and operates under a user-specified time step that must satisfy certain stability criteria. For this study, model simulations were conducted using time steps on the order of minutes.

In combination, PRZM and RIVWQ simulated temporal and spatially varying applications of diazinon in the watershed; the transport of diazinon into and along the stream network by drift, runoff, erosion, and subsurface sources; adsorption-desorption to soil and sediment; and degradation in soil, water, and sediment from photolytic and metabolic processes.

Model Setup

Watershed Delineation

The drainage area of the Main Drainage Canal encompasses 38,000 acres in Butte County, California, upstream of the U.S. Geological Survey (USGS) monitoring station 392144121492301, Main Drainage Canal at Gridley Road. The external watershed delineation was completed by the USGS and made available for use in this study in a geographical information system (GIS) format. The delineation process was difficult in certain areas because of the relatively flat topography and complex drainage network having multiple intersections and bidirectional canals and waterways.

Sub-Watersheds and Link Node Network

Model resolution was based on the available data (primarily the County Meridian Township-Range-Section which was the basis of diazinon use data), the study budget, and model stability considerations. The channel network was defined starting with the National Hydrography Dataset (*5*) as shown in the upper left hand corner of Figure 2. A subset of principal channels was represented in the model based on their linkage to the outlet channel being monitored (Node 2). Model nodes were selected to correspond with tributary junctions and monitoring locations. Additional intermediate nodes were inserted to provide surface drainage entry locations into the channel system and to preserve numerical stability.

The watershed was delineated into a number of sub-watersheds that share a common surface drainage entry location. A total of 70 sub-watersheds were defined as shown in Figure 2. Delineation was based on the publication "Study of Diazinon Runoff in the Main Canal Basin During the Winter 2000-2001 dormant spray season" (*11*), a review of topographic maps (1:24,000 scale), and best professional judgment. The drainage area of the Main Drainage Canal (approximately 15,400 ha) has little relief (~12 m total gradient). Available topographic data (5-ft or approximately 1.5-m intervals) were not precise enough to accurately define drainage divides within the drainage area and made it difficult for the USGS to define the outer watershed boundary. For example, on the 1:24000 topographic maps, there are many areas with one or more miles between topographic intervals. Many of the drainage divides were assumed to occur midway between channels because the resolution of topographic data prevented a more exact drainage definition.

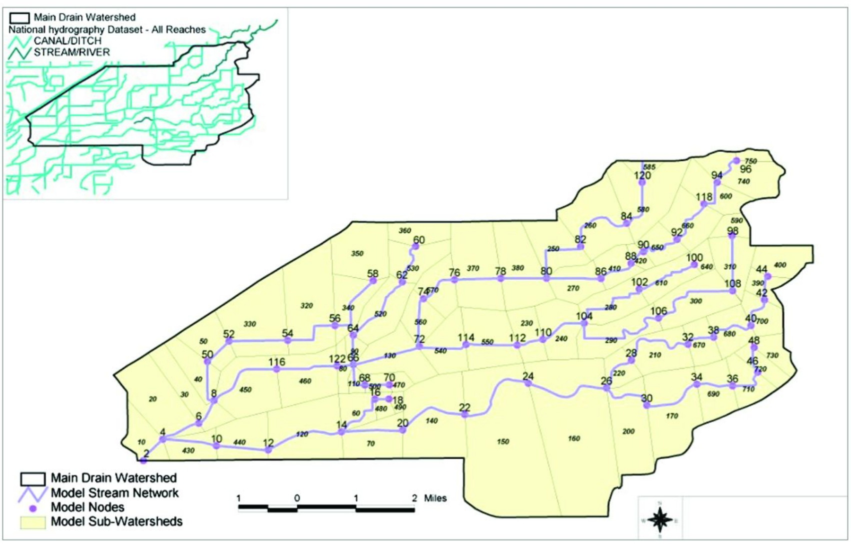


Figure 2. Sub-Watersheds and Link Node network – Model Representation of Main Drainage Canal Watershed. (see color insert)

PRZM Input Data

Water and diazinon mass originating from the sub-watersheds were predicted by conducting 147 unique PRZM simulations. Each simulation was defined by the intersection of land areas designating different combinations of soil, land use, weather, and diazinon use. Discussion on individual data sources is provided below.

Soils

The National Resources Conservation Service (NRCS) office in Chico provided maps and soil properties for the section of the county that includes the Main Drainage Canal area. Soil delineations for the watershed were digitized as part of this study (Figure 3). Soil properties were processed into a format required for model input.

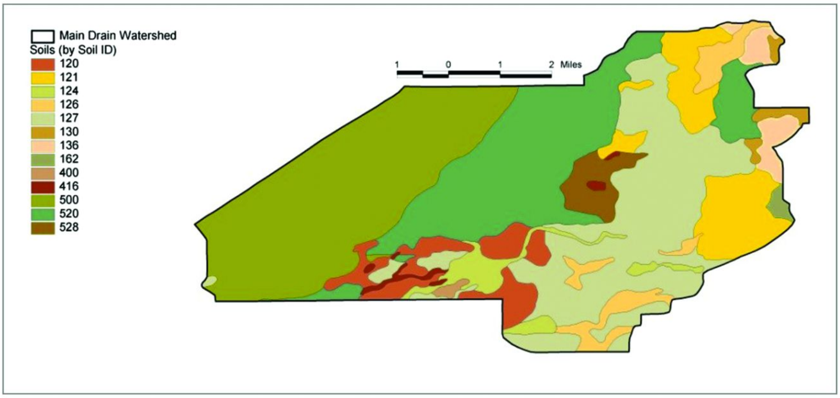


Figure 3. Soils – Digitized from NRCS Preliminary Mapping (no published soil survey in print) (see color insert)

Land Use

Detailed land use data for Butte County were obtained from the California Department of Water Resources 1994 Land Use Survey (Figure 4). For agronomic model inputs, specific land use categories were grouped into broader categories based on similarity in agriculture or impact on model configuration (Figure 5). Bi-annual Farmland Mapping and Monitoring Program (FMMP) data were reviewed to ensure that land use changes between 1994 and 2002 would not significantly compromise results.

Crop Parameters

Parameter estimation guidelines in the PRZM manual were used to derive cropping dates for emergence, maturation, and harvest, in addition to other crop parameters for interception storage, active root depth, areal coverage, and maximum canopy height.

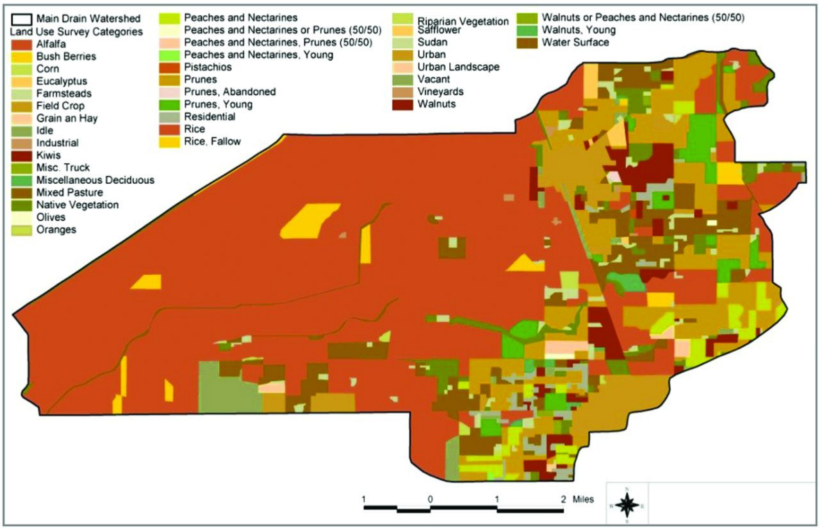


Figure 4. All Land Use Attributes in Main Drainage Canal Watershed from California Department of Water Resources 1994 Butte County Land Use Survey. (see color insert)

Weather Data

Precipitation and temperature data were obtained from the National Climatic Data Center (*13*) for the National Weather Service station at Oroville, CA (46521). For days with missing values, data from the next closest station at Willows, CA (49699) were used. The alternate station was used less than 5% of the time for precipitation and less than 20% for temperature values. The Oroville station is approximately 13.5 km (closest point) to 29 km (farthest point) from the watershed border. The fill-in data from the Willows station is approximately 50 km from the watershed center. The elevations of the Oroville and Willows stations are approximately 52.1 and 71.0 m above sea level, respectively. The elevation of the watershed ranges from approximately 21.3 to 30.5 m above sea level.

Diazinon Environmental Fate Properties

Environmental fate properties for diazinon were obtained from a modeling study of diazinon conducted by USEPA (*12*) as seen in Table I.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

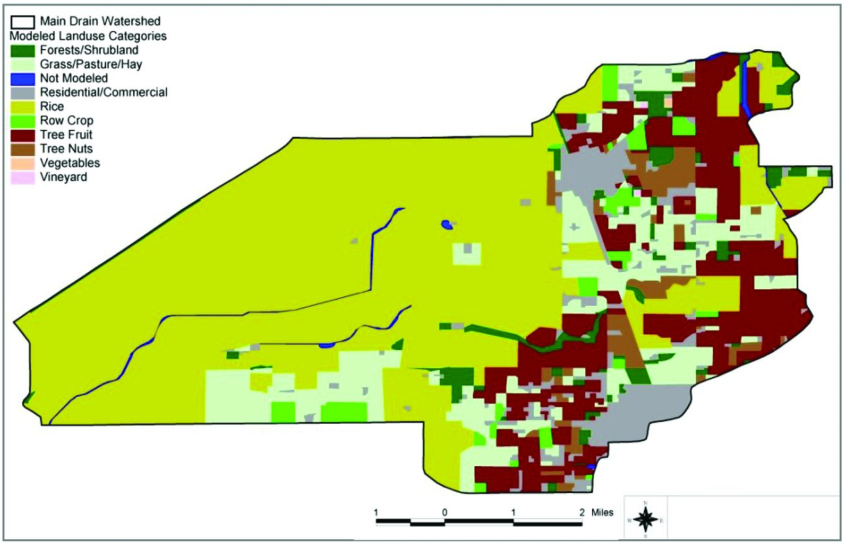


Figure 5. Grouped Land Use Data for Model Configuration in Main Drainage Canal Watershed from California Department of Water Resources 1994 Butte County Land Use Survey. (see color insert)

Table I. Diazinon Properties

Property[a]	*Value*
Molecular weight	303.3 g mol^{-1}
Solubility	40 mg L^{-1}
Henry's Law Constant	1.4 x 10^{-7} atm-m^3 mol^{-1}
K_{oc}	758 mL g^{-1}
Foliar degradation, T½	4.0 d
Washoff	0.5 /cm rainfall
Aerobic soil metabolism, T½	41.1 d
Anaerobic soil metabolism, T½	82.2 d
Soil photolysis, T½	20 hours
Water decay rate, T½	82.2 d
Sediment decay rate, T½	164.4 d

[a] Note: T½ = half-life

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Diazinon Applications

Diazinon use was obtained from the California Department of Pesticide Regulation (CDPR) Pesticide Use Report (PUR) database (*14*). The PUR database reports all agricultural uses of registered pesticides by active ingredient and crop, including application date and rate by County Township, Range, and Section (COMTRS). All records of diazinon use in the CDPR database over the 10-year simulation period (1992-2001) within the study area were simulated with the model. Land use data were used to better pinpoint applications for those COMTRS units (square mile sections) that straddled the watershed divide. Urban and homeowner uses were not simulated in the model as these use patterns have been discontinued. Historical uses of diazinon in the watershed are tabulated and mapped in Figure 6. Diazinon use was concentrated in the eastern, upper portions of the watershed.

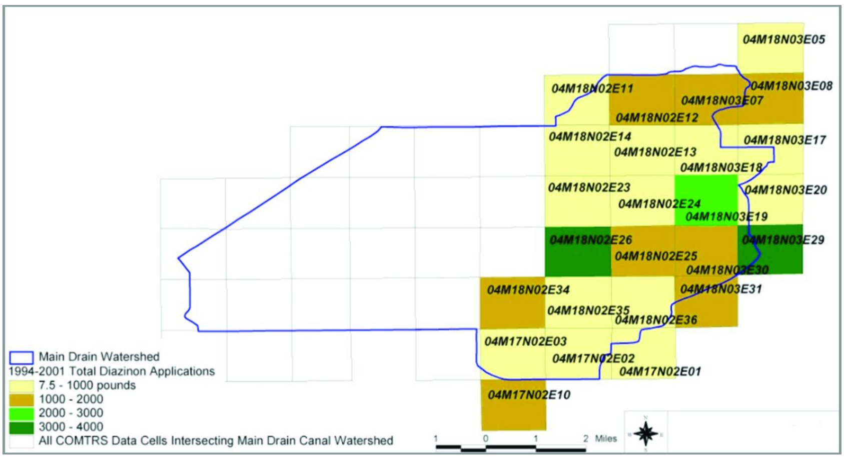


Figure 6. Applications – 1994-2001 – PUR cells with applications shown. Table shows crops and amounts in each COMTRS area. (see color insert)

A total of 147 PRZM simulations were required to represent unique combinations of soils, land use, and diazinon applications in the watershed (Figure 7). These unique areas are displayed with the sub-watershed drainage area and the river channel/link-node network that form the complete representation of the Main Drainage Canal model. A given PUR point may be found in multiple unique PRZM runs if the COMTRS cell intersects with multiple soils. Output from a PRZM simulation was assigned to one or more sub-watersheds depending on whether those soil-crop-application conditions occurred in that sub-watershed. Output for a sub-watershed was calculated by area weighting the appropriate percentage of unique simulations that define the soil-land use-application conditions in the sub-watershed. Output from each sub-watershed enters the stream network at the downstream node (e.g., area 370 drains to and enters node 76).

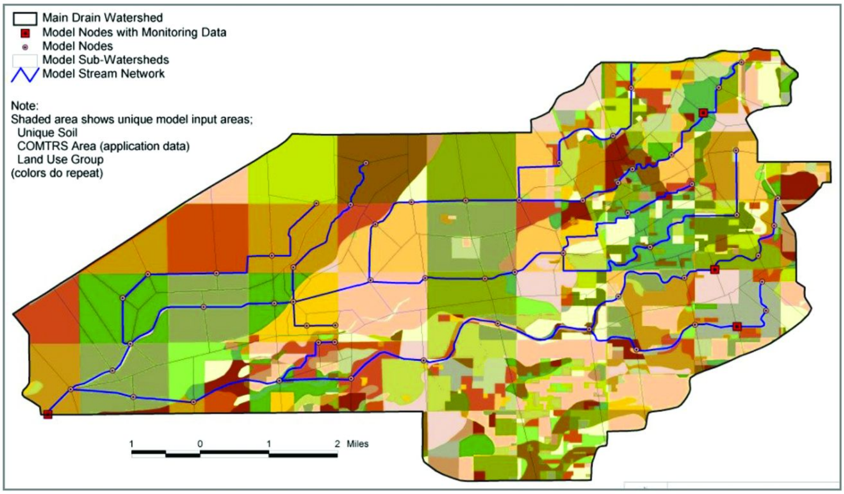


Figure 7. Unique Model Input Intersect: Soil, Application Data, and General Landuse in addition to Sub-Watersheds and Link Node Network (with monitoring locations designated). (see color insert)

RIVWQ Input Data

RIVWQ utilizes a number of input parameters to define the channel system, including link-node topology (designating which nodes drain into which other nodes), stage-storage-discharge relationships (relating channel geometry, frictional resistance, and dispersion), and sediment properties (bulk density, organic matter, and water-sediment transfer coefficients). Channel characteristics were based on limited observations from a field reconnaissance trip to the watershed in 2002, interviews with Peter Dileanis (USGS), Fred Thomas (CERUS Consulting), and inferred from Briggs and Oliver (*11*). Initial drift loads were based on USEPA default values for modeling aerial and airblast (predominate ground application method) using 5% of the application rate across the surface area of the water body. Values were refined during calibration.

Model Calibration and Parameter Sensitivity Analysis

Model performance was evaluated by comparing model predictions to measured streamflow and diazinon concentrations at model nodes where sufficient monitoring data were available. Graphical outputs were compared visually to evaluate model performance. The time-series dataset was poorly populated, making statistical analyses difficult. Streamflow data for USGS gauge number 392144121492301, Main Drainage Canal at Gridley, were provided by Peter Dileanis, USGS, Sacramento District office. Monitoring results for diazinon were

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

obtained from six sources, some unpublished, including the CVRWQCB Staff Report July 2000; Water Resources Investigations Report 02-4101; NWISWeb data for the nation; and unpublished data by the USGS. In addition, the 319(h) studies provide in-field runoff data and water samples collected from interior drainage canals. Figure 7 identifies the four locations with monitoring data available for at least short periods of time between 1994 and 2001.

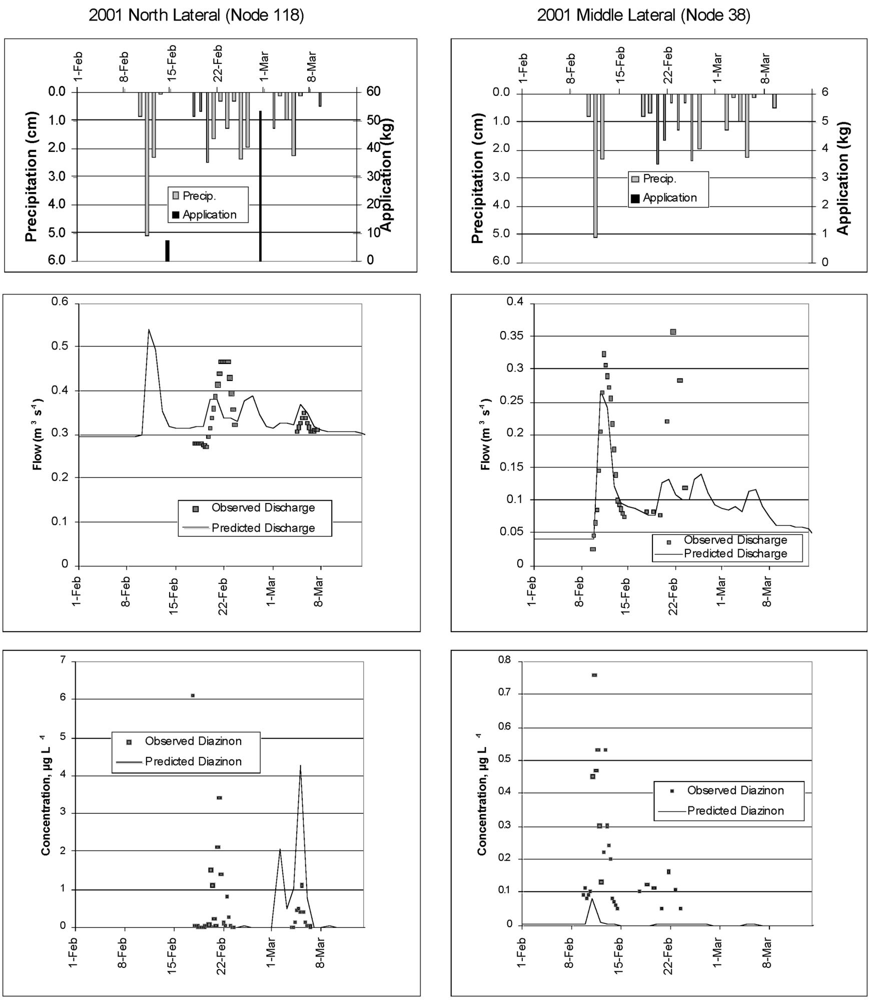
Sensitivity analyses were performed on selected input parameter values, including diazinon degradation rate constants, spray drift loads, channel cross-sectional geometry, and channel storage routing coefficients. The study initially involved the use of PRZM version 3.12, which did not consider subsurface lateral inflow into the receiving water system. This feature was added to PRZM and became a component to the sensitivity analysis. Degradation rates, drift parameters, crop values, and sedimentation values resulted in minor differences in the results. The most sensitive parameters were related to base flow and flow attenuation as discussed below.

Input parameter values were adjusted within realistic ranges in an attempt to better reproduce event timing, magnitude, and duration. Cross-sectional geometry was refined during the calibration process upon receipt of additional data from Dileanis and Thomas. These adjustments provided a relatively small impact on model predictions. Base flow and other subsurface lateral return flow were incorporated into the model and proved to be both highly sensitive and improve predictions of streamflow magnitude, event duration, and, consequently, diazinon event concentration magnitude and duration. Implementing other storage/attenuation mechanisms (Muskingum routing, dead storage) provided incremental improvements in model performance. The storage term compensated for various attenuation factors that exist in the agricultural landscape that were not specifically represented, including interior features of the sub-watersheds (depressions, wetlands, ponds, channel obstructions and side pools, and smaller ditches/canals/streams). Subsurface flow was the primary calibration parameter. Curve numbers were adjusted for the lower basin, which is predominately rice land use. Drift loads were adjusted in some areas of the basin in order to improve model predictions.

Calibration results are presented in Figures 8 and 9. Figure 8 compares predicted versus observed streamflow and diazinon concentration at four locations for 2001, the year with the best record of diazinon concentration in terms of sample frequency. The top panel presents daily precipitation (cm) for reference and interpretation purposes. The middle panel presents streamflow (m^3 s^{-1}) and the lower panel contains diazinon (μg L^{-1}). Monitoring locations are provided in Figure 7. Figure 9 presents results for 1994, 2000, and 2001 on the Main Canal (node 2). Observed streamflow data were not available for 1994 and 2000 for comparison. It was noted in the data supplied by CVRWQB that the 2000 data were mostly obtained through ELISA analysis, which showed a bias towards higher concentrations when compared to GC/MS results. In general, runoff event timing and duration tracked observed data. Predictions of streamflow during runoff events were generally within several cfs in the North (node 118), Middle (node 38), and South (node 36) laterals, but up to 150 cfs (4.24 m^3 s^{-1}) in the Main Drainage Canal.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

In general, diazinon concentrations were within several µg L^{-1} of measured values. Diazinon concentrations in the Middle Lateral (node 38) appeared to be consistently under predicted during 2001 (Figure 8), but the difference was within 1 µg L^{-1}. Streamflow was under predicted in the Main Drainage Canal (node 2) during 2001. Other locations had no consistent over- or under prediction between streamflow or diazinon exposure events. System modifications that improved the performance at these locations (nodes 38 and 2) adversely impacted model performance elsewhere in the system.



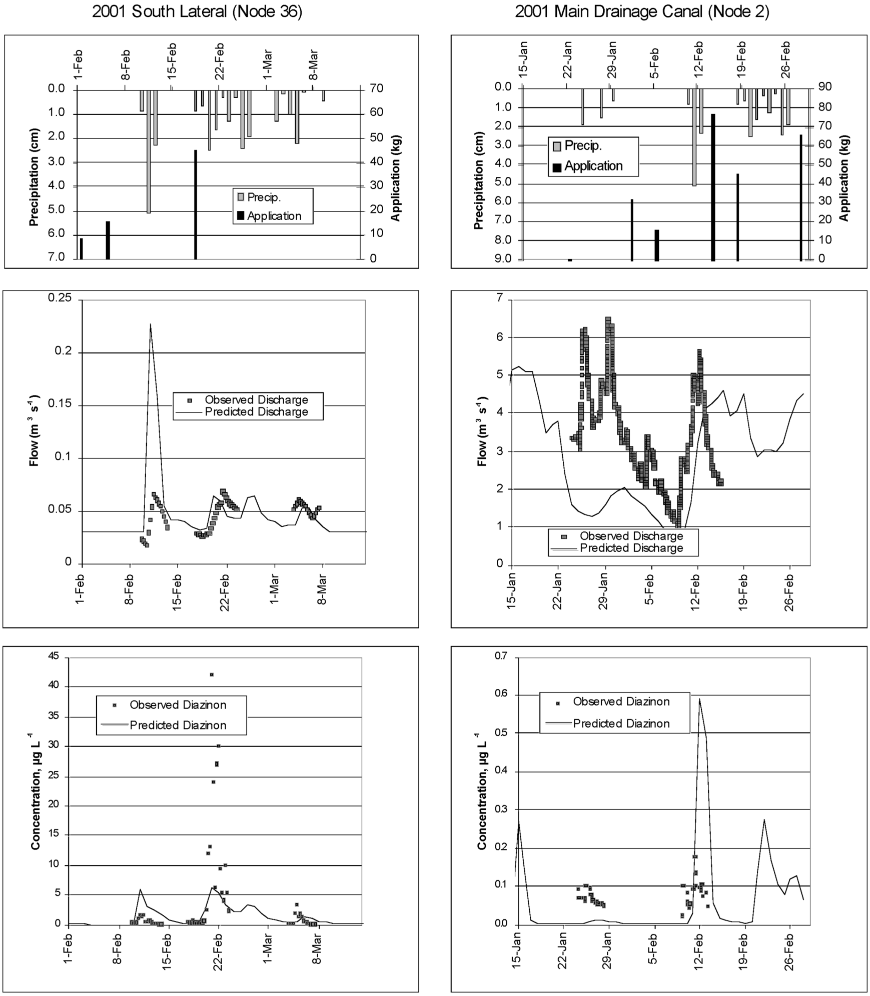


Figure 8. Calibration Results for Year 2001.

The model could not reproduce the observed concentrations of diazinon seen around February 21, 2001, in the North Lateral canal (node 118; Figure 8) because there was no record of diazinon use in the PUR database. Either the observed concentrations represented an unreported use of diazinon in the watershed or boundary condition inflow from external uses (i.e., an external source of water upstream of this location). Water flow entering the watershed at the North Lateral was accounted for by increasing baseflow during the calibration process. However, external loading of chemical was not included. It may be possible that application dates in the PUR are incorrect for areas contributing to this location because model predictions from March 1 to March 8 were anomalously high.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

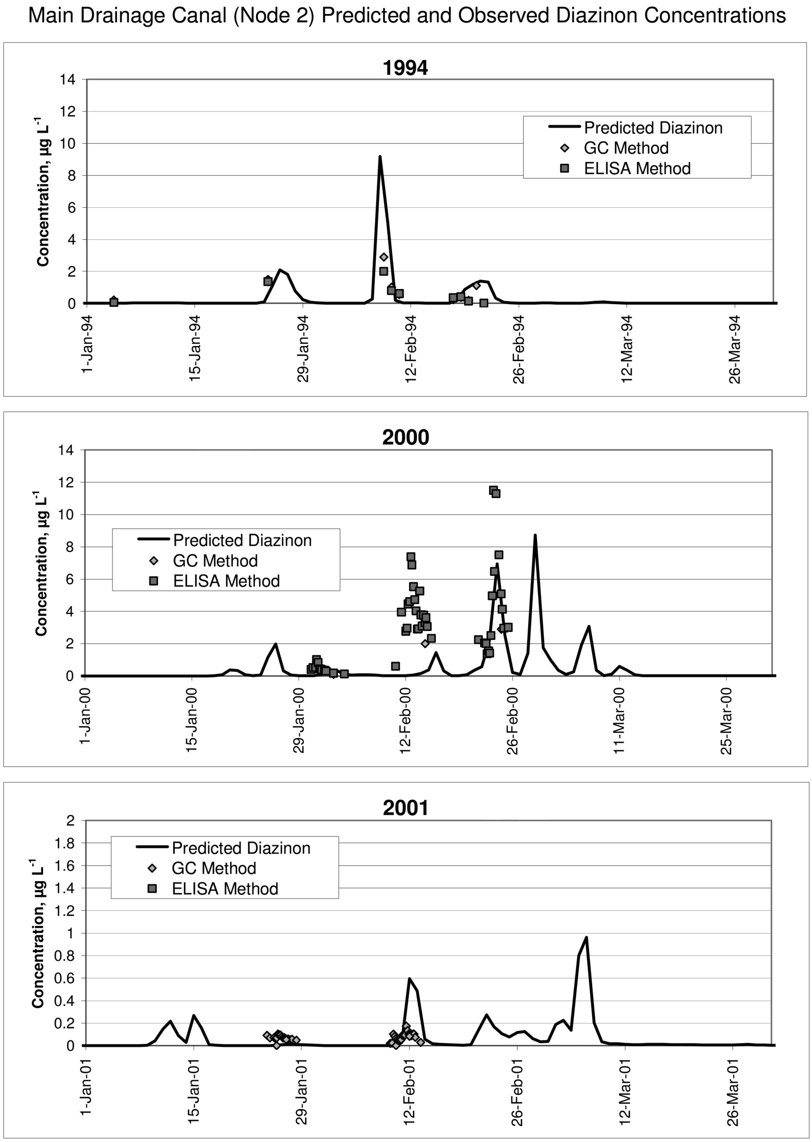


Figure 9. Calibration Results for Years 1994, 2000, and 2001.

Environmental chemistry properties for diazinon were not adjusted during calibration. Reducing degradation half-lives for PRZM may improve model performance later in the season, but uncertainties in other areas of model configuration did not provide sufficient justification for changing degradation rates. As a result, diazinon properties remained consistent with those used in earlier simulations by the U.S. Environmental Protection Agency (*12*, *15*). The final configuration was determined to be the best compromise for the system at large.

Simulations of Historical Uses of Diazinion

Predicted concentrations of diazinon in the Main Drainage Canal (Node 2) for the simulation period 1992 through 2001 are presented in Figure 10. The figure also presents daily precipitation for the Oroville weather station and model predictions of streamflow for the same period. Simulations reflect actual use of diazinon in the watershed as reported in the PUR database use for the same period. The figure illustrates seasonal and annual variability in precipitation, streamflow, and diazinon concentration.

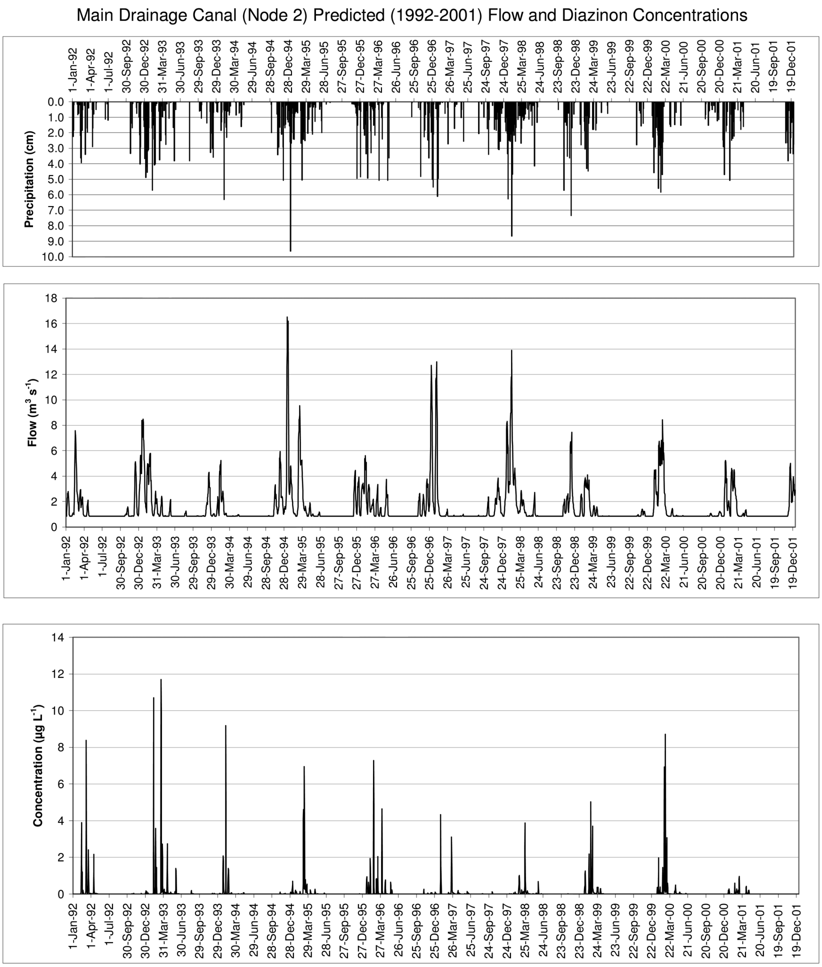


Figure 10. Predicted Streamflow and Diazinon Concentration in Main Drainage Canal for Simulation Periods 1992-2001.

Annual maximum diazinon concentrations are summarized in Table II for four points of interest, the Main, North, Middle, and South canals. Both Figure 10 and Table II illustrate the relative difference between years when relatively high (1992, 1993, 1994, and 2000) and low concentrations (1997, 1998, 1999, and 2001) were observed. Similar tables can be generated for other endpoints (e.g., 96-hour durations). Peak concentrations of diazinon ranged from 0.96 μg L^{-1} (2001) to 11.7 μg L^{-1} (2000) in the Main Drainage Canal. The highest concentration (27.6 μg L^{-1}) was predicted in the Middle Lateral for 2000.

Table II. Simulated Maximum Annual Concentration of Diazinon in Main Drainage Canal and Laterals

	Max. Annual Concentration in Water (μg L^{-1})			
Year	*Main Drain Node 2*	*North Node 118*	*Middle Node 38*	*South Node 36*
1992	8.38	10.70	8.45	7.02
1993	11.70	17.80	19.50	15.20
1994	9.18	7.59	11.80	10.10
1995	6.94	4.66	5.06	16.50
1996	7.28	5.23	6.47	10.60
1997	4.32	3.97	17.30	2.16
1998	3.87	7.36	3.93	7.70
1999	5.03	15.80	18.60	4.91
2000	8.72	22.10	27.60	19.60
2001	0.96	4.27	0.34	6.20

The predominant source of diazinon loading was from runoff (Table III). Drift and subsurface transport pathways were relatively small. Furthermore, diazinon pulses coincided with rainfall events as opposed to application events. There were no noticeable spikes on the days without rain, and it is unlikely that applications were occurring during rainfall events.

Based on 2001 use patterns, source loadings were concentrated in the eastern, upper part of the watershed (Figure 11). The lower basin, primarily planted in rice, has negligible use of diazinon. Subbasins generating the highest loadings to the aquatic environment included those numbered 150, 160, 690, 710, 720, and 730 on the South Lateral and 580, 600, and 740 on the North Lateral. These sub-watersheds were characterized as having large percentages of soils of Hydrologic Soil Groups C or D (Figure 3) and significant acreage of stone fruit treated with diazinon (Figure 6).

Table III. Simulated Mass Loadings of Diazinon to Receiving Water System from Runoff, Subsurface and Drift Sources

Year	*Mass (kg)*	*Runoff (%)*	*Subsurface (%)*	*Drift (%)*
1992	8.42	99.75%	0.13%	0.11%
1993	15.76	98.08%	1.84%	0.09%
1994	7.42	98.21%	1.69%	0.12%
1995	12.35	99.21%	0.74%	0.06%
1996	9.55	96.09%	3.78%	0.13%
1997	5.64	99.80%	0.03%	0.16%
1998	3.83	90.13%	9.71%	0.15%
1999	7.98	97.69%	2.24%	0.07%
2000	21.32	98.86%	1.11%	0.04%
2001	1.98	99.70%	0.12%	0.19%

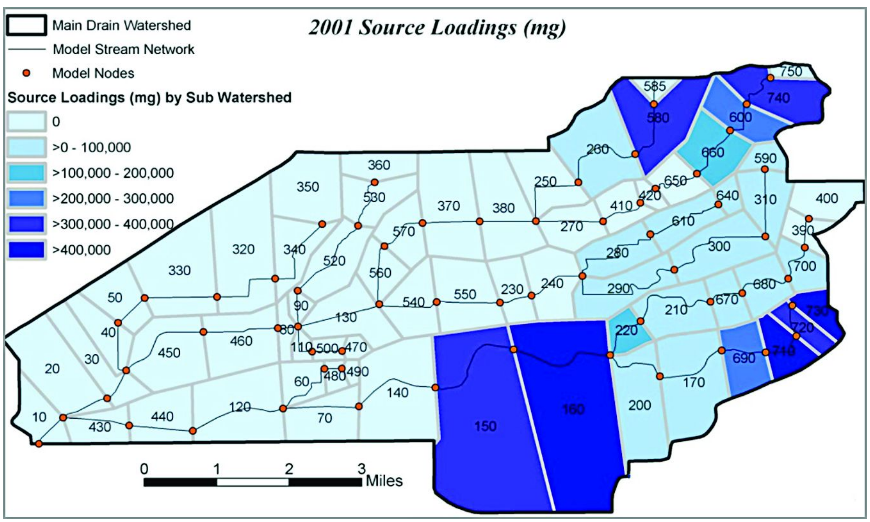


Figure 11. Aquatic Loadings of Diazinon by Sub-Watershed for 2001. (see color insert)

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Diazinon applications in the watershed generally occur from December through March with the highest use in January and February. An additional, but lesser, use of diazinon occurs in the watershed in the late spring/summer months (May through September). The application window for diazinon on dormant orchards coincides with the wet season (December through March) with the months of highest use corresponding with the wettest months of the year (January and February). Thus, the majority of diazinon use is during periods when runoff events are most likely to occur. Periods of highest concentration are also predicted to occur during the December to March, although in some years elevated concentrations were predicted to occur through May.

Management Scenarios

Management practices were added to product labels for diazinon use on dormant orchards in the San Joaquin and Sacramento River basins in 2004 to minimize the transport of diazinon to aquatic ecosystems. Practices included ground application only during the dormant season, requiring a 3.0 m vegetative filter strip (VFS) to reduce runoff, and a 30.5 m application setback to reduce drift, limiting applications if soils are saturated or if rainfall is forecast within a 48-hour period, encouraging optimum timing for application based on larvae count/development, and restricting applications based on wind speed and wind direction to minimize spray drift.

The impact on each practice was evaluated by comparing model predictions of diazinon concentrations in the Main Drainage Canal and mass loadings of diazinon into receiving streams to model predictions of baseline conditions. For the purpose of this assessment, baseline conditions were defined as current uses of diazinon, based on the last several years of PUR records, and standard agronomic practices in place prior to the recent stewardship program recently promoted by the Coalition for Urban/Rural Environmental Stewardship (CURES) and implemented on product labels. Model simulations were conducted using 10 years of historical weather data (1992-2001) to evaluate diazinon transport to receiving water streams in a probabilistic fashion (i.e., under a range of low, moderate, and high runoff conditions).

A 12 x 25 scenario matrix was developed consisting of variations in application frequency, rate, and rainfall forecasting restrictions (*16*) with variations in percent of crop treated, application setback requirements (drift reduction buffers), VFS widths, and maintenance of inter-row VFS (*13*). The scenario matrix (Tables IV and V) includes and expands on the management practices recently implemented on product labels. The matrix also provides a sensitivity analysis on use conditions that could occur; for example, if all candidate crop acreage in the watershed were treated at the maximum label rate.

Table IV. Application Conditions Simulated in Scenario Matrix

Application Scenario	*Applications per Year*	*Rainfall Window*[a]
A	3/yr at max rate	no restriction
B	2/yr at max rate	no restriction
C	1/yr at max rate	no restriction
D	3/yr at max rate	24-hr window
E	2/yr at max rate	24-hr window
F	1/yr at max rate	24-hr window
G	3/yr at max rate	48-hr window
H	2/yr at max rate	48-hr window
I	1/yr at max rate	48-hr window
J	3/yr at max rate	72-hr window
K	2/yr at max rate	72-hr window
L	1/yr at max rate	72-hr window

[a] Note: Rainfall window refers to management practice prohibiting application if rainfall is forecast within the designated period (e.g., within the next 24 hours)

Application Factors

Each application scenario consisted either of 1, 2, or 3 applications per year at the label rate of 2.24 kg ha^{-1} per application. The number of applications reflected options permissible on product labels. Application dates and intervals were based on an analysis of the PUR data for the years 1998 to 2002. When three applications were simulated, applications were scheduled to occur over 7-day intervals centered on February 2nd, 20th, and 27th. When two applications were simulated, the applications were centered on February 20 and 27. When a single application, was simulated, the window was centered at February 20. In the analyzed time period, the 7-day windows around February 2nd, 20th, and 27th accounted for 12.5%, 27.6%, and 19.1% the total applications, for a total 59.2% of all applications around the three dates.

Scenarios were designed to simulate the effect of restricting applications within 24, 48, or 72 hours of a forecasted rainfall event. If rainfall of one inch or more occurred within the target window, applications were shifted to occur before or after the originally targeted application date. The scenario assumed all applications would occur, but the timing would shift if the potential for rainfall was forecast. The 12 application scenarios are summarized in Table IV. The applications factors are listed in Table VI.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Table V. Reduction Factors Used in Management Scenario Matrix[a]

Option	*FRAC_ STRM[b]*	*FRAC_ DRFT[c]*	*FRAC_ APP[d]*	*RUN_ FRAC[e]*	*Comment[f,g]*
0	1.00	0.05	1.00	1.00	100% crop treated
1	1.00	0.05	0.50	1.00	50% crop treated
2	1.00	0.05	0.25	1.00	25% crop treated
3	1.00	0.05	1.00	0.489	10′-VFS, 100% crop treated
4	1.00	0.05	0.50	0.489	10′-VFS, 50% crop treated
5	1.00	0.05	0.25	0.489	10′-VFS, 25% crop treated
6	1.00	0.05	1.00	0.373	20′-VFS, 100% crop treated
7	1.00	0.05	0.50	0.373	20′-VFS, 50% crop treated
8	1.00	0.05	0.25	0.373	20′-VFS, 25% crop treated
9	1.00	0.05	1.00	0.177	50′-VFS, 100% crop treated
10	1.00	0.05	0.50	0.177	50′-VFS, 50% crop treated
11	1.00	0.05	0.25	0.177	50′-VFS, 25% crop treated
12	1.00	0.05	1.00	0.67	50%IRC, 100% crop treated
13	1.00	0.05	0.50	0.67	50%IRC, 50% crop treated
14	1.00	0.05	0.25	0.67	50%IRC, 25% crop treated
15	1.00	0.05	1.00	0.27	100% IRC, 100% crop treated
16	1.00	0.05	0.50	0.27	100% IRC, 50% crop treated
17	1.00	0.05	0.25	0.27	100% IRC, 25% crop treated
18	1.00	0.032	0.50	1.00	No setback, 50% crop treated
19	1.00	0.018	0.50	1.00	25’ setback, 50% crop treated
20	1.00	0.012	0.50	1.00	50’ setback, 50% crop treated
21	1.00	0.008	0.50	1.00	100’ setback, 50% crop treated
22	2.00	0.032	0.50	1.00	no setback, 2x width, 50% treated
23	2.00	0.018	0.50	1.00	25’ setback, 2x width, 50% treated
24	2.00	0.012	0.50	1.00	50’ setback, 2x width, 50% treated,
25	2.00	0.006	0.50	1.00	100’ setback, 2x width, 50% treat.

[a] Distances of 10, 20, 25, 50, and 100 ft equal 3.0, 6.1, 7.6, 15.2, and 30.5 m. [b] FRAC_STRM: Fraction of fields within drift receiving area. [c] FRAC_DRFT: Fraction of application rate hitting water surface. [d] FRAC_APP: Fraction of crop acreage treated. [e] RUN_FRAC: Runoff/erosion reductions for VFS and inter-row vegetative cover. [f] IRC: Inter-row vegetative cover. [g] VFS: Vegetated filter strip.

Table VI. Application Factors in 12 x 25 Scenario Matrix

Factor	*Variation*
Number of applications	1, 2, or 3 applications per year
Rainfall forecast restriction	0, 24, 48, and 72-hr restriction

Management Factors

Twenty-five runoff/drift conditions were simulated for each of the 12 application scenarios (Table V). The conditions included both management factors to mitigate diazinon transport and a sensitivity analysis to address uncertainty in model parameterization. The management factors (21 conditions) include reducing treated acreage, using VFS, maintaining inter-row vegetative filter strips, and implementing buffer strips to reduce direct spray drift to adjacent ditches and streams. Four additional conditions were simulated to address uncertainty in estimates of potential ditch and stream exposed to drift.

The 25 management conditions (Table VII) were simulated by applying reduction factors to scale drift and/or runoff loadings of diazinon from the agricultural system (predicted by the PRZM model) to the river system (predicted by RIVWQ).

Table VII. Management Factors in 12 x 25 Scenario Matrix

Factor	*Variation*
Crop treatment	25%, 50%, 100% of crop acreage treated
Vegetative filter strip	0, 10, 20, and 50 ft (0, 3.0, 6.1, and 15.2 m)
Inter-row vegetative filters	0%, 50%, and 100% vegetative filter cover
Drift buffer	0, 25, 50 and 100 ft (0, 7.6, and 15.2 m)
Drift reception area	Baseline and 2x baseline

The three crop treatment percentages reflect the fact that not all fields/orchards are treated in a given year. An analysis of previous application years (1998-2002) showed that between 13% and 31% of the potential crop area (as mapped in 1994 Butte County land use survey, Figure 4) received applications. The 25% scenario most accurately reflected recent yearly applications, whereas 50% and 100% treatments, although not typical, were still possible given the current labels.

Runoff loading reductions resulting from vegetative filter strips of variable widths were represented using empirical reduction factors incorporated in the SWAT model (*17*). The filter trap efficiency provided in SWAT is based on empirical data and is represented as:

$$trap_{ef} = 0.367\ (width_{filtstrip})^{0.2967}$$

in which $trap_{ef}$ is the fraction of the loading trapped and $width_{fs}$ is the width in meters of the filter strip.

Reductions from inter-row vegetative filters was based on research by Watanabe and Grismer (*18*) in which observed diazinon runoff, as a percent of applied active ingredient, was 8.6%, 5.8%, and 2.3% with 0%, 50%, and 100% inter-row VFS cover, respectively. In rainfall simulation based studies, the authors achieved similar results when a 50 mm hr^{-1} rainfall event was used and had lower diazinon losses with lower intensity rainfall events. Their high-intensity rainfall results were used for this study as conservative estimates of effectiveness.

The base drift fraction scenario assumed 5% drift with all stream surface area potentially close to a field receiving an application. Drift reductions to conform to the 30.4 m setback and wind speed/wind direction management practices were based on airblast model predictions using AgDRIFT (*19*). Drift loads predicted by the AgDRIFT model were as follows: 7.6 m = 1.78%, 15.2 m = 1.23%, and 30.4 m = 0%. A high-resolution analysis of field proximity to ditches and streams was not incorporated into the model setup. A sensitivity analysis was included to address uncertainty in the surface area of ditches and streams receiving spray drift. For the sensitivity analysis, the potential receiving area was doubled. This factor likely represented a more conservative estimate of drift. Reduction factors used for each scenario are summarized in Table VII. Definitions for each factor are provided below:

- FRAC_STRM: Fraction of fields within drift receiving area. A value of 1.0 indicates all stream surface area receives the drift rate (determined with the FRAC_DRFT). A value less than 1.0 indicates a reduction.
- FRAC_DRFT: Fraction of application rate hitting water surface (function of VFS width or drift setback.)
- FRAC_APP: Fraction of crop acreage treated.
- RUN_FRAC: Runoff/erosion reductions for VFS and inter-row vegetative filters. The factors were applied to runoff/erosion loads, not drift or subsurface sources.

Scenario Results

Scenarios were evaluated by comparing annual loadings of diazinon to water, predicted by the model from runoff, drift, and subsurface sources, and by comparing annual maximum concentrations predicted at the outlet of the Main Drainage Canal to baseline conditions. Scenarios used the same historical weather data simulated with the baseline scenario in order to provide a side-by-side comparison. The upper 10th percentile values calculated from the annual series were used for the comparison. Baseline conditions were represented as 25% of crop treatment at a single application per year. Comparing individual scenario results in Figure 12 provided a means to evaluate the relative impacts of individual factors.

- Number of applications. Increasing the number of applications resulted in an increase in diazinon concentration of 111% with two applications and 151% with three applications. These results were not directly proportional to the total increase in applied diazinon mass because of the stochastic nature of rainfall and the temporal aspects of degradation and other dissipation mechanisms.
- Rainfall restriction. The benefits of restricting applications based on forecasted rainfall varied on a storm-by-storm basis. Relatively little benefit occurred in the upper 10th centile concentration. The 24-hour restriction provided a reduction of 3.5%, but the 72-hour restriction increased concentration by approximately 10%. The increased concentration associated with the 72-hour restriction was associated with a greater mass of diazinon on surface soils at the onset of the storm event associated with the upper 10th centile concentration. The mass increase resulted from condensed applications.
- Percent crop treated. Increasing the percent of treated crop from 25% to 50% and 100% percent resulted in increased concentrations of 100% and 298%, respectively.
- Vegetative filter strips. Vegetative filter strips (VFS) reduced diazinon concentrations by 51%, 63%, and 82% with VFS widths of 3, 6.6, and 15.2 m, respectively (C5, C8, and C11 compared to C2). These results reflected optimal conditions. In practice, VFS must be maintained to minimize and prevent channel formation and short-circuiting.
- Inter-row vegetative filters. Inter-row vegetative filters reduced concentrations by 33% and 72% with coverage of 50% and 100%, respectively.
- Drift buffers. The 7.6, 15.2, and 30.4 m setback distances provided relatively little impact on the upper 10th centile diazinon concentrations and total period mass loadings. Drift reduction had the greatest impact on shallow headwater ditches and streams, which were not included in the link-node representation of the channel system, and in reducing low-level concentrations of diazinon between runoff events during the application season.
- Drift reception area. Doubling the drift load to account for uncertainty in the surface area exposed to drift proved to be a relatively insensitive parameter because of the dominance of runoff in total mass loadings and high exposure events.

The recent label practices are represented as 25% crop treatment, a single application per year, a 24-hour rainfall window, and a 3.0 m VFS. The 30.4 m setback for drift reduction was not included with these other factors in scenario F5. The relative benefit of the drift buffer was minor as discussed above and as shown between scenarios F18 and F20. In combination, the label practices were predicted to provide a 53 percent reduction in diazinon loadings to the water and a 52 percent reduction in the upper 10^{th} centile annual maximum concentration.

Elimination of diazinon transport to aquatic systems was not predicted to occur with the recent label changes. However, the management practices specified on the label predicted considerable reductions in diazinon loadings and concentrations in the Main Drainage Canal. Similar reductions are likely to occur in other areas of the Sacramento River basin that have similar use density and climate.

In summary, the greatest reductions in diazinon loadings and aquatic concentrations were predicted to occur with adjacent VFS, inter-row vegetative filters, and decreased diazinon use (number applications and percentage of crop treated). Lesser impacts were predicted to occur with drift buffers and rainfall restrictions, although these practices may reduce impacts in shallow headwater ditches during small storm events.

Management options and refinements that had been considered, but could not be evaluated, include the following:

- Vegetative filter ditches. Research in this area was being initiated in the Sacramento River watershed (*20*), but was not available at the time for model development, validation, and application.
- Sophistication in simulating Vegetative Filter Strips. Results presented here reflect reduction factors applied to edge-of-field loadings based on empirically derived data. More sophisticated methods can be employed to address chemical mass balance within the VFS in a temporal context (e.g., ability to address variability in storm magnitude and potential flushing of accumulated residues). Several options include the linkage of PRZM simulations as a runoff-run on model, and the use of models like VFSMOD or REMM (*21*) that were designed to simulate pesticide attenuation and retention processes in VFS.
- Water holding. Containing runoff water for 72 hours prior to downstream release has been recommended in recent stewardship programs (*22*), but was not simulated herein. Water holding may be practical in certain areas of the Main Drainage Canal because of the high density of rice acreage that could conceivably be used for storage. Studies have shown that rice fields can effectively reduce diazinon transport to downstream water bodies (*23*, *24*). Water holding can be represented in various ways in the PRZM-RIVWQ modeling system and/or through linkages with the Rice Water Quality model.
- Sophistication in simulating drift loads. Greater sophistication can be employed in simulating drift as a function of setback distance, wind speed, and wind direction. This would require a more detailed spatial characterization of the proximity of treated fields to nearby ditches, streams, and other potential receiving water bodies along with a stochastic or probabilistic representation of wind speed and direction.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

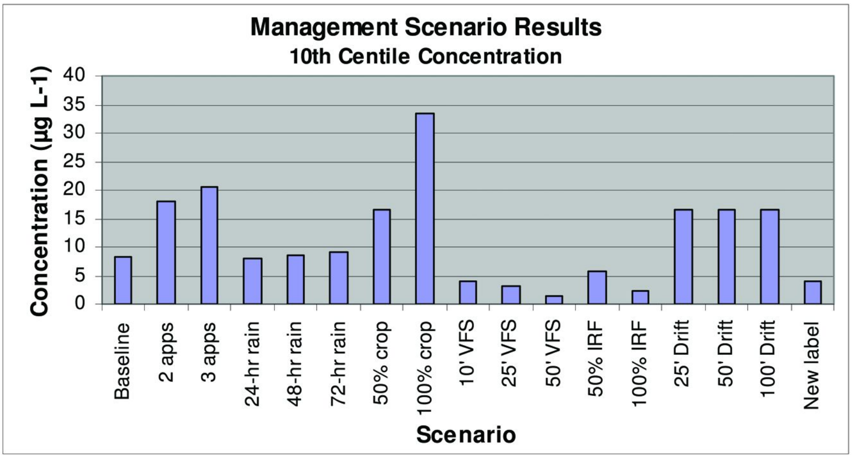


Figure 12. Comparison of upper 10th centile concentrations for select management practices. Baseline approximates pre-2004 label practices, apps=number of applications, x-hr rain=rainfall restriction window, % crop= % of crop treated, VFS=width of vegetative filter, IRF=percent coverage of inter-row vegetative filter, Drift=setback distance, New label = suite of management factors on 2004 label.

Post-Label Monitoring

Monitoring data for diazinon from 1999 through 2010 for the Bay Delta Estuary watershed system are presented in Figure 13. The watershed as defined herein includes the Sacramento River and San Joaquin River watersheds, as well as the drainage area below the confluence of these rivers. The outlet of the watershed is located approximately at the base of the Golden Gate Bridge. The monitoring data contain a five-year period immediately prior to label changes in 2004 and a five-year period after label changes (Figure 13). The data used to generate Figure 13 were obtained from the California Department of Pesticide Regulation (CDPR) and the National Water Information System (NWIS) database operated by the USGS (downloaded March 2011). Both data sources provide the latitude and longitude coordinates of the water sample collection location. With these coordinates, Arc GIS 9.3 was used to narrow down the samples to those collected within the Bay Delta Estuary watershed. The 2004 monitoring data are not depicted in the figure because it was a transition year for label implementation. Overall, a decrease in the percentage of samples with detectable amounts of diazinon in the watershed has occurred since the label change (46% to 20% of samples). Diazinon concentration in samples below levels of quantification were populated with half of the provided level of quantification. A total of 2,352 samples were used to generate the box plots. Between the two periods, the median diazinon value decreased from 0.02 µg L^{-1} to 0.0015 µg L^{-1}.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

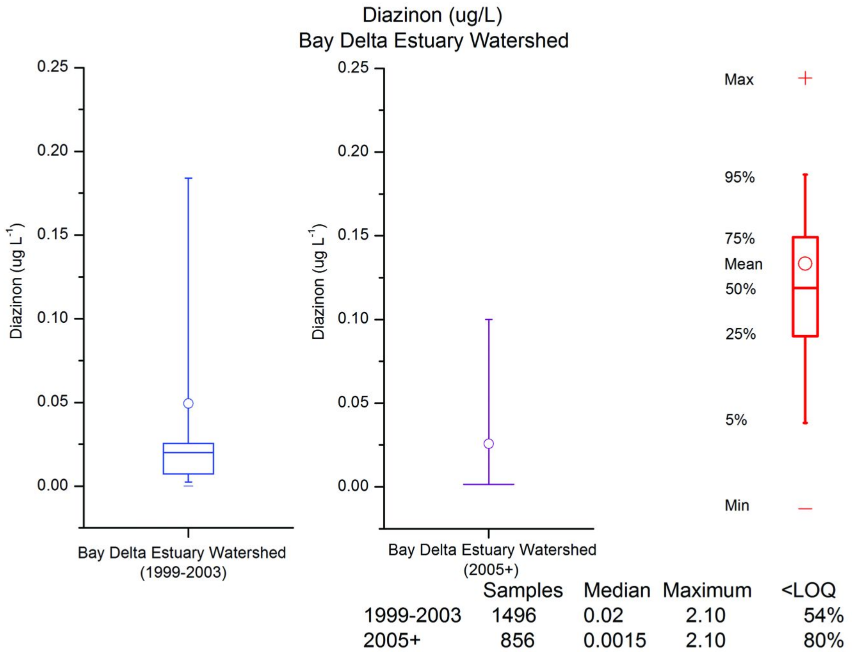


Figure 13. Statistical summary of monitoring data for diazinon in the Bay Delta estuary watershed before and after label changes (see color insert)

There are several factors that may have contributed to the apparent decrease in diazinon concentrations. This includes changes in management practices as directed by the label and use. As illustrated in Figure 14, diazinon use decreased from 90,700 to 34,000 kg in the period 2000-2008 in the Bay Delta Estuary watershed system. During this period, non-agricultural uses of diazinon were canceled and agricultural uses declined in favor of other insecticides. Figure 14 was generated using the California Department of Pesticide Regulation's Pesticide Use Reporting (PUR) database, which quantifies the yearly use of all registered pesticides. Registered uses include agricultural fields, pastureland, parks, golf courses, cemeteries, and roadsides rights-of-way.

Watershed-wide improvements have been documented in a number of sub watersheds surrounding the Sacramento River, Feather River, Sacramento Slough, and Sutter Bypass (*25*). Approximately 48% of the river miles listed as diazinon-impaired in 2002 within the Lower Sacramento Basin have been removed from the CWA Section 303(d) Impaired Water Bodies List for diazinon impairments.

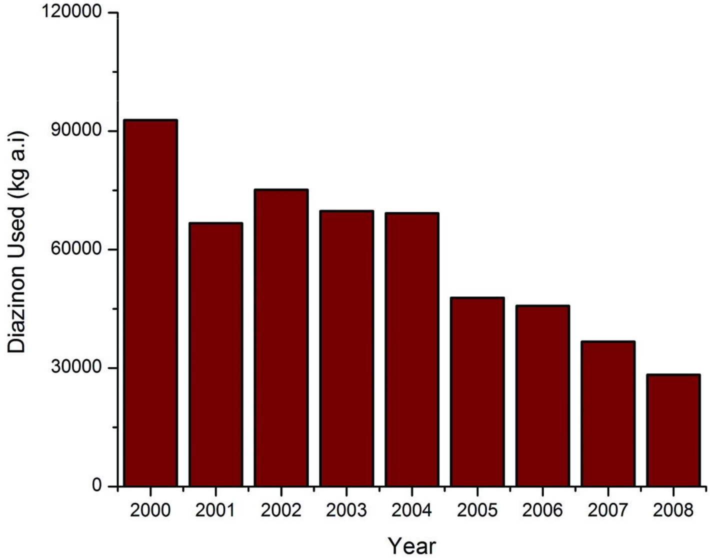


Figure 14. Registered Diazinon use in Bay Delta Estuary watershed from 2000 to 2008.

Conclusions and Recommendations

In combination, PRZM and RIVWQ simulated temporally and spatially varying applications of diazinon and its fate and transport in the watershed. Sufficient data existed to characterize important factors in the movement of diazinon to non-target areas, including variability in soils, weather, and diazinon use. Detailed information was not readily available on diazinon degradation under local conditions, channel cross-sectional geometry, and localized drainage and water management. Areas of greatest uncertainty were in precise characterization of drainage, representing the impacts of smaller ditches and streams, and in predicting drift loads and transport with lateral subsurface flow.

The predominant source of diazinon loading in the aquatic system was predicted to occur from surface runoff. Drift and subsurface transport pathways were relatively small by comparison. Subbasins generating the highest diazinon loads were in the upper eastern portion of the watershed and characterized as having large percentages of soils of Hydrologic Soil Groups C or D (i.e., relatively high silt and clay content) and substantial acreage of stone fruit treated with diazinon. The lower basin, primarily planted in rice, has negligible use of diazinon.

In general, the periods of highest concentration in surface waters were predicted to occur from December through March. In some years, elevated concentrations were predicted to extend into May. This coincided with the period of highest diazinon use and the wettest period of the year, when runoff events are most likely.

Among the management scenarios evaluated, the greatest reductions in diazinon loadings and aquatic exposure concentrations were predicted to occur with adjacent VFS, inter-row vegetative filters, and decreases in diazinon use (number applications and percentage of crop treated). Less impact was predicted with drift buffers and rainfall restrictions, although simulations indicated that implementation of these practices may reduce concentrations in shallow headwater ditches and during smaller runoff events in the Main, North, Middle, and Lateral canals.

Management practices added to diazinon labels in 2004 for applications to dormant orchards in the San Joaquin and Sacramento River basins were predicted to provide considerable reductions in diazinon loadings and concentrations in the Main Drainage Canal. In combination, the label practices were predicted to provide a 53% reduction in diazinon loadings to ater and a 52% reduction in peak concentration.

Monitoring data collected in the past six years (2004-2010) since label changes were implemented showed a reduction in the numbers of samples with detectable residues and in the median diazinon concentration. Modeling results indicated that reductions were attributable to the implementation of label changes, cancellation of non-agricultural uses of diazinon, and an overall decrease of use in the area. Nearly half of the river miles listed diazinon-impaired in 2002 within the Lower Sacramento Basin have been removed from the CWA Section 303(d) Impaired Water Bodies List for diazinon impairments.

Acknowledgments

This study was conducted through the Sacramento River Toxic Pollutant Control Program (SRTPCP) under a grant funded by the U.S. Environmental Protection Agency (USEPA) Region 9 to the Sacramento Regional County Sanitation District (SRCSD). The authors would like to acknowledge the following individuals, agencies, and organizations for providing information, review, or other assistance during the course of the study and the preparation of this manuscript: Jerry Troyan and Kristi Walters, Sacramento Regional County Sanitation District (SRCSD); Kathy Russick, Sacramento River Watershed Program (SRWP); Danny McClure and Kelly Briggs, Central Valley Regional Water Quality Control Board (CVRWQCB); Peter Dileanis, U.S. Geological Survey (USGS); Fred Thomas, CERUS Consulting; Joe Connell, University of California Cooperative Extension; Michael Oliver, Research Consultant; Robert Ehn, for Makhteshim-Agan of North America; Romeo Favreau, University of California, Davis; Lei Guo, California Department of Pesticide Regulation; Mary Nett, Water Quality Consulting; Nick Poletika, Dow AgroSciences LLC; Mark Grismer, University of California, Davis; Charles Crawford, U.S. Geological

Survey; Mark Russell, DuPont Agricultural Products, Ron Parker, U.S. Environmental Protection Agency; and Joshua Allen, Waterborne Environmental, Inc. Note: Although this chapter has been reviewed and approved in accordance with U.S. EPA requirements, its contents do not necessarily reflect U.S. EPA views or policy.

References

1. U.S. Environmental Protection Agency (USEPA). Pesticide Root Zone Model Field and Orchard Crop Scenario Metadata. Pesticides: Science and Policy. Updated September 28, 2004. http://www.epa.gov/oppefed1/models/water/metadata.htm.
2. U.S. Environmental Protection Agency (USEPA). Interim Reregistration Eligibility Decision: Diazinon. EPA 738-R-04-006; Office of Pesticide Programs, May 2004.
3. U.S. Geological Survey (USGS). NWISWeb Data for the Nation. http://waterdata.usgs.gov/nwis (verified July 21, 2004).
4. U.S. Geological Survey (USGS). USGS National Water Quality Assessment Data Warehouse.http://water.usgs.gov/nawqa (verified Nov. 11, 2004).
5. U.S. Geological Survey (USGS). National Hydrography Dataset (NHD). http://nhd.usgs.gov/ (verified Nov. 11, 2004).
6. Central Valley Region Water Quality Control Board (CVRWQCB). *Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Orchard Runoff Into the Sacramento and Feather Rivers*; 2003.
7. Sacramento River Watershed Program (SRWP). *Annual Monitoring Report: 2000-2001*; June 2002.
8. U.S. Environmental Protection Agency (USEPA). Tier two screening model shell for pesticide aquatic exposure assessment. *(P)RZM (E)XAMS model shell*, version (5).0 user's manual; Environmental Fate and Effects Division, Office of Pesticide Programs, 2006. http://www.epa.gov/oppefed1/models/water/index.htm#przmexamsshell.
9. Suárez, L. A. *PRZM_3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.12.2*; National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency: Athens, GA, 2005.
10. Parker, R.; Arnold, J. G.; Barrett, M.; Burns, L.; Carrubba, L.; Neitsch, S. L.; Snyder, N. J.; Srinivasan, R. Evaluation of Three Watershed-Scale Pesticide Environmental Transport and Fate Models. *J. Am. Water Resour. Assoc.* **2007**, *43* (6), 1424–1443.
11. Briggs, K. A.; Oliver, M. *Technical Memorandum: Study of Diazinon Runoff in the Main Canal Basin During the Winter 2000-2001 Dormant Spray Season*; SRWP OP Focus Group, 2002.
12. U.S. Environmental Protection Agency, (USEPA). Revised Tier 2 EEC's for Diazinon. Memorandum dated November 14, 2000 from R. David Jones,

Ph.D., Senior Agronomist to Danette Drew, Health Effects Division, 33 pages.

13. National Climatic Data Center. *Climate Data Online*. http://www.ncdc.noaa.gov/oa/ncdc.html (verified July 21, 2004).
14. California Department of Pesticide Regulation (CADPR). Pesticide Use Reporting (PUR) Database, 2004. http://www.cdpr.ca.gov/docs/pur/purmain.htm.
15. U.S. Environmental Protection Agency (USEPA), 2000a. *Environmental Risk Assessment for Diazinon*, Revised Science Chapter; October 2000, 77 pages.
16. Central Valley Region Water Quality Control Board (CVRWQCB). *Draft Program of Implementation Report for the Control of Diazinon in the Sacramento and Feather Rivers*; California Environmental Protection Agency, May 2002.
17. Neitsch, S. L.; Arnold, J. G.; Kiniry, J. R.Williams,J. R.; King, K. W. *Soil And Water Assessment Tool, Theoretical Documentation*, Version 2000; Grassland, Soil And Water Research Laboratory, Agricultural Research Service, 2002.
18. Watanabe, H.; Grismer, M. Numerical modeling of diazinon transport through inter-row vegetative filter strips. *J. Environ. Manage.* **2003**, *69*, 157–168.
19. Teske, M. E.; Bird, S. L.; Esterly, D. M.; Ray, S. L.; Perry, S. G. *A User's Guide for AgDRIFT® 2.03*; Technical Note No. 95-10; CDI: Princeton, NJ, U.S.A., 2001.
20. Denton, D. L.; Moore, M. T.; Cooper, C. M.; Wrysinski, J.; Williams, W. M.; Miller, J. L.; Reece, K.; Crane, D.; Robins, P. Mitigation of Permethrin in Irrigation Runoff by Vegetated Agricultural Drainage Ditches in California. In *Synthetic Pyrethroids: Occurrence and Behavior in Aquatic Environments*; ACS Symposium Series; Gan, J., Spurlock, F., Hendley, P., Weston, D. P., Eds.; American Chemical Society: Washington, DC, 2008; Vol. 991.
21. Winchell, M. *A Comparison of Four Models for Simulating the Effectiveness of Vegetative Filter Strips at Reducing Off-Target Movement of Pesticides*. Prepared by Stone Environmental, Inc., for CropLife America, 2010; 81 pages.
22. Coalition for Urban/Rural Environmental Stewardship (CURES). *Management Practices for Protecting Surface Water During Dormant Orchard Applications*; 2004.
23. Kröger, R.; Moore, M.; Cooper, C. M.; Holland, M. M. Diazinon Accumulation and Dissipation in *Oryza sativa* L. Following Simulated Agricultural Runoff Amendment in Flooded Rice Paddies. *Water Air Soil Pollut.* **2009**, *201*, 209–218.
24. Moore, M. T.; Kröger, R.; Cooper, C. M.; Cullum, R. F.; Smith, S.; Locke, M. A. Diazinon Reduction and Partitioning Between Water, Sediment, and Vegetation in Stormwater Runoff Mitigation through Rice Fields. *Pest Manage. Sci.* **2009**, *65*, 1182–1188.

25. Central Valley Region Water Quality Control Board (CVRWQCB). Reporting watershed improvement (SP-12). *Improving California Central Valley Watersheds: Diazinon Reduction in the Feather and Sacramento Rivers*, 2010; 21 pages.

Chapter 16

Estimating Pesticide Retention Efficacy for Edge-of-Field Buffers Using the Riparian Ecosystem Management Model (REMM) in a Southeastern Plains Landscape

Thomas L. Potter,* R. Richard Lowrance, David D. Bosch, and Randall G. Williams

USDA-ARS, Southeast Watershed Research Laboratory, P.O. Box 748, Tifton, GA 31793
***tom.potter@ars.usda.gov**

Erosion and agrichemical runoff are persistent natural resource concerns. Practices designed to reduce water quality impacts include replacing conventional with conservation-tillage management and maintaining and restoring riparian forests and wetlands. Data and models describing ecosystem-scale responses to these practices are needed to effectively assess their risk reduction potential. We used the Riparian Ecosystem Management Model (REMM) to evaluate riparian buffer system response to herbicide runoff from farm fields managed conventionally (CT) or under a common conservation-tillage practice, strip-tillage (ST). Measured hydrologic and water quality data from a seven-year field study conducted in south central Georgia (USA) were used. Inputs from the CT-system were about 2 times higher than from the ST-system. Simulated outputs from the buffer tracked the input pattern. However, the model indicated that ST-system inputs were attenuated at a lower rate during transport through the buffer. Findings were explainable by examining model processes and agreed with published studies that herbicides transported primarily in the dissolved form and delivered in subsurface flow have lower rates of retention in vegetated buffers. This has implications for

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

assessing impacts of theses conservation practices at watershed scales.

Introduction

Erosion and agrichemical runoff are persistent natural resource concerns (*1*). Remedial strategies include conservation programs that promote use of reduced and or no-tillage management (*2*). Substantial emphasis is also placed on maintaining and restoring riparian forests and wetlands as buffers for water resource protection (*3*). Many decades of research have demonstrated that riparian forest buffers provide important ecosystem services including pollutant attenuation in cropland runoff. The Riparian Ecosystem Management Model (REMM) developed at the USDA-ARS Southeast Watershed Laboratory in Tifton, Georgia (USA) simulates processes in these systems (*4*).

REMM's initial version evaluated surface and subsurface hydrology; sediment transport and deposition; carbon, nitrogen, and phosphorus transport, removal, and cycling, vegetation growth and management options, such as vegetation type, buffer zone size, and biomass harvesting (*4*). REMM applications focusing on hydrologic processes and nutrient dynamics are described in numerous reports (*5–9*). Recently pesticide processes including transport, sorption, degradation and sequestration, and plant uptake within these buffer systems were added to the model. We used this version to evaluate riparian buffer system response to measured edge-of-field loads of two widely used herbicides in surface runoff and subsurface flow from farm fields in conventional and strip-tillage management in south-central Georgia (USA). Strip-tillage (ST) is a commonly used conservation tillage practice in the region. ST involves planting crops into 15-cm wide strips tilled into cover crop residue mulch. A long-term study conducted by our research group showed that when ST was used for rotational cotton (*Gossypium hirsutum* L.) and peanut (*Arachus hypogaea* L.) production a 2-fold decrease in surface runoff and a 2-fold increase in lateral subsurface flow were observed when compared to conventional-tillage (CT) management (*10*). CT in this case involved operations that provided a crop residue free soil surface for planting. Studies also showed that the shift in runoff partitioning between surface and subsurface flow increased transport of a relatively mobile herbicide, fluometuron (*N*, *N*-dimethyl-*N′*-[3-(trifluoromethyl) phenyl] urea), and its degradate desmethylfluometuron (DMF) in subsurface flows (*11*). These observations identified a need to assess how the region's riparian buffer systems may respond as tillage practices and contaminant transport pathways change.

Objectives of this study were to evaluate the utility of REMM for buffer system design relative to control of non-point source pesticide inputs to surface waters and examine how increased use of conservation-tillage in Southeastern (USA) landscapes may impact pesticide retention and attenuation efficacy by riparian buffer systems.

Material and Methods

Input Data

Measured temperature, rainfall, and irrigation, edge-of-field surface and lateral subsurface flow volumes, sediment in surface runoff, sediment organic carbon, and dissolved concentrations of two herbicides pendimethalin (*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitro-benzenamine) and fluometuron and fluometuron's principal soil degradate, DMF, in runoff and lateral subsurface flow were used as model inputs. Data were collected in gently sloping (3–4%) 1-ha field in Tift County, Georgia (USA) equally divided down-slope into two tillage blocks, ST and CT. Soil is classified in the Tifton series (fine-loamy, kaolinitic, thermic, Plinthic Kanidult). Tillage practices were established in 1999 and maintained annually. A rye (*Secale cearale* L.) cover crop was planted after crop harvest each autumn. A burn-down application of glyphosate was made about one month prior to planting in each of the following springs. With the ST-system, crops were planted in 15-cm strips tilled into the cover crop residue. In the CT-system area, crops were planted into beds of freshly-tilled soil free of surface residue. Tillage was accomplished with a chisel plow followed by disking and bedding. Planting dates and crop management followed recommended practices. Soil properties, crop management, and hydrologic and water quality monitoring were described in prior publications (*10–13*).

Data used in simulations were aggregated across each of the three 0.15-ha sub-plots within each tillage block. Results spanned seven years, 2000-2006, during which, four cotton and three peanut crops were produced. Pendimethalin was applied to peanut and cotton crops and fluometuron to cotton. Commercial formulations of each active ingredient (AI) were broadcast at planting with the exception of a post-directed fluometuron application to cotton in June 2001. AI application rates, 0.9 to 1.0 kg ha^{-1}, were based on label recommendations and weed pressure assessment.

Sediment bound concentration of each analyte in each sample was computed using equation 1 with C_s = sediment concentration (ug g^{-1}); C_d = dissolved concentration (ug mL^{-1}); K_{oc} = sediment water partition coefficient (mL g^{-1}); f_{oc}= fraction organic carbon in sediment. Linear partitioning was assumed.

$$C_s = C_d*K_{oc}*f_{oc} \qquad 1$$

Pendimethalin's K_{oc}, 16000 mL g^{-1}, was obtained from sediment and water partitioning measurements made on runoff samples collected from an adjacent field (*13*). DMF and fluometuron K_{oc}'s, 226 and 100 mL g^{-1}, respectively were medians of eight published values (*14*). Daily loads into the buffer system were computed using equations 2 and 3 with M_d = mass dissolved (kg); M_s = mass sediment bound (kg); V_w = water volume (L); and C_{sed} = concentration sediment (g L^{-1})

$$M_d = C_d*V_w \qquad 2$$

$$M_s = C_s*C_{sed}*V_w \qquad 3$$

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Model Description

REMM uses a three zone conceptual model of a riparian system. Measured or simulated inputs enter the riparian system in zone 3 which starts at the "edge-of-field" and exits from zone 1 which is adjacent to a stream channel or other water body (*8*). We use the term "edge-of-buffer" to describe discharges from zone 1. Within each zone vegetation (grass, conifers and or deciduous trees), and characteristics of each of three soil layers, and zone width are user specified. Weather inputs are from climate records and or climate generators. Hydrologic, carbon and nutrient cycling, and plant growth processes in each zone are simulated on a daily time step (*4*). Outputs are daily flows and contaminant loads by soil layer in each zone. With the exception of recently added pesticide processing functions, descriptions of model processes and functions are provided in published reports (*4*, *8*).

As indicated, pesticide fate and transport processes were recently added to REMM. The same equations and algorithms used in the Root Zone Water Quality Model (*15*) were used. Within each soil layer pesticides may be reversibly or irreversibly adsorbed by soil or degraded. Reversible binding is based on linear equilibrium partitioning between soil water and soil organic matter. Irreversible binding and degradation are described by pseudo-first order rate equations. Additionally plant uptake is evaluated for soil layer 1 based on octanol-water partition coefficient and irreversible binding in the litter layer by first order kinetics. In all cases, time-step increments are daily.

Model Base Case and Parametization

Data collected from several studies on riparian systems located on the same farm where runoff plots were located were used (*16*). The soils at this study site, Tifton loamy sand in the cropped uplands and Alapaha loamy sand (fine-loamy, siliceous acid, thermic Typic Fluvaquents) in riparian areas commonly associated in South Georgia landscapes. Soil properties are similar with the Alapaha soil having a higher water table for much of the year due to its lower landscape position (*16*). The ratio of the combined buffer zone to cultivated field width (40/60) in these studies was used as a metric to establish zone widths for our simulations. The small difference in zone widths between the ST and CT related simulations was due to the small difference in slope length between the two fields (Table I). Vegetation scenarios were grass, conifers and deciduous trees (GCD) in zones 3 to 1 or grass in each zone (GGG).

Pesticide properties were derived from a combination of measured, literature, and in some cases default estimates (Table II). Rate constants for irreversible pesticide binding to soil and liter were estimated. This process, frequently termed "bound-residue-formation", is commonly reported in soil pesticide degradation studies; however kinetic data that effectively describe the process are not generally available (*17*).

Table I. Base case for simulations†

	Riparian Buffer		
	Zone 1 edge-of buffer	*Zone 2*	*Zone 3 edge-of-field*
Length (m)‡	CT = 7.6 ST = 7.0	CT = 7.6 ST = 7.0	CT = 7.6 ST = 7.0
Soil (cm)	Layer 1 = 30 Layer 2 = 70 Layer 3 = 150	Layer 1 = 30 Layer 2 = 70 Layer 3 = 150	Layer 1 = 30 Layer 2 = 70 Layer 3 = 150
Slope (%)	2.0	3.8	2.6
Vegetation§ GGG GCD	 grass grass	 grass conifers	 grass deciduous trees

† Gibbs Farm configuration (*16*). ‡ CT= conventional-tillage; ST = strip-tillage. § GGG = grass-grass-grass; GCD = grass-conifers-deciduous trees

Table II. REMM pesticide property parametization – base case

Symbol	*parameter*	*units*	*fluometuron*	*DMF*	*pendimethalin*
S_{aq}	aqueous solubility†	mg L^{-1}	111	528	0.33
K_{oc}	soil organic carbon water partition coefficient ‡,§	mL g^{-1}	100	200	16000
H_b	irreversible binding#	$t_{1/2}$;days	365	365	365
H_d	soil aerobic degradation‡	$t_{1/2}$;days	71	261	75
B	Walker exponent (water)§		0.8	0.8	0.8
T_{ref}	reference soil temperature	^oC	20	20	20
E_a	activation energy§		54	54	54
K_{ow}	octanol-water partition coefficient†		240	240	15800
pK_a	acid dissociation constant		NA	NA	NA
$H_{d(an)}$	soil anaerobic degradation	$t_{1/2}$;days	378§	378#	16†

† Footprint database (*18*). ‡ experimental (Potter unpublished). § literature (*14*, *15*, *19*). # estimated.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Results and Discussion

Edge-of-Field Loads

Daily outputs of the three target compounds from fields in each tillage system, here termed the edge-of-field loads, were summed to yield their mass contributed to the buffer system for the seven-year monitoring period (Table III). Computations showed that fluometuron use in the CT-system resulted in the greatest cumulative load (13 g; 0.55 % of applied). DMF, a fluometuron degradate, and pendimethalin (5.7 g; 0.3 % of applied) inputs were 35 and 56 % less respectively. The cumulative ST-system edge-of-field fluometuron load was about 40% of the CT-system. The ST-system DMF load was within 20% of the corresponding fluometuron load. The pendimethalin ST-system was 96% less than the CT-system load. The ST-system's much larger impact on pendimethalin edge-of-field loss was directly linked to a 5-fold reduction in sediment associated loss (*11*, *12*). Pendimethalin has a relatively high K_{oc} (Table II) and binds to soil strongly; thus reduction in sediment loads reduced pendimethalin runoff loss (*12*). Another factor that likely reduced ST-system pendimethalin loss was strong binding of the portion of the compound intercepted by the cover crop mulch during application (*13*).

Mass Balance Assessment

Cumulative attenuation within each zone in the buffer system was evaluated by dividing the difference between inputs and outputs zone by the zone 3 input (edge-of-field). Results were expressed as cumulative percent attenuation for the duration of the simulation (Table III). Use of this approach was supported by a mass balance assessment performed by summing daily inputs and outputs and the amount attenuated, i.e. mass, degraded, sequestered, and or taken up by vegetation, within each zone and soil layer for the entire simulation period. Comparison of the difference between inputs and outputs by zone with the amount removed by these attenuation processes agreed within 0.0001% indicating that the model effectively conserved mass during simulations.

Edge-of-Buffer Outputs

Simulated outputs were in all cases lower when inputs were from the ST-system. Results also indicated lower overall edge-of-buffer pendimethalin loss, less fluometuron and DMF loss with the GGG than the GCD vegetation pattern, and greater relative attenuation of all compounds when inputs were from the CT-system versus the ST-system (Tables III and IV).

The lower overall pendimethalin discharge from the buffer indicated by these computations was attributable to lower input (Table III) and the compound's high K_{oc} (Table II), tendency for sediment-bound transport, and high rates of sediment removal as water moved through buffers. This is in agreement with literature reviews of vegetated buffer mitigation efficacy that reported high attenuation rates for sorbing compounds, like pendimethalin (*20*). Transport of fluometuron and DMF was primarily in the dissolved form (*12*) and computed discharge from the buffer was greater (Table III).

Table III. Edge-of field (zone 3) pendimethalin, fluometuron, and DMF input and their edge-of-buffer output (zone 1) mass (g) for simulations with grass in zone 3 and either conifers or grass in zone 2, and deciduous trees or grass in zone 1

	pendimethalin		*fluometuron*		*DMF*	
	tillage					
Zone vegetation pattern	CT†	ST†	CT	ST	CT	ST
Z3 (input)	5.7	0.22	13	5	8.5	4.5
Z1 (output)‡						
GCD	0.9	0.06	4	2	2.3	2.1
GGG	0.8	0.06	3.6	1.8	1.8	1.9

† CT = conventional-tillage; ST = strip-tillage. ‡ GCD = grass (Z3), conifers (Z2), deciduous trees (Z1); GGG = grass (Z3), grass (Z2), grass (Z1).

Table IV. Cumulative percent pendimethalin, fluometuron, and DMF attenuation by zone for simulations for the two buffer vegetation patterns, GGG and GCD in zones Z3, Z2, and Z1, respectively‡

	pendimethalin		*fluometuron*		*DMF*	
	tillage					
Zone vegetation pattern‡	CT†	ST†	CT	ST	CT	ST
Z3						
GCD	50	61	45	42	46	36
GGG	53	62	46	43	46	47
Z2						
GCD	80	70	63	54	65	49
GGG	81	72	67	57	69	51
Z1						
GCD	84	72	69	59	73	54
GGG	87	75	72	63	79	58

† CT = conventional-tillage; ST = strip-tillage. ‡ GCD = grass, conifers, deciduous tress; GGG = grass, grass, grass.

Inspection of model processes indicated that vegetation impacts were likely due to increased evapo-transpiration (ET) from grass as compared to the trees in zones 2 (conifers) and 1 (deciduous), during summer months when most herbicide runoff occurred. Higher ET when grass was assigned to these zones resulted in drier soil conditions, greater potential for infiltration into soil, and less runoff. Although simulations suggested that the fully grassed buffers may have increased herbicide retention efficiency, the impact on cumulative attenuation with the buffers was small, 3 to 6% (Table IV). This is not surprising in light of a recently

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

published investigation comparing atrazine and metolachlor retention by grass and grass with poplar buffers. There was no significant difference in retention due to vegetation type (*21*).

A greater impact was indicated when the source of the inputs to the buffer were compared. Computed cumulative attenuation for the ST- was 9 to 21 % less than for the CT-system inputs (Table III). Greater attenuation of inputs from the CT-system were linked to the fact that >90 % of the CT-system load of all three compounds was in surface runoff. Relative ST-system surface load of DMF and fluometuron was 50% with the remainder delivered to the buffer in seepage and lateral subsurface flow. For pendimethalin there was no subsurface or seepage inputs to the buffer. This compound has a low tendency to leach. Data also showed that cumulatively the CT-system when compared to the ST-system runoff had a greater fraction of the pendimethalin bound to sediment. The relative amounts were 53% sediment-bound for the CT- and 27% for the ST-system.

The relative distribution between surface and subsurface flow and fraction bound to sediment in runoff impacted the percent attenuation in the buffer since there is increased potential for trapping compounds entrained in surface runoff. Highly effective sediment retention in vegetated buffers is a contributing factor (*20*) and generally the greater the fraction sediment-bound a compound is in runoff the more it will be retained. REMM effectively captured the process.

A second process involves the potential for compounds dissolved in surface runoff to be sorbed by the thatch layer in grass buffers and the litter layer when surface runoff enters a forested buffer. In REMM the sorptive process is irreversible thus litter or thatch sorption serves as a sink. In addition, compounds dissolved in runoff will contact organic matter in surface soils when runoff infiltrates. This process, described as reversible in REMM served to retain and attenuate pesticides in surface flows. Model results indicated that litter and soil organic matter sorption were primary factors in attenuating fluometuron and DMF in surface runoff since their transport is primarily in the dissolved form.

Attenuation within the Buffer

A decreasing trend in cumulative percent attenuation of each compound moving from zones 3 to 1 was observed (Table IV). This is in general agreement with published studies in which attenuation was measured within vegetative buffers (*20*, *22*). Overall the data analysis served to emphasize that buffers likely have a greater capacity to retain pesticides with high K_{oc} and when they are delivered to buffers from CT- versus ST-systems.

Zhang et al. (*22*) in their review showed that for many pesticides removal efficiency can be effectively described using equation 4.

$$Y = K^*(1-e^{-(b^*\text{distance})}) \qquad \mathbf{4}$$

Y= percent attenuation; K = buffer capacity (0<K≤100); b = probability of pollutant removal per unit distance; and d = distance traveled in meters. REMM results for the GGG scenario were fit to this equation using Sigma Plot Version 11 (*23*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

R^2 values were all >0.996 indicating that the equation effectively predicted simulated buffer system response. Fitted parameters for each compound and input scenario are compiled in Table V with equations plotted in Figure 1. Trends for the capacity parameter, K, mirrored cumulative edge-of-buffer outputs described above with CT-> ST-system inputs and pendimethalin>DMF>fluometuron. In the case of the pollutant removal parameter, b, the trend for all three compounds was ST->CT-system input. The one exception was a nearly 2-fold greater "b" for pendimethalin ST-system input to the buffer. We do not have an explanation of what appears to be an anomalous result. It may be linked to the fact that pendimethalin ST-system input was more than an order magnitude less than the other compound-input combinations and loads were dominated by a few events.

Table V. Cumulative percent pendimethalin, fluometuron, and DMF attenuation (Y) as function of distance (m) in buffer: data fit to equation: $Y = K*(1-e^{-(b*distance)})$‡

	pendimethalin		*fluometuron*		*DMF*	
	tillage					
parameter	CT†	ST†	CT	ST	CT	ST
R^2	0.996	0.999	0.997	0.999	0.999	0.999
"K"	100	75	80	66	91	63
"b"	0.09	0.24	0.11	0.14	0.09	0.12

‡ Reference (*22*). † CT = conventional-tillage; ST = strip-tillage.

The close fit to the data and tracking of expected trends provided strong support for the conclusion that REMM effectively simulated buffer system response and that equation and fitted parameters may be useful for buffer design. The equation provides a simple means of estimating attenuation as a function of buffer width when compound specific K and b values are available. Dosskey et al. (*24*) showed that for sediment and water retention in buffers values for these parameters could be predicted using a combination of field length, Universal Soil Loss Equation factor C, and soil textural class. It is possible that pesticide related parameters may be estimated similarly. Investigations are needed to confirm this.

Another potential use of equations relating buffer width to cumulative percent attenuation of the herbicides is in comparison of the relative efficacy of the two conservation practices, tillage and buffer systems on herbicide attenuation. This can be done by computing cumulative percent attenuation associated with the tillage practices using Table III edge-of-field data, inserting the value into the corresponding CT-system exponential decay equation (Table V) and solving for distance (buffer width). Computations indicate that buffer widths of 36, 13, and 8 m for pendimethalin, fluometuron and DMF respectively would be equivalent to the impact of implementing ST in this landscape.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

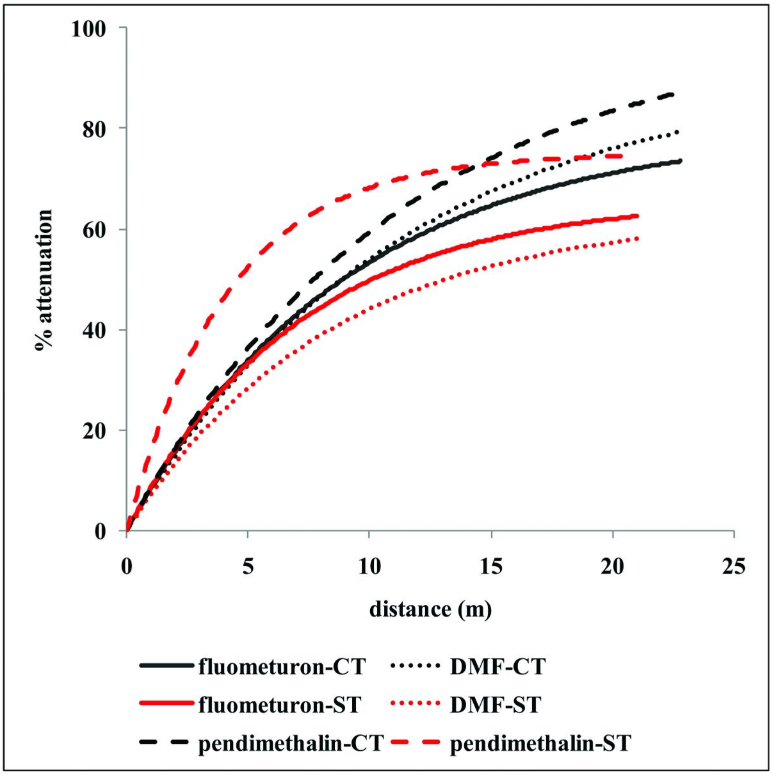


Figure 1. Computed percent attenuation of pendimethalin, DMF, and fluometuron as a function of distance traveled with an all grass buffer system using REMM simulated outputs by zone (Table V).

Finally it should be noted that these equations represent buffer response with inputs and outputs integrated over relatively long time periods. For individual storm events the buffer width-percent attenuation relationships may be highly variable. "Extreme" events are of particular concern since they may overwhelm buffer capacity and result in little of no pesticide attenuation in the buffer. This behavior is highlighted in Table VI and in the discussion on REMM use for event tracking below.

Event Tracking

To illustrate REMM's potential for tracking event dynamics, edge-of-field inputs, edge-of-buffer outputs and computed percent attenuation for each compound for two largest daily inputs from the CT-system are summarized in Table VI. For pendimethalin, the largest input representing 28% of the cumulative edge-of-field load resulted in no output, i.e. 100% attenuation. The next largest event representing 11% of the cumulative edge-of-field load resulted in an edge-of-buffer load representing 60% of the cumulative total discharged from the buffer. In this case, attenuation within the buffer was only 9%. The large

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

difference in response may be explained by antecedent moisture conditions prior to events. Weather and irrigation records indicated that there was combined 20 mm in the week prior to the first event whereas there was more 68 mm in the same time-frame prior to the second. Data indicated that the buffer was wetter prior to the second event; thus, there was less infiltration of runoff that entered the buffer. In turn pendimethalin retention was reduced with more of the compound reaching the edge-of-buffer. Similar, although less dramatic, responses were indicated for fluometuron and DMF.

Event dynamics indicated by simulations emphasized the importance of "extreme" events in pesticide discharges from farm fields and buffer systems. This includes storms close to the time of application and following periods when rainfall creates high antecedent soil water conditions in fields and buffers.

Table VI. Daily edge-of-field inputs and edge-of-buffer outputs and estimated percent attenuation, and rainfall plus irrigation for the two largest edge-of-field daily inputs during simulations. DAT = days after treatment

Compound *event date*	*DAT* *days*	*input*† *g day*$^{-1}$	*output*‡ *g day*$^{-1}$	*attenuation* *%*	*rainfall + irrigation mm*
pendimethalin					
3-Jun-05	11	1.60 (28%)	<0.001	100	43
6-Jun-05	13	0.65 (11%)	0.55 (60%)	9	40
fluometuron					
21-Jun-01	3	2.0 (16%)	1.0 (24%)	52	25
6-Jun-05	13	1.3 (10%)	1.0 (24%)	24	42
DMF					
6-Jun-05	13	0.48 (6%)	0.37 (16%)	23	42
10-Jul-05	48	0.29 (3%)	0.25 (11%)	13	122

† percent of cumulative edge-of-field input in parenthesis. ‡ percent of cumulative edge -of- buffer output in parenthesis.

Conclusions

REMM was used to evaluate riparian buffer system response to edge-of-field loads of two herbicides, pendimethalin and fluometuron, and a common fluometuron degradate, DMF, from fields maintained in conventional and strip-tillage management. Two buffer vegetation conditions were examined, a buffer with grass in each of REMM's three zones, and one with grass, conifers, and deciduous trees successively from field to stream. Measured inputs were obtained from a study comparing tillage impacts on water quality and quantity during rotational cotton and peanut production over a seven-year period in South Central Georgia (USA). Simulations provided outputs indicating that grass buffers may be slightly more effective in retaining these herbicides and that retention increased for the high K_{oc} compound pendimethalin. Outputs also indicated that edge-of-buffer loads from fields in conservation-tillage were lower than from

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

the conventionally-tilled system but the rate of attenuation within the buffer was lower for inputs from the conservation-tillage system. Finally, REMM outputs emphasized the importance of "extreme events" on pesticide losses from buffers and that a two-parameter exponential decay equation describing attenuation and buffer length relationships (*22*) effectively fit REMM results. The equation may be useful for buffer system design.

Generally, buffer system responses simulated by REMM were explainable by examining model processes and in agreement with published studies describing pesticide behavior in vegetated buffer strips. Results should provide model users with confidence in using REMM for pesticide risk assessments. However we emphasize that whether REMM predicted the correct magnitude of residues leaving buffers was not addressed in this paper. Work to calibrate and validate REMM predictions using available data sets that include edge-of-buffer inputs and outputs is in progress.

Acknowledgments

Special thanks to USDA-ARS employees Sally Belflower, Margie Whittle, Ernest Harris, Lorine Lewis, and Rickey Fletcher who assisted in data collection in tillage studies and to Timothy Strickland for review of this manuscript. The University of Georgia Coastal Plain Experiment Station provided land and irrigation.

References

1. USDA-NRCS. Summary Report: 2007 National Resources Inventory; Natural Resources Conservation Service, Washington, DC, and Center for Survey Statistics and Methodology, Iowa State University, Ames, Iowa. http://www.nrcs.usda.gov/technical/NRI/2007/2007_NRI_Summary.pdf, 2009.
2. Alleto, L; Coquet, Y.; Benoit, P.; Heddadj, D.; Barriuso, E. *Agron. Sustainable Dev.* **2010**, *30*, 367–400.
3. USDA. Buffers common sense conservation; USDA- Natural Resources Conservation Service, Washington, D.C. http://www.nrcs.usda.gov/feature/buffers/#Anchor-WhatBuffer, 2010.
4. Lowrance, R.; Altier, L. S.; Williams, R. G.; Inamdar, S. P.; Sheridan, J. M.; Bosch, D. D.; Hubbard, R. K.; Thomas, D. L. *J. Soil Water Conserv.* **2000**, *55*, 27–34.
5. Inamdar, S. P.; Lowrance, R. R.; Altier, L. S.; Williams, R. G.; Hubbard, R. K. *Trans. ASAE* **1999**, *42*, 1691–1707.
6. Dukes, M. D.; Evans, R. O. *Trans. ASAE* **2003**, *46*, 1567–1579.
7. Gerwig, B. K.; Stone, K. C.; Williams, R. G.; Watts, D. W.; Novak, J. M. *Trans. ASAE* **2001**, *44*, 505–512.
8. Lowrance, R.; Williams, R. G.; Inamdar, S. R.; Bosch, D. D.; Sheridan, J. M. *J. Am. Water Resour. Assoc.* **2001**, *37*, 1445–1455.

9. Cerruci, M.; Conrad, J. M. *J. Am. Water Resour. Assoc.* **2003**, *39*, 1167–1180.
10. Bosch, D. D.; Potter, T. L.; Truman, C. C.; Bednarz, C. W.; Strickland, T. C. *Trans. ASAE* **2005**, *48*, 2137–2144.
11. Potter, T. L.; Bosch, D. D.; Strickland, T. C.; Truman, C. C. In *Proceedings 30th Southern Conservation Agricultural Systems Conference*; Endale, D. M.; Tifton, Georgia, 2008; pp 128−131. http:// www.ag.auburn.edu/auxiliary/nsdl/scasc.
12. Potter, T. L.; Truman, C. C.; Bosch, D. D.; Bednarz, C. W. *J. Environ. Qual.* **2004**, *33*, 2122–2131.
13. Potter, T. L.; Truman, C. C.; Strickland, T. C.; Bosch, D. D.; Webster, T. M. *J. Environ. Qual.* **2008**, *37*, 839–847.
14. Locke, M. A.; Zablotowicz, R. M.; Steinreide, R. W.; Kingery, W. L. *J. Agric. Food Chem.* **2007**, *55*, 844–851.
15. Wauchope, R. D.; Rojas, K. E.; Ahuja, L. R.; Ma, Q.; Malone, R. W.; Ma, L. *Pest Manage. Sci.* **2004**, *60*, 222–239.
16. Lowrance, R. R.; Sheridan, J. M. *J. Environ. Qual.* **2005**, *34*, 1851–1859.
17. Barriuso, F.; Benoit, P.; Dubus, I. G. *Environ. Sci. Technol.* **2008**, *42*, 1845–1854.
18. Footprint. *The FOOTPRINT Pesticide Properties DataBase*; Database collated by the University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704). http://www.eu-footprint.org/ppdb.html, 2009.
19. USEPA. Reregistration Eligibility Decision (RED) for Fluometuron. USEPA Office of Prevention, Pollution, and Pesticides, Washington, D.C. http://www.epa.gov/oppsrrd1/REDs/fluometuron_red.pdf, 2005.
20. Krutz, L. J.; Senseman, S. A.; Zablotowicz, R. M.; Matocha, M. A. *Weed Sci.* **2005**, *53*, 353–367.
21. Caron, E.; Lafrance, P.; Auclair, J-C; Duchemin, M. *J. Environ. Qual.* **2010**, *39*, 617–629.
22. Zhang, X.; Liu, X.; Zhang, M.; Dahlgren, R. A.; Eitzel, M. *J. Environ. Qual.* **2010**, *39*, 76–84.
23. SyStat. *SigmaPlot for Windows*, version 11.0; Systat Software, Inc.: San Jose, CA, 2008.
24. Dosskey, M.; Helmers, M. J.; Eisenhauer, D. E. *J. Soil Water Conserv.* **2008**, *63*, 232–241.

Chapter 17

Comparison of Models for Estimating the Removal of Pesticides by Vegetated Filter Strips

Michael F. Winchell,*[,1] Russell L. Jones,[2] and Tammara L. Estes[1]

[1]Stone Environmental, 535 Stone Cutters Way, Montpelier, VT 05602, USA
[2]Bayer CropScience, 17745 South Metcalf, Stilwell, KS 66085, USA
*mwinchell@stone-env.com

Publication Date (Web): December 21, 2011 | doi: 10.1021/bk-2011-1075.ch017

Vegetated filter strips (VFSs) established at the downslope edge of agricultural fields have long been recommended as a management practice to reduce sediment, nutrients, and pesticides in surface runoff before it enters water bodies. Recently VFSs have been mandated as label requirements for plant protection products in Europe and North America. Several simulation models have been developed to predict the amount of pesticide active ingredients and their metabolites removed from runoff flowing through these strips. Removal efficiency is a function of several parameters and must be predicted on an event basis. The predictions of four simulation models (APEX, PRZM-BUFF, REMM, and VFSMOD) were compared using three data sets. Conditions simulated included a range of soil properties, slopes, rainfall events, and pesticide characteristics. All four models predicted reductions of pesticides in the VSFs consistent with the observed reductions, with VFSMOD simulations in closest agreement with the measured data across the three data sets.

Introduction

Use of VFSs as agricultural best management practices (BMPs) has gained in popularity over the past 15 years, in part due to the National Conservation Buffer Initiative of the US Department of Agriculture, Natural Resources Conservation Service (NRCS) (*1*). Increasingly, of VFSs use is recommended or required on pesticide labels as a mitigation measure to reduce pesticide runoff. In order to estimate the effectiveness of VFSs, one of two approaches is generally employed. The first involves designing and conducting field experiments to assess VFS effectiveness in reducing pesticide mass transport at the field edge. The second approach involves use of simulation models to evaluate buffer system efficacy in removing pesticides from runoff. Recent reviews of field studies have shown that a wide range in VFS effectiveness has been observed in the field (*2–4*), making it difficult to generalize their effectiveness. Furthermore, the characteristics of a VSF that affect pesticide removal efficiency have been shown to be more complex than simply buffer width (*5*), as has been the current approach until recently.

An unpublished report (*6*) reviewed five currently available simulation models for evaluating VFS effectiveness in reducing pesticide runoff from treated agricultural fields. This chapter reports on a follow-up study designed to compare the performance of four of these models using three different datasets (additional details of the study are provided in an unpublished report available upon request (*7*)).

Materials and Methods

Models Evaluated

APEX (*8*) is a farm/small watershed scale model for simulating the effects of agricultural management practices on water quality and agricultural productivity. It is a physically-based, continuous, distributed parameter model which can be used to model up to 4,000 distinct and hydrologically connected "subareas." The APEX model can be obtained from http://www.brc.tamus.edu/simulation-models/epic-and-apex.aspx.

PRZM-BUFF is a modified version of the field scale model PRZM used to evaluate the effectiveness of VFSs and unmanaged buffers in reducing pesticide runoff, erosion, and spray drift to downstream areas. PRZM-BUFF, is configured as a run-off / run-on model with main field water and chemical mass from runoff and erosion input as boundary condition inflows into adjacent untreated areas. Multiple PRZM simulations are performed to simulate various portions of the field and surrounding areas. Requests for the model can be made at http://www.waterborne-env.com/.

REMM (*9*) is a field scale model for evaluating the movement of water, sediment, and nutrients in riparian zones adjacent to agricultural fields and includes subsurface lateral flow and ground water in addition to overland runoff. REMM was modified in 2008 to include simulation of pesticide behavior. A preliminary version was used in this study. Inquiries about the model and its current status can be made by contacting Randy Williams (randy.williams@ars.usda.gov) or R. Richard Lowrance (Richard.lowrance@ars.usda.gov).

VSFMOD links a field-scale, storm-based numerical simulation model (*10*) with a pesticide trapping equation (*4*). The model is capable of simulating runoff and infiltration of water, sediment transport, and pesticide trapping through VFSs. The software, users manual, and associated publications can be obtained from the author R. Munoz-Carpena at http://carpena.ifas.ufl.edu/VFSMOD.

Study Site Descriptions

Three data sets, one from Europe and the other two from North America, were used for the comparison of model predictions. The study sites differed in soil, topographic, and climatic characteristics. Environmental fate properties of the four pesticides investigated also varied widely (see Table I). The study sites and buffer characteristics are described in the following sections and in Table II.

Table I. Pesticide Properties at Each Study Site

Study Site	*Pesticide*	*Koc (mL g^-1^)*	*Half-Life (days)*
Gibbs Farm	Alachlor[a]	54	30
Velbert- Neviges	Pendimethalin[b]	12,500	97
Sioux County	Atrazine[c]	171	61
Sioux County	Chlorpyrifos[a]	9,930	30.5

[a] Source: (*11*). [b] Source: (*12*). [c] Source: (*13*).

The Gibbs Farm data set was obtained during field studies near Tifton, Georgia (*14*, *15*). A grassed VFS located at the endge of the farm field was 8 m wide (field to buffer area ratio of 11.5). Inputs and outputs to the VFS were monitored continuously for three years from 1992 through 1994. For model comparison described in this chapter, the model PRZM was used to simulate the loadings of runoff, sediment, and pesticide coming from the adjacent field into the VFS. PRZM was parameterized using the known field characteristics and pesticide application dates and rates for each year. Reductions in runoff, sediment and pesticide (alachlor, a compound weakly to moderately sorbed to soil) through the buffer were measured over the period from 1992 through 1994. The annual averages of these reductions (as a percent of the fluxes entering the buffer) were compared with the results each each of the VFS models.

Velbert-Neviges is a data set generated in North Rhine-Westphalia, Germany (*12*). The VFS was a three meter wide grass buffer strip (field to buffer area ratio of 2.3) on a silty loam soil with a 10% slope. The plot draining to the VFS received simulated rainfall representing six events spread over two years (1998 and 1999). The size of the rainfall events ranges from 60 mm to 71 mm, and occurred between 3 and 23 days after pesticide application. In each of these events, the buffer also received simulated rainfall. The reduction in runoff, sediment, and pendimethalin, a compound highly sorbed to soil, was simulated by each of the models and compared with the reductions observed in the field for each event.

Table II. Buffer Characteristics at Each Study Site

			Sioux County, Iowa[e]			
Parameter	*Gibbs Farm*	*Velbert- Neviges*	*Treatment 1*	*Treatment 2*	*Treatment 3*	*Treatment 4*
Treated Area (m^2)	11,000	10.5 (15)[c]	N/A	N/A	N/A	N/A
Buffer Width[a] (m)	8	3	4.6	4.6	4.6	4.6
Buffer Length[b] (m)	120	1.5	4.6	4.6	0.46	0.46
Buffer Slope (%)	2.5	10	5.25	5.25	5.25	5.25
Effective Field to Buffer Area Ratio	11.46	2.33[d]	15	30	150	300
Buffer Vegetation Type	Bermuda grass	Pasture grass mix	Brome grass / bluegrass	Brome grass / bluegrass	Brome grass / bluegrass	Brome grass / bluegrass
Soil	Loamy sand	Silty loam	Silty clay loam	Silty clay loam	Silty clay loam	Silty clay loam

[a] Distance parallel to slope. [b] Distance perpendicular to slope. [c] Area was 15 m^2 for 1 event. [d] Ratio was 3.33 for 1 event [e] No treated area; synthetic run-on matrix was applied directly to buffer)

Sioux County is a data set from a study conducted in the northwest corner of Iowa (*16*). The 12 VFSs were 4.6 m in length (simulated field to buffer ratios of 15 and 30 were tested) and were on a silty clay loam soil with a 5% slope. Flow uniformity was investigated by applying a simulated runoff matrix (water, sediment, and pesticide) to 100% of the plot area (uniform) or to only 10% of the plot area (concentrated). In each of these events, the VFS itself received simulated rainfall. The pesticides evaluated at the Sioux County site were atrazine (a compound with moderate sorption to soil) and chlorpyrifos (a compound fairly strongly sorbed to soil but less so than pendimethalin).

Parameterization and Conduct of Simulations

Uncalibrated simulations using best estimates of model parameters were conducted. Models were parameterized, using as consistent values as possible, while considering that each model has somewhat different requirements and recommendations for implementation. The inputs and outputs from the VFSs at each of the study sites used for comparison between observed and simulated represented the total runoff, sediment, and pesticide loads.

For the Sioux County site, sensitivity of predicted reductions in runoff, sediment, and pesticide to changes in a few key input parameters was evaluated. Included in this analysis were saturated hydraulic conductivity (the curve number was substituted for PRZM), Manning's N, and the antecedent soil moisture.

Results and Discussion

Gibbs Farm

Simulations were continuous from 1992 through 1994. Total runoff reductions and sediment were evaluated for 1993 and 1994 only. Of the four models, VFSMOD provided the closest agreement to the observed values in both years (runoff reduction differences of +2% and -31% in 1994 and 1994 respectively), followed by APEX, PRZM-BUFF, and REMM. Observed reductions in sediment were low in 1993 compared to all model predictions and the observed reductions in 1994. In the later year, all four models predicted a reduction of sediment within 10% of the observed value. The comparisons of simulated versus observed reductions in alachlor are shown in Figure 1. The "percent reduction" was calculated as shown in equation 1.

$$PctRed = 100 * [1 - (PestOut / PestIn)] \qquad \text{Eqn. 1}$$

where, PctRed = percent reduction in buffer (%)
PestOut = pesticide leaving buffer (mass)
PestIn = pesticide entering buffer (mass)

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

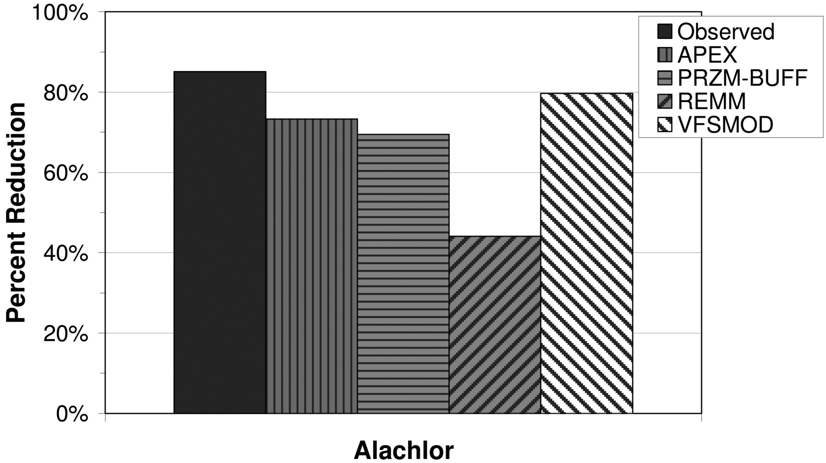


Figure 1. Total Alachlor Mass Reduction, 1992-1994, at Gibbs Farm.

The observed total reduction in alachlor mass over the three-year period was approximately 85%. The model simulations of alachlor reductions with VFSMOD were closer to the observed data than the other three models (5% less than observed). APEX and PRZM-BUFF showed greater deviations from the observed reductions, predicting reductions of 12% and 16% less than the observed value respectively. REMM prediction of alachlor reduction was 41% lower than the observed value.

Velbert-Neviges

The model simulations evaluated six events during the two year period with simulated reductions in runoff, sediment, and pesticide (pendimethalin) compared to the observed results (*12*). Simulated versus observed reductions for pendimethalin are shown in Figure 2. A comparison of predicted versus observed expressed as mean absolute error (absolute value of predicted minus observed) in runoff, sediment, and pendimethalin is shown in Figure 3. The calculation of mean absolute error is shown in equation 2.

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|obs_i - sim_i| \qquad \text{Eqn. 2}$$

where, MAE = mean absolute error

obs_i= i^{th} observed buffer reduction (%)

sim_i = i^{th} simulated buffer reduction (%)

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

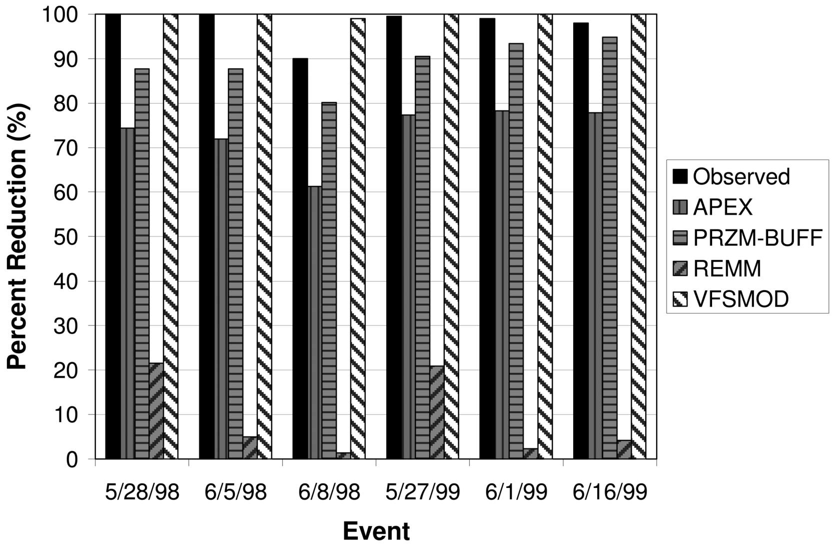


Figure 2. Total Pendimethalin Mass Reduction over the six Velbert-Nevige Events.

The observed runoff reduction at Velbert-Neviges was high, greater than 95% for all but one of the six events. For all six events, VFSMOD was closest to the observed runoff reduction, often within 5% (Figure 3). APEX, PRZM-BUFF, and REMM under-predicted the runoff reduction, by 40% or more. Observed sediment reductions in the buffer were greater than 90% for all six events. All four models performed well in predicting the sediment reduction, generally within 15% of the observed reductions (Figure 3). The observed pendimethalin reductions (Figure 2) were all greater than 90%, showing strong similarity to sediment behavior. This is not surprising given pendimethalin's high sorption coefficient and tendency for sediment-sorbed transport. The VFSMOD simulations were generally closest to the observed pendimethalin reductions, followed by PRZM-BUFF, APEX, and then REMM (Figure 3). The low percent differences (between observed and simulated) in runoff, sediment, and pendimethalin reductions obtained using VFSMOD can be in part attributed to VFSMOD's method for calculating pesticide reduction as a function of infiltration and sediment trapping within the buffer (along with several other factors). The reductions predicted by REMM were lower than the other three models, and did not follow the high sediment reductions that REMM predicted. This behavior was not expected and the reason for it could not be determined.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

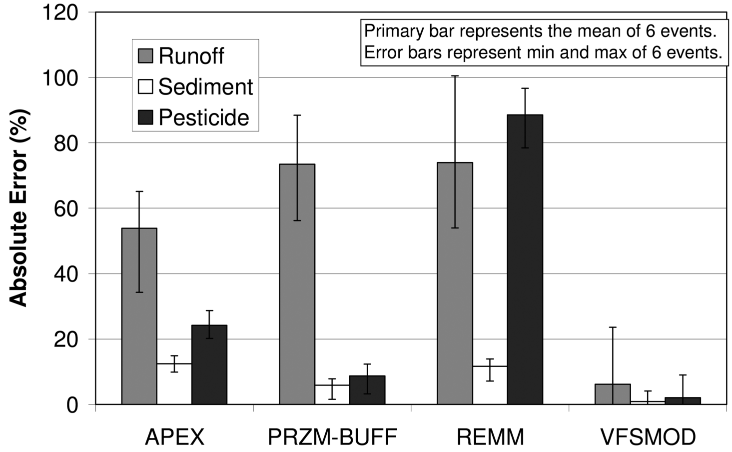


Figure 3. Mean Absolute Error in Buffer Reductions over the six Velbert-Neviges Events.

Sioux County, Iowa

Simulations evaluated four different scenarios, three replicates each, totaling 12 runoff events. The models were run in an event-based mode for each of the 12 events with assumed antecedent soil moisture equal to half the soil field capacity. Simulated reductions in runoff, sediment, and two pesticides, atrazine and chlorpyrifos (with contrasting soil adsorption behavior), were compared with the observed results (*16*). The comparisons of simulated versus observed reductions in atrazine, and chlorpyrifos are shown in Figures 4 and 5, respectively. A comparison of predicted versus observed expressed as mean absolute error in runoff, sediment, atrazine, and chlorpyrifos is shown in Figure 6.

In these simulations, APEX consistently over-predicted the amount of runoff reduction in the buffer, while the other three models tended to under-predict runoff reduction. Reductions in runoff were higher for sheet flow conditions than for concentrated flow conditions. Sheet flow was characterized by uniform shallow flow across a VFS, while concentrated flow was characterized by uneven flow depth across a VFS buffer, some sections with deeper and faster flow and some sections with shallower slower flow.

Trends for sediment reduction were not as clear as for runoff. VFSMOD results were closest to the observations for the sheet flow conditions, while APEX was closest to the observations for the concentrated flow conditions. REMM generally under-predicted the sediment reduction by the VFS. PRZM-BUFF always predicted 100% reduction in sediment. This behavior was attributed to its simplified treatment of sediment processes.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

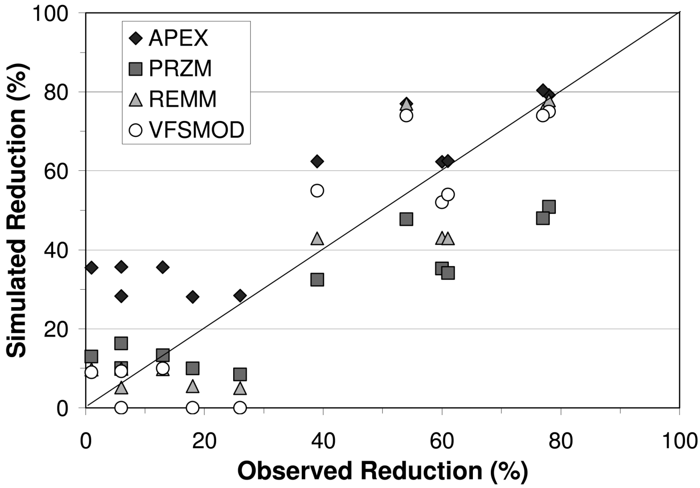


Figure 4. Total Atrazine Reduction in the 12 Sioux County Plots. (Sheet flow conditions area represented by the data points for each model with higher observed reductions (> 40%) while the concentrated flow conditions are represented by the data points for each model with lower observed reductions (< 30%).)

Atrazine simulations followed a similar pattern to the runoff simulations. This was expected since the compound is weakly sorbed by sediment and tends to dissolve in runoff. Three of the four models did well at predicting atrazine reductions for the sheet flow conditions (data points further from the origin in Figure 4), with PRZM-BUFF tending to under-predict the amount of reduction. Under concentrated flow conditions (data points nearer the origin), APEX indicated higher atrazine reduction under concentrated flow conditions compared to the predictions of other models as well as the experimental data. Overall, REMM performed slightly better than all the other models for total atrazine reduction.

For chlorpyrifos reduction (Figure 5) VFSMOD had the closest agreement with the observations (slightly better than APEX), with a tendency to under-predict the amount of pesticide reduction (summary statistics of model performance are presented in Table IV). APEX provided the closest estimate to measured values of the four models for concentrated flow conditions, but under-predicted the reductions under sheet flow conditions. REMM consistently under-predicted the reduction for both flow regimes, while PRZM-BUFF had a tendency to over-predict the reductions for the concentrated flow and under-predict the reductions for the sheet flow conditions.

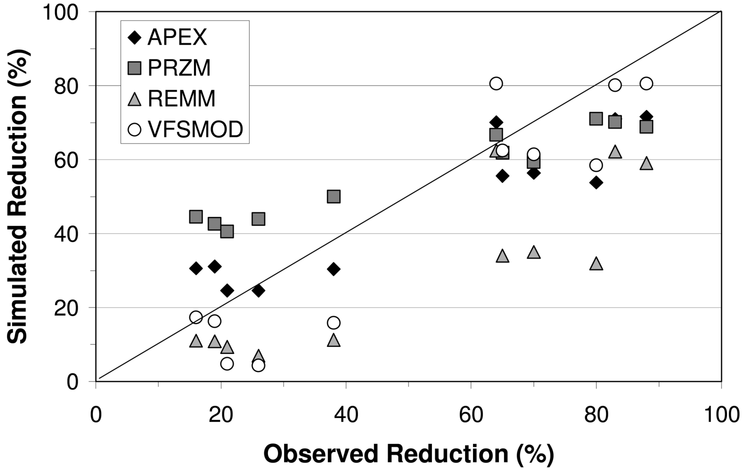


Figure 5. Total Chlorpyrifos Reduction in the 12 Sioux County Plots.)Sheet flow conditions area represented by the data points for each model with higher observed reductions (> 60%) while the concentrated flow conditions are represented by the data points for each model with lower observed reductions (< 40%).)

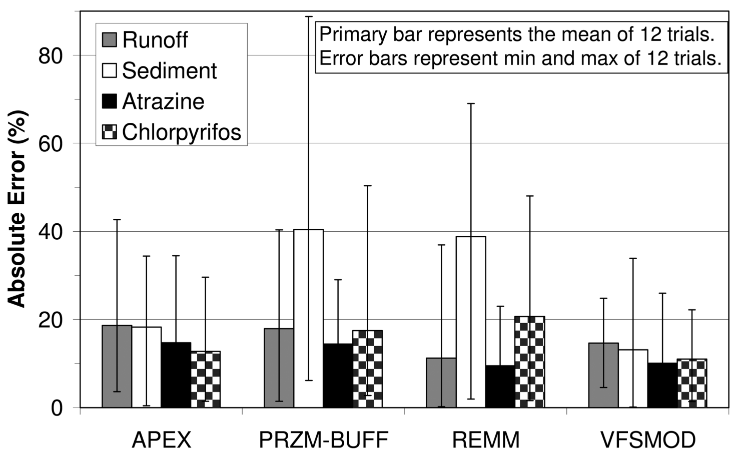


Figure 6. Mean Absolute Error in Buffer Reductions in the 12 Sioux County Plots.

Parameter distributions sampled for the limited sensitivity analysis are shown in Table III. Results showed that VFS reductions in runoff, sediment, atrazine, and chlorpyrifos were sensitive to changes in saturated hydraulic conductivity (or curve number with PRZM), with APEX being the most sensitive. All models showed little sensitivity to changes in Manning's N value, with only APEX showing any sensitivity to Manning's N. Sensitivity to initial soil moisture was negligible for APEX and low for the other models. Likely, this was due to the fact that by the time surface runoff enters a VFS the VFS surface soil will be close to saturation as a result of the rainfall, minimizing the importance of the soil moisture prior to the start of the rainfall event. However, antecedent soil moisture will still be important in determining the magnitude of a runoff event, and hence, the potential for pesticide mass to move off-field and into the VFS. These results highlight the importance of appropriately parameterizing the infiltration components of these models, as infiltration not only affects soluble pesticide reductions in the buffer, but also sediment deposition processes and sorbed pesticide reductions.

Table III. Model Sensitivity Analysis Parameter Distributions

Distribution Percentile	*Ksat Layer 1 (cm/hr)*	*Ksat Layer 2 (cm/hr)*	*Ksat Layer 3 (cm/hr)*	*CN*	*Manning's N Value*	*Initial Soil Moisture (% Field Capacity)*
1	0.82	0.28	0.48	82.3	0.40	1.0
10	1.97	0.66	1.15	73.9	0.43	10.0
50	5.73	1.93	3.36	60.7	0.47	50.0
90	16.71	5.61	9.78	45.7	0.56	90.0
99	39.88	13.40	23.35	33.9	0.61	99.0

Comparison of Model Predictions

Simulations using the three datasets (covering a wide range of buffers, storms, and pesticide properties) provided 73 data points to compare the models against each other and observed data. From these data points, the error (including the sign) and the absolute error (the absolute value of the simulated reduction minus the observed reduction) were calculated for each of the data points. The models were ranked for each data point according to the magnitude of the absolute error in the prediction. The mean and standard deviations of the rank and the arithmetic average of the absolute error, and the arithmetic average of the error (which indicates the positive or negative bias in the model, and results are summarized in Table IV. Also this analysis was performed with relative error in addition to absolute error, but the results are not included here for simplicity since the overall conclusions do not change, although there are changes in comparisons involving individual data points.

Table IV. Comparison of Model Performance

Statistic	*Parameter*	*APEX*[a]	*PRZM-BUFF*[a]	*REMM*[a]	*VFSMOD*[a]
Rank	Pesticide	2.6 (1.0)	2.6 (1.0)	3.0 (1.1)	1.9 (1.1)
	Runoff	2.5 (1.1)	3.2 (0.9)	2.6 (1.2)	1.8 (0.9)
	Sediment	2.7 (0.9)	2.8 (1.1)	3.0 (1.2)	1.6 (0.8)
Mean Absolute Error (%)	Pesticide	16 (10)	16 (14)	31 (31)	9 (8)
	Runoff	30 (20)	37 (28)	35 (32)	12 (9)
	Sediment	19 (17)	31 (31)	30 (24)	12 (17)
Mean Error (%)	Pesticide	-0.9 (18.7)	-5.3 (21.2)	-28.1 (33.9)	-3.0 (11.1)
	Runoff	-8.0 (35.9)	-36.5 (28.8)	-30.1 (36.7)	-6.2 (14.4)
	Sediment	-6.6 (25.4)	27.4 (34.7)	-23.8 (30.5)	-1.8 (20.7)

[a] Numbers in parentheses represent the standard deviation of the individual values.

Results show that the mean error statistics are almost entirely negative (PZRM-BUFF sediment is the only positive mean error value), indicating that the models were conservative, and, on average under-predicted VFS effectiveness. In addition, based on mean absolute error and the rank, VFSMOD simulations are consistently closer to the observations than the other three models. The order of the other three models depended on whether pesticide, runoff, or sediment is being considered. As might be expected, the standard deviations in the absolute error were smaller for the models with the lower mean absolute errors. Furthermore, all of the models will, on average, simulate the buffer effectiveness at reducing runoff, sediment, and pesticides within approximately 30% of field observations (based on absolute error).

This study has made numerous comparisons of model simulations with field observations. Implicit in these comparisons has been that the “observations” are accurately reflecting field conditions over the entire buffer. However, conducting field experiments to measure runoff, sediment, and pesticide loadings into and out of vegetative buffers is difficult, and field observations have various levels of uncertainty associated with them. While it is beyond the scope of this study to quantify these uncertainties, it is important to consider this when assessing model performance and comparing specific simulations to the observed data.

Conclusions

In our comparison of the performance of the four models, VFSMOD provided the best overall performance based on differences between predicted and observed pesticide, runoff, and sediment retention by the VFS. The other models evaluated in this study (APEX,PRZM-BUFF, and REMM) were found to make predictions of VFS effectiveness for pesticide removal that deviated from the effectiveness observed in the field studies by less than 31% on average (based on the absolute error). These results should provide risk assessment scientists and regulators with increased confidence for the evaluation of VFS performance as a mitigation strategy.

Acknowledgments

Funding for this project was provided by the European Crop Protection Association, Bayer CropScience, Monsanto Company, and Syngenta. The PRZM-BUFF simulations were performed by Amy Ritter and Mark Cheplick, Waterborne Environmental; the VSFMOD simulations were performed by George Sabbagh, Bayer CropScience. Additional information on the data sets was provided on the Velbert-Neviges data set by Christine Klein, SCC Scientific Consulting; on Gibbs Farm by Richard Lowrance and Randy Williams, USDA/ARS; and on Sioux County, Iowa by Nick Poletika, Dow AgroSciences.

References

1. USDA Natural Resources Conservation Service. *Conservation Buffers to Reduce Pesticide Losses*; 2000; p 21. http://www.in.nrcs.usda.gov/technical/agronomy/newconbuf.pdf.
2. Arora, K.; Mickelson, S. K.; Helmers, M. J.; Baker, J. L. *J. Am. Water Resour. Assoc.* **2010**, *46* (3), 618–647.
3. Reichenberger, S.; Bach, M.; Skitschak, A.; Frede, H.-G. *Sci. Total Environ.* **2007**, *384*, 1–35.
4. Sabbagh, G. J.; Fox, G. A.; Kamanzi, A.; Roepke, B.; Tang, J. Z. *J. Environ. Qual.* **2009**, *38* (2), 762–771.
5. Lacas, J. G.; Voltz, M.; Gouy, V.; Carluer, N.; Gril, J. J. *Agron. Sustainable Dev.* **2005**, *25*, 253–266.
6. Winchell, M.; Estes, T. *A Review of Simulation Models for Evaluating the Effectiveness of Buffers in Reducing Pesticide Exposure*; US EPA MRID #47773401; unpublished report, 2009.
7. Winchell, M. *A Comparison of Four Models for Simulating the Effectiveness of Vegetative Filter Strips at Reducing Off-Target Movement of Pesticides*. US EPA MRID #48451401, Unpublished report, 2010.
8. Williams, J. R.; Izaurralde, R. C.; Steglich, E. M. *Agricultural policy/environmental extender model theoretical documentation*; BREC Report #2008-17; Blackland Research and Extension Center: Blackland, TX, 2008; p 130.
9. Lowrance, R. R.; Altier, L. S.; Williams, R. G.; Inamdar, S. P.; Bosch, D. D.; Sheridan, J. M.; Thomas, D. L.; Hubbard, R. K. *The Riparian Ecosystem Management Model: simulator for ecological processes in riparian zones*; USDA-ARS Conservation Research Report 46; 2002.
10. Muñoz-Carpena, R.; Parsons, J. E.; Wendell, G. J. *J. Hydrol.* **1999**, *214*, 111–129.
11. Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Augustijn-Beckers, P. W.; Burt, J. P. *Rev. Environ. Contam. Toxicol.* **1992**, *123*, 1–155.

12. Pätzold, S.; Klein, C.; Brümmer, G. W. *Soil Use Manage.* **2007**, *23*, 294–305.
13. Giddings, J. M.; Anderson, T. A.; Hall, L. W., Jr.; Hosmer, A. J.; Kendall, R. J.; Richards, R. P.; Solomon, K. R.; Williams, W. M. *A Probabilistic Aquatic Ecological Risk Assessment of Atrazine in North American Surface Waters*; Society of Environmental Toxicology and Chemistry (SETAC): Pensacola, FL, 2005; p 432.
14. Lowrance, R. R.; Vellidis, G.; Wauchope, R. D.; Gay, P.; Bosch, D. D. *Trans. ASAE* **1997**, *40* (4), 1047–1057.
15. Sheridan, J. M.; Lowrance, R.; Bosch, D. D. *Trans. ASAE* **1999**, *42* (1), 55–64.
16. Poletika, N. N.; Coody, P. N.; Fox, G. A.; Sabbagh, G. J.; Dolder, S. C.; White, J. *J. Environ. Qual.* **2009**, *38*, 1042–1052.

Publication Date (Web): December 21, 2011 | doi: 10.1021/bk-2011-1075.ch018

Chapter 18

Sources of Pyrethroid Insecticides in California's Urban Watersheds: A Conceptual Model

Kelly D. Moran[1,*] and Patti L. TenBrook[2]

[1]TDC Environmental, LLC, 4020 Bayview Avenue, San Mateo, CA 94403
[2]U.S. Environmental Protection Agency, Region IX, 75 Hawthorne Street, San Francisco, CA 94105
[*]kmoran@tdcenvironmental.com

Pyrethroid insecticides have been linked to widespread aquatic toxicity in California's urban watersheds. To assist with the identification of the specific applications or activities linked to pyrethroids discharges, a conceptual model of the transport of pyrethroids from urban areas to surface waters was developed. This model is based on a review of scientific and engineering literature, pesticide product labels, California pesticide sales and reported use data, pesticide user surveys, and unpublished data from municipal urban runoff programs and municipal wastewater treatment plants. The conceptual model categorizes urban pesticide use patterns and disposal practices, and identifies pathways linking pesticide applications with surface waters. The model assumes that the bulk of pesticide applications are made to sites specified on product labels, but considers both legal and illegal disposal practices. The model was developed to serve as a tool to prioritize further investigations of use patterns, formulations, and transport mechanisms, and to develop measures to prevent and respond to water quality and compliance problems associated with urban pyrethroid use.

Introduction

Pyrethroid insecticides have been detected in surface waters—in both the water column and sediments—in areas subject to runoff and discharges from urban areas in California and other states (*1–12*). More importantly, toxicity to aquatic organisms has been linked to pyrethroids in numerous studies (*13–23*). In addition, reports submitted by regulated entities in California to regulatory agencies indicate incidents of toxicity due to pyrethroids (*24–29*).

Weston and Lydy (*19*) reported that nearly all samples collected in urban areas, or downstream of urban areas, in a study of the Sacramento-San Joaquin Delta, California, were toxic to the amphipod *Hyalella azteca*, and the toxicity was linked to pyrethroid insecticides. In the same study, very few detections of pyrethroids, and no toxicity due to pyrethroids were reported in samples from agricultural areas. The presence of pyrethroids in urban surface waters has been linked to particular outdoor and indoor pesticide use patterns that may lead to direct runoff to surface waters, or to indirect discharge via storm drains and sanitary sewer systems/wastewater treatment plants (*30*).

Professional applications account for nearly 90% of pyrethroid use in urban areas in California (*31*). Since professional pesticide applicators are trained, certified, and overseen by regulators, it is reasonable to expect that they carefully follow all instructions and restrictions on pesticide labels. This means that appearance of pyrethroid insecticides in surface waters is largely the result of legal use.

Instructions on pesticide labels are intended to mitigate risks to human health and the environment. Under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA, 7 U.S.C. §136 et seq.), the U.S. Environmental Protection Agency (U.S. EPA) Office of Pesticide Programs (OPP) uses data submitted by pesticide registrants, as well as other available data and modeling, to estimate concentrations of pesticide expected in surface water if the pesticide is used according to the label. While OPP has many scenarios available for modeling agricultural pesticide use, the tools and information available to model urban scenarios are limited (e.g., detailed urban pesticide use data).

Urban pesticide fate models will need to consider recent work by Jorgenson et al. (*32*, *33*), which has shown that factors such as surface composition and pesticide formulation significantly affect transport of pyrethroids from urban surfaces. Models will also need to include realistic urban loss rates. Wittmer et al. (*34*) reported that although urban pesticide use rates were lower than in agriculture, the rate of pesticide loss (fraction washed off) from urban areas was up to ten times higher than in agricultural areas. This is consistent with findings of Blanchoud et al. (*35*) that the contribution to surface water from urban pesticides in the Marne River, France, was similar to the contribution from agricultural pesticides (~11 tons/year), although 100 times more pesticide had been applied for agricultural use.

We describe a conceptual model that is designed to capture transport pathways and processes from urban pyrethroid application sites to surface waters. By categorizing urban pesticide use patterns to pervious and impervious surfaces, by identifying pesticide disposal practices, and by identifying transport pathways

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

and mechanisms linking pesticide applications with surface waters, this model will be a tool that can be used to identify which factors contribute most to pyrethroid transport to surface waters. The model includes realistic assessments of urban pesticide use and use patterns in California based on estimates of urban pesticide use and surveys of pesticide applicators. It considers all urban water conveyances (e.g., driveways, gutters, storm sewers, sanitary sewers, ditches, canals, etc.) and their pervious/impervious character. The model will serve as a tool to prioritize the importance of factors (e.g., use patterns, pesticide product formulations, and/or transport mechanisms) that determine transport of pyrethroids in urban areas.

Background

Most North American urban areas rely on two separate drainage systems—a wastewater (sewage) system and a storm drainage system. Wastewater systems are designed to carry wastewater from toilets and indoor drains to municipal wastewater treatment plants (sewage treatment plants). Separate storm drainage systems are designed to convey storm water runoff to urban waterways, usually without any type of treatment. Although some older cities transport both sewage and runoff in the same pipe, problems with sewage overflows during storm events in the late nineteenth and early twentieth centuries (*36*) triggered construction of municipal separate storm drain systems, which are now the norm.

To protect human health and water quality, modern cities convey wastewater from homes and businesses to centralized municipal wastewater treatment plants. Wastewater conveyance systems are not sealed systems; piping often is not watertight. As a result, stormwater and groundwater—and any pollutants they may be carrying—can enter wastewater collection systems and be conveyed to wastewater treatment plants.

Municipal wastewater treatment plants serve as processing facilities rather than disposal facilities. Wastewater treatment plants have varied treatment processes, designs, and capacities. In most cases, wastewater treatment plants provide physical separation of solids from liquids, biological treatment, and effluent disinfection. Wastewater treatment plants have three general outputs: water, solids, and air emissions. Effluent water may flow into creeks, rivers, estuaries, or the ocean. In some cases, waterways receiving discharges have little other flow (these are called "effluent dominated" waters). Recycled wastewater has growing use for irrigation, toilet flushing, industrial use, and even as an input to drinking water systems (*37*). Wastewater solids, commonly called sewage sludge or "biosolids," may be reused in agriculture or in urban gardens, disposed of in landfills, or incinerated, generating waste ash (*38*).

When it rains in an urban area, storm water runoff flows through engineered storm drain systems into urban waterways. Outdoor urban drainage system design focuses on moving water quickly away from structures, to prevent flooding and to ensure that roads and sidewalks remain usable during rainstorms. Engineered drainage systems are necessary in all but the lowest density areas because urbanization increases the quantity of water that runs off when it rains by replacing

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

natural *pervious* surfaces, where water infiltrates into soils, with *impervious* surfaces like buildings, streets, walkways, driveways, and patios, where water does not infiltrate into soils, but flows freely to the engineered drainage system.

When it is not raining, storm drains convey a variety of non-rain water discharges to waterways, such as excess irrigation runoff; wash water from cleaning outdoor surfaces (like buildings, driveways, and walkways); water from emptying swimming pools, spas, and fountains; vehicle wash water; and water released while flushing drinking water systems. Together, storm water runoff and other runoff flows are called "urban runoff."

Water running off of urban areas carries pollutants from urban surfaces into storm drains and waterways. In most of the nation's urban areas, water that runs off outdoors areas does not receive any type of treatment before it is discharged. Storm drains may discharge into creeks, rivers, estuaries, or the ocean. Most storm drainage systems have multiple discharge locations. For example, urban runoff from the ~70 km^2 Chollas Creek watershed (San Diego CA) flows into Chollas Creek through 800 separate storm drain outfalls (*39*). The most common design—gravity flow pipes—can convey runoff flows to waterways in minutes (*40*).

The movement of pollutants in outdoor urban watersheds is highly dependent on the nature of the ground surface where the pollutant is deposited. It has long been known that common urban watershed pollutants—including metals, other organic chemicals, and particles—wash off impervious surfaces much more efficiently than they wash off from pervious surfaces (*41*). The fundamental difference in pollutant washoff between pervious and impervious surfaces has formed a unifying theme in the modern stormwater quality management profession (*42*). Across the nation, state and local governments have adopted requirements to minimize impervious surface area in new urban development (*43*, *44*).

Drainage system design significantly affects pollutant levels in urban runoff. Traditional hardscape design that directs runoff through paved gutters through pipes to waterways provides little opportunity for pollutant removal. Drainage system designs incorporating specially engineered pervious areas (e.g., treatment swales, ponds, or gardens) remove significant fractions of pollutants from urban runoff (*45*). Some lower density urban areas use unpaved drainage systems like ditches, that remove pollutants but were not specifically designed for pollutant removal. These systems are less efficient than engineered treatment systems (*46*).

Model Development

We present a conceptual model that identifies—and determines the relative importance of—sources and transport pathways for pyrethroid insecticides in the urban environment. The model is based on knowledge of pest pressures and pesticide use patterns commonly observed in California, estimates of pesticide use in urban areas of California, prior work in modeling urban stormwater runoff, information about application practices from pesticide labels, and recent studies of factors affecting washoff potential of pyrethroid insecticides applied to various kinds of impervious urban surfaces. The model is specific to pyrethroid pesticides as they are used in California urban areas. As such, it omits some transport pathways that might be important for less hydrophobic pesticides, different urban use patterns, or in areas with different groundwater, surface water or drainage system characteristics. Some aspects of the model will be broadly applicable to other pesticides and other regions, particularly the concept of the relative importance of applications to pervious versus impervious surfaces.California's most urbanized areas are located in regions characterized by dry summers and mild, wet winters. As a result, indoor and outdoor pest control is a year-round challenge. Surveys of urban pesticide users in California have identified ants as the most commonly treated pests in urban areas (*47–51*). Other common urban pests include snails/slugs, spiders, termites, rodents, fleas, cockroaches, and flies (*47–51*).

Pyrethroid insecticides are commonly used for ant and termite control. A typical use of pyrethroid insecticides for ant control involves perimeter spraying around buildings plus spraying outside surfaces where ants are observed (e.g., window frames, eaves, garages, porches, and other impervious surfaces). Perimeter spraying involves a broadcast application in a band around the building, up to 10 feet away from the building plus 2-3 feet up the building wall starting at the foundation. When conducting perimeter spraying, professional applicators report treating all ground surfaces—including impervious surfaces (*50*). In 2009, the U.S. EPA requested that user instructions for pyrethroid products labeled for non-agricultural outdoor use be modified to allow only spot or crack and crevice treatments to impervious outdoor surfaces, with the exception that perimeter sprays may be applied to building walls starting at the foundation and up to a maximum height of 3 feet.

While most termite control involves subterranean treatments, pre-construction foundation treatments soak exposed soil that is subsequently covered by a building foundation. In 2009, U.S. EPA requested that labels for pyrethroid products used for pre-construction termite treatment include requirements to prevent runoff from the treatment site (*52*).

The California Department of Pesticide Regulation (DPR) maintains a rich Pesticide Use Reporting (PUR) database of pesticide use information (*53*). In addition, DPR keeps records of pesticide sales (*54*). All pesticide use, both agricultural and non-agricultural, by licensed, professional applicators must be reported to DPR. Non-professional applications (e.g., by homeowners) are not reported. TDC Environmental (*31*, *55–57*) has used PUR data, along with pesticide sales data to estimate urban pesticide use in California. Most important, the TDC Environmental reports estimate what portion of pesticides are used by professional vs. non-professional applicators. Pesticide user surveys by the University of California and others (*47–50*) provide insight as to what portions of pyrethroid applications are outdoors above ground (i.e., typically ant treatments) vs. indoors (i.e., commonly ant, flea, or cockroach treatments) or underground (i.e., termite treatments). This information is incorporated into the urban conceptual model.

In 1998, the Water Environment Federation and the American Society of Civil Engineers published a manual called "Urban Runoff Quality Management"

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

(*42*) that provides a history of studies of urban runoff water pollution and the development of urban runoff pollution control programs. The manual provides a discussion of hydrologic characteristics unique to urban areas, as well as an analysis of data collected in the U.S. EPA's Nationwide Urban Runoff Program (*58*). A key observation of this early work is the importance of the relationship of degree of imperviousness to urban runoff. The portion of pyrethroid applications to pervious vs. impervious surfaces in an urban area is a critical component of the model presented here.

A final component of the model incorporates findings of recent studies regarding the washoff potential of various pesticides, most importantly the effects of surface composition (*32*, *33*, *59*) on washoff rates. In urban runoff literature, the term "washoff" is used to describe the total quantity of a pollutant—both dissolved and attached to particles—that is washed off of a surface by urban runoff.

Model Development Approach

Consistent with the two separate urban water drainage systems in most urban areas, the conceptual model was developed in two sections – urban runoff and wastewater. The urban runoff portion of the model focuses on the sources of pyrethroids that flow into the urban stormwater drainage system. The wastewater portion of the model identifies the sources of pyrethroids that flow into municipal wastewater treatment plants. With a few exceptions that are detailed below, outdoor pyrethroid use falls into the urban runoff portion of the conceptual model and indoor pyrethroid use falls into the wastewater portion of the conceptual model.

The focus of this conceptual model is on use of pyrethroids in urban areas; agricultural use is not addressed. Indirect transport of pyrethroids to surface waters through pathways other than the two urban water drainage systems (such as runoff from agricultural fields treated with pyrethroid-containing sewage sludge or leachate from municipal non-hazardous solid waste landfills containing disposed pyrethroids) is beyond the scope of this model because it does not ordinarily occur in urban watersheds. Since pyrethroid manufacturing and packaging facilities do not exist in most urban areas—and facility air emissions, solid waste management, and effluents are controlled by other (non-pesticide) environmental regulatory programs—manufacturing-related releases have not been included in the conceptual model. Due to pyrethroids' low volatility (*60*), the conceptual model does not address air transport pathways.

Finally, the model incorporates several assumptions, some for simplicity, some due to data gaps. Two major assumptions are: 1) sanitary and storm sewer systems are separate; and 2) both professional and non-professional pesticide applicators generally follow application instructions on pesticide labels with regard to application locations and that any misuse involves modified application rates or incidental applications to adjoining surfaces. For purposes of this model, except for pyrethroids leaked from collection containers or spilled during transport, solid waste management systems (e.g., garbage and hazardous waste collection systems) are assumed to remove pyrethroids from urban areas.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Pyrethroid Urban Use Patterns

TDC Environmental (*31*) identified some important information about urban pyrethroid use. First, pyrethroids are divided into two groups according to product formulation and non-agricultural label instructions, which generally correlate with urban use locations, use levels, and photostability. The pyrethroids most heavily used in outdoors in urban areas (bifenthrin, cyfluthrin, β-cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, γ-cyhalothrin, λ-cyhalothrin, permethrin, and tralomethrin) are photostable pyrethroids primarily formulated as concentrates, granules, and ready-to-use liquids designed to be applied on and around buildings and in landscaped areas. Regarding these pyrethroids:

- Reported professional use, which is primarily for controlling pests on and around buildings, accounts for about 90% of total use;
- Use of these pyrethroids is higher in California urban areas than in California agricultural areas;
- Permethrin was the most heavily used (based on quantity applied in 2003-2008); and
- Two pyrethroids—cypermethrin and bifenthrin—accounted for most of the pyrethroid-related toxicity units applied in California urban areas in 2007-2008.

The second group of pyrethroids identified by TDC Environmental (*31*) are the pyrethroids designed and labeled for primarily indoor use for pet treatments and those sold only in low-concentration formulations like aerosols and foggers. With one exception (etofenprox), this group is comprised of relatively photosensitive pyrethroids: allethrins, cyphenothrin, etofenprox, imiprothrin, resmethrin, sumithrin (also called d-phenothrin), tetramethrin, and tau-fluvalinate.

A user-based approach was selected for development of the conceptual model. The conceptual model divides pesticide users into two groups: Professionals and Non-Professionals. "Professionals" are people engaged for hire in the business of pest control. "Non-professionals" are individuals who use pesticides at home (home and garden applications) and maintenance staff who apply pesticides at multifamily residential, industrial, commercial, and institutional facilities. Most available pesticide use data sources (e.g., (*47–50*, *53*, *61*) distinguish between professional and non-professional pesticide users. Professionals and non-professionals also differ in product selection, user training, and pesticide product sales channels (*61*).

Table 1 summarizes pyrethroid use by each of these two user groups. Information in Table 1 was obtained from pesticide product labels, California pesticide sales and reported use data, pesticide user surveys and retail shelf surveys (*47–51*, *53*, *54*, *61–66*).

Pyrethroid Insecticide Sources in Urban Watersheds

The conceptual model begins with pyrethroid sources. A "source" is defined here as the first event that transfers pyrethroids from enclosed containers into the

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

urban environment. This event—called a "release" for modeling purposes—may occur during intentional use (e.g., pyrethroid applications), cleanup activities associated with applications, as a result of an accidental spill, or through disposal of unused product. Each of these types of releases is a potential source of pyrethroids in urban waterways. The approach used to address each pyrethroid source in the conceptual model is described below.

Table 1. Urban Pyrethroid Insecticide Use Overview

Professional Pyrethroids Applications in Urban Areas	*Non-Professional Pyrethroids Applications in Urban Areas*
Structural pest control around residential and non-residential buildings, such as: • Outdoor broadcast spraying around buildings • Spot and "crack and crevice" treatments near buildings and outdoor living areas • Indoor sprays, fogging, and crack and crevice treatments • Termite control applications by underground injection or soil trenching and backfill • Pre-construction termiticide treatments (soil treatment prior to foundation construction) Landscape maintenance and related activities, such as broadcast or spot treatments to lawns and gardens, golf courses, parks, cemeteries, and road, rail, and utility rights of way Mosquito control applications by mosquito abatement agencies (ground sprays, ground-based fogging, or regional aerial spraying) Sewer manhole treatments	Structural pest control by residents or by staff of multifamily residential, industrial, commercial, and institutional facilities, such as: • Outdoor spot or broadcast spraying around buildings and outdoor living areas • Indoor sprays and fogging Landscape maintenance by residents or by staff of multifamily residential, industrial, commercial, and institutional facilities, such as broadcast or spot treatments in lawns and gardens Outdoor fogging to control mosquitoes Use of treated consumer products, such as: • Insecticide-treated clothing • Preserved wood • Pet collars Pet shampoos and spot-on treatments Human head lice and scabies shampoo and lotion treatments (regulated by the Food & Drug Administration) Sewer manhole treatments by maintenance and field staff

Applications

The primary way that pyrethroids are released to the urban environment is through legal (i.e., according to label instructions) applications to control pests. Both outdoor and indoor pyrethroid applications have pathways to surface waters. The urban runoff model addresses all outdoor pyrethroid applications, which fall into three broad categories: outdoor structural pest control, landscape maintenance and related activities, and mosquito control applications. The wastewater model addresses all indoor pyrethroid applications, impregnated materials, human and pet treatments, applications into the wastewater collection system at manholes, and one special case of underground applications—those occurring immediately adjacent to sewer lines.

Cleanup

Cleanup of mixing equipment, application containers, and applicator clothing may generate pyrethroid-containing wastewaters. Pesticide product labels include disposal instructions for unused product and for rinsate. For pyrethroid insecticides, this typically includes instructions to rinse equipment over the application area, and never to place unused product down any indoor or outdoor drain. In both the wastewater and urban runoff portions of the model, this type of cleanup is treated as part of the application itself.

Clothes washing generates a sewer discharge that is addressed in the wastewater conceptual model. Some products, like head lice shampoos and pet flea treatments, must be washed off after the appropriate treatment period. The wash water is assumed to be discharged into an indoor drain that flows to the wastewater system.

Since improper cleanup likely occurs occasionally despite efforts to prevent it (*47*, *48*), both portions of the model include improper cleanup activities to the extent that these activities involve unique drainage pathways. Whether or not the pesticide application occurs outdoors, improper cleanup that occurs indoors (e.g., in a sink connected to the sewer system) is considered in the wastewater model.

Disposal and Spills

The conceptual model accounts for both proper and improper disposal of unused and spilled pyrethroids. Unused pyrethroids and spill cleanup waste should be disposed of through the solid waste management system (proper disposal), either as business or household hazardous waste.

Since professionals regularly apply pesticides, it is generally assumed that they use all of pyrethroid products they purchase. In contrast, non-professionals tend to apply pesticides less frequently. Although pesticides are usually purchased for immediate application, the quantity purchased is often greater than the immediate need (*47–49*, *51*). Non-professionals frequently dispose of unused pesticides (*47–49*, *51*).

Despite precautions and regulatory controls, pyrethroid products may be spilled while in use, while in the urban portion of the wholesale or retail distribution system, or while enroute for disposal. Proper spill cleanups involve application of adsorbents to soak up any liquids and collecting pyrethroid-containing waste into a container that is sealed prior to disposal in the solid waste management system.

Improper disposal, though undesirable, is likely to occur (*47–49*, *51*, *67*). The conceptual model design recognizes that improper disposal may occur wherever

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

pyrethroids are handled—outdoors or indoors. Non-professionals commonly dispose of unused pesticides as non-hazardous waste via household garbage collection (usually improper disposal, but state laws vary) (*47–49*, *51*, *67*). When surveyed, a few percent of non-professionals admit that they have used gutters and drains for disposal (*47–49*, *51*). Since improper spill cleanups have also been documented and they can result in discharges to surface water, these are included in the conceptual model as well. Both the urban runoff and wastewater portions of the model address spills and improper disposal to the extent that these involve drainage pathways that are not associated with ordinary pyrethroid applications (e.g., disposal directly into drains).

Urban Runoff Conceptual Model

The urban runoff portion of the conceptual model focuses on connections between outdoor application, cleanup, and spill, disposal locations and surface waters. For convenience, the urban runoff model is divided into two parts. The first part links pyrethroid sources—the initial releases of a pyrethroid into the outdoor urban environment—and the outdoor location where the pyrethroid release occurs. The second part outlines the pathways for subsequent transport of these pyrethroids to surface waters.

Pyrethroid Insecticide Sources in Urban Runoff

The location where a pyrethroid is first released into the open environment determines the potential pathways available for transport to surface waters. Figure 1 shows the locations where pyrethroids are first released into the outdoor urban environment, including outdoor applications, as well as improper outdoor cleanup, spills, and disposal.

The conceptual model focuses on the three major categories of outdoor pyrethroid applications: structural pest control, landscape maintenance, and mosquito control (see Table 1 above). Structural pest control applications may occur outdoors, above ground, underground (injection or trenching), or indoors (which is considered in the wastewater model).

One special type of structural pest control application—pre-construction termiticide treatments—occurs on outdoor pervious surface (a building foundation site), but soon after the application, the treatment site is covered by a building foundation. If a rainstorm occurs before the foundation is completed, the pyrethroids could be washed away from the application site.

Pyrethroids behave like other chemicals deposited on outdoor urban surfaces. When an equivalent quantity of the same pyrethroid product formulation is applied to an impervious surface and a pervious surface of the same area, and both surfaces receive an equal amount of rainfall, the quantity of pyrethroids that washes off of the impervious surface is ten to one hundred times larger than the quantity washed off of the pervious surface (*32–34*). Recognizing the effect of the degree of perviousness on pyrethroid transport into urban waterways, the model subdivides outdoor, above ground locations into pervious

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

and impervious surfaces. The heavy lines in Figure 1 highlight the connection between professional structural pest control—the heaviest use of pyrethroids in urban areas (*31*)—and impervious surfaces.

Pyrethroid Insecticides Transport to Surface Waters via Urban Runoff

The second part of the urban runoff conceptual model outlines the connections between outdoor pyrethroid release locations and surface waters (see Figure 2). Pyrethroids occurring outdoors in urban areas have three primary fates: 1) degradation, 2) sequestration on surfaces, soil, or in organisms, or 3) removal by washing into drainage systems. Only pyrethroids occurring on exposed outdoor impervious and pervious surfaces have the potential to be washed into drainage systems and ultimately into surface waters.

Washoff may occur when it rains ("storm flows") or as a consequence of incidental water flows between storms ("dry weather flows"). After washoff, pyrethroid fate depends on the characteristics of the event that triggers the washoff and drainage system design. Ultimately, assuming pyrethroids are similar to other pesticides (*34*, *35*), only a small percentage of the total quantity of pyrethroids used outdoors is likely to reach urban waterways—but this small fraction of has proven sufficient to cause toxicity test failures.

Since much larger fractions of pyrethroids wash off of impervious surfaces than off of pervious surfaces, the heavy lines in Figure 2 highlight the connection between impervious surfaces and surface waters. Figure 2 shows a connection to the wastewater portion of the conceptual model to account for the small fraction of urban runoff that flows into the wastewater collection. These flows, called "inflow" by wastewater system operators, are one of the sources of pyrethroids described in the wastewater portion of the model.

Storm Events

Urban runoff during storm events has been a focus of regulatory programs because storm events are normally associated with higher pollutant loads—and often (but not always) with higher pollutant concentrations (*68*). Pyrethroid monitoring data similarly show that storm flows convey higher total loads than dry weather flows and generally contain higher pyrethroid concentrations (*1*, *19*, *24–26*). Like the pyrethroid washoff experiments described above, these monitoring data suggest that the processes involved in pyrethroid transport to surface waters from outdoor urban surfaces are consistent with urban runoff transport processes for other pollutants.

During a storm event, pyrethroid washoff depends not only on surface composition (pervious or impervious), but also on the rain volume, intensity, timing relative to the pyrethroid application, and the product formulation (*32*). Urban runoff drainage systems normally transport runoff to creeks within minutes—so quickly that the pyrethroids in runoff are unlikely to achieve equilibrium partitioning between solid and solution phases (*69*). Negligible degradation is expected in such short time frames (*60*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

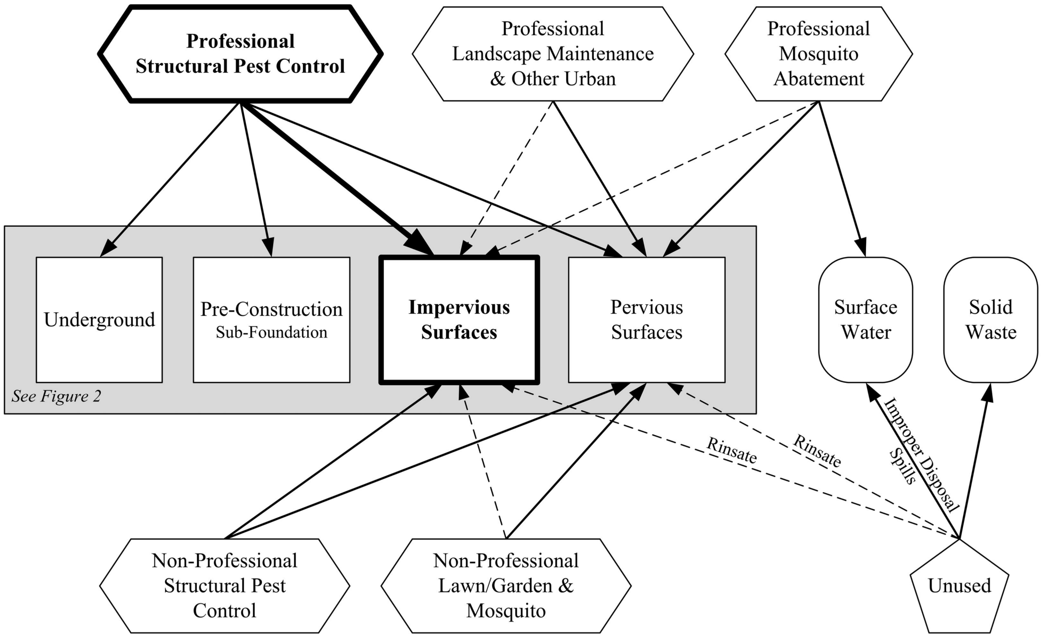


Figure 1. Urban Runoff Conceptual Model Part 1 - Initial Release of Pyrethroid Insecticides into the Outdoor Urban Environment (Line weight indicates relative importance of release)

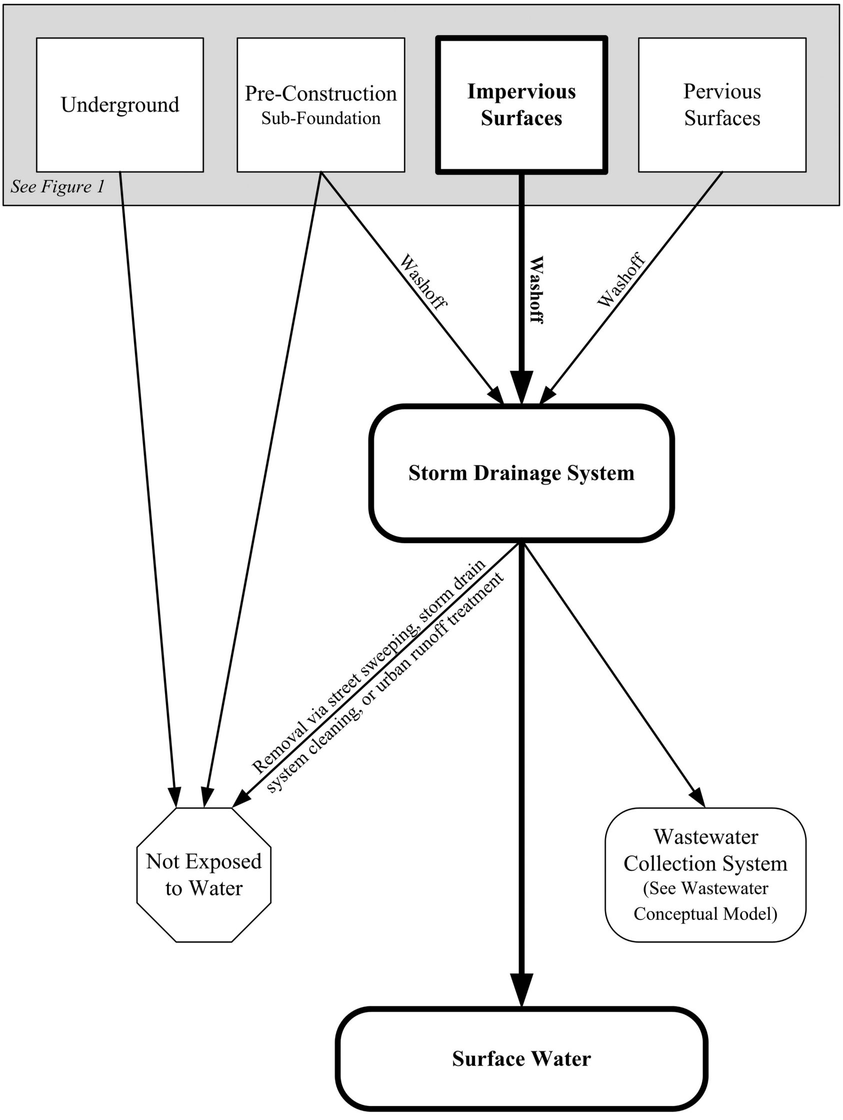


Figure 2. Urban Runoff Conceptual Model – Part 2: Connections Between Outdoor Pyrethroid Insecticide Release Locations and Surface Waters (Line weight indicates relative importance of connection)

Flow rates in stormwater collection systems depend on storm volumes, intensities, and drainage system design. When flow rates are high, runoff particles wash through the system. At very high flow rates, previously deposited particles may be re-suspended and carried to waterways.

Dry Weather Flows

Between storm events, other water flows like irrigation overflow and cleaning water can transport pollutants to urban waterways. Non-rain flows typically have relatively low flow rates and volumes, which makes them relatively inefficient at washing pollutants off of outdoor urban surfaces (some of which are never contacted by such flows). Consequently, they usually mobilize smaller pollutant quantities than stormwater runoff flows (*68*). Nonetheless, pyrethroid concentrations in dry weather runoff from urban watersheds sometimes exceed published toxicity thresholds for *Hyalella azteca* (*1*).

When flow rates are low, pyrethroids may adhere to particles that settle out in drainage systems. Most of these pyrethroids are likely washed to creeks by subsequent storm flows. Depending on the time period between storms, some degradation may occur in the drainage system, where degradation rates may be slowed due to lack of sunlight. Pyrethroid removal from the drainage system during street sweeping (open gutters only) or catch basin sump cleaning is likely minimal, because past studies of drainage system cleaning have shown that these important operational practices ordinarily provide little water quality benefit (*45*, *58*).

Wastewater Conceptual Model

The wastewater portion of the conceptual model (Figure 3) shows the primary pathways for pyrethroid insecticides transport into and out of municipal wastewater treatment plants.

The sources of pyrethroid insecticides in wastewater fall into five categories:

1. *Applications with inevitable discharges*. These include pet shampoos, as well as non-pesticide head lice shampoos and scabies lotion treatments, all of which must be washed off after treatment periods.
2. *Indirect post-application discharges*. After pyrethroids are applied indoors, pyrethroids may degrade, remain indefinitely on the treated surface, or be transferred to solid waste or to wastewater by subsequent cleaning activities. The conceptual model captures indirect wastewater discharges associated with cleaning treated surfaces. For example, mopping treated surfaces, hosing down treated kennels, using sponges or towels that are subsequently rinsed, or shampooing treated carpets creates pyrethroid-containing wastewaters that normally are poured into indoor drains connect to the sewer system. Pets receiving spot-on treatments or wearing impregnated collars may subsequently be bathed

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

indoors by owners, groomers, or veterinarians. Another class of indirect discharges is associated with clothes washing. Pyrethroid-treated clothing and clothing worn by both professional and non-professional applicators will almost certainly be washed in clothing washing machines that drain to the sewer system.

3. *Cleanup, spills, and illegal disposal*. Improper cleanup, spills, or improper disposal may cause pyrethroid discharges in sinks, toilets, tubs, or other indoor drains.
4. *Groundwater infiltration*. When groundwater infiltrates into the sewer system, it may carry pyrethroids applied underground in the immediate vicinity of the sewer lines. Due to pyrethroids' high K_{oc} values, their subterranean movement is likely limited (*60*).
5. *Urban runoff inflow*. The final group of pyrethroid discharges to the sewer system occurs outdoors. Even when urban drainage systems are separated, urban runoff finds its way into the sewer system. During dry weather, runoff from targeted neighborhoods may be intentionally directed to the sewer system as a means of removing pollutants (e.g., bacteria, metals, PCBs) that otherwise would have flowed directly into waterways. In wet weather, sewer system flows increase, often significantly, due to a combination of infiltration of groundwater into sewer lines and runoff flowing into manholes and outdoor drains connected to the sewer system. During storm events, stormwater flowing through manholes may wash off pyrethroids used for manhole treatments.

Pyrethroids that are not degraded during wastewater treatment plant processing will be discharged into surface water with the plant's water effluent, carried into recycled water distribution systems, or transferred to the plant's solid waste stream (sewage sludge). Pyrethroids have been detected in both wastewater treatment plant water effluent and sewage sludge (*19*, *70*).

Use of the Conceptual Model

The conceptual model provides a framework for identifying the specific applications or activities linked to pyrethroid discharges and the pathways for pyrethroid transport to urban waterways. This framework is being used today by government agency and corporate managers to inform near-term risk management decisions addressing the widespread aquatic toxicity associated with pyrethroids in urban watersheds.

The model was developed to serve as a tool to prioritize use patterns, formulations, and transport mechanisms for development of mitigation measures to address water quality and compliance problems associated with urban pyrethroid use. Because it was designed to mesh with available pyrethroid use and washoff data sets, the model highlights data gaps that should be priorities for future research, such as conducting dry weather and storm event wastewater treatment plant influent sampling to determine the contribution of storm water inflow

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

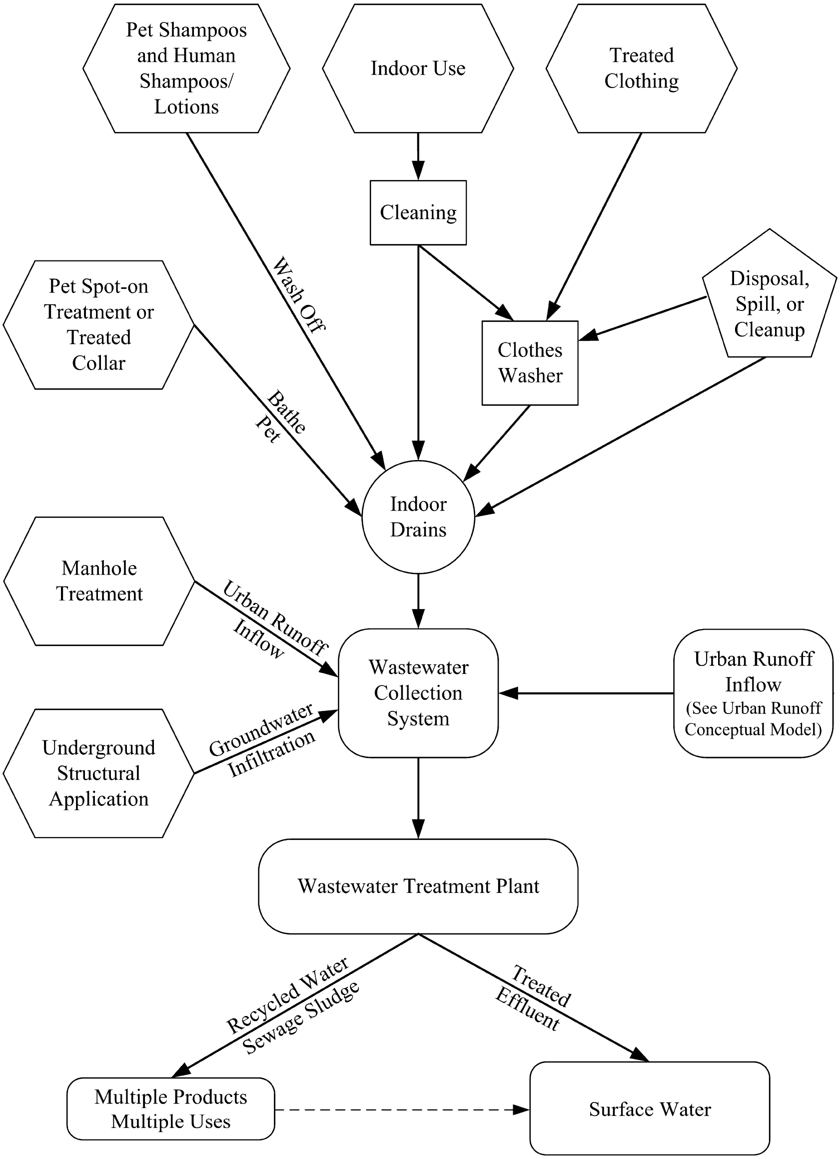


Figure 3. Wastewater Conceptual Model

to wastewater treatment plants. Another research priority highlighted by the conceptual model is obtaining a quantitative breakdown by application location for pyrethroids applied by professionals for structural pest control. California's pesticide use reporting system contains a wealth of data on professional urban pyrethroid applications; however, structural pest control application data do not distinguish among above ground, underground, pre-construction termiticide, and indoor applications. The conceptual model also can inform the selection and

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

design of experiments to test hypotheses about the relative importance of various pyrethroid sources and the relative effectiveness of risk mitigation strategies.

Well-informed conceptual models are the first step toward development of numeric watershed models (*71*). Because this conceptual model has been designed on the basis of the same urban runoff scientific literature that has informed a generation of numeric urban runoff models, it provides a strong foundation for future development of numeric models capable of estimating pyrethroid concentrations in urban waterways on the basis of urban use quantities and use patterns.

Acknowledgments

Development of this conceptual model was made possible in part by funding from the California Stormwater Quality Association and a grant from the American Recovery and Reinvestment Act of 2009 and the Clean Water State Revolving Fund through the California State Water Resources Control Board and the San Francisco Estuary Partnership. The contents of this document do not necessarily reflect the views or policies of the funding organizations. Although this chapter has been reviewed and approved in accordance with U.S. EPA requirements, its contents do not necessarily reflect U.S. EPA views or policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. Special thanks to Dr. Gail Chesler for her peer review of the wastewater portion of the model.

References

1. Weston, D. P.; Holmes, R. W.; Lydy, M. J. Residential Runoff as a Source of Pyrethroid Pesticides to Urban Creeks. *Environ. Pollut.* **2009**, *157* (1), 287–924.
2. Hintzen, E. P.; Lydy, M. J.; Belden, J. B. Occurrence and Potential Toxicity of Pyrethroids and Other Insecticides in Bed Sediments of Urban Streams in Central Texas. *Environ. Pollut.* **2009**, *157* (1), 110–116.
3. Hladik, M. L.; Kuivila, K. M. Assessing the Occurrence and Distribution of Pyrethroids in Water and Suspended Sediments. *J. Agric. Food Chem.* **2009**, *57* (19), 9079–9085.
4. Lao, W.; Tsukada, D.; Greenstein, D. J.; Bay, S. M.; Maruya, K. A. Analysis, Occurrence, and Toxic Potential of Pyrethroids and Fipronil in Sediments from an Urban Estuary. *Environ. Toxicol. Chem.* **2010**, *29* (4), 843–851.
5. Schmidt, C. *Sediment Pyrethroid Sampling in Irrigation Canal/Ditch System, Missoula, Montana*; Montana Department of Agriculture: Helena, MT, Mar 2010.
6. Anderson, S.; Cherr, G.; Morgan, S.; Nisbet, R. *Pacific Estuarine Ecosystem Indicator Research (PEEIR) Consortium: Modeling & Integration Component, Year 4 Annual Report*; University of California: Bodega Bay, CA, Jul 2005.

7. AQUA-Science. *Acute Toxicity of Sacramento Area Urban Creeks to Ceriodaphnia dubia, Final Technical Report*; Central Valley Regional Water Quality Control Board: Sacramento, CA, Aug 2007.
8. Bondarenko, S.; Spurlock, F.; Gan, J. Analysis of Pyrethroids in Sediment Pore Water by Solid-Phase Microextraction. *Environ. Toxicol. Chem.* **2007**, 2587–2593.
9. Budd, R.; Bondarenko, S.; Haver, D.; Kabashima, J.; Gan, J. Occurrence and Bioavailability of Pyrethroids in a Mixed Land Use Watershed. *J. Environ. Qual.* **2007**, *36* (4), 1006–1012.
10. Lowe, S., Anderson, B. S., Phillips, B. M. *Investigations of Sources and Effects of Pyrethroid Pesticides in Watersheds of the San Francisco Estuary, Final Project Report*; SFEI Contribution #523; San Francisco Estuary Institute: Oakland, CA, 2007.
11. Woudneh, M. B.; Oros, D. R. Quantitative Determination of Pyrethroids, Pyrethrins, and Piperonyl Butoxide in Surface Water by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry. *J. Agric. Food Chem.* **2006**, *54* (19), 6957–6962.
12. Woudneh, M. B.; Oros, D. R. Pyrethroids, Pyrethrins, and Piperonyl Butoxide in Sediments by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry. *J. Chromatogr., A* **2006**, *1135* (1), 71–77.
13. Amweg, E. L.; Weston, D. P.; You, J.; Lydy, M. J. Pyrethroid Insecticides and Sediment Toxicity in Urban Creeks from California and Tennessee. *Environ. Sci. Technol.* **2006**, *40* (5), 1700–1706.
14. Anderson, B. S.; Phillips, B. M.; Hunt, J. W.; Clark, S. L.; Voorhees, J. P.; Tjeerdema, R. S.; Casteline, J.; Stewart, M.; Crane, D.; Mekebri, A. Evaluation of Methods to Determine Causes of Sediment Toxicity in San Diego Bay, California, USA. *Ecotoxicol. Environ. Saf.* **2010**, *73* (4), 534–540.
15. Anderson, B. S.; Phillips, B. M.; Hunt, J. W.; Voorhees, J.; Clark, S.; Mekebri, A.; Crane, D.; Tjeerdema, R. S. Recent Advances in Sediment Toxicity Identification Evaluations Emphasizing Pyrethroid Pesticides. In *Synthetic Pyrethroids*; Gan, J., Spurlock, F., Hendley, P., Weston, D., Eds.; ACS Symposium Series 991; American Chemical Society: Washington, DC, 2008; pp 370−399.
16. Holmes, R. W.; Anderson, B. S.; Phillips, B. M.; Hunt, J. W.; Crane, D. B.; Mekebri, A.; Connor, V. Statewide Investigation of the Role of Pyrethroid Pesticides in Sediment Toxicity in California's Urban Waterways. *Environ. Sci. Technol.* **2008**, *42* (18), 7003–7009.
17. Werner, I.; Deanovic, L. A.; Markiewicz, D.; Khamphanh, M.; Reece, C. K.; Stillway, M.; Reece, C. Monitoring Acute and Chronic Water Column Toxicity in the Northern Sacramento-San Joaquin Estuary, California, USA, Using the Euryhaline Amphipod, *Hyalella azteca*: 2006 to 2007. *Environ. Toxicol. Chem.* **2010**, *29* (10), 2190–2199.
18. Werner, I.; Vasi, M.; Markiewicz, D. *Surface Water Ambient Monitoring Program (SWAMP) Toxicity Testing and Toxicity Identification Evaluation, Final Technical Report*; California State Water Resources Control Board: Sacramento, CA, Apr 2007.

19. Weston, D. P.; Lydy, M. J. Urban and Agricultural Sources of Pyrethroid Insecticides to the Sacramento-San Joaquin Delta of California. *Environ. Sci. Technol.* **2010**, *44* (5), 1833–1840.
20. Weston, D. P.; Amweg, E.; Mekebri, A.; Ogle, R. S.; Lydy, M. J. Aquatic Effects of Aerial Spraying for Mosquito Control over an Urban Area. *Environ. Sci. Technol.* **2006**, *40* (18), 5817–5822.
21. Weston, D. P.; Holmes, R. W.; You, J.; Lydy, M. J. Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides. *Environ. Sci. Technol.* **2005**, *39* (24), 9778–9784.
22. Ding, Y.; Amanda, D. H.; Heather, M. F.; Michael, J. L. Distribution and Toxicity of Sediment-Associated Pesticides in Urban and Agricultural Waterways from Illinois, USA. *Environ. Toxicol. Chem.* **2010**, *29* (1), 149–157.
23. Brown, J. S.; Sutula, M.; Stransky, C.; Rudolph, J.; Byron, E. Sediment Contaminant Chemistry and Toxicity of Freshwater Urban Wetlands in Southern California. *J. Am. Water Resour. Assoc.* **2010**, *46* (2), 1–18.
24. Riverside County Flood Control and Water Conservation District. Santa Margarita Watershed Annual Report Fiscal Year 2006-2007 Appendix G: Santa Margarita Region Monitoring Annual Report; prepared for the Riverside County Municipal Co-Permittees for submittal to the to California Regional Water Quality Control Board San Diego Region; Riverside, CA, 2007.
25. Riverside County Flood Control and Water Conservation District. Santa Margarita Watershed Annual Report Fiscal Year 2007-2008 Appendix G: Santa Margarita Region Monitoring Annual Report; prepared for the Riverside County Municipal Co-Permittees for submittal to the to California Regional Water Quality Control Board San Diego Region; Riverside, CA, 2008.
26. Riverside County Flood Control and Water Conservation District. Santa Margarita Watershed Annual Report Fiscal Year 2008-2009 Appendix G: Santa Margarita Region Monitoring Annual Report; prepared for the Riverside County Municipal Co-Permittees for submittal to the to California Regional Water Quality Control Board San Diego Region; Riverside, CA, 2009.
27. Weston Solutions. *Toxicity Identification Evaluation (TIE) of County of San Diego and Copermittees Chollas Creek Stormwater Sample*; Report to County of San Diego and Copermittees; Carlsbad, CA, 2006.
28. Weston Solutions. *Toxicity Identification Evaluation (TIE) of County of San Diego and Copermittees Chollas Creek Stormwater Sample*; Report to County of San Diego and Copermittees; Carlsbad, CA, 2007.
29. Weston Solutions. *Toxicity Identification Evaluation (TIE) of County of San Diego and Copermittees Agua Hedionda Creek Stormwater Sample*; Report to County of San Diego and Copermittees; Carlsbad, CA, 2008.
30. TDC Environmental, LLC. *Pesticides in Urban Runoff, Wastewater, and Surface Water: Annual Review of New Scientific Findings 2010*; prepared for the San Francisco Estuary Partnership; San Mateo, CA, 2010.

31. TDC Environmental, LLC. *Pesticides in Urban Runoff, Wastewater, and Surface Water: Annual Urban Pesticide Use Data Report 2010*; prepared for the San Francisco Estuary Partnership; San Mateo, CA, Mar 2010.
32. Jorgenson, B. C.; Young, T. M. Formulation Effects and the Off-Target Transport of Pyrethroid Insecticides from Urban Hard Surfaces. *Environ. Sci. Technol.* **2010**, *44* (13), 4951–4957.
33. Jorgenson, B. C.; Wissel-Tyson, C.; Young, T. M. *Factors Contributing to the Off-Target Transport of Pyrethroid Insecticides From Urban Surfaces*. University of California, Davis, CA. Unpublished work, 2011.
34. Wittmer, I. K.; Scheidegger, R.; Bader, H.-P.; Singer, H.; Stamm, C. Loss Rates of Urban Biocides Can Exceed Those of Agricultural Pesticides. *Sci. Total Environ.* **2011**, *409* (5), 920–932.
35. Blanchoud, H.; Moreau-Guigon, E.; Farrugia, F.; Chevreuil, M.; Mouchel, J. M. Contribution by Urban and Agricultural Pesticide Uses to Water Contamination at the Scale of the Marne Watershed. *Sci. Total Environ.* **2007**, *375* (1−3), 168–79.
36. Burian, S. J.; Nix, S. J.; Pitt, R.; Durrans, S. R. Urban Wastewater Management in the United States: Past, Present, and Future. *J. Urban Technol.* **2000**, *7* (3), 33–62.
37. *Wastewater Reclamation and Reuse*; Asano, T., Ed.; Water Quality Management Library; CRC Press: Boca Raton, FL, 1998; Vol. 10.
38. McFarland, M. J. *Biosolids Engineering*; McGraw-Hill: New York, 2001.
39. Weston Solutions. *Chollas Creek TMDL Source Loading, Best Management Practices, and Monitoring Strategy Assessment*; prepared for the City of San Diego; Carlsbad, CA, Sept 2006.
40. American Society of Civil Engineers; Water Environment Federation. *Design and Construction of Urban Stormwater Management Systems;* ASCE; WEF: New York, NY, Alexandria, VA, 1992.
41. Field, R.; Heaney, J. P.; Pitt, R. *Innovative Urban Wet-Weather Flow Management Systems*; Technomic Pub. Co.: Lancaster, PA, 2000.
42. Water Environment Federation; American Society of Civil Engineers. *Urban Runoff Quality Management*; WEF; ASCE: Alexandria, VA, Reston, VA, 1998.
43. U.S. EPA. *Incorporating Low Impact Development into Municipal Stormwater Programs*; EPA 901-F-09-005; U.S. Environmental Protection Agency: Washington, DC, 2009.
44. Arnold, C. L. J.; Gibbons, C. J. Impervious Surface Coverage: The Emergence of a Key Environmental Indicator. *J. Am. Planning Assoc.* **1996**, *62* (2), 243–258.
45. Minton, G. *Stormwater Treatment*; Sheridan Books: Seattle, WA, 2005; pp 20−21.
46. Burton, G. A.; Pitt, R. *Stormwater Effects Handbook : a Toolbox for Watershed Managers, Scientists, and Engineers*; Lewis Publishers: Boca Raton, FL, 2002; pp 35−37.
47. Flint, M. L. *Residential Pesticide Use in California: A Report of Surveys Taken in the Sacramento (Arcade Creek), Stockton (Five-Mile Slough) and the San Francisco Bay Areas with Comparisons to the San Diego Creek*

Watershed of Orange County, California; University of California Statewide IPM Program, University of California Davis: Davis, CA, March 15, 2003.

48. Wilen, C. *Survey of Residential Pesticide Use and Sales in the San Diego Creek Watershed of Orange County, California*; University of California Statewide IPM Program, University of California Davis: Davis, CA, Oct 2001.
49. Wilen, C. *Survey of Residential Pesticide Use in the Chollas Creek Area of San Diego County and Delhi Channel of Orange County, California*; University of California Statewide IPM Program, University of California Davis: Davis, CA, Sept 2002.
50. Pyrethroid Working Group and Meta Research, Inc. *California 2009 Urban Pesticide Use Pattern Study*; Sacramento, CA, Dec 2010.
51. Sacramento Stormwater Quality Partnership. *Residential Pesticide Use Survey, Summary and Report of Findings*; Meta Research: Sacramento, CA, Nov 2004.
52. U.S. EPA. *Notice to Manfacturers, Producers, Formulators, and Registrants of Pesticide Products*; Pesticide Registration Notice 2008-1; U.S. Environmental Protection Agency: Washington, DC, 2008.
53. California Department of Pesticide Regulation Pesticide Use Database. http://www.cdpr.ca.gov/docs/pur/purmain.htm.
54. California Department of Pesticide Regulation Pesticide Sales Database, http://www.cdpr.ca.gov/docs/mill/nopdsold.htm.
55. TDC Environmental, LLC. *Pesticides of Interest for Urban Surface Water Quality: Urban Pesticide Use Trends Annual Report 2008*; prepared for the San Francisco Estuary Project; San Mateo, CA, Jul 2008.
56. TDC Environmental, LLC. *Pesticides of Interest for Urban Surface Water Quality: Urban Pesticide Use Trends Annual Report 2007*; prepared for the San Francisco Estuary Project; San Mateo, CA, Jun 2007.
57. TDC Environmental, LLC. *Pesticides of Interest for Urban Surface Water Quality: Urban Pesticide Use Trends Annual Report 2006*; prepared for the San Francisco Estuary Project; San Mateo, CA, Jun 2006.
58. U.S. EPA. *Final Report of the Nationwide Urban Runoff Program*; PB-84-185545; U.S. Environmental Protection Agency: Washington, DC, 1983.
59. Jiang, W.; Gan, J.; Haver, D. Sorption and Desorption of Pyrethroid Insecticide Permethrin on Concrete. *Environ. Sci. Technol.* **2011**, *45* (2), 602–607.
60. Shamim M. T.; Hoffmann M., D.; Melendez, J.; Ruhman M. A., Ecological Risk Characterization for the Synthetic Pyrethroids. In *Synthetic Pyrethroids*; Gan, J., Spurlock, F., Hendley, P., Weston, D., Eds.; ACS Symposium Series 991; American Chemical Society: Washington, DC, 2008; pp 257−309.
61. Kreidich, N. I.; Flint, M. L.; Wilen, C. A.; Zhang, M. *Tracking Non-residential Pesticide Use in Urban Areas of California*; University of California Statewide IPM Program, University of California Davis: Davis, CA, Jun 2005.
62. TDC Environmental, LLC. *San Francisco Bay Area Retail Store Survey*; prepared for the San Francisco Estuary Project; San Mateo, CA, Sept 2005.

63. TDC Environmental, LLC. *San Francisco Bay Area Retail Store Survey*; prepared for the U.S. EPA Region IX; San Mateo, CA, Nov 2003.
64. Osienski, K.; Lisker, E.; Budd, R. *Surveys of Pesticide Products Sold in Retail Stores in Northern and Southern California, 2010*; California Department of Pesticide Regulation: Sacramento, CA, 2010.
65. Clarke, D.; Joshel, C. University of California Statewide IPM Program, Davis CA. Unpublished shelf surveys of pesticides retail stores from 2003-2008 in the Sacramento, Davis, and Woodland California area, 2008.
66. U.S. EPA Pesticide Products Label System. http://oaspub.epa.gov/pestlabl/ppls.home.
67. Kreith, F.; Tchobanoglous, G. *Handbook of Solid Waste Management*, 2nd ed.; McGraw-Hill: New York, 2002; Chapter 10.
68. Duke, L. D.; Lo, T. S.; Turner, M. W. Chemical Constituents in Storm Flow vs. Dry Weather Discharges in California Storm Water Conveyances. *J. Am. Water Resour. Assoc.* **1999**, *35* (4), 821–836.
69. Bondarenko, S.; Putt, A.; Kavanaugh, S.; Poletika, N.; Gan, J. Time Dependence of Phase Distribution of Pyrethroid Insecticides in Sediment. *Environ. Toxicol. Chem.* **2006**, *25* (12), 3148–3154.
70. U.S. EPA. *Treating Contaminants of Emerging Concern: A Literature Review Database*; EPA-820-R-10-002; U.S. Environmental Protection Agency: Washington, DC, 2010.
71. U.S. EPA. *Guidance on the Development, Evaluation, and Application of Environmental Models*; EPA/100/K-09/003; U.S. Environmental Protection Agency: Washington, DC, 2009.

Chapter 19

Use of the EPA Storm Water Management Model (SWMM) for Diagnosis of Pesticide Off-Target Movement from Residential Areas

Scott H. Jackson[1,*] and Michael Winchell[2]

[1]BASF Corporation, 26 Davis Drive, Research Triangle Park, NC 27709
[2]Stone Environmental Inc., 535 Stone Cutters Way, Montpelier, VT 05652
[*](919) 547-2349, scott.jackson@basf.com

The goal of this work was to determine if the SWMM model could be used to understand off-site pesticide loss from a housing development. The causes of unintentional exposures can often be difficult to determine, and therefore, hampers stewardship efforts. We used the model in an effort to discover which conditions are most likely to contribute to pesticide micro-constituents being found in storm drain water samples. Modeling results agreed with a University of California Cooperative Extension study that indicated inadvertent applications to impervious surfaces contributed the greatest mass loss. One conclusion from this work is that the use of a model such as SWMM can be helpful as a diagnostic tool for determining factors that contribute to pesticide loss from residential areas. A series of mitigation management practices could be developed based on this effort.

Introduction

We rely on chemicals as part of everyday life for agriculture, manufacturing, and domestic purposes. Environment Canada, for example, has estimated that there are more than 10,000 substances in use according to their Domestic Substances List (*1*). Recently, there has been concern that some frequently used products such as plastics, plastic additives, flame retardants, detergents, disinfectants, cosmetics, pharmaceuticals, and pesticides may be found in urban waters. Pesticides can be used for maintenance of landscaping, structural protection from termite attack or for elimination of nuisance pests such as ants or cockroaches. The use of pesticides in the urban environment poses unique challenges whether they are used around homes, apartment building or other commercial structures. Since urban structures typically drain directly into storm drain systems, detection of pesticides moving off target has been exacerbated. Scientists and regulators have struggled to place off-target exposures of urban pesticides in perspective. Their exact origin has not always been clearly understood. Various government agencies have been monitoring storm water quality (*2*, *3*) for some years. Is it possible to identify the sources of the off-target contamination? Some of the monitoring work has focused on housing subdivisions, which act as one hydrologic unit. Since the developments are essentially closed systems, they provide a unique opportunity to examine pesticide use practices using a model. This issue has been understood and predicted in agriculture using models either at the edge of field or on a watershed scale. However, the urban environment poses unique challenges that are not yet fully met. Among these challenges is the need for a tool that can help describe and predict how various practices might contribute to off-target movement. The goal of this work was to determine if we could use a model to identify those practices contributing to off-target movement and establish how landscape characteristics influence off-target movement (*4*, *5*).

Methods

Modeling Approach and Scenario

The EPA Storm Water Management Model (SWMM Ver. 5.0) is a dynamic rainfall-runoff simulation model used for single event or long-term (continuous) simulation of runoff in urban areas (*6*). The runoff component of SWMM operates on a series of subcatchment areas that receive precipitation and generate runoff and pesticide loads. The routing portion of SWMM transports this runoff through a system of pipes, channels, and storage/treatment devices. SWMM tracks the runoff generated within each subcatchment, along with the flow rate, flow depth, and quality of water in each pipe and channel during a simulation period. The model is run on sub-daily time steps, the duration of which is chosen by the user. In a 2006 study commissioned by CropLife America (*7*), the SWMM model was recommended as the most promising model for evaluating pesticide residues in the urban environment; for this reason, SWMM was chosen as the tool for use in this study.

The area selected for investigation is located in Aliso Viejo, a suburb located in Orange County, California (Figure 1). A water quality monitoring location is at the outlet of a detention pond that collects storm water from several outfalls draining a high-density residential development (Figure 2).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Figure 1. Study area location

Figure 2. Monitoring site

To evaluate the effectiveness of the modeling method, it was necessary to select a pesticide for evaluation. We selected fipronil as it is limited to a very specific uses and is applied only by Certified Pest Control Operators, unlike other pesticides such as pyrethroids which have many homeowner uses, including broadcast lawn applications. Fipronil exposure in Southern California storm water is attributed to the use of the product for control of nuisance ants. Ant treatments are restricted to spray perimeter bands measuring one foot up the side of the structure, and one foot out from the structure. Since use of the product is restricted to professional applicators and it has such a restrictive use pattern, fipronil was a good test candidate for modeling to determine how management practices may impact losses of the pesticide in stormwater.

Model Development

Subcatchment Delineation

The first step in building the SWMM model was to define watershed subcatchments and hydrologic connectivity. Standard methods for performing watershed and subcatchment delineation in an undeveloped landscape—such as the use of GIS and digital elevation models (DEMs)—are not effective in an urban environment. This is because the natural topography and hydrologic flow paths are often altered by roads, structures, and storm water collection systems. In order to accurately represent the contributing area and hydrologic connectivity in an intensely developed area like the housing development in Aliso Viejo, additional data such as storm water collection system maps were required.

To delineate the subcatchments in the Aliso Viejo subdivision, storm water collection system maps in CAD format were obtained from the planning department of the City of Aliso Viejo. These maps showed the locations of storm drains, subsurface culverts, and outfalls. They also described culvert characteristics, including their diameter, length, and connectivity. These data were used to define the hydrologic connectivity, or "plumbing", within the subdivision. The storm water maps, along with aerial photography and 5-foot contours obtained from the city's planning department, provided the basis for the delineation of subcatchment boundaries. Two separate watersheds, consisting of a total of seven separate "primary" subcatchments were defined. Both watersheds flowed into the same detention pond and outfall. The two watersheds and their "primary" subcatchment delineation are shown in Figure 3. The aerial imagery of the site on the left side of the figure can be compared with the SWMM depiction of the subcatchments on the right side of the figure. The term "primary" is used to indicate that these subcatchments represent the hydrologic boundaries of areas draining through a common culvert. These subcatchments were further delineated into "secondary" subcatchments as described below.

Figure 3. Subcatchment delineation

Secondary Subcatchment Delineation

Subcatchments in SWMM represent both hydrologic watershed divides as well as land units with different physical and chemical (pesticide) characteristics within a common watershed. The "primary" subcatchments discussed in the previous section were delineated based on the hydrologic divides within the study area. However, within each of those primary subcatchments, there were many different landscape areas with different physical and chemical (pesticide) characteristics. For example, there are roof areas, lawn areas, road and sidewalk areas, natural areas, and others. In order to describe the different characteristics and behavior of the different landscape areas with respect to build-up and wash-off of the pesticide (or chemical), they must be represented in SWMM as separate subcatchments.

Our conceptual model for how pesticides are applied in an urban environment required that we divide the landscape into seven different classifications, each representing a "secondary" subcatchment within a "primary" subcatchment. These seven classifications were roof, impervious surface, lawn, lawn buffer, landscape, landscape buffer, and brush areas. The characteristics of each of these areas were defined as follows:

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

- Roof: Roofs were delineated to represent impervious areas which do not have any pesticide build-up and have zero depression storage.
- Impervious surface: Impervious, non-roof areas were delineated to represent impervious areas which could have pesticide build-up and have some depression storage.
- Lawn: Lawn areas were delineated to represent pervious areas which could receive pesticide build-up and are also irrigated.
- Lawn Buffer: Lawn buffers are impervious areas adjacent to lawns. These areas can have pesticide build-up from direct application or off-target application. These buffers can also receive off-target irrigation. For this study, the buffer distance around the lawns was set to 3 feet.
- Landscape: Landscape areas were delineated to represent pervious areas which could receive pesticide build-up and are also irrigated. They were distinguished from lawn areas since they were believed to be less likely to receive pesticide build-up.
- Landscape Buffer: Landscape buffers are impervious areas adjacent to landscaped area. These areas can have pesticide build-up from direct application or off-target application. These buffers can also receive off-target irrigation. For this study, the buffer distance around the lawns was set to 3 feet.
- Brush: These areas were delineated to represent natural areas which do not receive pesticide build-up and are not irrigated.

The seven landscape classes described above were manually digitized for the study watershed. Figure 4 shows an example of the delineation of roof (brown areas), impervious (tan areas), and lawn (green areas) over a small section of the study area. Figure 5 shows all seven landscape areas delineated over a broader section of the subdivision.

For each of the seven primary subcatchments, there were seven secondary subcatchments, each representing a different landscape classification. This resulted in 49 independent SWMM subcatchments that could each be parameterized independently. The parameterization of the subcatchments is described in the next section.

Subcatchment Parameterization

The major components of the model that required parameterization were the weather, topographic characteristics, soils, and pesticide build-up/wash-off characteristics. Each of these components is described in the following sections.

Weather and Irrigation

For this study, hourly precipitation data from nearby Irvine, California (*8*) were used as inputs to the model. The data were compiled for the period from January 2004 through December 2008. The monthly rainfall for January through April of 2007, the period during which model scenarios were evaluated is shown in Table1. Monthly evapotranspiration (ET) was also required as an input. Long-term average monthly ET values for the Orange County area (*8*) were assumed to apply to the Aliso Viejo study area.

One of the primary mechanisms for pesticide transport into urban drainage systems is believed to be over-irrigation and off-target irrigation onto impervious surfaces where pesticide has been applied. An irrigation schedule of approximately 0.5 cm every other day, resulting in approximately 2.54 cm per week was set as the baseline irrigation schedule. The irrigation was set to occur on all lawn, lawn buffer, landscape, and landscape buffer subcatchments in the study area. Alternative irrigation scenarios were investigated as part of the model evaluation.

Figure 4. Roof, impervious, and lawn delineation from aerial photos

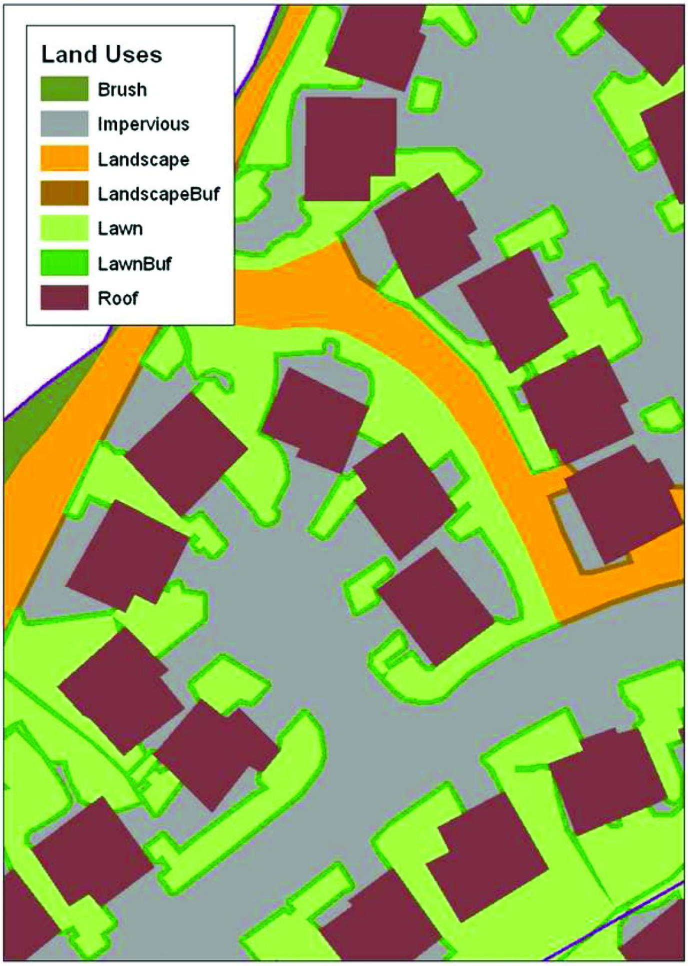


Figure 5. Landscape delineation of seven secondary subcatchments

Table 1. Monthly rainfall summary (Jan. – Apr. 2007)

Month	*Rainfall (cm)*
January	0.05
February	1.68
March	0.18
April	1.40

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Topographic Characteristics

The primary topographic characteristics required for the SWMM model were the area and slope associated with each subcatchment. The area was calculated based on the GIS delineation of the subcatchments from the aerial photography. In order to calculate the slope, a digital elevation model (DEM) was generated from 1.5 meter contours. Based on this DEM, the average slope or each subcatchment areas was determined. The area and average slope of each landscape class is shown in Table 2. This table shows that the predominant land use classes in the study watershed are impervious areas (roads, sidewalks, patios) and roofs, with the impervious buffers around the landscape areas covering the least amount of area. Slopes were highest in the natural brush and landscaped areas, with lower slopes for the impervious and lawn areas.

Table 2. Subcatchment landscape area summary

Name	*Total Area (ha)*	*Avg. Slope (%)*
Brush	3.9	23.4
Impervious	34.3	10.1
Landscape	17.5	22.7
Landscape Buffer	2.3	22.0
Lawn	19.5	9.9
Lawn Buffer	7.2	10.6
Roof	23.6	8.9

Soils

The portions of subcatchments that were pervious require that an infiltration model be parameterized. The infiltration model chosen for this study was the Green-Ampt model. This required the estimation of two parameters based on soil properties; the saturated hydraulic conductivity and the soil suction head. The soils for each subcatchment were characterized by overlaying the SSURGO soils mapping units (*9*) to determine the dominant soil for each subcatchment, then identifying the soil properties associated with those soils. The saturated hydraulic conductivity values were based directly on values contained in the SSURGO database. The soil suction head parameter values were estimated based on soil texture and were extracted from a published table (*10*).

Pesticide Build-up and Washoff

The SWMM model does not allow pesticide inputs to occur instantaneously at a specified rate and time over a given area. Instead, the water quality component of the SWMM model allows pesticids to build up over time during dry periods and then a portion to be washed off during wet periods. The build-up and washoff rates are based on functions defined by the user and can be defined independently for different land uses occurring within each subcatchment. The SWMM model offers the flexibility of defining a subcatchment to be composed of multiple land uses that have different pesticide build-up and washoff characteristics (the different land uses for our study site were described in previously). For example, one could define pesticide build-up to occur on only a small fraction of a subcatchment. It is through this model structure that a user is able to control the fraction of area that receives pesticide inputs.

The build-up function defined for the areas receiving pesticide in the study watershed was estimated based on the density of housing units in the study area and the typical application rate of the pesticide. SWMM offers three different build-up function options including a power, exponential, and a saturation function (*8*). The equation form chosen for this study was the power function, shown in equation 1. This build-up function resulted in a maximum of approximately 0.11 kg ha^{-1} of active ingredient. The shape of this function is shown in Figure 6. The build up plataeus at day 15, which represents the time for required for the full application area to have been treated. The assumption in this type of build-up function is that application are occurring randomly across different portion of the study area on different days. SWMM does not allow accommodation for any special circumstances, such as restricting applications on weekends.

$$B = \mathrm{Min}(C_1, C_2 t^{C3}) \qquad \text{Eqn 1.}$$

Where B = build-up (kg ha^{-1})
C_1= max possible build-up (kg ha^{-1})
C_2 = buildup rate constant (kg ha^{-1}-day)
T = time (days)
C_3= time exponent

SWMM offers three options for definining washoff; an exponential function, a rating curve, and an event mean concentration (*6*). The option chosen for this study was the exponential function. The form of this equation is shown in equation 2. The equation's coefficient values chosen were based on example SWMM input files and user manual recommendations. The shape of the washoff function is shown in Figure 7.

$$W = C_1 Q^{C2} B \qquad \text{Eqn 2.}$$

Where W = washoff (kg hr^{-1})
C_1= washoff coeficient (1 mm^{-1})
Q = runoff rate (mm hr^{-1})
C_2 = washoff exponent
B = build-up (kg)

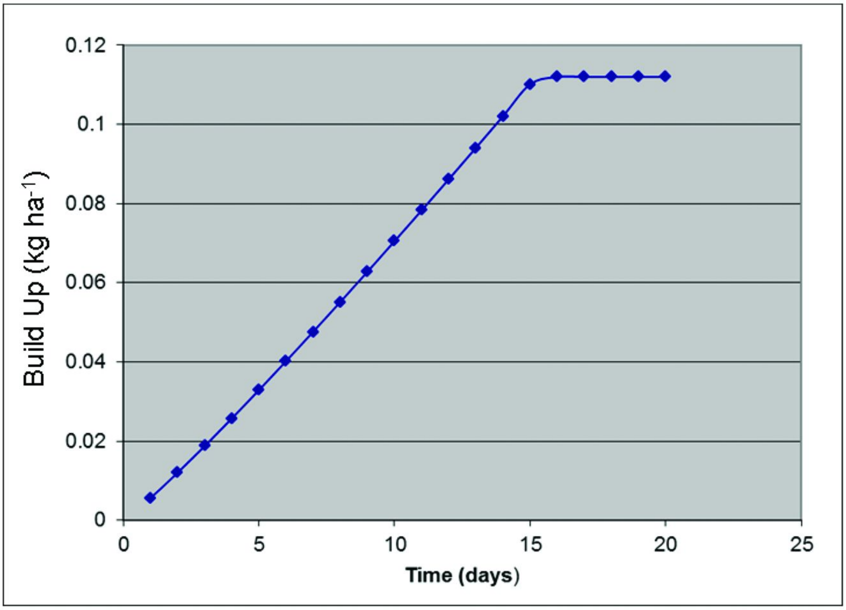


Figure 6. Pesticide build-up Function

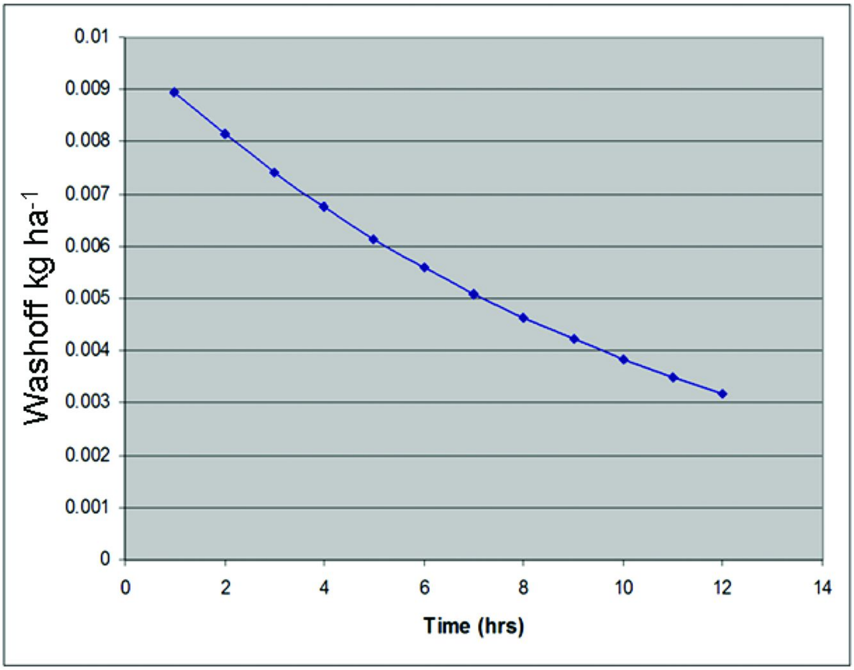


Figure 7. Pesticide washoff function

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Model Scenarios

Several model parameterization scenarios were investigated both to test sensitivity of model predictions to specific inputs and parameters. Three different inputs/parameters were investigated. The first was the saturated hydraulic conductivity of the pervious areas. This parameter is the primary control on surface runoff generation from lawns and landscape areas, and therefore impacts the amount of pesticide that can be transported from those areas. The second model parameter investigated was the percent of the impervious buffer area that was allowed to have pesticide build-up. This had a direct impact on the amount of pesticide available for direct runoff into the storm water collection system from either off-target irrigation or natural rainfall events. Finally, the frequency of irrigation was investigated. Irrigation frequency has a direct effect on the duration of dry days when build-up of pesticide can occur on both pervious and impervious surfaces. In total, six different scenarios were simulated, each of which varied one of the three inputs or parameters just described. These six scenarios are described in Table 3.

Table 3. SWMM simulation scenarios

Scenario	*Parameter/Input*	*Value*
1	High Hydraulic Conductivity	2.92 – 7.06 cm h^{-1}
2	Low Hydraulic Conductivity	0.13 cm h^{-1}r
3	Impervious Surface Area Build-up	1% of area
4	Impervious Surface Area Build-up	10% of area
5	Irrigation	0.71 cm, every third day
6	Irrigation	0.71 cm, every second day

Results and Discussion

Once the model was configured, the scenario was run for about 120 days. Both hydrology and pesticide loss predictions were based on the terminal outfall for the development. Model run results from the six scenarios are summarized in Table 3. Results from the most frequent irrigation scenario are summarized in Table 4.

Results from varying irrigation frequency can be found in Table 5. Results from varying irrigation frequeny can also be found presented graphically in Figures 8 and 9.

Tabular results from varing irrigation frequency do not provide much insight into how water additions might influence pesticide losses. However, an examination of Figures 8 and 9 indicate that daily losses from the development are influenced by irrigation pattern. In the more frequent irrigation scenario, pesticide losses average about 0.1 ug L^{-1} while the less frequent irrigation scenario produced losses of about 0.3 ug L^{-1}. One additional difference was spikes produced by rainfall events. In the more frequent irrigation scenario, pesticide spikes on rain days were more pronounced compared to the base irrigation runoff events (0.7 ug L^{-1}), while the less frequent irrigation scenario rainfall spikes were greater in magnitude (0.9 ug L^{-1}). Overall, pesticide losses were the same from the two irrigation scenarios but the loss patterns were different.

Table 4. Hydrologic input summary for the model run period.

	Runoff Quantity	
	Volume (ha-cm)	*Depth (cm)*
Total Precipitation	18.40	25.9
Evaporation Loss	2.03	2.8
Infiltration Loss	12.98	18.3
Surface Runoff	3.50	4.8
Final Surface Storage	0	0

Table 5. Influence of irrigation frequency on pesticide loss.

	1 Day (kg ha^{-1})	*2 Day (kg ha^{-1})*
Initial Buildup	0.00	0.00
Surface Buildup	1.34	1.34
Wet Deposition	0.00	0.00
Sweeping Removals	0.00	0.00
Infiltration Loss	0.00	0.00
BMP Removal	0.00	0.00
Surface Runoff	0.02	0.03
Remaining Buildup	1.34	1.34
Continuity Error (%)	0.00	0.00

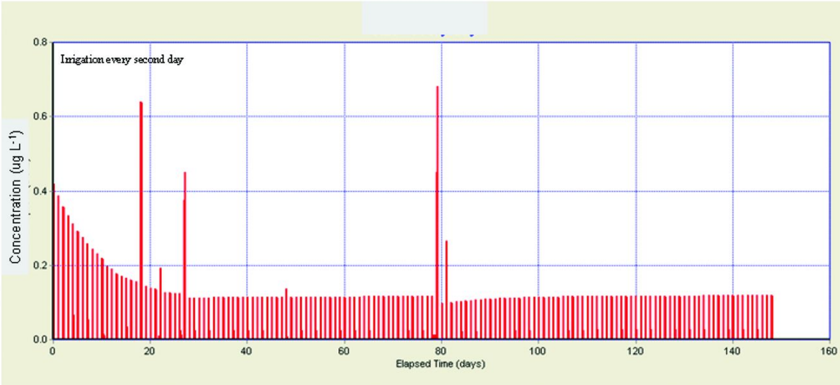


Figure 8. Plot of pesticide concentration moving from the development based on irrigations every second day.

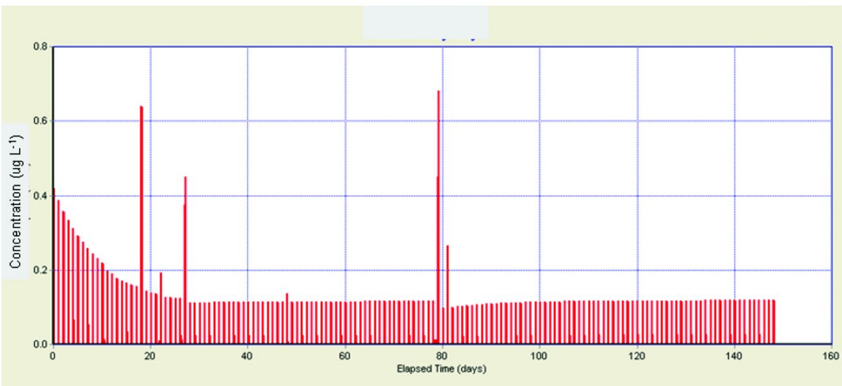


Figure 9. Plot of pesticide concentration moving from the development based on irrigations every third day.

Results from varying hydraulic conductivity can be found in Table 6. Results from hydraulic conductivity can also be found presented graphically in Figures 10 and 11.

Similarly, the irrigation scenario's tabular results from varying hydraulic conductivity do not provide much insight how soil permeability might influence pesticide losses. However, an examination of Figures 10 and 11 indicate that daily losses from the development are influenced by soil hydraulic conductivity. In the high hydraulic conductivity soil scenario, pesticide losses were fairly uniform for the modeled time period and did not produce pesticide loss spikes from rainfall events. By contrast, the lower soil hydraulic conductivity scenario

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

produced pesticide losses similar to the high hydraulic conductivity scenario but pesticide loss spikes were produced on some of the rainfall events. These spikes were the result of surface runoff generation occurring on pervious surfaces where some pesticide accumulation had occurred. Overall, pesticide losses were slightly greater for the low hydraulic conductivity scenario and the scenario produced runoff spikes on rain days.

Table 6. Influence of soil hydraulic conductivity on pesticide loss.

	High (kg ha⁻¹)	*Low (kg ha⁻¹)*
Initial Buildup	0.00	0.00
Surface Buildup	1.34	1.34
Wet Deposition	0.00	0.00
Sweeping Removals	0.00	0.00
Infiltration Loss	0.00	0.00
BMP Removal	0.00	0.00
Surface Runoff	0.02	0.03
Remaining Buildup	1.34	1.34
Continuity Error (%)	0.00	0.00

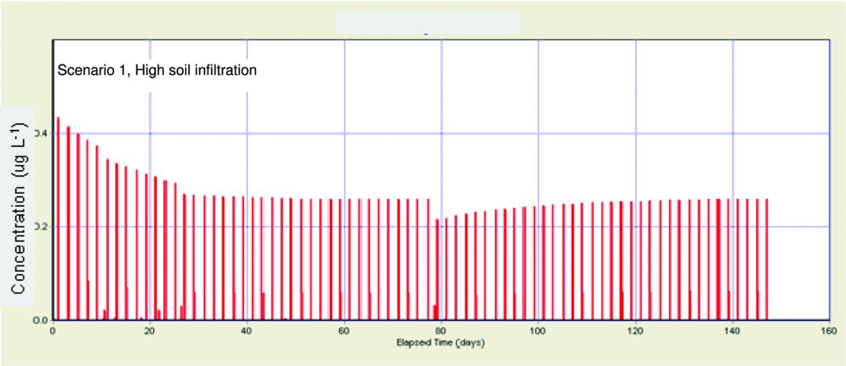


Figure 10. Plot of pesticide concentration moving from the development based on high soil hydraulic conductivity.

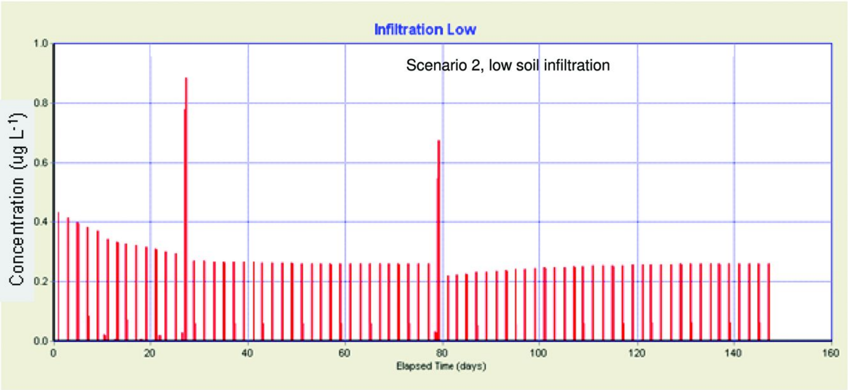


Figure 11. Plot of pesticide concentration moving from the development based on low soil hydraulic conductivity

Based on results presented in Table 7, it is evident that the amount of pesticide overtreatment impacted the amount of pesticide loss from the development. The amount of pesticide accumulating as pesticide build-up, as well as the quantity lost, are clear indicators of the difference between these two scenarios. Runoff results from the two overtreatment scenarios are also presented as plots in Figures 12 and 13.

Table 7. Influence of the pervious to impervious land percentages on pesticide loss. The header values (90/10) represent the percentage of the landscape receiving pesticide overtreatment.

	90/10 (kg ha^{-1})	*99/1 (kg ha^{-1})*
Initial Buildup	0.00	0.00
Surface Buildup	1.62	1.36
Wet Deposition	0.00	0.00
Sweeping Removals	0.00	0.00
Infiltration Loss	0.00	0.00
BMP Removal	0.00	0.00
Surface Runoff	0.27	0.03
Remaining Buildup	1.34	1.32
Continuity Error (%)	0.00	0.00

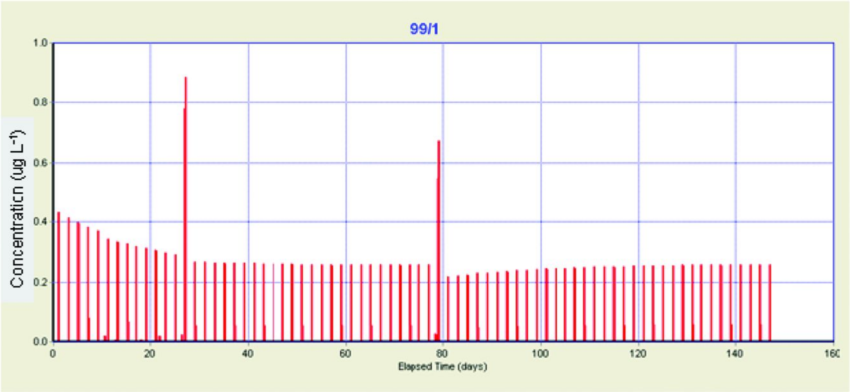


Figure 12. Plot of pesticide concentration moving off site for the 99/1 pervious to impervious pesticide overtreatment scenario.

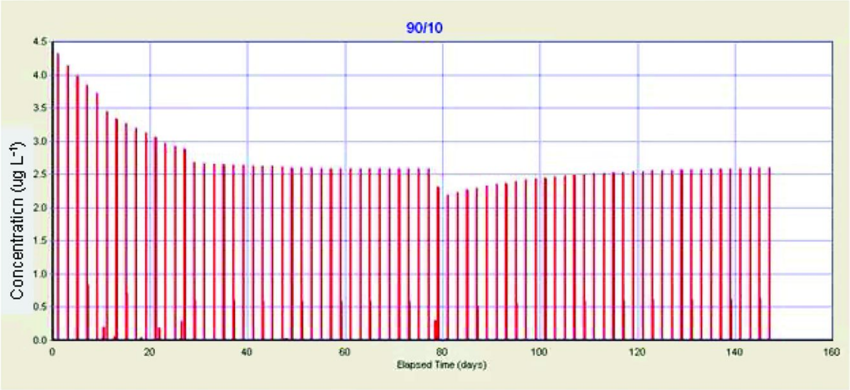


Figure 13. Plot of pesticide concentration moving off site for the 90/10 pervious to impervious pesticide overtreatment scenario.

Based on results in Figure 12 for the 99% pervious, 1% impervious scenario, runoff spikes were evident from rainfall inputs on two dates, while the mean loss of pesticide was about 0.3 ug L^{-1} with each irrigation event. The 90% pervious, 10% impervious overtreatment scenario plot is presented in Figure 13. The results presented in Figure 13 indicate that the mean runoff with each sprinkler event was about 3 ug L^{-1} and no runoff spikes occurred with rainfall events.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

By varying inputs in the six scenarios, we were able to determine which variables impacted pesticide loss from the development. Changing hydraulic conductivity and irrigation varied the pattern of pesticide loss but not the mass lost from the development. While patterns of loss were important, we focused the total mass lost in this work. By varying irrigation, spikes of pesticide loss were indicated, . however, irrigation frequency did not impact the magnitude of loss. Similarly spikes in pesticide loss were observed in the low but not the high hydraulic conductivity scenario but total mass loss did not differ between scenarios. None of the irrigation or hydraulic conductivity scenarios were as predictive as the pesticide overtreatment scenarios. The scenario indicating the greatest pesticide losses from the development was the 10% pesticide overtreatment scenario.

Subsequent to the completion of our modeling work, the University of California published an examination of treatment practices around homes where they could determine an accounting of mass loss (12). Their work focused on three application methods/practices, as follows: A) Spot treatment spraying ants anywhere they were seen including following trails, B) Perimeter spray only (labeled use), and C) Perimeter & spot treatments.

Results from the study in 2008 (*11*) were as follows from the treated properties: treatment A) 603 ug fipronil total, treatment B) 1 ug fipronil total, and treatment C) 363 ug fipronil total. The difference between treatments A and C was that treatment C included a spray-free zone on the properties. Both our modeling work and the subsequent study by the University of California confimed that losses of the active ingredient from properties only occurred when pesticide applications were made to impervious surfaces where water was then available to move that pesticide to storm drain systems. Applications of fipronil which closely followed the label led to little or no loss of substance. Our modeling work suggests that pesticide loss in storm drain water was proportional to the amount of impervious surface treated and that careful application of the product must be followed to ensure additional impervious areas do not get treated beyond what the label allows. This conclusion was supported by the finding of Greenberg et. al. (*11*). In summary, the modeling system was effective as a diagnostic tool for determining sources of pesticide losses to storm drain systems.

References

1. Environment Canada, Domestic Substances List Categorization and Screening Program. http://www.ec.gc.ca/substances/ese/eng/dsl/dslprog.cfm.
2. Flint, M. L. *Residential pesticide use in residential California: a report of surveys taken in Sacramento (Arcade Creek), Stockton (Five-Mile Slough), and San Francisco Bay Areas with comparisons to the San Diego Creek watershed of Orange County, California*; 2010. http//www.ipm.ucdavis.edu/PDF/PUBS/ncaliforniasurvey_1.pdf.
3. He, L.-H.; Ensminger, M.; Kelley, K.; Spurlock, F.; Goh, K. Monitoring Pesticides in Urban Stormdrain and Surface Waters in Four Metropolitan

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Areas of California; Presented at 238th ACS National Meeting, August 16−20, 2009, Washington, DC.

4. Lin, K.; Haver, D.; Oki, L.; Gan, J. Transformation and sorption of fipronil in urban stream sediments. *J. Agric. Food Chem.* **2008**, *56*, 8594–8600.
5. Gunasekara, A. S.; Truong, T.; Goh, K. S.; Spurlock, F.; Tjeerdema, R. S. Environmental fate and toxicology of fipronil. *J. Pestic. Sci.* **2007**, *32*, 189–199.
6. James, W.; Rossman, L. E.; Huber, W. C.; Dickinson, R. E.; James, W. R. C.; Roesner, L. A.; Aldrich, J. A. *Users's Guide to SWMM 5, Computational Hydraulic International, Guelph, Ontario, Canada*; 2008.
7. Cheplick, J. M.; Dasgupta, S.; Ritter, A. M.; Williams, W. M. *Model Review and Scenario Development for Urban/Residential Pesticide Runoff Model*; Waterborne Environmental, Inc.: Leesburg, VA, 2006; PROJECT ID WEI 252.04. http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OPP-2007-0319.
8. CIMIS – California Irrigation Management Information System, Station 75. http://wwwcimis.water.ca.gov/cimis/welcome.jsp.
9. Natural Resources Conservation Service, Soil Survey Geographic (SSURGO) Database. http://soildatamart.nrcs.usda.gov/.
10. Chow, V. T.; Maidment, D. R.; Mays, L. W. *Applied Hydrology*; McGraw-Hill: New York, 1988.
11. Greenberg, L.; Rust, M. K.; Klotz, J. H.; Haver, D.; Kabashima, J. N.; Bodarenko, S.; Gan, J. Impact of ant control technologies on insecticide runoff and efficacy. *Pest Manage. Sci.* **2010**, *66*, 980–987.

Chapter 20

The Challenges of Developing and Implementing Agricultural Environmental Management Practices

K. L. Mercer*

KMI, 750 Shannon Hill Drive, Paso Robles, California 93446
***klmercer@charter.net**

Escalating human populations will increase the need for intensified food production and contribute to ongoing environmental degradation. Augmenting food production, while protecting resources, will require increased implementation of existing management practices as well as rapid development of innovative ways to mitigate the environmental impacts of agriculture. Such change requires whole-farm considerations. This chapter provides an extensive field-level overview of the challenges of developing and implementing sound agricultural environmental practices on the Central Coast of California. The ubiquitous use of the term "management practices" by various practice paradigms is noteworthy as it causes confusion and results in unmet expectations. A single term, Agronomic*E* Practice, is proposed to signify that a practice promotes dual goals of cost-effective agricultural production and environmental protection. Potential solutions to implementation barriers are listed along with the call for innovations. This chapter addresses all practice categories with particular focus on pesticides.

Introduction

Human population is expanding and escalating food demands and environmental degradation from agriculture production (*1*, *2*). One of the primary challenges for today's agriculture is how to maintain future agricultural vitality without perpetuating threats to human health or natural systems.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Expectations are that agriculture will implement management practices to tackle impairments associated with fertilizer, irrigation and pesticide use, sedimentation and endangered species protection. In the face of documented impairments, agriculture has not met expectations. The question becomes what is preventing more rapid development and implementation of environmental management practices?

This chapter reviews what practices are being implemented by growers on the Central Coast of California. It explores the unique nature of developing and implementing agricultural environmental practices. It further addresses institutional, technical, social, financial, field research, and communication barriers to practice development and implementation of practices. Solutions are discussed to address the unique nature of solving agricultural environmental issues. These include more effective education, financial and regulatory incentives, adequate technical capacity, innovations, private/public collaborations and changing expectations.

Agriculture on the California Central Coast

The Central Coast of California grows roughly 118,115 hectares of irrigated crops (*3–8*). Commodities grown, in order of descending acreage, are cool season vegetables (i.e. leafy greens and brassicas), wine grapes, strawberries, sub-tropical fruits (i.e. lemons and avocados), tree fruits and nuts, warm season vegetables (i.e. tomatoes, peppers and squash) and ornamental crops. This region generates over $6 billion in gross revenue and much of the United States is dependent on the Central Coast for fresh fruits and vegetables. Based on commodity trade associations estimates, 70-85% of lettuce, 70-90% of broccoli, 15% of wine production and 50-53% of fresh and frozen strawberries are produced in this region. The viability of this area has national food supply implications and there is a concern that regulatory and economic factors may combine to displace Central Coast crops into other production areas.

The cosmetic nature of fresh produce is highly important as consumers expect blemish- and insect-free fruits and vegetables. This, combined with the relative short shelf-life of fresh produce, creates strong competition between growers for retail contracts and a slim margin of error on yield or quality.

The environmental issues on the Central Coast are not exceptional, albeit, they may be exacerbated by unique and sensitive local ecosystems. Impairments consist of water toxicity associated with pesticides, nutrients, bacteria and sedimentation from multiple sources including agriculture (*9*). Additionally, there are hotspots of endangered or threatened plant, animal, bird or amphibian species. These hotspots (*10*) are caused by transition between California's northern and southern and in-land and coastal microclimates, topography, ecosystems, human population distribution and land uses. Many endangered or threatened species are associated with aquatic or riparian habitats.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Grower Practices

Currently, there is poor understanding of what growers have done or are doing to protect the environment. Baselines are needed to enable measurement of progress. From 2005 to date, a water quality baseline has been produced from Central Coast ambient water quality monitoring data (*9*). Local pesticide monitoring data corroborate with data from previous national reports (*11*). In parallel, there needs to be a baseline of management practices to correlate with water quality improvement trends. Since a practice baseline does not currently exist, several lines of evidence are compared below to document the existing degree of practice implementation.

In 2006, the Central Coast Regional Water Quality Control Board (CCRWQCB) created a snapshot-summary of grower management practices based on information submitted by growers for enrollment in the Conditional Ag Waiver for Irrigated Lands (*12*). Of note, the highest level of practice adoption was where growers had the most direct control, where there was both public and private sector support, and where environmental protections directly reduced input costs. Growers reported that Pesticide Management Practices were adopted on greater than 88% of all acres using Integrated Pest Management (IPM), pest scouting, pest management thresholds, pest risk assessment models, sprayer calibration and proper pesticide mixing and loading. Similarly, growers adopted Fertilizer Management Practices on more than 75% of acres. Adoption of Irrigation Management Practices was appreciably lower and the level of adoption of Sediment Management Practices varied widely among crop groups.

In the 2004 Oso Flaco Nitrate and Sediment Assessment (*13*), greater than 80% of growers adopted practices such as irrigation scheduling and efficiency evaluations, drainage ditch installations, pesticide management, culvert/grades, tailwater return systems, soil sampling, more efficient use of N fertilizer, and plant tissue sampling which is used as an indicator of crop fertilizer sufficiency.

Grower comment letters submitted to the CCRWQCB in 2010 and 2011 (*14*) further substantiate levels of implementation. Types of practices normally implemented by all growers, across commodities, were consistent with practices reported above. Notably, many growers in all commodities practice organic farming. There is divergence in some practices among commodity groups as each commodity has unique production requirements. Growers of perennial crops such as grapes and sub-tropical trees use drip or micro-sprinkler irrigation and scheduling to avoid over-watering. These growers have largely discontinued the use of long-residual, pre-emergent herbicides. Weed control is done with mowing and/or targeted use of post-emergent, contact herbicides. Tillage is minimal. Many greenhouses recycle 100% of their irrigation run-off. Additionally, ornamental crops have reduced the use of pesticides of concern. For example, chlorpyrifos use decreased from a peak of 1,837.53 kg in 1996 to 425 kg in 2008. The use rate decreased from 0.997 kg/ha in 1991 to 0.718 kg/ha in 2008. And the number of hectares treated with chlorpyrifos decreased from 4,082 ha in 1996 to 591 ha in 2008. Diazinon was also reduced. Total use dropped from 885.42 kg in 1993 to 113.8 kg in 2008. Applications dropped from a peak of 1,115.86 kg in 1996 to 130.6 kg in 2008. Use rates decreased from 1.58 kg/ha in 2006 to 0.51

kg/ha in 2008. And the number of hectares treated with diazinon decreased from 2,278.46 in 1996 to 213.28 in 2008.

Central Coast Barriers to Implementation and Development of Environmental Management Practices

Collectively, there are a range of barriers that block development and/or implementation of management practices. Six categories of management practice barriers are considered below.

Institutional Barriers

Institutional barriers are associated with mandated policies or regulations over which growers have little control and which, in the end, diminish the likelihood of protections being implemented or developed.

The co-management of the water quality and food safety issue exemplifies how growers can be caught between regulations, agronomic requirements or contractual directives (*15*). In 2006, an *Escherichia coli* 1057:H7 outbreak among persons eating fresh spinach necessitated strong measures to protect leafy greens from contamination by human pathogens. Based upon available information, retailers encouraged growers to remove vegetated treatment systems with the goal of reducing wildlife habitat, pathogenic vectors, and microbial reservoirs. Subsequently, growers have become leery about further implementing practices which might trigger food safety liability or contractual issues. Contrarily, vegetated treatment systems and buffers are considered by many water quality professionals to be essential for protecting water quality. Hence, a practical impasse has been created.

In California, riparian habitat restoration and/or construction projects require multiple permits from numerous agencies. It is a multi-year process which may cost a permittee thousands of dollars. A few coordinated permits exist which pre-approve and pre-condition an "umbrella" permit held by one permittee. The Salinas River Channel Coalition has such a permit without which an individual permittee would have to obtain permits from seven agencies. Estimated costs are for every $100 spent in restoration activities, $200 would be required for permit related activities and fees. It would take an individual permittee three to five years to obtain approval for a two-year permit (*16*).

Regulations can be a deterrent to implementing management practices. Since 2008, negotiations of the CCRWQCB Conditional Ag Waiver (*14*) have frustrated stakeholders to the point that individual and non-profit efforts to protect the environment have been postponed. Frustration levels have prompted strong letters from elected officials to the State and Regional Water Quality Control Boards. One legislator wrote, "…So far, this hostile [regulatory] environment has curtailed, if not altogether stalled, the previous progress on agricultural water quality on the Central Coast. Efforts by most non-profits and agencies to proactively address water quality issues have come to a standstill" (*17*, *18*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Additionally, regulatory agencies vie for jurisdiction. In California, this situation creates a maze of duplicative and conflicting regulations. For instance, growers may implement a practice which protects water quality such as impounding irrigation water to reduce pesticide discharges; but may create unintended consequences such as reducing the amount of fresh water available for endangered species habitat in coastal lagoons and estuaries.

Technical Barriers

Since the 2008 economic downturn, technical resources and professional capacity have diminished. Many persons involved with agriculture rely on Natural Resource Conservation Service (NRCS) to provide growers with conservation assistance. Presently, the demand for assistance outstrips NRCS resources and the abilities of existing staff to assist eligible growers on the Central Coast. In 2010, only 47%, 87% and 66% of Environmental Quality Incentive Program (EQIP), Agricultural Water Enhancement Program (AWEP) and Conservation Reserve Program (CRP) applications, respectively, were awarded contracts (*19*). Regional Water Quality Control Board staff has stated that private sector consultants will make up deficiencies in technical capacity and provide technical assistance to growers. This might not be the case. There is an expected shortage of both licensed and experienced professionals because of an aging workforce (*20*). Of the 3,100 California licensed Pest Control Advisors, almost 40 percent are over 55 years of age, 35% are 45 to 55 and only 17 percent are 44 years or younger. Time will be required for private consultants to acquire necessary certificates or the experience to fill voids created by attrition or by new regulations. Disconcertingly, small farms and minority growers may not have equal access to technical services.

Ensuring that practices are technically suited to a particular location is a challenge. What may work in one place may not be effective in another. For example, vegetated ditches have been shown to be effective at removing pesticide contaminated sediments in the Midwest and southern parts of the United States; but not always on the Central Coast where ditches tend to be deep "v-shapes" to conserve valuable land for production. Regional differences in construction design accounts for reduced functionality where water borne pesticides or contaminated soils may not contact vegetation (*21*). Management practices may be inappropriate without fully understanding sources of pollution. Subsequently, management practices may seem ineffective or it may seem as if growers are not addressing impairments, when, in fact, the practices, per se, may be unsuitable.

In order to implement beneficial practices it is not sufficient to simply determine an impairment, but, also necessary to characterize temporal, spatial, seasonal and source influences to develop and adopt appropriate mitigative measures. Meals (*22*) suggests that characterization monitoring should occur at locations and at a frequency sufficient to detect change with enough sensitivity to determine the effectiveness of implemented practices. Measuring the impact of Management Practices is complicated. Greene-Lopez (*23*) listed the questions that need to be answered in order to understand the value of practices: 1) Do practices mitigate? 2) How are "effective or successful" practices defined? 3) Do water quality practices mitigate sufficiently to meet numeric standards? 4)

Is the discharge scenario under which the practice is "effective" the same as the discharge scenario that is actually causing the impairment? and 5) Since there are data gaps as to *how* agricultural impairments occur, can we definitively know how to address the root cause of the impairment?

A critical question is how long will it take to measure the positive effects of implemented practices? Meals (*22*) submits that watershed projects often fail to meet expectations because of the time that elapses between implementation and the point when improvements are detected in the watershed. Hydrology, vegetation, transport rate and path, residence time, pollutant sorption properties, weather, climate change, land-use changes and ecosystem linkages are all factors of lag time. Site specificity and the pollutant in question will vary lag times from weeks to years to decades. In order to accurately and effectively interpret data, and subsequently design effective practices, the lag time in a particular watershed must be known, or at the very least, estimated.

Field-level improvements may not equate to ecosystem-level improvements that can be directly and immediately measured. In the Quail Creek Project discussed below (*23*), growers realized significant pesticide reductions in farm-level discharges to below numeric objectives; however, these reductions were not reflected in samples taken in associated receiving waters. Unknown contamination likely pre-existed or was introduced from another source in the watershed before or at the time that mitigated irrigation water was discharged.

Other factors, such as watershed characteristics may contribute to impairments as well. It is common on the Central Coast for discharges causing impairments to be concentrated and channeled so that management practices designed for diffuse discharges have reduced effectiveness. Receiving water responses to management practices differ dramatically between highly modified systems such as dammed or channelized watersheds versus systems that are diluted by naturally-occurring base flows (*24*). Practices should account for this variability and not be treated as if they are universally applicable. One size does not fit all.

Social Barriers

It is difficult to sort grower attitudes and gauge the influence of demographics, tradition, political philosophy, or community peer pressure on practice implementation. Examples of attributes which influence a grower's likelihood to implement practices are discussed below.

Some commodity groups are ethno-centric. For instance, a large majority of strawberry growers are either Hispanic or Mixteca. Agricultural experience among members of this group varies from advanced to those who struggle with agricultural practices and economic performance. There are the obvious language barriers to discussions about management practices but these growers may also require supplemental and specialized training as they often prefer kinesthetic learning in the field in small groups with people they trust as opposed to classroom settings or large groups (*25*).

There are multiple risks associated with farming (*26*). Risk aversion predominates in agriculture. Farmers avoid risk as they are able and/or alleviate liability where risk cannot be avoided. They constantly assess yield, quality assurance, liability, market demands, operational flexibility and succession planning as part of risk/benefit analyses crucial to their operations. The less that is known about the success rate, the cost or the benefit of a practice; the riskier the practice will seem and the less likely the implementation.

A 2003 NRCS Survey (*27*) documented that growers were particularly concerned with the long-term nature of proposed practices in tenant situations. On the Central Coast, the impact of land tenure is often ignored by regulators, policymakers and technical professionals when considering what growers "should" do to address environmental impacts. Land tenure is very fluid and constantly shifting among annual crop growers. Many growers have developed a business strategy of owning base land and leasing additional land from other landowners. Anecdotal information indicates that in major watersheds on the coast as much as 80% of the land is rented. Hence, the grower may not be vested on the land or may not have assurances from the landowner that he will be on the ground for a long period of time.

One difference between growers and other parties interested in water quality (e.g. regulators and natural resource agency personnel) is the pace with which new ideas, trends and policy concepts are substituted for existing ones. Growers tend to require substantial time to cogitate and weigh options before they adopt change while others regularly amend their responses. This creates dissonance. In 2010, an unpublished survey of five stakeholder groups (growers, representatives from private industry, technical service providers, regulators and nonprofit/trade associations) documented that three of the five stakeholder groups perceived disconnects between development/implementation priorities and regulatory priorities. Plus, technical service providers and non-profit/trade associations indicated that development and implementation priorities cannot keep abreast of shifting regulatory priorities (*28*). Better understanding about the differential and consistent pace of change would better facilitate public problem solving processes.

Financial Barriers

No discussion of management practice barriers would be complete without discussing financial limitations. Often, the "average" and "gross revenue" are used to determine the ability of the regulated community to absorb the costs of a recommended regulation or initiative. These are misleading statistics. Net profit per hectare is much more relevant to the ability of an operation to absorb additional costs. Many high value crops have high gross revenue but very low net profit once fixed and variable costs and taxes are subtracted. Strawberries are a prime example. Gross revenue ranged over five years from $73,298.74 to $96,334.15 per hectare and net revenue ranged from $8,309.59 to $30,294.55 per hectare depending on market factors and production challenges (*29*). This is potentially a small return on investment, leaving little room for additional costs. Using more precise economic measurements in lieu of averages would provide clearer insight into income or revenue and a grower's financial resiliency to absorb the cost of implementing practices. For example, in Santa Barbara County, the average farm size is 212 ha, but, more than 60% of the farms have less than 24.28 ha. In terms of gross revenue, the average farm earns $496,715; whereas 46% and 52% of the farms earn less than $50,000 and $100,000, respectively (*30*). More work needs to be done to understand economic implications of regulations and policies: not only to the farm, but to local economies.

Field Research Barriers

Research and demonstrations need to be funded, supported and designed in ways to generate reproducible, significant and transferable results. Three field projects illustrate the challenges of developing management practices.

Collective Project - Starting in 2004, ambient monitoring data indicated there were chlorpyrifos and diazinon exceedances in Quail Creek, a subtributary of the Salinas River. No existing single practice was known to mitigate the impairments. Furthermore, there were no assurances that any combination of existing practices would be enough to reduce contaminants below levels of concern. Growers worked with four organizations to find solutions through the use of a new enzymatic product, Landguard™ OP-A, to hydrolyze organophosphate pesticides in irrigation water in combination with other practices. In previous projects, more than 90% of the organophosphate pesticides were hydrolyzed (*31*). A study was conducted to measure pesticide reductions associated with Landguard and water impoundment. Two catchment basins were dosed with Landguard™ per manufacturer instructions. Two ponds were sampled prior to treatment and then again after 24 hours before the sampling period began and every 72 hours thereafter for the duration of the project. Two sampling "passes" were made of the entire watershed while treatment ponds were discharging. In the end, LandguardTM substantially reduced organophosphate pesticide concentrations to levels that were either non-detectable or below levels of concern 0.025 ug/L for chlorpyrifos and 0.016 ug/L for diazinon. From an implementation point of view, growers learned that the best set of available practices was a combination of capturing pesticide contaminated water in existing catchment basins and then treating that water with Landguard™ prior to discharging (*24*). Uncertainty about Landguard's availability, price, dose, application rate, timing and the mode of application became barriers to wide-scale adoption. The strength of this effort was that it was privately funded and grassroots-driven and growers felt safe trying new approaches because of assured confidentiality. One drawback was that this effort was informal and produced few verifiable data. Another downside was that, to date, confidential data has not been shared with a broader audience.

One-Time Demonstration Project - This California Department of Conservation Watershed Coordinator Grant (*32*) project involved a one-time field demonstration which compared water quality discharges from soil treated with two different chlorpyrifos formulations for control of soil-borne insects. One area was treated with a granular formulation and the other was treated with a liquid formulation. When discharges were compared, there were no significant differences in chlorpyrifos levels regardless of the formulation used. Substitution of one formulation with another was not shown to be effective at mitigating chlorpyrifos exceedances. Discharges from both formulations exceeded the proposed numeric standards of 0.025 ug/L for chlorpyrifos and 0.016 ug/L for diazinon. This project exemplified the difficulties of developing effective management practices in the field. This project had inconsistent funding and staff due to state budget cuts. There were logistical and laboratory issues. Growers were reluctant to participate due to concerns about grant reporting requirements and enforcement vulnerability. Collaborative growers were pressured not to participate because of frustration over regulatory negotiations. These political challenges ultimately caused the grantee to cancel the grant.

Multi-Year Project - This was part of an EPA Strategic Agricultural Initiative grant to demonstrate and facilitate the adoption of pest management practices such as IPM and pest control methods such as alfalfa trap crops, use bug vacuums, and the use of biopesticides such as rosemary oil and mustard meal (*33*). The goal was to encourage adoption of low-risk, integrated pest management tools and strategies. Success was determined through grower surveys. Sixteen survey respondents applied fewer pounds of permethrin (17%), methyl bromide (7%), diazinon (4%), and chlorpyrifos (3%) than the county average. This creates an assumption that the project successfully reduced pesticide usage but results could have been confounded by growers motivated to transition to “safer” pesticides. Four out of five demonstrations resulted in growers adopting demonstrated management practices on all or part of their operations (546 hectares). Adoption of the bug vacuum was very low because costs seem high when compared to other treatments. The investment in bug vacuums ranged from $4,000-$60,000 depending on the number of rows, volume of air vacuum created and the type of dedicated tractor used (*34*).In the EPA study, likewise, the cost to efficacy ratio of the demonstrated biopesticides was prohibitive and resulted in low practical adoption. Alfalfa trap crops have become a commonly accepted practice but there are no reliable estimates of overall adoption.

A consultant, who worked on two of the projects discussed above, addressed the difficulties associated with developing and implementing meaningful and useful management practices in the field (*35*). She stated that it is not a simply a matter of replacing one practice with another practice as much as creating large-scale modifications and fundamental investments which can change the entire farming system. This requires time and consideration of multiple factors at each location where a practice may be used. It is very difficult under field trial conditions to assess the effectiveness of combinations of practices.

Finally, the two demonstration projects above which were performed to satisfy specific grant criteria did not include measuring practice effectiveness. Grant success was tracked through other means. This emphasizes the need to better coordinate public grant objectives with field-level conditions and needs.

Communication Barriers

Published surveys about insufficient practice implementation attribute communication barriers to the inability of professionals to adequately transfer information, and growers’ doubt as to the trustworthiness of communicated information (*27*, *36*, *37*). For instance, in 2003, NRCS documented that surveyed growers indicated clear and concise information was often not available and that information often conflicted about which management practices were most effective (*27*).

Over time, assorted paradigms have evolved in communicating about "management practices". Examples are: Integrated Pest Management (IPM), good agricultural practices (GAPs), best management practices (BMPs), agronomic, conservation, preservation, restoration, organic, sustainable, and food safety practices. Difficulty arises when persons ascribing to a particular paradigm attempt to communicate about management practices with persons outside of their paradigm. While the vocabulary is similar; the vernacular is not. This is problematic during collaborative problem solving attempts to address complex agricultural environmental issues. Regulators and the public become impatient because improvements are not immediately measureable, environmental professionals become frustrated that improvements are not happening at a faster pace, and agriculturalists become aggravated because locally relevant solutions are not readily available. All are interested in management practices but for different reasons.

Three common "management practice" paradigms are presented here for the purposes of illustration. This discusses the evolution, management practice approaches, and primary adherents of each paradigm.

The Conservation Paradigm - Since the Dust Bowl in the 1930's, a rich tradition of conservation has successfully reclaimed vast tracks of land in the Midwest from wind and water erosion. In its early stages, the conservation movement was focused on soil stabilization for production of agricultural crops and/or livestock. With time, conservation practices stressed the protection of natural resources as well as prevention of soil and water erosion and crop production considerations became secondary. This shift in focus was reflected in the name change in 1994 from the Soil Conservation Service to the Natural Resource Conservation Service (*38*). Today, this philosophical approach is typically embraced by the conservation community and natural resource professionals working for agencies and farmers and ranchers who may financially benefit from conservation practices.

The Conventional Agriculture Paradigm – In the 20th Century, there was transformation from an agrarian society to an industrial society in which farming became highly specialized via the Green Revolution. This transformation was driven largely by innovations from private/public partnerships and investments. In a historical context, this approach was seen as a modern and rational approach as new practices were vetted through empirical research. Growers embraced practices to increase productivity, decrease input costs or increase overall profitability. A new practice was generally adopted singly and substituted for an existing practice. No doubt, higher crop yields effectively acted as a land multiplier so that more food could be produced on less land (*39*). Today various stakeholders, such as resource managers, might denounce conventional farming because of its intensive and non-renewable exploitation of resources. This approach is currently the most widely practiced farming system. It is generally embraced by traditional growers, private industry suppliers, agriculturalists, and by consumers who demonstrate cost consciousness.

The Sustainable Farming Paradigm -Towards the late-20th Century, a subset of growers became concerned about agriculture's alienation from natural systems and the loss of the rural lifestyle. They responded with sustainable farming: "While the nature of conventional agriculture is production maximization through external inputs usage, sustainable agriculture is based on reduction of external inputs through maximization of knowledge and labor" (*40*). This paradigm is composed of three primary principles: environment, social equity and economics. Advocates are from a wide spectrum of progressive growers, trade associations and agricultural policy makers. Food retailers are major drivers of grower adoption and generally pass the costs along to the grower rather than to the consumer. The strength of the paradigm is that it promotes new ways to approach known problems. However, in spite of its holistic philosophy, sustainability often focuses primarily on environmental practices and economic considerations are unquantified or minimized. This paradigm could benefit from a strong economic analysis of financial benefits, environmental services, and the costs of associated documentation and tracking.

Barriers can have cumulative effects. For instance, in the absence of technical resources, growers may generate their own data. In a high-value cropping system where neighbors compete for contracts, grower-generated information about ways to improve productivity, while protecting the environment, could be a competitive advantage. Hence, growers may not be willing to openly communicate this information. In addition, grower generated information may not be helpful in public dialog as it may not be treated as a credible source. In this case, lack of technical capacity, a competitive marketplace, and communication barriers plus trust issues combine to inhibit the transfer of valuable practice information.

Solutions for Development and Implementation of Agronomic^{E} Practices

Much of this chapter has been dedicated to understanding the barriers to development and implementation of environmental management practices. Below is a discussion about potential solutions to overcome those barriers.

Standardized Terminology

The term "Management Practices" connotes a range of meanings. There is a need to create a standardized term for agricultural-environmental practices which broadly covers the dual goal of farming profitably while actively protecting the environment. For the sake of simplicity, the term, Agronomic^{E} Practice, is proposed. "Agronomic" emphasizes the farm as an intensively and profitably managed, interdisciplinary ecosystem. "*E*" emphasizes that the practice also protects the environment and/or creates ecosystem services. An Agronomic^{E} Practice accomplishes more than food production alone or environmental mitigation alone. Instead, it signifies an interconnection between financially sound farming and protection of all resources. Growers positively respond as this includes the long-term viability of their farm. This, subsequently, creates "buy-in" into the goal of a prosperous farm which prevents harm.

IPM is an example of an Agronomic^{E} practice. The National Road Map for Integrated Pest Management (*41*) defines IPM, as a "long-standing, science-based, decision-making process that identifies and reduces risks from pests and pest management related strategies. It coordinates the use of pest biology, environmental information, and available technology to prevent unacceptable levels of pest damage by the most economical means, while posing the least possible risk to people, property, resources, and the environment… IPM serves as an umbrella to provide an effective, all-encompassing, low-risk approach to protect resources and people from pests."

In order to make rapid change, there needs to be concerted efforts to develop additional Agronomic^{E} Practices, similar to IPM, to address other pollutant categories. For example, an idealized approach would be to prevent sediment runoff by putting a value on a cubic inch of soil in order to quantify losses from sedimentation, or conversely, calculate gains associated with retaining soil on the farm. This would require interdisciplinary efforts from conservationists, economists, and agronomists among other disciplines. However, the incentive to protect a quantifiable investment would stimulate a major shift in how landowners and operators view soil as a resource. There would be a vested interest in implementing or developing ways to prevent erosion and sedimentation.

The Environmental Defense Fund (EDF) philosophy epitomizes an Agronomic^{E} Practice approach. They have a strong record of finding solutions to environmental problems so that growers remain viable and simultaneously address environmental impacts. Their 2008 report, Farming for Clean Water, states that management practices must boost the farm while protecting the environment (*42*).

Education

There is agreement that practical information about management practices is critical. The question is "how does education correlate with management practice implementation?" In 2007, a survey of 2,000 growers was conducted by University of California Agriculture and Natural Resources (*43*) to measure how actions and attitudes were shaped by water quality educational efforts. In general, 75.7% of survey respondents had previously participated in water quality education. Positive correlates were found. Seventy-two percent of educated growers versus 55% of uneducated growers found education was useful in determining what water quality management practices to implement.

Another survey addressed barriers to the adoption of practices in the South (*36*) and explored how the method of delivering information impacts adoption and implementation of practices. Today, most extension personnel convey innovative technologies through a "diffusion of innovation" (DOI) model. In the DOI model, a new technology passes through concept, research, demonstration and implementation phases and information is provided by a technical expert to growers at critical points in development. The underlying assumption is that inventive growers will voluntarily adopt innovations and other growers will follow the lead of progressive growers. According to this study, this model "is increasingly seen as outdated … and incapable of adequately accounting for and addressing complex farming systems" (*44*). New and effective means of communication are needed to educate about practices which address agricultural environmental issues.

Incentives

The current overarching policy for environmental protection involves short-term investment by a few private individuals to create long-term benefits for society. In this situation, it would seem that society should have a vested interest and motivation to provide growers with resources and incentives necessary to facilitate environmental improvements. The gross revenue of high-value crops may prevent eligibility for USDA conservation program payments that exist for other commodities. Environmental protection incentives then must come from other sources: cost savings, markets, or other social initiatives.

The economic "carrot" and regulatory "stick" approach to forging agricultural/environmental or business/environmental interconnections is often discussed in relation to financial incentives. Proposed carrots are generally an economic incentive (e.g. conservation program payments, market based solutions such as resource trading, or compensatory mitigations). Another iteration of carrot and stick comes from the concept of voluntary adoption of management practices as the reward versus regulated and prescribed practices as the punishment. Often, regulators and policy makers will use the abeyance of regulation in exchange for some desired action; however, this approach is losing favor as more is known about the level of environmental impacts and the public is subsequently demanding immediate actions to meet perceptions of pollution.

Market creation through preferential purchasing encourages a "value" choice in which consumers pay more for environmentally friendly commodities and produce. This is analogous to how the organic farming industry has successfully commanded a premium for organic products. In another example, some sustainably certified vineyards recently have begun to receive premiums (*45*) or regulatory preferential treatment (*12*) for their certification status.

Ensure Adequate Technical Capacity

Practical application and active participation are keys to successful information transfer (*47*). This requires seasoned technical professionals who are adequately and reliably supported; but as noted, there is an anticipated shortage of appropriately trained technical professionals. In order to effectuate change, a sufficient number of well-trained, experienced technical professionals must be available to educate, demonstrate, and develop new practices, assist with implementation and measure the effectiveness of implemented practices.

Innovation

In 2008, the Environmental Defense Fund (EDF) projected that in order to meet water quality goals within adopted deadlines, nitrogen and phosphorous loads would have to be reduced by 44% and 27% respectively, despite expected population increases of 30% between 2000 and 2030. The report stated current conservation efforts, while laudable, were not sufficient and current conservation adoption rates would not succeed in achieving goals for another 40 years (*48*). The report called for innovations of all types: large, industrial, technical-fixes to small, farm-level brainstorms. The ability of growers to solve problems may be one of the most overlooked of resources. Successful growers own and operate farms through persistence, innovation, organization, risk-taking (*46*) and improvisation. Growers solve a myriad of daily environmental issues as a function of the intensively managed ecosystems which are the crux of farming. Tapping growers' unique problem solving skills is essential to accelerate change.

Since current practices appear incapable of achieving expectations within established timelines, it would follow that technological breakthroughs and innovative approaches are needed to provide alternative practices to meet objectives. In recent years, technology has been viewed by some as a "double edged sword, contributing to an overall improvement in productivity while simultaneously degrading public health, deteriorating the environment and threatening the sustainable resources" (*49*). However, if technical innovations can increase farm profitability and provide environmental benefits they should be rapidly conceived, evaluated, developed and deployed in order to boost agricultural production to meet projected food demands. Agricultural market demand coupled with relevant technologies could potentially provide the momentum and catalyst to encourage private investment in further development and exponential advancements to leapfrog over current barriers to sustained improvements.

Public/Private Collaborations

One of the best examples of public/private collaborations is the three-way partnership between growers, EDF and public sector funding in three Chesapeake Bay Watersheds and with the Iowa Soybean Association. These partnerships have formed On-Farm Networks which allow farmers to collect and collate data from their own farms and to evaluate the effectiveness and economics of different management practices (*50*). On-Farm Networks have demonstrated improvements. For example, in one watershed, nitrogen reductions were approximately 29,484 kg from sidedress applications and 36,240 kg from pre-plant applications.

The future role of the private sector as a participant in solving environmental issues remains nebulous. Some companies have resources and technical staff to innovate while other companies may be so focused on maintaining their core businesses that they miss opportunities to develop innovative technologies. Innovations may be spun off to or originate from smaller businesses. These entrepreneur-style businesses are often under-capitalized and cannot sustain the

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

research and marketing efforts necessary to bring a great idea to market. There is currently a market development void for these innovative ideas. Finding ways to harness the talent and innovation existing in private industry will be indispensible in solving future agricultural environmental problems.

Changing Expectations

Currently, if actions by growers are not sufficient to achieve mitigation expectations, then, a grower has three options: he may develop new practices, substitute another crop (which may or may not be an option, depending on the land or local markets), or develop the land for another use (i.e. quit farming).

Setting realistic expectations is one of the best, first steps in building momentum for change. Unrealistic expectations, milestones and standards can be disincentives. Changing how society views impairments or how we measure effectiveness can lead to a more productive problem solving.

The question of changing expectations is an emerging policy discourse (*51*). "Scientists are now suggesting that efforts should focus less on restoring ecosystems to their original state and more on sustaining new, healthy ecosystems that are resilient to further environmental change." Most ecosystems are "sufficiently altered in structure and function to qualify as novel systems, and that management activities are experiments, blurring the line between basic and applied research. Responses to specific management manipulations are context specific". Trying to return ecosystems to an ideal or a historical state may not be possible, and management activities with that intent may perpetuate problems or create additional issues.

A recent publication by the Public Policy Institute for California echoes the need to change approaches, expectations and current systems relative to California water management (*52*). Instead of having a system in which all interests are pitted against each other it would be more beneficial to develop a system in which "water is managed more flexibly and comprehensively for the benefit of both the economy and the environment."

Conclusions

There are multiple barriers to development and implementation of management practices which reduce the impacts of farming activities on the environment. The barriers discussed in this chapter are: institutional, technical, social, financial, field research challenges, and communication barriers.

From a communication standpoint, the term "management practice" has a variety of meanings. There needs to be one term to standardize expectations about agricultural environmental practices to avoid confusion or unmet expectations. The term Agronomic^{E} Practices is used here to designate practices which promote productive and profitable farming in a way which protects the environment. In essence, Agronomic^{E} Practices create a prosperous farm that prevents harm.

Clearly, current state of environmental degradation created by agriculture demands attention. Potential solutions exist, but they will not be inexpensive or easy to actualize. Possible solutions include: education, economic or regulatory incentives, utilization of growers' problem solving acumen, sufficient technical capacity, technological innovations, public/private collaborations and changing expectations.

Solutions will not occur without social and private investment in innovative outcomes. The situation necessitates an ever-increasing and critical need for creative problem solving. It will take vision in the 21st century to move beyond current technical expertise and regulatory trajectories and embrace innovative approaches and systems to nurture ecosystems, ensure safe drinking water and protect an extraordinary food production system. It will take leadership to see the problems differently, and change expectations, if necessary, in order to realize desired outcomes.

References

1. FAO, Economic and Social Development Department, World Food Summit. *Food Requirements and Population Growth*; Technical background document 1-5; 1996; Vol. 1, Chapter 4. http://www.fao.org/docrep/003/w2612e/w2612e4a.htm.
2. Hunt, J.; Markiewicz, D.; Pranger, M. *Summary of Toxicity in California Waters: 2001-2009*; Prepared for the Surface Water Ambient Monitoring Program, November 2010. http://www.swrcb.ca.gov/water_issues/programs/swamp/docs/reports/tox_rpt.pdf.
3. *Monterey County Crop Report*; 2010. http://Ag.co.monterey.ca.us/assets/resources/assets/163/cropreport_2010.pdf?.
4. *San Benito County Crop Report*; 2009. http:www//cosb.us/wp-content/uploads/2009-crop-report.pdf.
5. *San Luis Obispo County Crop Report*; 2010. http://www.slocounty.ca.gov/Assets/AG/croprep/crop+report+year+2010.pdf.
6. *Santa Barbara County Agricultural Production Report*; 2010. http://www.countyofsb.org/uploadedFiles/agcomm/crops/2010.pdf.
7. *Santa Clara County Agricultural Crop Report*; 2010. http://www.sccgov.org/SCC/docs%2FAgriculture%2C%20Division%20of%20%28DIV%29%2Fattachments%2F2010CropReportFINAL.pdf.
8. *Santa Cruz County Crop Report*; 2010. http://www.agdept.com/content/cropreport_10.pdf.
9. About ambient water quality monitoring by Central Coast Water Quality Preservation, Inc. (CCWQP), posted on Central Coast Ambient Monitoring Program (CCAMP) website. http://www.ccamp.org/ccamp/Reports.html.
10. Dobson, A. P.; Rodrigues, J. P.; Roberts, W. M.; Wilcove, D. S. Geographic Distribution of Endangered Species in the United States. *Science* **1997**, *275* (5299), 550–553.
11. Gilliom, R. J.; et al. *The Quality of our Nation's Waters - Pesticides in the Nation's Streams and Ground Water*; U.S. Geological Survey 1992 – 2001; Circular 1291; 2006.

12. *About 2006 Conditional Agricultural Waiver for Irrigated Lands Management Practice Checklist*; Central Coast Regional Water Quality Control Board; 2007. URL discontinued and unavailable.
13. *Cachuma Resource Conservation District (CRCD): 2004 Oso Flaco Nitrate and Sediment Assessment*; 2008. URL unavailable.
14. About Central Coast Regional Water Quality Control Board Conditional Ag Waiver for Irrigated Lands. http://www.swrcb.ca.gov/rwqcb3/water_issues/programs/ag_waivers/ag_order.shtml.
15. Bianchi, M. L.; Mercer, K. L; Crohn, D. M. Resolving Conflicting Priorities Concerning Food Safety Issues in Leafy Green Vegetables. In *Proceedings of the 23rd Vertebrate Pest Conference*; Timm, R. M., Madon, M. B., Eds.; University of California: Davis, 2008; pp 7−15.
16. Din, D., Executive Director, Salinas River Channel Coalition. About permitting requirements in the Salinas Valley. Unpublished personal communication.
17. Correspondence from the Honorable Congressman Sam Farr to State Water Quality Control Board. May 4, 2010.
18. Correspondence from the Honorable Congressman Sam Farr to Central Coast Regional Water Quality Control Board. February 18, 2011.
19. Mountjoy, D., Assistant State Conservationist for Field Operations, NRCS. About USDA program applications versus awarded contracts. Unpublished personal correspondence. February 29, 2011.
20. Cline, H. *Pest Control Advisor Workforce Aging, Dwindling*; Western Farm Press: October 31, 2006. http://westernfarmpress.com/pest-control-adviser-workforce-aging-dwindling.
21. Moore, M. T.; et al. Mitigation Assessment of Vegetated Drainage Ditches for Collecting Irrigation Runoff in California. *J. Environ. Qual.* **2008**, *37*, 486–493.
22. Meals, D. W.; Dressing, S. A. Lag Time in Water Quality Response to Best Management Practices: A Review. *J. Environ. Qual.* **2010**, *39*, 85–96.
23. Greene-Lopez, S. Technical Program Manager, Central Coast Agricultural Water Quality Coalition. About Quail Creek. Unpublished project report, 2010.
24. Greene-Lopez, S. Technical Program Manager, Central Coast Water Quality Preservation, Inc. About management practices. Unpublished correspondence, 2010.
25. Santibanez, M. P. Cachuma Resource Conservation District (CRCD). *Strawberry Farmers Survey*; Unpublished report, January 2008.
26. Miller, A.; Dobbins, C.; Pritchett, J.; Boehlje, M.; Ehmke, C. *Risk Management for Farmers*; Staff Paper 04-11; September 2004.
27. Brant, G. *NRCS: Barriers and Strategies Influencing the Adoption of Nutrient Management Practices*; Technical Report 13.1; March 2003. http://www.ssi.nrcs.usda.gov/publications/2_tech_reports/T025_nutrient_management.doc.
28. Mercer, K., President, KMI. About barriers to management practices. Unpublished Survey, 2010.

29. *Agricultural Resources Study, Ventura County Initial Study Assessment Guideline, Analysis of Proposed Mitigation Parcel, C. 1*. URL unavailable. Document available through keyword search with report title.
30. Mercer, K., Watershed Coordinator, Southern San Luis Obispo and Santa Barbara Counties Agricultural Watershed Coalition. *About Appendix A, Four Year Guadalupe Settlement Fund Grant Summary*; Correspondence with CCRWQCB; September 5, 2008. http://www.swrcb.ca.gov/rwqcb3/board_info/agendas/2008/sept/item20/item20_att1.pdf.
31. Anderson, B. S.; et al. *Pesticide and Toxicity Reduction Using Vegetated Systems and Landguard OP-A*; Data summary and final report; CCRWQCB: San Luis Obispo, CA, 2008. URL unavailable.
32. California Department of Conservation, Watershed Coordinator Grant Program. Grant Number 3007-205; Unpublished final report, June 30, 2010.
33. US Environmental Protection Agency, Strategic Agricultural Initiative, Food Quality Protection Act, Grant #X8-00902001-0; Unpublished final report, January 2010.
34. Pickel, C.; Zalom, F.; Walsh, D.; Welch, N. Vacuums provide limited Lygus control in strawberries. *Calif. Agric.* **1995**, *49* (2), 19–22.
35. Antinetti, R., Water Quality Consultant. About implementing agricultural environmental protection practices. Unpublished interview. February 8, 2011.
36. Rodrigues Baide, J. M. M.S. thesis, Auburn University, Auburn, AL, 2005.
37. Drost, D.; et al. Barriers to Adopting Sustainable Agricultural Practices. *J. Extension* **1996**, *34* (6), 6FEA1.
38. *75 Years of Helping People Help the Land*; USDA NRCS; 2010. http://www.ca.nrcs.usda.gov/news/75/index.html.
39. Dimitri, C.; Effland, A.; Conklin, N. *The 20th Century Transformation of U.S. Agriculture and Farm Policy*; ERS Information Bulletin; June 2005; No. 3. http://ageconsearch.umn.edu/bitstream/59390/2/eib3.pdf.
40. Roling, N. G.; Jiggins, J. Policy Paradigm for Sustainable Farming. *Eur. J. Agric. Educ. Ext.* **1994**, *1* (1), 23–43.
41. IPM Centers. *National Road Map for Integrated Pest Management*; May 17, 2004. http://www.ipmcenters.org/ipmroadmap.pdf.
42. Friedman, S.; Heimlick, R.; Jackson, B.; McLellan, E. *Farming for Clean Water: Innovative Solutions to Reduce Chesapeake Bay Farm Runoff*; Center for Conservation Incentives at Environmental Defense; 2007. http://www.edf.org/page.cfm?tagID=17394.
43. Bianchi, M. L.; Lubell, M.; Mercer, K. L. *Attitudes and Actions Survey*; ANR, University of California, 2007. URL unavailable.
44. Vanclay, F.; Lawrence, G. Farmer Rationality and the Adoption of Environmentally Sound Practices; a Critic of the Assumption of Traditional Extension. *Eur. J. Agric. Educ. Ext.* **1994**, *1* (1), 59–90.
45. O'Connor, K., Executive Director, Central Coast Vineyard Team. About Sustainability in Practice (SIP) certification. Unpublished personal correspondencem February 27, 2011.

46. Canadian Farm Business Management Council (CFBMC). About Farmer Characteristics. *So You Want to be a Farmer*; 1999. http://agmarketing.extension.psu.edu/business/pdfs/sowantfarmr.pdf.
47. Thoms, K. J. *They're Not Just Big Kids: Motivating Adult Learners*. http://frank.mtsu.edu/~itconf/proceed01/22.html.
48. US Environmental Protection Agency. *The Next Generation of Tools and Actions to Restore Water Quality in the Chesapeake Bay. A Draft Report Fulfilling Section 202(a) of Executive Order 13508*; September 9, 2009. http://executiveorder.chesapeakebay.net/file.axd?file=2009%2F9%2F202(a)+Water+Quality+Draft+Report.pdf.
49. Matus, K. J. M. Policy Incentives for a Cleaner Supply Chain: The Case of Green Chemistry. *J. Int. Affairs* **2010**, *64* (1), 121–136.
50. Friedman, S., Regional Director for the Chesapeake Bay at EDF. About On-Farm Networks. Unpublished personal correspondence. December 21, 2009.
51. University of Colorado at Boulder. Conservation Strategies Just Shift with Global Environmental Change, Ecologists Urge. *ScienceDaily*; February 7, 2008. http://www.sciencedaily.com/releases/2008/01/080131101747.htm (Retrieved February 26, 2011).
52. Hanak, E.; et al. *Managing California's Water: from Conflict to Reconciliation*; Public Policy Institute of California, Part II; February 2011. http://www.ppic.org/makin/publication.asp?1+944.

Chapter 21

Food Safety and Surface Water Quality

Karen Lowell[1] and Mary Bianchi[2,*]

[1]L&L Consulting, 334 Maher Rd., Royal Oaks, CA 95076
[2]University of California Cooperative Extension, 2156 Sierra Way Ste C, San Luis Obispo, CA 93401
[*]mlbianchi@ucdavis.edu

On-farm management practices that protect or improve water quality have come into conflict with food safety guidance in California's Central Coast region. Growers report finding themselves forced to choose between meeting their natural resource conservation goals and legal obligations to protect surface water quality, or meeting the food safety guidelines and/or requirements of public and private food safety programs. Research shows water quality management practices reduce sediments, nutrients, and pesticides from agricultural discharges but often fail to meet water quality objectives. Food safety concerns related to wildlife presence, and pathogen persistence in irrigation tailwater and sediments from irrigation and sediment control structures further reduce grower incentives to retain these management practices in the face of market related guidance that suggests they be removed.

Introduction

Management Practices (MPs) to control nonpoint source pollutants have long been implemented for resource conservation and improvement of surface water quality. In the wake of several high profile foodborne illness outbreaks linked to produce sourced from the Central Coast of California, industry leadership and a range of regulatory bodies have increased focus on field operations and development of appropriate Good Agricultural Practices (GAPs) to minimize risk of pathogen contamination. On-farm management practices in many California Central Coast produce growing operations have changed in response to this increased focus on food safety concerns (*1*).

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Growers in the Central Coast of California must balance water quality and food safety mandates within the confines of a wide range of biological, legal, and market forces that impact farm management. The intersection of surface water quality and food safety issues involves a myriad of social, environmental, legal and policy issues. Understanding this nexus is essential in water quality discussions, hence the inclusion of this chapter in a text on surface water quality.

For reasons that will be explained below, water quality MPs and food safety GAPs are often perceived by food safety professionals to be at odds. As a result of increasing pressure to demonstrate field management practices that minimize risk of pathogen contamination of fresh produce, growers in California's Central Coast region report finding themselves in an untenable position – forced to choose between meeting their natural resource conservation goals and legal obligations to protect surface water quality, or meeting the food safety guidelines and/or requirements of public and private food safety programs (*1*).

Co-Managing for Water Quality and Food Safety

As growers manage farming operations they must consider a wide range of biological, legal and market forces that impact their operations. Co-management considers the implications of a management decision in multiple dimensions (*1*, *2*). In the context of food safety discussions, co-management has been defined as an approach to minimize microbiological hazards associated with food production while simultaneously conserving soil, water, air, wildlife and other natural resources (*1*). For example, a water or sediment control basin may allow water conservation and mitigation of discharge water, but food safety inspectors may be concerned about pathogen risk from recycled tailwater and/or the risk of feces from wildlife attracted to a water source. Placement of the basin, use of selective fencing, choice of crops planted closest to the basin and other considerations would all be part of co-management considerations.

The efficacy of many MPs is well documented in the literature, much of it contained in this volume. However, demonstrating the value of a MP in a specific cropping system and location may yield less definitive results; such is the case for many MPs in irrigated mixed vegetable, row crop production operations in the Central Coast of California. When water quality fails to meet target objectives, the value of MPs may be questioned, particularly if there is perceived to be a potential for food safety risk.

Both surface water quality and food safety are of critical importance in public health. Research regarding risks to food safety and how to effectively mitigate them must be considered alongside research documenting benefits of MPs to address water quality concerns. Effectively managing these dual concerns is extremely challenging in produce growing operations in the Central Coast. This challenge stems from the necessity for practitioners to make decisions with information that offers incomplete or inconclusive guidance in a regulatory/business environment that demands decisive action and demonstrated effectiveness.

A lack of management practice implementation by farmers is commonly cited as the cause of continued water quality impairment by nonpoint source pollutants in produce operations in the Central Coast. Regulatory requirements proposed by the Central Coast Regional Water Quality Control Board (*3*) mandate that increased implementation of effective practices result in water quality that meets specific (often numeric) objectives. Both regulatory and industry pressures similarly define management practice guidelines to ensure that produce is free of pathogenic contaminants. In both food safety and water quality objectives, the target objective is elusive, and clear guidance on meeting objectives is difficult to discern from available research results. Statistical significance, biological significance, and progress towards meeting regulatory objectives or guidelines are all potential measuring sticks of management practice effectiveness.

The following examples from recent research illustrate the complexity of using research results to guide management practices for surface water quality:

- *Research results that show measurable reductions which are biologically and statistically significant but do not meet regulatory targets*: A vegetated treatment system combining several existing management practices reduced turbidity from 800-1000 NTU to 20-40 NTU (*4*). Reductions in turbidity were statistically significant. Results were an order of magnitude reduction in turbidity, and the final level approached the point at which lower impacts to juvenile fish would be expected (*5*) indicating biologically significant changes. However, levels still exceeded regulatory targets.
- *Research results that show measurable reductions which may or may not be statistically significant but are not biologically meaningful and do not meet regulatory targets:*

    - Two-fold reductions in chlorpyrifos concentrations (*6*) indicate statistically significant reductions in in-stream concentrations, but will not be meaningful biologically until the concentrations drop below the LC50 (median lethal concentration) for organisms of interest.
    - A vegetated ditch may lower nitrate concentrations from 35 mg/L to 33 mg/L. Though the reduction is measurable, it is not biologically meaningful, nor does it meet current numeric standards of 10 mg/L for drinking water, nor the lower levels recommended for aquatic life protection (*7*, *8*).

Just as water quality standards may be unrealistic given long standing water quality issues and the ability of MPs to mitigate contamination, zero tolerance for pathogen contamination in the production area is virtually unattainable for produce growers. The ability to precisely define and manage contamination risk in the growing environment is extremely challenging given knowledge gaps and incomplete understanding of how contamination episodes occur (*1*).

Implementation of food safety guidelines has generated numerous research projects to evaluate the effectiveness of food safety standards, and additional pressure to demonstrate the effectiveness of MPs addressing water quality. The information presented here is based on fresh produce growing operations in the Central Coast of California and looks at the available research where impacts of MPs on reductions of pesticides and/or nutrients and pathogens are measured. However, increased incidence of foodborne illness associated with consumption of fresh produce (*9*, *10*) and emerging industry and regulatory pressures have led to increased scrutiny in all produce growing regions.

Changing Management Practices

In a 2009 survey of leafy greens growers in the Central Coast of California, growers report being told that wildlife, non-crop vegetation and water bodies pose a risk to food safety (*11*). Many of the pathogens of concern in food safety, including *Escherichia coli* O157:H7 and *Salmonella,* can be found in fecal matter from some wildlife species. Lack of information and understanding of factors that determine actual risk presented by wildlife creates one of the most significant challenges for co-management. For example, in an investigation following the 2006 *E. coli* O157:H7 outbreak linked to spinach sourced from the region, the outbreak strain of the pathogen was found in soil, sediments, surface water, and cattle and wild pig feces near the growing area (*12*, *13*). However, the pathway by which the pathogen entered the supply chain was never conclusively determined (*14*). Many wildlife studies report pathogen prevalence in fecal matter samples from wild animals, but often do not provide detailed information about the population from which samples were collected, nor other information necessary to fully define or manage risk.

In addition to incomplete understanding about which animals may carry pathogens and at what prevalence rates, there is very little information about what animals use the types of farm vegetation and water bodies targeted for removal due to food safety concerns. This additional uncertainty, coupled with a regulatory/business climate that demands zero tolerance of pathogens, compounds the challenge of managing food safety risk factors at the field level. A thorough discussion of the food safety risk posed by wildlife and their habitat is not the focus of the present work. See Lowell *et al.* (*1*) for a review of this issue.

Despite the uncertainties just outlined, grower surveys provide clear evidence that in response to pressure from auditors, inspectors and other food safety professionals some conservation practices are now being removed and/or discontinued. For example, twenty-one percent (21%) of growers surveyed in 2007-2008 reported that they had removed or abandoned conservation practices specifically installed to address water quality issues. Respondents to the 2009 grower survey reported they were told by food safety professionals that plants in ditches or ponds, hedgerows or windbreaks, rangeland, natural lands not grazed and wetland or riparian vegetation all presented food safety risk. These planted areas were perceived to be a food safety threat because they provide harborage for wildlife (*11*).

The food safety professionals that growers refer to in the surveys are guided by a growing body of regulation and industry guidelines. Industry leadership and federal agencies charged with food safety oversight in fresh produce have sought

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

strategies to address heightened concern about field level pathogen contamination of produce. In California and Arizona, the U.S. Department of Agriculture (USDA) based marketing agreements called Leafy Green Marketing Agreements (LGMA) are administered through collaborative agreements between federal and state agencies. Signatories of the LGMA agree to adhere to specific GAPs aimed at reducing food safety risk. Joint efforts by the USDA and Food and Drug Administration (FDA) are underway to craft rules to address preventative controls for pathogen contamination in fresh produce.

The USDA has proposed a National LGMA (*15*) and a new rule by FDA is expected in 2012. The President signed the FDA Food Safety Modernization Act into law January 4, 2011. The new law is intended to strengthen FDA's ability to detect, prevent and respond to food safety problems, including food safety issues related to imported food (*16*).

Numerous private inspection services administered by produce buyers and third party auditing services are also used to evaluate field level management targeting food safety concerns. Food safety guidelines that are publicly available rarely prescribe on-farm management decisions. For example, a private company audit available online (*17*) notes that animal tracks throughout the growing area are grounds for rejection of a crop. The checklist directs the auditor to reject the crop, not to tell the grower what to do to address the concern. Yet growers report that they are often directed by food safety inspectors to reduce the likelihood of wildlife movement near crops by removing habitat that might encourage their presence (*1*, *11*, *18*).

Co-Management: Evaluating Impact of Management Decisions in Multiple Dimensions

Growers find themselves defending MPs that food safety professionals find concerning without clear data to demonstrate effectiveness of the MP. Just as lack of certainty regarding risk presented by wildlife presents co-management challenges, lack of certainty regarding benefits of water quality MPs presents co-management challenges. An evaluation of both the risk and benefit of the MPs targeted in food safety concerns can be organized around two questions: 1) what water quality benefit is demonstrated? 2) what food safety risk can be documented? We also consider what impact a food safety practice, for example use of bare ground buffers, may have on both food safety and water quality. Because cropping systems, soil conditions, historic water quality issues, and management practices selected by growers differ among regions, the following section will focus on literature from the Central Coast region where it is available. We occasionally include consideration of work done outside the region when it has been widely cited in local co-management discussions. The review is not intended to demonstrate an exhaustive summary of the literature, but rather to illustrate co-management challenges using the information that has informed the debate in the region.

Vegetative Treatment Systems (VTS)

Several different USDA Natural Resources Conservation Service (NRCS) conservation practices may fall under the broad category of VTS – including Filter Strip, Grassed Waterway, Vegetated Treatment Area, and Constructed Wetland (*19–22*). A handful of studies have been done to examine the effectiveness of a range of locally adapted VTS implemented in the Central Coast Region. Table 1 summarizes the VTS from 4 studies done in irrigated row crop settings in the region. Additional details are provided below.

Hunt *et al.* (*23*, *24*) measured the effectiveness of two vegetated pond systems in reducing concentrations of both pesticides and nutrients. Both ponds were originally constructed to retain sediment. The first was a two pond system with floating pennywort (*Hydrocotyle ranunculoides*) established to help increase denitrification and microbial populations, and increase sedimentation by decreasing flow through rates. The second was a single pond system vegetated with three aquatic plants: duckweed (*Lemna* sp.), watercress (*Nasturtium* sp.), and pennywort. The VTS system was able to significantly reduce turbidity, nitrates, phosphates and pesticides detected at the outflow compared to the levels found at the inflow of each VTS. In VTS-2, chlorpyrifos concentrations averaged 52% lower at the VTS outlet than at the inlet. Water concentrations of most other pesticides averaged 20-90% lower at VTS outlets.

Anderson *et al.* (*25*) tested a vegetated ditch system consisting of a three part VTS with sedimentation area, vegetated drainage ditch and a Landguard® application reach. Vegetation in the ditch was rushes (*Juncus phaeocephalus* and *J. patens*) and pennywort, and the ditch was seeded with creeping wild rye and red fescue. As the trials progressed, naturally occurring Bermuda grass also grew in the ditch. The system was effective at reducing pesticide concentrations, especially when used in conjunction with Landguard® treatment. While some pesticides (organochlorines and pyrethroids) showed declines after treatment in the sedimentation and vegetated sections of the ditch, diazinon (an organophosphate) was not sufficiently removed during the VTS residence times observed in the study. Landguard® was able to effectively reduce diazinon.

Cahn *et al.* (*26*) did not find reductions of sediment, nutrients and pathogens in vegetated treatment systems under Central Coast irrigated row crop conditions. In their work, runoff from sprinkler irrigation of a row crop in experimental plots was directed to either a bare dirt ditch or a grass lined ditch. The V-shaped ditch constructed for the study was planted to creeping wild rye and red fescue; volunteer grain rye and barley were also present in the final vegetation cover. The vegetated ditch treatment did not consistently reduce the concentration of suspended sediments and nutrients in the run-off from the experimental plots. The authors note that the short residence time in the system is probably the cause of the inefficiency. While turbidity is not the focus of this review, it is noteworthy that addition of 5ppm or less of polyacrylamide (PAM) to the irrigation water resulted in an average 90% reduction in turbidity, and approximately 70% reductions

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

in total N and P in the outflow water. The researchers note that much of the vegetation was above the flowing water and thereby had less impact on flow rate and mitigation of contaminants in the discharge water. The system design and flow rate tested in this research are fairly typical of systems in use in the region. The authors note that the sediment rates in the system were high due to the use of sprinkler irrigation in a highly erodible soil, again conditions common in many productive areas in the region.

Los Huertos and Krone-Davis (*27*) studied four VTS in on-farm studies including two vegetated drainage ditches, a tailwater recover basin and a constructed wetland. VTS 1 was a ditch with established pennywort, watercress, duckweed, and ditchgrass (*Ruppia* spp) and filamentous algae; a flashboard riser was used to regulate residence time in the system. During the study period, a die off of the established vegetation was noted, and at re-growth, preferential flow was observed to allow the water to pass through the system with less effective contact with the vegetation. VTS 2 was a ditch with established pennywort and also employed a flashboard riser to regulate residence time. VTS 3 was a dual, irrigation/tailwater recovery pond with a dense mat of pennywort. VTS 4 was two large, shallow wetlands separated by a culvert. The grower managing VTS 4 attempted to establish a rice crop in the wetland. When this did not succeed the grower planted California tule (*Scirpus* spp). This system also had abundant filamentous algae.

None of the tested VTS in the study reduced nitrate, phosphorus or sediment loads in outflow water. In addition to problems with preferential flow (noted in VTS 1) Los Huertos and Krone-Davis (*27*) note that insufficient residence time and lack of adequate C source for denitrifying bacteria may reduce VTS effectiveness.

In summary, research conducted in irrigated row crops in the Central Coast region suggests that the effectiveness of VTS and vegetated ditches can vary based on site specific characteristics, and the design and maintenance of the practice. They may be highly effective in the circumstances for which they were designed, but are sometimes expected to perform in circumstances for which they were not designed. Under these circumstances, they may not be effective in mitigating the root causes of water quality impairments.

The value of VTS as described above is best demonstrated in systems receiving low volume of water with low levels of pollutants and contaminants. The impact is less evident in typical narrow V-shaped ditches and treatment ponds receiving high volumes of water with high levels of pollutants and contaminants. Supporting practices, appropriate design, residence time, contaminant load, turbidity, and contact with vegetation all influence the effectiveness of VTS. Overall, the research provides a reminder that efficacy of conservation practices varies widely.

In addition to uncertainty regarding the ability of VTS to handle the volume of water and contaminants typically discharged from irrigated row crops, difficulty in maintaining these practices may reduce their effectiveness. Local soils vary in texture and structure, with some being more challenging for establishment of effective VTS than others. Cahn *et al* (*26*) note that the soils in their study area were easily eroded and showed higher sediment levels than are typically reported for irrigation runoff, though they note that this was in part the result of the irrigation method. Author visits to farms in the area illustrate instances where water flows around the vegetation in a VTS, making little contact with it. In such cases, the effectiveness of the system is compromised.

Sediment Retention Systems

Sediment detention basins (also called sediment ponds or settling ponds) hold storm water and tail water, allowing sedimentation before water is discharged, thus preventing sediment from entering nearby water bodies. They may also reduce flooding risk by managing surges in runoff (*28*). Sediment basins are well established management practices in many Central Coast growing environments. Although they do not completely address water quality concerns, they are widely accepted as at least partially effective as a component of a suite of practices to reduce nutrient, sediment and contaminant loads in water. Hunt *et al*. (*23*, *24*) and Anderson *et al.* (*4*) demonstrated that a significant portion of some pesticides are removed with sediments as they settle out.

In addition to water quality objectives, sediment retention systems prevent soil from being transported downstream where it will accumulate in lower gradient channels and waterways. Sediment basins, therefore, play a critical role in reducing flooding frequency by detaining runoff and keeping local drainages open during winter storm events. In the Central Coast, particularly along the Salinas River and its tributaries, flood control has been the subject of much discussion and tension (*29*). If food safety requirements result in the abandonment of sediment basins, then downstream farm flooding will increase unless channel dredging is increased. Because flooded ground has strict wait periods before cropping is allowed (*30*), co-management with these systems may be particularly complicated.

Tailwater Recovery Systems

Tailwater Recovery Systems collect, store, and transport irrigation runoff for reuse in the irrigation system (*31*). Tailwater is a necessary part of surface irrigation systems, particularly furrow systems, to allow sufficient opportunity time for infiltration of irrigation water at the lower end of the field. Tailwater systems allow increased irrigation efficiency, remove standing water that might damage the crop, reduce the potential for environmental impacts from pollutants leaving the farm, and may reduce water costs. These systems can provide benefits in conservation of groundwater, environmental benefits in management of nonpoint source pollutants from both irrigation waters and storm flows and also provide economic benefits to producers (*31*, *32*). One, or sometimes two, ponds are designed to capture runoff from one or more irrigation sets and to capture sediments carried in tailwater. As with VTS, the ability of tailwater ponds to trap sediments and associated pesticides and nutrients is dependent on residence time (*33*, *34*). Tailwater return systems are recommended for furrow irrigation systems in which chemigation has occurred (*35*).

Table 1. Summary of Vegetated Treatment Systems features and effectiveness in mitigating contaminants

	Hunt et al., 2008 *(24)*		***Cahn et al, 2011*** *(26)*	***Anderson et al., 2011*** *(54)*	***Los Huertos and Krone-Davis, 2011*** *(27)*			
	VTS 1	*VTS 2*			*VTS 1*	*VTS 2*	*VTS 3*	*VTS 4*
Production Type	Row crops	Green-houses	Row Crops	row crops	sprinkler/drip irrigated row crops, mixed vegetables	greenhouse/ nursery/cut flower operation	sprinkler irrigated row crops, mixed vegetables	sprinkler/drip irrigated row crops, mixed vegetables
Drainage Area	50 acres	35 acres	not described	120 acres	200 acres tile drainage	20 greenhouses	450 acres	160 acres
VTS Type	pond	pond	vegetated drainage ditch	3 part VTS with sedimentation area, vegetated drainage ditch and a Landguard application reach	vegetated drainage ditch	vegetated drainage ditch	dual, irrigation tailwater recovery ponds	2 large, shallow constructed wetlands separated by culvert
VTS area including perimeter roads	0.15 acres	0.2 acres	52 m long/3 m wide/1 m deep ditch	300 m long/3.25 m width (top)/1.25 m width (bottom)/1 m deep	approx. 305 m long/1.8 m wide	approx 305 m long	not given	both ponds together approx. 0.5 acre
VTS volume (cubic meters)	640	1,350	not described	total of three sections of system 18,000 L	not given	not given	not given	not given
mean flow rate (L/s)	1	6.80	not described	up to 15	not given	not given	not given	not given

Continued on next page.

Table 1. (Continued). Summary of Vegetated Treatment Systems features and effectiveness in mitigating contaminants

	Hunt et al., 2008 (24)		*Cahn et al, 2011* (26)	*Anderson et al., 2011* (54)	*Los Huertos and Krone-Davis, 2011* (27)			
	VTS 1	*VTS 2*			*VTS 1*	*VTS 2*	*VTS 3*	*VTS 4*
Residence time	7.4 days	2.3 days	45 minutes	approximate time to pass through sedimentation and vegetated ditch stages 3.5 to 5 hours	not given	not given	not given	not given
Change after passage through VTS								
Turbidity (NTU)	-0.96	-0.63	none detected	- >90% for sedimentation and vegetated ditch stages of VTS	none detected	not noted	none detected	none detected
Total Nitrate (mg/L)	-0.34	-0.14	none detected	not measured	none detected	-12.3	none detected	none detected
Total Phosphate (mg/L)	-0.86	+ 0.18	none detected	not measured	none detected	+15.4	none detected	none detected
			Vegetation noted to be growing primarily above water, thereby reducing impact on flow rate	No evidence of preferential flow	No evidence of preferential flow initially, then a die off with some preferential flow noted after re-establishment of vegetation			

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

In the Central Coast region, crops are typically irrigated with ground water and occasionally ground water blended with tertiary treated waste water. Sea water intrusion in many coastal growing areas has led to acute pressure to minimize ground water use. Coupled with pumping costs, water shortages provide a strong incentive for growers to use tailwater reuse systems.

Co-Management: Food Safety Risk and Water Quality MPs

Four types of risk may be considered: 1) risk that MPs will increase the likelihood of pathogen-bearing animals in or near the crop area; 2) risk that pathgens will amplify in MPs targeting water quality; 3) pathogen risk in reclaimed sediments from sediment retention basins; and 4) pathogen risk in tailwater.

The first is generally linked to wildlife, and risk presented by their fecal matter. Food safety guidelines (*30*) call for a minimum 5 foot radius no harvest buffer around fecal matter and a 3 foot radius no harvest buffer around evidence of animal incursion into the crop. Some private guidelines, as noted earlier, may lead to rejection of a crop if abundant evidence of animal presence is seen (*1*).

Information about pathogen risk from specific animals, and what animals are more likely to visit a crop area based upon proximity of various landscape features is very scarce (*1*, *36*). Some growers report that removal of vegetation has led to increased presence of birds in the crop areas as they seek irrigation risers for perches. Others report that removal of dense vegetation close to the ground discourages rodents. Anecdotal evidence of this nature is widely shared among those working on food safety issues, but is difficult to quantify or apply across diverse growing environments.

There is not a large body of literature either from the region or beyond regarding the risks of pathogens in VTS, agricultural drainage sediments and tailwater. Survival and/or amplification of pathogens in water and sediments that are returned to cropland is an area of active research. An appropriate water quality standard for foliar contact water has not been conclusively defined (*37*), but generally the recreational water quality standard is used (</= 126 MPN (or CFU)/100 mL (rolling geometric mean n=5) and </= 235 MPN(or CFU)/100 mL for any single sample (*30*).

Both Cahn *et al.* (*26*) and Los Huertos and Krone-Davis (*27*) tested pathogen movement through the VTS described In Table 1. Cahn *et al.* (*26*) placed a suspension of rifampicin resistant *E. coli* mixed with sand in small porous bags positioned in the field from which irrigation run off was received. Bags were removed after the first irrigation event of the study period. They tested for this introduced *E. coli*, total generic *E. coli,* and coliform bacteria. *E. coli* measured in the outflow was not significantly reduced from that at the inflow, with the exception of one instance when less *E. coli* was found in a PAM treatment.

Los Huertos and Krone-Davis (*27*) likewise found no significant decrease in *E. coli* concentration between the inlet and outflow water. However, they did find that the number of exceedences of the LGMA standard for foliar contact water was lower for *E. coli* measured at the outlet than for *E coli* measured at the inlet. In this work, no *E. coli* was introduced, rather total coliform, fecal coliform and

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

generic *E. coli* were measured. Thus, the source of the bacteria was not known in their work.

In wetlands, *E. coli* may be reduced by competition with native microorganisms, predation by other organisms, solar radiation, allelopathogens exuded by plants or non-ideal conditions (e.g. cold). The presence of plants in wetlands has been demonstrated to reduce pathogen survival (*38*, *39*) more effectively than algae (*40*). Diaz *et al.* (*41*) found 66–91% reduction of *E. coli* concentrations and 86–94% reduction of enterococci concentrations in four constructed wetlands in the San Joaquin Valley region of California. The authors report that hydraulic residence time (HRT) of less than a day can achieve approximately 70% reduction of bacteria indicator retention, and suggest that smaller systems may be effective. Knox *et al.* (*42*) studied two systems, one a natural flow through wetland, the other a degraded channelized wetland, both receiving drainage from a flooded/sprinkler irrigated pasture area in the Sierra Foothills region of California. Their work demonstrated that wetlands may become less effective at reducing pathogen movement, as well as nutrient and sediment movement if channels develop that allow water to flow through them more rapidly with less contact with vegetation. Data such as this incentivizes use of these treatment systems for control of pathogens entering waterways, at the same time that food safety may discourage their use.

Sediment Retention Systems

Food safety concerns related to use of sediment retention basins may take several forms. The Central Coast region receives very little rainfall between the months of May through November, the busiest part of the growing season, and many natural water sources dry out. Local wildlife may therefore be attracted to water sources, even non-pristine ones such as sediment basins. For this reason, growers report food safety concerns of sediment retention basins related to the risk of wildlife attracted to the growing environment. Birds are often observed in and near these water sources.

A second concern related to the use of sediment retention basins relates to survival of pathogens in sediments. As with tailwater, growers in the region are cautioned that application of captured sediment to crop land may present a food safety risk (*11*). Justification for this caution is found in a broader body of literature considering pathogen survival in sediments in non-agricultural settings. For example, Czajkowska *et al.* (*43*) examined survival of *E. coli* O157:H7 in bottom sediments from Polish lakes and rivers in a lab experiment. They report survival times of 25-39 days at 6^{o}C or 10-30 days at 24^{o}C. Locally, investigation of the growing environment from which the 2006 spinach outbreak crop was sourced found the outbreak strain of *E. coli* O157:H7 in sediment, as well as water and soil (*13*). Other literature has examined survival of pathogens in soil environments, which is also relevant for risk assessment as sediments removed from the retention basin are typically returned to crop land.

There is a fairly extensive body of literature examining survival of pathogens in soil, though much of it considers pathogens added with soil amendments (e.g.

manure or compost) or irrigation water (*44*, *45*). Local research has demonstrated that generally survival of attenuated *E. coli* O157:H7 in soil is short lived when applied in irrigation water (*46*), a spray (*47*) or when mixed with sand and placed in the growing environment in a small porous satchel (*48*). Koike *et al.* (*48*) also demonstrated however, that survival of pathogens may be greatly influenced by the material with which they are added. In on-farm trials this research found that when spinach plants inoculated by spraying with attenuated *E. coli* O157:H7 were disked in shortly after inoculation, the pathogen was detectable in the soil environment for over 100 days.

As the above illustrates, co-managing for food safety and sediment management in growing operations requires information about pathogen movement, survival, and actual risk. While some information is available to guide risk analysis it is far from complete and thus, again creates challenges for co-management.

Tailwater Recovery Systems

Similarly, management of food safety risks associated tailwater return systems requires information regarding presence of pathogens in irrigation water, potential for pathogen contamination of irrigation flows as they move through the production area, and risks associated with retention ponds or basins and the sediments removed from the basins (*42*, *49*, *50*). Current LGMA guidance does not specify evaluation of risks from tailwater. The FDA Commodity Specific Food Safety Guidelines for the Lettuce and Leafy Greens Supply Chain does include “Things to consider - Evaluating risks of using tailwater”, but does not include information on mitigation of risks (*50*).

Bare Ground Buffers

The above descriptions have focused on the mitigation of sediment, nutrient and pesticide contaminants in agricultural discharge water. Migitation of water quality in surface flow may also be addressed by a variety of practice standards, e.g. grassed road surfaces and Grassed Waterways (*20*). A brief summary of findings related to the water quality benefits of vegetated buffers in a wide range of systems may be found in Appendix J of Lowell *et al.* (*1*). A co-management challenge has emerged for such vegetated buffers zones. In addition to discouraging the presence of non-crop vegetation and water bodies, growers report pressure to maintain bare ground buffers adjacent to crops. Such buffers allow easy detection of animal intrusion, but could actually *increase* food safety risk if surface flow from surrounding areas reaches crops without filtration through a vegetative buffer.

In the Central Coast region, rangeland adjacent to produce growing areas presents a unique food safety challenge as surface flow may carry pathogens from manure into waterways and cropland. This may present direct food safety risk if surface flow carries contaminated water to crops. It may also present an indirect risk if surface water becomes contaminated and thus increases the presence of pathogens in all animals in the landscape who may drink from the contaminated water source.

Research in systems typical of the region has demonstrated that pathogen movement by overland flow from range lands may be reduced when perennial forage and/or grasses act as a barrier to reduce movement of manure and water downslope (*49*). Lewis *et al.* (*51*) report that for every 10m of buffer length, a 24% reduction in fecal coliform bacteria is observed when surface flow from dairy farms and grazing ranches is directed through vegetative buffers or grassed waterways, In rangeland systems, manure deposition is typically spread across a wide area, and water flow is not concentrated. The benefits relate to both mechanical trapping of manure, and increased infiltration of water as it moves across the landscape (*49*).

To the extent that bare ground buffers increase the likelihood of pathogens reaching surface waters, they represent a potential conflict for both food safety and water quality objectives. In this case co-management is not complicated by a lack of information so much as by the desire to maintain a practice to monitor risk (e.g. bare ground allows visible evidence of animal incursion).

Removal of Riparian Vegetation

Riparian vegetation, one of the features targeted for removal for food safety reasons, has numerous roles in the landscape. Robust riparian vegetation is considered essential for protection of surface waters. Vegetation roots stabilize stream banks, may modify water movement (*52*), and act as a filter, trapping sediment and pollutants from upslope sources (*53*). Riparian zones may influence water quality directly by chemical uptake and cycling of nutrients by plants, or indirectly. Indirect influences include supplying chemically active C sources to soils and channels to support heterotrophic bacteria, which may facilitate biological processes to reduce contaminants (e.g. nutrients, pesticides or pathogens) (*54*).

Local research by Anderson *et al.* (*54*) reports a significant correlation between macrophyte cover on stream banks and the species richness and number of mayfly (Ephemerotoptera) taxa in a section of the Salinas River heavily influenced by agricultural drainage. This indicator suggests reduced toxicity impacts from contaminants. As a large percentage of the production ground in the region borders waterways, the potential for adverse impact on riparian vegetation is significant. For example, Hardesty and Kusunose (*55*) surveyed leafy greens growers in Monterey and Fresno Counties and report 72.7% of growers produce on land adjacent to riparian areas. Numerous laws and ordinances are in place to protect riparian habitat in the Central Coast region because of the critical role this vegetation plays in protecting both surface waters and stream banks (see Section B, (*56*)). In addition to its role in water quality protection, riparian vegetation is a critical component of wildlife conservation efforts in the Central Coast region. For a review of this topic see Lowell *et al.* (*1*).

Legal Challenges for Co-Management

Co-management challenges play out in produce fields around the region, but they are also emerging in the court room. Buyers of fresh produce and food safety professionals evaluate the risk of pathogen contamination in the growing environment. Growers are obligated to respond to input from these individuals as failure to do so will lead to lost market for their crop. But growers must also comply with a wide range of laws governing water quality and other protected resources.

Environmental advocacy groups have noted the increased emphasis on food safety and the attending shift from water quality concerns with alarm. A recent challenge has emerged as a non-profit group, the Monterey Coastkeeper, filed suit against Monterey County Water Resources Agency (MCWRA). Coastkeeper alleges MCWRA is polluting the waters of the Central Coast and the United States by failing to regulate agricultural operation discharge waters with pollutants in excess of protective standards, such as pesticides and nitrates (*57*). In addition, the Regional Water Quality Control Board (RWQCB) is engaged in a series of discussions with local growers to address discharge water quality standards through an Agricultural Waiver, which guides grower compliance with water quality objectives. Growers find themselves faced with mounting pressure to respond, but few options that all agree will address water quality concerns in their operations. As noted in the review of field research from the region, Polyacrylamide (PAM) and Landguard®, an enzymatic treatment that helps break down organophosphate pesticides, have emerged as new tools for growers managing water quality in discharge water. However, growers report frustration that these products have not yet been embraced by the Regional Water Quality Control Board (RWQCB) which enforces the Clean Water Act for agricultural discharge water, and so are unsure if they are acceptable as mitigation strategies for discharge water in a Farm Plan. Pressure from food safety inspectors make maintenance of vegetated treatment systems and riparian habitat less appealing while at the same time, regulators and advocacy groups are demanding effective water quality, including robust riparian vegetation.

Growers must consider numerous existing laws at federal, state, and county levels that could come into play as they make food safety management decisions. The major categories in which actions taken to address food safety concerns are likely to lead to conflict with laws and ordinances include the following: water/wetland management; stream bank protection measures; water quality; pesticide use and protection of birds/fish/animals/plants designated endangered, threatened or otherwise protected. Organic growers may be particularly challenged as language in the National Organic Program (NOP) regulation requires that organic growers demonstrate maintenance or improvement of the natural resources of the operation, including soil and water quality, as well as support biodiversity (*58*).

There are several examples of direct conflict as growers co-manage their operations. Growers have cited food safety concerns as the motivation for actions that resulted in violations of California Water Code, as well as violations of the federal Clean Water Act (*56*). The violations have included removal of wetland

and willow vegetation, filling a lake/wetland area, diverting surface flow without a permit, and grading of a streambed and riparian vegetation.

Other compliance tensions focus on wildlife management. For example, in a Central Coast case, a landowner with deer grazing in a lettuce crop requested depredation permits. After granting repeated depredation permits, and removal of 40 deer, the Fish and Wildlife Service advised the land owner to use other management practices (e.g., fencing) to address the problem. The land owner threatened to sue California Department of Fish and Game for failure to authorize depredation permits as this did not allow him to manage food safety risk as he felt he must (*56*). Understanding food safety co-management challenges, including legal tensions, is increasingly critical if adoption of management practices addressing water quality is to be successful among produce growers.

Emerging Priorities Suggest Future Co-Management Complexity

In addition to tensions surrounding water quality management, growers may face regulatory guidance to maintain vegetated practices for other purposes as well, creating additional challenges for food safety co-management. Recent legal decisions have added vegetated practices as a condition for the use of certain pesticides. In July 2002 Washington Toxic Coalition sued the EPA in the U.S. District Court for the Western District of Washington, claiming that EPA had failed to protect federally listed salmonids, and further had failed to adequately consult with National Marine Fisheries Services (NMFS) concerning the effects of pesticides on federally listed salmonids, their habitat and their Critical Habitat. Language requiring or strongly encouraging vegetative buffers has emerged from the NMFS Biological Opinions that resulted from the Washington Toxic Coalition vs. EPA lawsuit, modifying existing pesticide labels (e.g. see buffer requirements on Capture 2EC-CAL EPA Reg. No. 279-3114 and Dimilin 2L EPA Reg. No. 400-461) (*56*). It is reasonable to assume that language, both in pesticide labeling and in guidance for endangered species protection will direct growers to maintain exactly the kinds of non-crop vegetation that growers are reporting pressure to remove in response to food safety concerns.

Riparian habitat management is likely to be another area of increased scrutiny in assessment of the impact of on-farm management for food safety. Waterways in the central portion of the Central Coast region flow into the Monterey Bay National Marine Sanctuary, the largest marine sanctuary in the continental United States and an area of exceptional significance for wildlife and commercial fisheries. Riparian areas provide essential habitat for birds, mammals, fish (including the federally listed as Threatened steelhead trout (*Oncorhynchus mykiss*), and amphibians (including frogs, toads, snakes and salamanders). In addition to the water quality protection services they provide, the unique qualities of riparian zones may make them habitat for a particularly diverse population of wildlife (*59*). Many creeks and rivers within the Central Coast region, including the Salinas River are designated as Critical Habitat for the steelhead, which is federally listed as Threatened (*60*). Riparian vegetation is critical to maintain adequate water quality and habitat features for this endangered species (*61*, *62*). The riparian corridors along Central Coast rivers and streams provide critical habitat connectivity for large and small mammals, southern steelhead and neotropical migratory birds (*63*). As pressure mounts to support conservation mandates, lawsuits like the one filed by the Washington Toxin Coalition have the potential to force tensions among different co-management objectives into conflict.

Summary

Growers of fresh agricultural products must consider a wide range of biological, legal and market forces as they manage their farming operations. While this chapter focuses on fresh produce production in California's Central Coast, recent changes in federal legislation suggest that the co-management of natural resources and food safety is of concern nationally.

Alongside consideration of research regarding the benefits of MPs in addressing water quality must be research regarding the potential risks of these practices to food safety. Just as the information regarding the value of water quality management practices provides imprecise estimate of their value in mitigating water quality concerns, so does the information regarding the food safety risks of these practices present an incomplete and imprecise estimate of the risk they present to food safety. The lack of certainty creates tremendous challenges for the growers who must make management decisions with complex legal, social, regulatory and market forces often incentivizing conflicting actions.

While it is not the scope of the work presented here to fully explore this issue, it is important to note that many of the most pressing challenges to co-management relate to liability and public risk perception of food safety issues. Addressing the impact of these factors on co-management will require more than new regulations and increasing scrutiny of on-farm operations. As increased regulatory action by both government and industry for food safety in the growing environment evolves, it will be essential to deliberately consider the values that guide the weighting of priorities, as both foodborne illness and poor water quality carry public health risks.

References

1. Lowell, K.; Langholz, J.; Stuart, D. Safe and Sustainable: Co-Managing for Food Safety and Ecological Health in California's Central Coast Region. San Francisco, CA. and Washington, D.C: The Nature Conservancy of California and the Georgetown University Produce Safety Project, 2010.
2. Crohn, D.; Bianchi, M. Research Priorities for Coordinating Management of Food Safety and Water Quality. *J. Environ. Qual.* **2008**, *37* (4), 1411–1418.
3. RWQCB. Conditional Waiver of Waste Discharge Requirements for Discharges from Irrigated Lands No. R3-2010-0040, 2011. http://www.waterboards.ca.gov/centralcoast/water_issues/programs/ag_waivers/docs/2010_0040_ag_order.pdf (verified 8 March 2011). California Regional Water Quality Control Board, Central Coast Region.

4. Anderson, B. S.; Phillips, B. M.; Hunt, J. W.; Largay, B.; Shihadeh, R. Pesticide and toxicity reduction using vegetated treatment systems and Landguard OP-A. Data Summary and Final Report. Central Coast Regional Water Quality Control Board, San Luis Obispo, CA, 2008.
5. Thompson, L.; Larsen, R. E. Fish Habitat in Freshwater Streams. ANR Publication 8112, 2004. http://ucanr.org/freepubs/docs/8112.pdf.
6. CMP (Cooperative Monitoring Program). Supplemental Water Quality Monitoring for Organophosphate Pesticides and Aquatic Toxicity. Central Coast Conditional Ag Waiver Cooperative Monitoring Program, 2009. Accessed at http://www.ccamp.org/ccamp/documents/SupplementalOPToxReport_Final052809.pdf.
7. Camargo, J. A.; Alonso, A.; Salamanca, A. Nitrate toxicity to aquatic animals: a review with new data for freshwater invertebrates. *Chemosphere* **2005**, *58*, 1255–1267.
8. RWQCB Central Coast. Interpreting Narrative Objectives for Biostimulatory Substances Using the Technical Approach for Developing California Nutrient Numeric Endpoints. Central Coast Ambient Monitoring Program Technical Report California Central Coast Water Board, April 2, 2009. Accessed at http://www.swrcb.ca.gov/rwqcb3/water_issues/programs/tmdl/303d/appendix_j.pdf.
9. DeWaal, C. S.; Bhuiya, F. Outbreaks by the numbers: fruits and vegetables 1990–2005. International Association for Food Protection Poster Presentation P3-03, July 8–11, 2007, Orlando, Florida. Posted at http://www.cspinet.org/foodsafety/IAFPPoster.pdf (Accessed 15 March 2011).
10. Sivapalasingam, S.; Friedman, C. R.; et al. Fresh produce: A growing cause of outbreaks of foodborne illness in the United States, 1973 through 1997. *J. Food Prot.* **2004**, *67* (10), 2342–2353.
11. Resource Conservation District. Challenges to Co-Management for Food Safety and Environmental Protection: A Grower Survey. Salinas, CA: Resource Conservation District of Monterey County, 2009.
12. Jay, MT.; Cooley, M.; Carychao, D.; Wiscomb, G. W.; Sweitzer, R. A.; Crawford-Miksza, L.; Farrar, J. A.; Lau, D. K.; O'Connell, J.; Millington, A.; Asmundson, R. V.; Atwill, E. R.; Mandrell, R. E. *Escherichia coli* O157:H7 in feral swine near spinach fields and cattle, central California coast. *Emerging Infect. Dis.* **2007**, *13* (12), 1908–1911.
13. Cooley, M.; Carychao, D.; Crawford-Miksza, L.; Jay, M. T.; Myers, C.; Rose, C.; Keys, C.; Farrar, J.; Mandrell, R. Incidence and tracking for Escherichia coli O157:H7 in a major produce production region in California, 2007. Online: http://www.plosone.org/article/info:doi/10.1371/journal.pone.0001159.
14. California Food Emergency Response Team. Investigation of an Escherichia coli O157:H7 Outbreak Associated with Dole Pre-Packaged Spinach (FINAL). San Francisco and Alameda, CA: California Department of Health Services and U.S. Food and Drug Administration, 2007.
15. USDA Agricultural Marketing Service. Marketing Orders and AgreementsProposed National Marketing Agreement Regulating Leafy

Green Vegetables; Recommended Decision and Opportunity to File Written Exceptions to Proposed Marketing Agreement No. 970. Docket Number: AO-FV-09-0138; AMS-FV-09-0029; FV09-970-1, 2011. http://www.ams.usda.gov/AMSv1.0/leafygreensagreement.
16. FDA. Food Safety Modernization Act, 2011. http://www.fda.gov/Food/FoodSafety/fsma/default.htm.
17. MacDonald's Risk Assessment Reguirements. http://diamondproduce.com/grower/blackdog/yuma/risk%20assessment.pdf.
18. Beretti, M.; Stuart, D. Food Safety and Environmental Quality Impose Conflicting Demands on Central Coast Growers. *Calif. Agric.* **2008**, *62* (2), 68–73.
19. USDA-NRCS. Conservation Practice Standard Filter Strip Code. 393, USDA-NRCS field office technical guide, 2006. http://efotg.sc.egov.usda.gov/references/public/CA/393std-8-06.pdf.
20. USDA-NRCS. Conservation Practice Standard Grassed Waterway Code 412, USDA-NRCS field office technical guide, 2010. http://efotg.sc.egov.usda.gov/references/public/CA/412std-06-2010.pdf.
21. USDA-NRCS. Conservation Practice Standard Vegetated Treatment Area Code 635, USDA-NRCS field office technical guide, 2009. http://efotg.sc.egov.usda.gov/references/public/CA/635std-11-09.pdf.
22. USDA-NRCS. Conservation Practice Standard Constructed Wetland Code 656, USDA-NRCS field office technical guide, 2008. http://efotg.sc.egov.usda.gov/references/public/CA/656-std-6-08.pdf.
23. Hunt, J. W.; Anderson, B. S.; Phillips, B. M.; Largay, B.; Watson F.; Harris, K.; Hanson, E.; Beretti, M.; Schafer, R.; Brown, K.; Bern, A. L.. Effectiveness of agricultural management practices in reducing concentrations of pesticides associated with toxicity to aquatic organisms. Data Summary and Final Report. Central Coast Regional Water Quality Control Board, San Luis Obispo, CA, 2007.
24. Hunt, J.; Anderson, B.; Phillips, B.; Tjeerdema, R.; Largay, B.; Beretti, M.; Bern, A. Use of toxicity identification evaluations to determine the pesticide mitigation effectiveness of on-farm vegetated treatment systems. *Environ. Pollut.* **2008**, *156*, 348–358.
25. Anderson, B.; Phillips, B.; Hunt, J.; Largay, B.; Shihadeh, R.; Tjeerdema, R. Pesticide and toxicity reduction using an integrated vegetated treatment system. *Environ. Toxicol. Chem.* **2011**, *30* (5), 1036–1043.
26. Cahn, M. D.; Suslow, T. V.; Sbodio, A. Evaluation of vegetation and polymers to control sediment, nutrients, and bacteria in irrigation run-off from vegetable fields on the central coast of California. Central Coast Agriculture Water Quality ARRA-08-332-550 Draft Final Report 2_24_11, 2011.
27. Los Huertos, M.; Krone-Davis, P. Demonstrating the Compatibility of Water Quality and Food Safety through Research and Implementation. Central Coast Agriculture Water Quality ARRA-08-332-550 Draft Final Report 2_24_11, 2011.

28. NRCS (USDA Natural Resources Conservation Service). Natural Resource Conservation Service Field Office Technical Guide. Conservation Practice Standards, 2008. http://www.nrcs.usda.gov/technical/Standards/nhcp.html.
29. Entrix, Inc. Salinas River Channel Maintenance Program Biological Assessment. Monterey County Water Resources Agency, Salinas, CA, 2009.
30. LGMA. Commodity specific food safety guidelines for the production and harvest of lettuce and leafy greens. August 4 version, 2010. http://www.caleafygreens.ca.gov/sites/default/files/LGMA%20Accepted%20Food%20Safety%20Practices%2008.04.2010_0.pdf (verified 8 March 2011).
31. Schwankl, L. J.; Pritchard, T. L.; Hanson, B. R.. Tailwater Return Systems. ANR Publication 8225, 2007. http://ucanr.org/freepubs/docs/8225.pdf.
32. Bouldin, J. L.; Bickford, N. A.; Stroud, H. B.; Guha, G. S. Tailwater Recovery Systems for Irrigation: Benefit/Cost Analysis and Water Resource Conservation Technique in Northeast Arkansas. *J. Arkansas Acad. Sci.* **2004**, *58*, 23–31.
33. Berg, R. D.; Carter, D. L. Furrow Erosion and Sediment Losses on Irrigated Cropland. *J. Soil Water Conserv.* **1980**, *35*, 267–270.
34. Long, R. F.; Hanson, B. R.; Fulton, A. E.; Weston, D. P. Mitigation techniques reduce sediment in runoff from furrow-irrigated cropland. *Calif. Agric.* **2010**, *64* (3), 135–140.
35. EPA. Management measures for irrigated sources. In Guidance Specifying Management Measures for Sources of Nonpoint Pollution in Coastal Waters, 1993. Accessed at http://www.epa.gov/owow/NPS/MMGI/Chapter2/ch2-2f.html.
36. Atwill, E. R. Implications of Wildlife in E. coli Outbreaks Associated with Leafy AWQA. AWQA Accomplishments 2007-2008. Agriculture Water Quality Alliance (www.awqa.org): Salinas, CA, 2008.
37. Suslow, T. V. Standards for Irrigation and Foliar Contact Water. Washington, DC. The Georgetown University Produce Safety Project, 2010.
38. Brix, H. Do macrophytes play a role in constructed wetlands? *Water Sci. Technol.* **1997**, *35*, 11–17.
39. Vacca, G.; Wand, H.; Nikolausz, M.; Kuxchk, P.; Kastner, M. Effect of plants and filter material on bacterial removal in pilot-scale constructed wetlands. *Water Res.* **2005**, *39* (7), 1361–1373.
40. Garcia, M.; Soto, F.; Gonzalez, J. M.; Becares, E. A comparison of bacterial removal efficiencies in constructed wetlands and algae-based systems. *Ecol. Eng.* **2008**, *32*, 238–243.
41. Diaz, F. J; O'Geen, A. T.; Dahlgren, R. A. Efficacy of constructed wetlands for removal of bacterial contamination from agricultural return flows. *Agric. Water Manage.* **2010**, *97*, 1813–1821.
42. Knox, A. K.; Dahlgren, R. A.; Tate, K. W.; Atwill, E. R. Efficacy of Natural Wetlands to Retain Nutrient, Sediment and Microbial Pollutants. *J. Environ. Qual.* **2008**, *37*, 1837–1846.
43. Czajkowska, D.; Boszczyk-Maleszak, H.; et al. Studies on the survival of enterohemorrhagic and environmental *Escherichia coli* strains in wastewater

and in activated sludges from dairy sewage treatment plants. *Polish J. Microbiol.* **2008**, *57* (2), 165–171.
44. Ibekwe, M.; Watt, P. M.; Shouse, P. J.; Grieve, C. M. Fate of Escherichia coli O157:H7 in irrigation water on soils and plants as validated by culture method and real-time PCR. *Can. J. Microbiol.* **2004**, *50*, 1007–1014.
45. van Overbeek, L. S.; Franz, E.; Semenov, A. V.; de Vos, O. J.; van Bruggen, A. H. C. The effect of the native bacterial community structure on the predictability of E. coli O157:H7 survival in manure-amended soil. *Lett. Appl. Microbiol.* **2010**, *50*, 425–430.
46. Harris, L. J. Survival of attenuated Escherichia coli O157:H7 ATCC 700728 in field inoculated lettuce. Final Report Center For Produce Safety and California Leafy Greens Research Program, 2010. https://cps.ucdavis.edu/amass/documents/researchproject/32/Harris_CPS-CLGRP_FinalReport.pdf (Accessed March 15, 2011).
47. Suslow, T.; Cahn, M.; Smith, R.; Koike, S.. Comparison of surrogate E. coli survival and epidemiology in the phyllosphere of diverse leafy green crops. Final Report Center For Produce Safety and California Leafy Greens Research Program, 2010. https://cps.ucdavis.edu/amass/documents/researchproject/102/Suslow_CPS-finalreport.pdf.
48. Koike, S., Cahn, M.; Smith, R.; Suslow, T. Examination of the survival and internalization of E.coli on spinach under field production environments. Final Report Center For Produce Safety and California Leafy Greens Research Program, 2010. https://cps.ucdavis.edu/amass/documents/researchproject/106/Koike_CPS%202008_Final%20Report_4-1-10.pdf (Accessed March 15, 2011).
49. Tate, K. W.; Atwill, E. R.; Bartolome, J. W.; Nader, G. A. Significant *Escherichia coli* Attenuation by Vegetative Buffers on Annual Grasslands. *J. Environ. Qual.* **2006**, *35*, 795–805.
50. Commodity Specific Food Safety Guidelines for the Lettuce and Leafy Greens Supply Chain, 2008. http://www.fda.gov/downloads/Food/FoodSafety/Product-SpecificInformation/FruitsVegetablesJuices/GuidanceComplianceRegulatoryInformation/UCM169008.pdf.
51. Lewis, D. J.; Atwill, E. R.; Lennox, M. S.; Pereira, M. D. G.; Miller, W. A.; Conrad, P. A.; Tate, K. W. Reducing microbial contamination in storm runoff from high use areas on California coastal dairies. *Water Sci. Technol.* **2009**, *60*, 1731–1743.
52. Dosskey, M. G.; Vidon, P.; Gurwick, N. P.; Allan, C. J.; Duval, T. P.; Lowrance, R. The role of riparian vegetation in protecting and improving chemical water quality in streams. *J. Am. Water Resour. Assoc.* **2010**, *46*, 261–277.
53. Kocher, S. D.; Harris, R. Riparian Vegetation, Forest Stewardship Series, University of California, Department of Agriculture and Natural Resources, Publication No. 8240, 2007.
54. Anderson, B. S.; Hunt, J. W.; Phillips, B. M.; Nicely, P. A.; Gilbert, K. D.; de Vlaming, V.; Connor, V.; Richard, N.; Tjeerdema, R. S. Ecotoxicologic impacts of agriculture drainwater in the Salinas River (California, USA). *Environ. Toxicol. Chem.* **2003**, *22*, 2375–2384.

55. Hardesty, S. D.; Kusunose, Y. Growers' compliance costs for the leafy green marketing agreement and other food safety programs. UC Small Farm Program Research Brief, ANR University of California, 2009. http://www.sfc.ucdavis.edu/docs/leafygreens.pdf.
56. The Nature Conservancy (TNC). Comments for FDA Docket (FDA-2010-N-0085) Submitted by The Nature Conservancy, July 23, 2010. http://www.regulations.gov/#!documentDetail;D=FDA-2010-N-0085-0410.1.
57. Abraham, K. Monterey Coastkeeper sues Water Resources Agency over farming pollution. *Monterey County Weekly*, Oct. 21, 2010.
58. National Organic Standards Board (NOSB). Formal Recommendation of the National Organic Standards Board (NOSB) to the National Organic Program (NOP), Biodiversity Conservation, May 6, 2009. http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5078051&acct=nosb (Retrieved Dec. 15, 2010).
59. Naiman, R. J.; Decamps, H.; Pollock, M. The Role of Riparian Corridors in Maintaining Regional Biodiversity. *Ecological Applications* **1993**, *3* (2), 209–212.
60. National Marine Fisheries Service (NMFS). Designation of critical habitat for 7 salmon and steelhead ESUs in California, 2005. http://swr.nmfs.noaa.gov/chd/Final_CHD_4b2_Report-Aug_05-part_1.pdf.
61. Thompson, L. C.; Voss, J. L.; Larsen, R. E.; Tietje, W. D.; Cooper R. A.; Moyle, P. B.. Role of hardwood in forming habitat for southern California steelhead. Presented at Sixth California Oak Symposium: Today's Challenges, Tomorrow's Opportunities, October 9−12, 2006, Rohnert Park, CA.
62. Rundio, D. E.; Lindley, S. T. Seasonal Patterns of Terrestrial and Aquatic Prey Abundance and Use by Oncorhynchus mykiss in a California Coastal Basin with a Mediterranean Climate. *Trans. Am. Fish. Soc.* **2008**, *137*, 467–480.
63. Penrod, K.; Hunter, R.; Marrifield, M.. Missing Linkages: Restoring Connectivity in the California Landscape, Conference Proceedings. Co-sponsored by California Wilderness Coalition, The Nature Conservancy, U.S. Geological Service, Center for Reproduction of Endangered Species, and California State Parks, 2001.

Editors' Biographies

Kean S. Goh

Kean S. Goh is an Environmental Program Manager of the Surface Water Protection Program at the California Department of Pesticide Regulation and an Associate at the Department of Environmental Toxicology at the University of California, Davis. Dr. Goh directs the statewide surface water monitoring, mitigation studies, analytical methods development and regulatory program to prevent pesticide runoff into surface water. He has published over 35 journal articles and book chapters. He serves as an advisor to graduate students and lectures on the environmental fate of pesticides and the management of arthropod vectors.

Brian L. Bret

Brian L. Bret is a regulatory manager for Dow AgroSciences and is the company's IR-4 Specialty Crops coordinator. Dr. Bret is responsible for obtaining and maintaining state registrations to meet the needs of western growers and urban professionals and for developing and implementing strategic responses to address regulatory issues in the western states.

Thomas L. Potter

Thomas L. Potter is a research chemist at the USDA-Agricultural Research Service Southeast Watershed Research Laboratory. Dr. Potter leads a multi-disciplinary group of scientists in investigations of land management and agronomic practices on fate and transport of pesticides at field, farm and watershed scales. Collectively he has more than 30 years experience as a research scientist, teacher and consultant. His areas of technical expertise include human and ecological risk assessment, elucidation and simulation of pesticide environmental fate and transport, and pesticide residue analysis.

Jay Gan

Jay Gan is a Professor of Environmental Chemistry at University of California, Riverside. Dr. Gan conducts research on environmental fate and transport of pesticides and emerging organic contaminants, with an emphasis on water quality and risk mitigation. Dr. Gan is the author of over 175 journal articles and 20 book chapters. He is also the senior editor of two ACS books.

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Dr. Gan teaches environmental chemistry courses to undergraduate and graduate students. Dr. Gan is a Fellow of American Association for the Advancement of Science (AAAS), American Society of Agronomy (ASA), and Soil Science Society of America (SSSA).

Subject Index

D

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

H

I

J

L

M

N

O

P

R

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

S

T

U

V

W

X

In Pesticide Mitigation Strategies for Surface Water Quality; Goh, K., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.