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UNIVERSITY OF CALIFORNIA
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Constructed Wetlands as a Mitigation Strategy to Reduce
Pesticide Loads in Agricultural Tailwater

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Environmental Sciences

by

Robert Livingston Budd

December 2009

Dissertation Committee:

Dr. Jianying Gan, Chairperson

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The Dissertation of Robert Livingston Budd is approved:

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University of California, Riverside

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The text of this dissertation, in part or in full, is a reprint of the material as it appears in Budd, R., Bondarenko, S., Haver, D., Kabashima, J., and J. Gan, (2007) Occurrence and bioavailability of pyrethroids in a mixed land use watershed. *Journal of Environmental Quality* 36:1006-1012, and Budd, R., O'Geen, A., Goh, K., Bondarenko, S., and J. Gan. (2009) Efficacy of constructed wetlands in pesticide removal from tailwaters in the Central Valley, California. *Environmental Science and Technology* 43(8):2925-2930. The co-author Jay Gan listed in the publications directed and supervised the research that forms the basis for this dissertation. I would like to thank my committee members; Jay for keeping me on track of my research, Dr. Michael Anderson for answering a plethora of questions regarding the conceptual model, and Dr. James Sickman, who gave me the opportunity to try my hand at teaching. I would especially like to thank Dr. Svetlana Bondarenko, who for which I would have been stuck on day one without. I would also like to thank all my lab mates I shared counter space over the years, especially Mae Grace for bearing Azkaban with me, Wesley Hunter, Fred Ernst, Katie, Laura, Greg, and Timmy. I owe my everlasting gratitude to numerous others; my family for unwavering support, Quresh Latif for making graduate school much more bearable, Marka Fenske for beaver talks, Beth Moore for housing me during the multitude of sampling trips, Betsy Dionne for letting me be me, the ultimate frisbee team for all the bruises that I happily paid for, and the staff at Coffee Depot for keeping me awake during the long hours of writing.

I would like to dedicate my entire dissertation to my father, Robert W. Budd, who was a constant source of inspiration and support through all my endeavors, and always told me that “Education is never wasted”.

ABSTRACT OF THE DISSERTATION

Constructed Wetlands as a Mitigation Strategy to Reduce Pesticide Loads in Agricultural Tailwater

by

Robert Livingston Budd

Doctor of Philosophy, Graduate Program in Environmental Sciences
University of California, Riverside, December 2009
Dr. Jianying Gan, Chairperson

Pyrethroid and organophosphate pesticides have been found in numerous waterways throughout the United States. Monitoring studies within the San Diego Creek watershed in Orange County, California, confirmed that runoff from agricultural fields are a primary contributor to pesticide loads within these waterways. As a mitigation option for non-point pesticide pollution, constructed wetlands were investigated in this study to reduce pesticide loading in agricultural tailwaters. Multiple wetlands located along the San Joaquin River in the Stanislaus County were observed over two consecutive irrigation seasons. The wetlands were found to be very effective at reducing pyrethroid concentrations (52 – 100%) and moderately effective at reducing chlorpyrifos concentrations (52 – 61%) under two flow regimes, with loads reduced by 95 – 100% in the outgoing water. Vertical transport of pyrethroids was found to be negligible, and less than 10% of chlorpyrifos was found to leach below 16 cm in the wetland floors. A significant increase in removal efficiencies between seasons within one portion of the

wetland was observed, and was attributed to a dramatic increase in vegetation and decreased flow rates. Pyrethroids overwhelmingly sorbed to suspended solids greater than $0.7 \mu\text{m}$ (62 – 93%), with resulting apparent partitioning coefficients (K_{da}) ranging from 1.9×10^4 to 3.1×10^5 . The freely dissolved concentrations of permethrin represented approximately 26 – 39% of its total mass in water samples with a decreasing trend in concentrations toward the outlet, signaling a decrease in the bioavailable fraction in the outgoing flow. Pesticide concentrations mimicked organic carbon content of the deposited sediment particle fractions. The highest concentrations were associated with larger particles comprised of aggregates of organic and decomposed plant material, which are less susceptible to sedimentation. This observation helps explain why the sediment basin was not effective at removing pesticides from the tailwater. Effective wetland lengths ($L_{1/2}$) necessary to reduce pesticide concentrations by 50% were estimated to be less than 100 m for cyhalothrin, cypermethrin and permethrin under low flow ($0.03 \text{ m}^3 \text{ s}^{-1}$), but reaching 267 m under high flow conditions ($0.07 \text{ m}^3 \text{ s}^{-1}$). The degradation studies indicate that the pesticides have the potential for persisting within the wetland system between irrigation seasons. While the half-lives of λ -cyhalothrin, cypermethrin, esfenvalerate, and permethrin were less than 1 yr ($r^2 > 0.48$) under anaerobic conditions, no detectable dissipation occurred for most pesticides *in situ* during the dry season. Bifenthrin was found to be relatively stable in all sediments, indicating its potential for prolonged persistence within the wetland systems. The results from this study indicate that constructed wetlands may act as a sink for most pyrethroids, and the removal is achieved through sedimentation and sediment trapping by vegetation and gravity.

However, accumulation of pesticides over time, and the associated environmental risks of the accumulated pesticide residues, should be further understood if constructed wetlands are to be widely used as a management practice.

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Chapter 1

General Introduction and Objectives

Pesticides are an important water quality component of agricultural return flow. One or more pesticides have been detected in a majority of waterways surveyed throughout the United States (1). Pyrethroids are a class of general use insecticides that have been detected more frequently in environmental monitoring as regulations have increased usage away from organophosphate pesticides. In California, pyrethroids have been found in 75% of sediment samples of monitored streams within the Central Valley (2). Both pyrethroid and organophosphate chemicals have been shown to elicit toxic effects to sediment invertebrates at environmentally relevant concentrations (3,4).

The Central Valley contains over 7 million acres of irrigated land representing over 25,000 dischargers. During the irrigation season, up to 50% of the flow in the San Joaquin River (SJR) can originate from irrigation return flows. Beneficial uses of the SJR water include municipal and domestic water supply, irrigation, power, fresh water habitat for wildlife, and recreation (CVRWCB, 1998). The SJR appears on California's 303(d) list of impaired waters because it frequently exceeds total maximum daily loads (TMDLs) for the organophosphates chlorpyrifos and diazinon. In addition to these contaminants, the water quality control plan for the SJR recognizes the need to reduce other pesticides such as high levels of pyrethroids that have also been detected in sediments and water column (3,5).

There is a critical need to identify and evaluate best management practices (BMPs) that improve water quality from irrigation return flows. Constructed flow-through wetlands (CWs) have great potential to mitigate non-point source pollutants such as pesticides. Previous work has considered pesticide removal efficiency in various watersheds. The authors of those studies have made correlative inferences to adsorption to organic matter (6, 7), vegetation (6, 8), macrophytes and algae (9), the chemical properties (10, 11), and microbial degradation (12).

This study has several unique aspects not explored in previous studies and will further our understanding of the mechanistic behavior of CWs and their ability to serve as a cost effective mitigation strategy for removing pesticides. This study monitors a large range of pesticides over an extended period of time, which will allow for the analysis of wetland response to variations in hydrological conditions and inflow water quality parameters such as pesticide concentrations and organic matter levels. The use of passive sediment samplers in this study allows for both a temporal and spatial analysis of pesticide deposition. Also, this study will evaluate the partitioning of pesticides under field conditions.

The overall objective of this proposed study is to evaluate the efficacy of constructed wetlands (CWs) to mitigate pesticides in agricultural return flows in the San Joaquin Valley.

The specific objectives of this study were:

1. to determine primary land use contributor of pyrethroid pesticides in mixed land-use watersheds,

2. to determine if constructed wetlands are an effective mitigation strategy for reducing pesticide concentrations in agricultural return flow, and
3. to evaluate the important environmental parameters involved in the fate and transport mechanisms of pesticides within the wetland systems.

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Chapter 2

Background Information

Pesticide Use

Pesticides have been detected in most surface water systems throughout the United States. An intense literature evaluation found that there was one or more pesticides detected in 95% of samples collected from 1,600 streams within the U.S. (1). The California Department of Pesticide Regulation mandates the recording of pesticide usage within California. Figure 2.1 below shows the total registered usage for selected pyrethroid and organophosphate insecticides within California between 2000 – 2007.

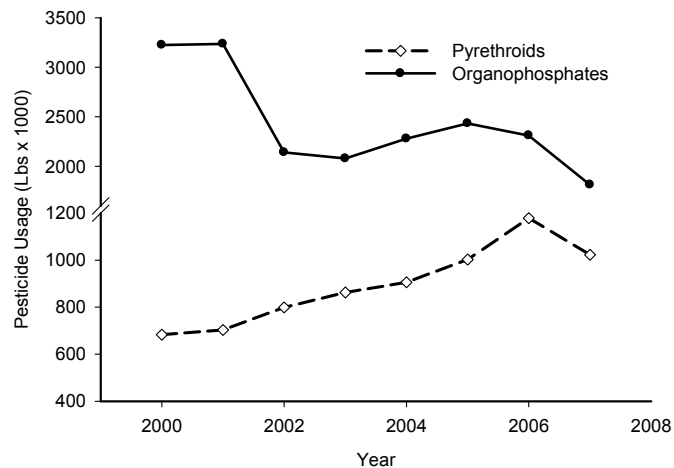


Figure 2.1. Pesticide usage of selected pyrethroid and organophosphates within California between 2000 – 2007.

Although organophosphates make up the lions share of total usage, the use of pyrethroid pesticides is predicted to increase as further restrictions to organophosphate use is mandated. A multiyear survey of pesticide usage in the San Joaquin Valley found a decrease in area treated with organophosphate insecticides with a concurrent increase in area treated with pyrethroids during the same period (2).

The use of insecticides in the Central Valley is significant. Table 2.1 below shows the amount of selected pesticides applied for agricultural purposes in 2004 in Stanislaus County, California. Although diazinon is being phased out of mainstream use, chlorpyrifos remains the most dominant organophosphate insecticide in total usage.

Table 2.1. Pesticide Use (lbs) in Stanislaus County, CA in 2007.

<i>Pyrethroids</i>	
Bifenthrin	9678
Cyfluthrin	145
Cypermethrin	37
Deltamethrin	16
Esfenvalerate	4710
Fenpropathrin	851
λ-Cyhalothrin	2604
Permethrin	6441
	24483
<i>Organophosphates</i>	
Chlorpyrifos	79597
Diazinon	5975
	85573

Pesticides in the Environment

Residue concentrations of pyrethroids in sediments have been detected in watersheds throughout the U.S., especially in California (3). Agricultural fields are a

well documented source of pyrethroids into sediment beds. Weston et al. (2004) detected pyrethroids in 75% of sediment samples collected within the agriculture dominated Central Valley of California (4). Pyrethroid residues have been frequently detected in the sediment from a number of urban streams in northern California (5, 6).

In high density agricultural areas, organophosphate and pyrethroid pesticides are often detected concurrently. Concentrations of both the pyrethroid esfenvalerate and organophosphate diazinon in agricultural storm water runoff draining into the San Joaquin watershed were found to be highly toxic to both fish and invertebrate species (7). The San Joaquin River appears on California's 303(d) list of impaired waters because it frequently exceeds total maximum daily loads (TMDLs) for the organophosphates chlorpyrifos (acute = 0.025 µg/L 1-hr ave., chronic = 0.015 µg/L 4-d ave.) and diazinon (acute = 0.16 µg/L 1-hr ave., chronic = 0.1 µg/L 4-d ave.). A survey study within the San Joaquin watershed found both diazinon and chlorpyrifos present at levels above those set for water quality standards in over 80% of samples analyzed (8).

Potential Fate

The fate and transport of pesticides in the environment is controlled by many variables. Environmental conditions such as temperature, hydraulics and hydrology of the system are the primary external forces that drive the movement of the pesticide. How a chemical interacts with the environmental conditions also depends on its physiochemical properties.

Pyrethroids

Pyrethroids are a class of general use insecticides. Most pyrethroids on the market today are second generation chemically stabilized forms of pyrethrum, the active ingredient derived from the chrysanthemum flower. Table 2.2 below lists some of the physicochemical properties of the pesticides of interest (9). The chemical structures of the chemicals of interest are shown in Figure 2.1. As evident from the water solubility and K_{oc} values, pyrethroids are extremely hydrophobic and tend to bind to organic matter, including DOM (10-12). Photolysis has been shown to be a potential degradation pathway for several pyrethroids including esfenvalerate, deltamethrin, and fenpropathrin (13). In natural systems however, the binding to DOM will limit photolytic degradation. Hydrolytic degradation will most likely be the primary route of abiotic degradation for pyrethroids in wetland systems. For most pyrethroids, hydrolysis occurs by cleavage of the ester bond resulting in carboxylic acid and alcohol byproducts. The rate of hydrolysis generally increases with increasing pH, resulting in more polar products (14). Sediment toxicity or bioavailability is usually estimated from the OC-based sediment concentration, as evidenced in the application of the Equilibrium Partitioning Theory (15). Due to their hydrophobic nature, the toxicity of pyrethroid residues in sediment will likely depend on their phase distribution, and specifically, the freely dissolved concentration in the sediment porewater, which can only be measured using selective sampling methods such as solid phase microextraction (SPME) (16,17).

Table 2.2. Select pesticide physiochemical characteristics.

Pesticide	MW	Solubility (ppm)	K_H	K_{oc} (soil)	$T_{1/2}$ (d) in soil
Bifenthrin	422.9	1.4×10^{-5}	7.2×10^{-3}	237,000	96.3 / 425 [†]
Cyfluthrin	434.3	2.3×10^{-3}	3.7×10^{-6}	124,000	11.5 / 33.6
Cypermethrin	416.3	4.0×10^{-3}	3.4×10^{-7}	310,000	27.6 / 55.0
λ - Cyhalothrin	449.9	5.0×10^{-3}	1.9×10^{-7}	326,000	42.6 / -
Deltamethrin	505.2	2.0×10^{-4}	3.1×10^{-7}	704,000	24.2 / 28.9
Esfenvalerate	419.9	6.0×10^{-3}	1.4×10^{-7}	-	38.6 / 90.4
Fenpropathrin	349.4	1.0×10^{-2}	6.3×10^{-7}	42,500	22.3 / 276
Permethrin	391.3	5.5×10^{-3}	1.4×10^{-6}	277,000	39.5 / 197
Chlorpyrifos	350.6	2	1.2×10^{-5}	5370	
Diazinon	304.4	40	1.1×10^{-7}	191	

[†]Aerobic/Anaerobic conditions

Pyrethroids are neurotoxins that restrict the sodium channel from closing during action potential propagation, thereby causing paralysis of the target organism. Although pyrethroids are fairly non-toxic to mammalian species, aquatic species have been shown to be sensitive to acute poisonings. The OC-normalized LC50 values for the amphipod *Hyalella azteca* have been calculated for λ -cyhalothrin (0.45 $\mu\text{g/g}$ OC), bifenthrin (0.52 $\mu\text{g/g}$ OC), deltamethrin (0.79 $\mu\text{g/g}$ OC), cyfluthrin, (1.08 $\mu\text{g/g}$ OC), esfenvalerate (1.54 $\mu\text{g/g}$ OC) and permethrin (10.83 $\mu\text{g/g}$ OC) (18). Several monitoring studies have attributed observed aquatic toxicity of benthic species to sediment contamination by pyrethroids (6, 8,19).

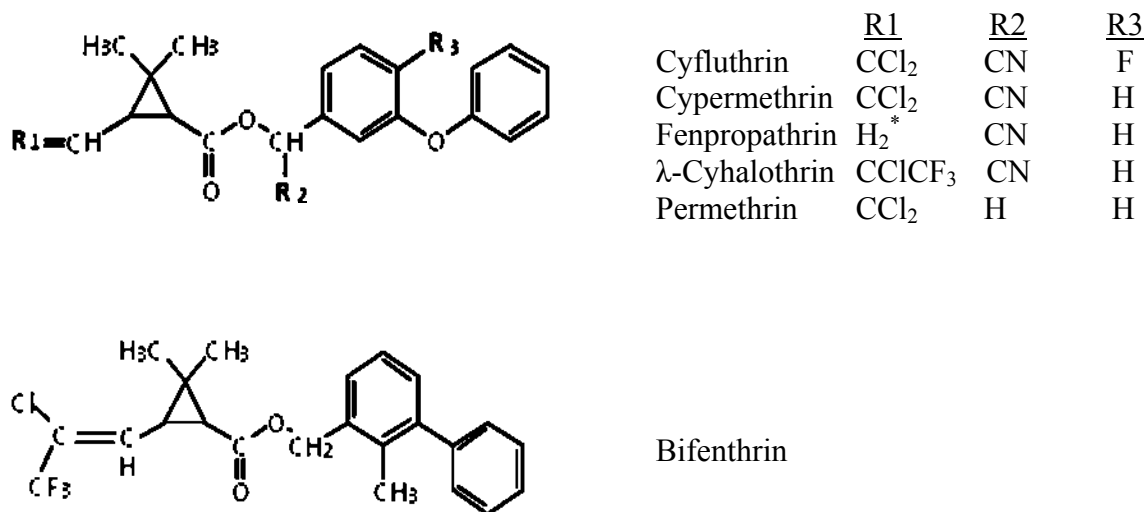


Figure 2.2. Chemical structure of select pyrethroid insecticides.

Organophosphates

Organophosphates are generally more soluble than pyrethroids, and therefore will partition into the aqueous phase more readily. Although organophosphates have a fairly high vapor pressure, organophosphates have been shown to not partition into the air phase to any significant amount in natural systems (20). As with pyrethroids, there is generally a positive correlation between pH and rate of hydrolysis. However, photolytic degradation (both direct and indirect) is much more prevalent for organophosphates in natural water systems (14). Laboratory tests have shown the rates of the various degradation pathways to follow a hierarchy of biodegradation > chemical hydrolysis > photolysis. However, all of the pathway rates are shown to vary dramatically under environmental conditions of various pH, sunlight and DOM to bind, which has led to a

significantly increased persistence of many organophosphates found in the environment (20).

Organophosphates are comprised of two main groups; thionate triesters (P=S) and oxonates (P=O) (8). All organophosphates are acetylcholinesterase inhibitors and are toxic to mammalian species. Although organophosphates were touted as safe because of their relatively short half-lives, their acute toxicity to human and aquatic organisms is a serious environmental concern that has contributed to the restricted use of some organophosphate products (20, 21).

Best Management Practices

Runoff from agricultural fields is a major contributor of water quality contaminants including excess sediments, nutrients and pesticides. Efforts have been made to reduce the stress on downstream aquatic systems by reducing the contaminant loading. Many best management practices, or “BMPs”, have been employed to inhibit transport. Some of the most popular BMPs include edge-of-field buffers, vegetated ditches, and constructed wetlands. Buffers and vegetated ditches have shown promise in their ability to reduce pesticide concentrations in downstream samples (3, 22, 23). Constructed wetlands operate under the same general principles as vegetated ditches, but could theoretically maintain efficacy under high discharge rates and accommodate a much larger drainage area.

Constructed Wetlands

A constructed wetland (CW) may cause the removal of a contaminant via physical (sedimentation and trapping), chemical and biological processes that are favorable for removal. As a result of these processes, it is commonly considered that wetlands have a beneficial effect on water quality (24, 25). Previous studies have demonstrated the ability of CWs to retain both sediment and nutrients (26). Other important factors controlling the water purification capacity of wetlands include rate of contaminant inflows, residence time of water in the wetland, availability of organic matter and other substrates for growth of microbes, and nutrient uptake demand by plants (27, 28). The desired effect is removal from the outgoing stream by increasing the retention time within the wetland and decreasing the $t_{1/2}$ by providing optimum conditions for biotic or abiotic degradation. Physical removal may be a result of adsorption of the contaminant by soil, and elimination of contaminant associated with the suspended sediment due to sedimentation and physical trapping (e.g., vegetation). Most studies have shown a positive correlation between vegetation density and pesticide removal due to increased sorption to macrophytes and organic matter (29) or a reduction in hydraulic conductivity (30). Sorption to plants have been shown to be the primary sink in highly vegetated agricultural ditches (22). Degradation of pesticides in wetland sediments is often enhanced by microbial populations that have been previously exposed (31). The potential of algal blooms to biotransform pesticides has also been noted in wetland systems (32).

A CW may be more chemically reactive, due to the presence of favorable conditions, such as pH and redox conditions, that may lead to enhanced chemical transformation of the contaminant. The redox potential of the system has been shown to have a dramatic affect on persistence and degradation rates of pesticides in wetland soils (33). For example, the persistence of chlorpyrifos in sediments increased significantly under anaerobic conditions ($t_{1/2}$ =125 – 746d) in comparison to aerobic soils ($t_{1/2}$ = 1.8 – 4.9d) (21).

The biotic degradation pathway is dependent on several factors including microbial population, density, contaminant concentration and the bioavailable fraction. The enhanced degradation may be a result of more favorable chemical and microbial conditions that have evolved over the course that the CW has been exposed to runoff. For instance, abundant nutrients may have been imported from the runoff into the CW over time, which can greatly increase the densities as well as diversities of microorganisms in the sediment. It is also likely that repetitive exposure to the same pesticides over time may cause induction and adaptation of sediment microbes so organisms capable of rapidly degrading the pesticides may establish in the CW (34, 35). Although pesticide degrading bacteria populations may become augmented in agricultural runoff waters, the binding of hydrophobic chemicals such as pyrethroids to sediment has been found to hinder microbial degradation (36). The aging of sediment has also been shown to increase sequestration of hydrophobic chemicals into the nanopores and matrices of organic matter, which further decreases accessibility to microbial degradation (37).

Flow-through wetlands are expected to be large sinks for pesticides due to sediment deposition, plant uptake and microbial degradation. Several studies have shown the potential for CWs in the role of removing pesticides from agricultural return flow. The vast majority of previous studies have focused on organophosphate insecticides (29-30, 38-41, 56) and herbicides (32, 42-44). In particular, the retention of chlorpyrifos within constructed wetlands has been well characterized (29,40, 56). A mass balance of a simulated runoff experiment found that 66% of diazinon partitioned to sediment and plant compartments within the constructed wetland (39).

Very little work has been done detailing constructed wetlands potential for removing pyrethroid insecticides from the water column. However, Moore et al. (2009) found that a constructed wetland length of 217 m was necessary to reduce λ -cyhalothrin and cyfluthrin concentrations from a 1% pesticide runoff originating from a 14 ha contributing area (45). Cooper et al. (2003) found that oxbow lakes were totally effective in removing the pyrethroids cyfluthrin and λ -cyhalothrin from the water column (46), and densely vegetated agricultural ditches have been observed to be capable of removing bifenthrin and λ -cyhalothrin (22). In the aforementioned studies, pesticide removal efficiencies were shown to vary between chemical, design, hydrology and vegetation characteristics. Overall, CWs have shown potential to mitigate non-point source pollutants such as pesticides.

Hydrology and Hydraulics

The hydrologic and hydraulic properties of the wetland will have a dramatic effect on the transport of the pesticide through the system (47). Pesticide removal efficiency has been shown to decrease considerably with increasing flow (42). These characteristics control the time frame in which the pesticide will remain in the wetland and be subject to attenuation. The concepts and equations discussed below are a summary of those presented by Persson and Whittgren (2003) (48). The primary driving force of a wetlands capacity to remove contaminants from the water column is the retention time, or how long it takes to move through the system. Retention time (R_t) is calculated by the equation:

$$R_t = \frac{V}{Q} \quad (\text{eq. 2.1})$$

where V = the volume of the wetland (m^3) and Q is the flow rate (m^3/s). The above equation represents the theoretical retention time. Because of shortcutting and interactions with the physical characteristics of the wetland, the theoretical retention time (R_t^{nom}) typically varies dramatically from the true retention time (R_t^{mean}). Figure 2 below illustrates the potential flow regimes for a tracer moving through a wetland. The R_t^{mean} is always smaller than the R_t^{nom} , implying that there is a certain percentage of wetland volume that is not involved in retention processes. Therefore, an important variable to

measure wetland efficiency is the effective volume V_{eff} , which is denoted by the equation: $V_{\text{eff}} = t_{\text{mean}}/t_{\text{nom}}$.

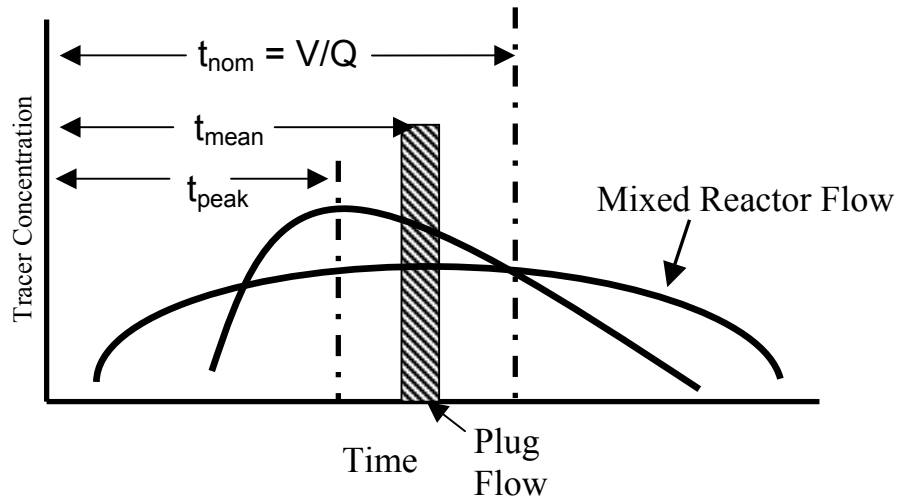


Figure 2.3. Potential movement of a parcel through a wetland.

Figure 2.3 illustrates both plug flow (zero order system) and complete mixing (first order) models of movement. It is generally accepted that in reality movement through a wetland follows a combination of the two models, referred to as the tank-in-series model, with N number of cells of mixing within the system depending on the degree of mixing. The hydraulic efficiency, denoted by $\lambda = t_{\text{peak}} / t_{\text{nom}}$ can be used to compare the relative shortcutting patterns between wetlands.

Storm water runoff is also an important parameter to consider in wetland performance. Contaminant transport and loadings into receiving waterbodies have been shown to be greatest after storm events (3, 8, 49). This would have a double negative

effect, as pesticides would be pushed farther through the system, and the establishment of enhanced microbial populations in the upper layers would be washed away. Total suspended solid has been shown to increase in effluent from CWs during large storm events (50).

Sedimentation

Pyrethroids, and organophosphates to a lesser extent, readily sorb to organic matter and suspended solids in the water column. Therefore the rate of sedimentation is a critical process to evaluate in the efficiency of wetlands to remove pesticides from the water column. Deposition is dependent on hydrologic residence time, wind and wave action, sediment particle size and texture, flocculation of suspended particles and vegetation (51). Sedimentation velocity can be estimated using Stoke's Law in systems with laminar flow (52). Particle size plays an important part not only for determining sedimentation rates, but also the spatial distribution of pesticides. For instance, pyrethroids tend to bind to finer grained particles and dissolved organic matter. Therefore it is possible to detect higher concentrations associated with sediment further downstream, after the larger particles have settled out (53).

Pesticide Adsorption/Desorption

An important physical mechanism for pesticide removal in CWs is adsorption to surface sediment. The adsorption potential is known to depend on the properties of both the contaminant itself and the sediment (most noticeably, OM). The partitioning to the solid phase is influenced not only by the quantity of organic matter, but also the binding

characteristics of the organic matter (54, 55). There is a general trend in increasing sorption with aromaticity of the sorbent. For instance, humic acid has been shown to have a higher binding capacity than fulvic acid (10). In addition, pesticides have been shown to become less available to degradation with longer exposure periods, a concept known as 'aging' of the sediment (37). The K_d of several organophosphates were shown to increase dramatically after only one month of aging (21).

Conceptual Model

Constructed wetlands have the potential for removing pesticides from agricultural tailwater that would otherwise pass directly into the main waterway via irrigation ditches. The slower flow resulting from a wider surface area should enhance sedimentation processes. Also, the dense vegetation should provide sorption sites as well as enhancing trapping of suspended solids. The environmental parameters of the wetlands should provide an ideal environment for pesticide retention, especially those with physiochemical properties that favor sorption such as pyrethroids and some organophosphates.

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Chapter 3

Occurrence and Bioavailability of Pyrethroids in a Mixed Land Use Watershed

ABSTRACT

The shift in land use patterns within many urban areas has the potential to influence the magnitude and nature of non-point source pollution. The presence of pyrethroid insecticides in urban surface streams is of particular concern due to the broad spectrum toxicity of pyrethroids to aquatic organisms and the widespread use of pyrethroid products for agricultural and urban pest control. Sediment samples were collected throughout a mixed land use watershed in southern California during two sampling periods and analyzed for a suite of pyrethroids. Bifenthrin and fenprothrin were found most frequently in the sediment samples, with the highest concentrations associated with sites adjacent to large commercial nurseries. Sediments from residential areas or residential-commercial mixed areas had fewer detections and significantly lower concentrations than the nursery runoff sediments. No apparent difference was found between wet and dry season concentrations, which may be attributed to the fact that the lack of flow under dry weather conditions rendered pyrethroid residues immobile. Organic carbon-normalized sediment concentrations were poorly correlated with the freely dissolved porewater concentrations measured by solid phase microextraction

(SPME), suggesting factors other than sediment organic carbon content should be considered when relating concentrations to potential toxicities.

INTRODUCTION

With the increasing encroachment of urban sprawl, there has been a dramatic shift in land use patterns within many watersheds. For instance, land use designated for agriculture within the San Diego Creek-Newport Bay Watershed in Orange County, California, decreased from 22% to 12% between 1983 and 1993, while residential and commercial areas increased from 48% to 64% during that same period (<http://www.epa.gov/region09/water/tmdl/final.html>). Similar to other regions in the United States, such transitions have significantly accelerated over the last decade. There is a concern that this shift in land use will result in an increase of non-point source pollution; in particular pesticides and nutrients originating from residential pest control and lawn care. In recent studies, residues of pyrethroid insecticides were frequently detected in the sediment from a number of urban streams in northern California (1 – 4). Although chemistry data were unavailable, a sediment toxicity survey also suggested a potential association between the observed toxicity in sediments collected within the Upper Newport Bay in southern California and pyrethroid residues (5).

Pyrethroids are a class of insecticides used for controlling a wide range of pests in both agricultural and urban environments. In Orange County, the total amount of pyrethroids reported by licensed applicators for structural pest control increased from 2,500 lbs. in 1990 to 72,500 lbs. in 2004 (<http://www.cdpr.ca.gov/docs/pur/purmain.htm>). A potentially much more significant, but poorly regulated or recorded, use of pyrethroids is by homeowners, as evidenced by the sale of numerous pyrethroid-containing products

at retail stores and garden centers (4). On the other hand, although traditional agriculture has greatly diminished, hundreds of commercial nurseries ranging from <1 to 200 ha in size are distributed throughout Orange County. These nurseries are sites of concentrated pyrethroid use (6, 7). Therefore, the San Diego Creek-Newport Bay Watershed represents an urban watershed with mixed land uses. To identify sources and successfully implement regulatory measures such as the Total Maximum Daily Load (TMDL) program, it is important to delineate the role of land use types in non-point source pollution.

Temporal variance in sediment pesticide concentrations is influenced by environmental conditions. Contaminant transport and loadings into receiving waterbodies have been shown to be greatest after storm events (8 – 10). Due to the strong affinity of pyrethroids to solid surfaces, large storms may be the most significant contributor to offsite movement of pyrethroids. Further downstream, transport may be a result of movement of finer particles and dissolved organic matter (DOM) (7). However, at present the seasonality of pyrethroid runoff is poorly understood.

Given the strong hydrophobicity of pyrethroids, the toxicity of pyrethroid residues in sediment will likely depend on their phase distribution, and specifically, the freely dissolved concentration in the sediment porewater that can only be measured using selective methods such as solid phase microextraction (SPME) (11, 12). Numerous studies show that the freely dissolved concentration in the sediment porewater is most indicative of bioaccumulation potential or toxicity effects of hydrophobic contaminants. However, monitoring for pyrethroids so far only employed conventional methods based

on exhaustive solvent extraction. The correlation between the measured total chemical concentrations and toxicity was therefore indirect and generalized.

The objectives of this study were to understand relationships of sediment contamination by pyrethroids and land use patterns in a mixed land use setting, to evaluate seasonal effects on pyrethroid occurrence in the sediment, and to examine the potential bioavailability of sediment-associated pyrethroid residues.

MATERIALS AND METHODS

Study Sites

The San Diego Creek Watershed encompasses 112 square miles within Orange County, CA (Figure1). The San Diego Creek provides over 90% drainage to the Upper Newport Bay that serves as a protected marine estuary and a habitat for hundreds of species of birds, fish, mammals and native plants. Many migratory bird species also depend upon the aquatic system during their winter routes.

Sampling sites were chosen based on sediment availability and site accessibility. The sampling sites were grouped into agriculture, commercial-residential mix, and residential based on the surrounding land use (Figure1). Agriculture sites were located adjacent to fields used for a variety of crops, and at stormwater discharge points of large commercial nurseries. Agriculture sites were located in small drainages that connected to the main channels, and flow at these sites was restricted to stormwater runoff.

Residential sites included small tributaries that received runoff primarily from residential areas. These sites were generally located in unlined channels with thicker surrounding

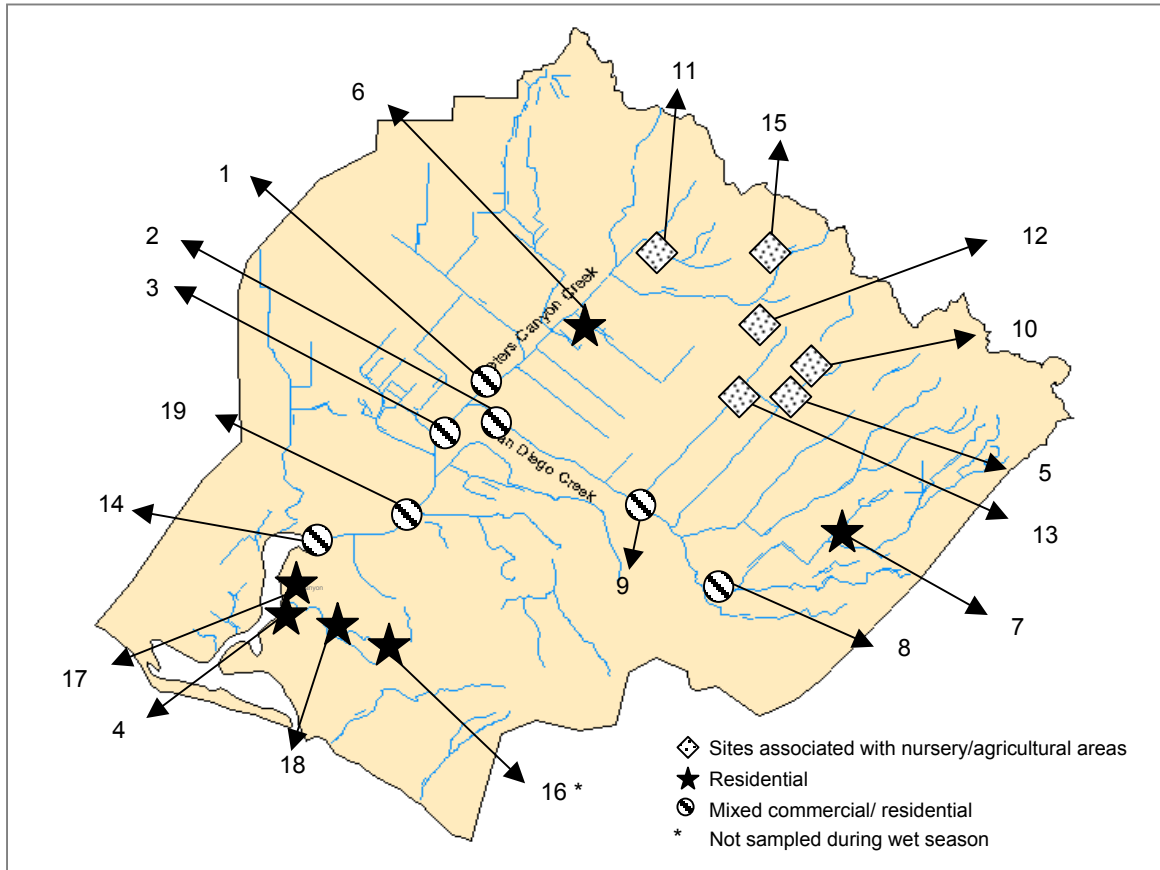


Figure 3.1. Site locations for sediment collection within the San Diego Creek Watershed in Orange County, California.

vegetation and slow moving water. Commercial-residential mix sites were located within the main tributaries of San Diego Creek and Peters Canyon that ran adjacent to areas of high density commercial and residential land use. The commercial-residential mix sites were usually concrete lined channels with several storm water drainage inputs. Stream flow was relatively constant at these sites.

Sediment Sampling

Sediment samples were collected at locations distributed throughout the San Diego Creek-Newport Bay Watershed during each sampling event (Figure 1). The samples were collected during two time periods to capture storm runoff deposits (April-May, 2005) and dry season conditions (August, 2005). Nineteen samples were collected during the dry season and eighteen samples were collected during the wet season at the same sites. Sediment was collected using a hand scoop into a 500-ml glass jar. The top layer of sediment (about 3 cm) was collected to represent the most recent sediment depositions. The sampling at each site was biased toward areas with finer sediments. All samples were transported to the laboratory within 4 h from the time of sampling and were kept at 4 °C in the dark before analysis. Aliquots of the homogenized sediment samples were air dried, sieved through a 1-mm sieve, and analyzed for total organic carbon (TOC) content at the University of California, Division of Agricultural and Natural Resources Analytical Laboratory in Davis, CA using a high-temperature combustion procedure.

Chemicals

Standards of bifenthrin (98.8%), permethrin (97.0%) and cypermethrin (95.1%) were obtained from FMC (Princeton, PA). Cyfluthrin (92%) and deltamethrin (99.4%) were obtained from Bayer CropScience (Stilwell, KS). Esfenvalerate (98%), lambda-cyhalothrin (98.7%), and fenpropathrin (99.7%) were obtained from Chem Service (West Chester, PA), Syngenta (Bracknell, Berks, UK), and Valent (Walnut Creek, CA), respectively. All solvents and other chemicals used in this study were analytical grade or GC grade. Florisil (60-100 mesh) was purchased from Supelco (Bellefonte, PA). All glassware and sodium sulfate were baked at 400 °C for 4 h before use to prevent carryover contamination of pyrethroid residues.

Sediment Analysis

Sediment samples were analyzed using modified EPA methods 3550B, 3620, 3660, 8081 and the method published by You et al. (2004) (14). A 100-g aliquot of sediment was weighed into a 250-ml high density polypropylene centrifuge bottle and centrifuged at 7000 rpm for 25 min. After the overlying water was decanted, a 20-g subsample (wet weight) of the homogenized sediment was weighed into a 250-ml beaker and 100 μl of 500 $\mu\text{g l}^{-1}$ of decachlorobiphenyl solution was added as the surrogate. Anhydrous sodium sulfate (Na_2SO_4) was mixed into the sediment sample to remove excess water, followed by addition of 75 ml acetone-methylene chloride mixture (1:1, v/v). The sediment sample was placed in a Sonic 550 high-intensity ultrasonic processor (Fisher) for 5 min with a 3 s (on) and 1s (off) pulse cycle. The solvent extract was

decanted through a Whatman No. 41 filter paper (Whatman, Maidstone, UK) filled with 2 g of anhydrous Na₂SO₄ into a round bottom flask. The sonication procedure was repeated two additional times with fresh solvents. The sonicator probe was rinsed with acetone in between samples. The solvent extracts were combined and concentrated on a vacuumed rotary evaporator at 35 °C to approximately 5 ml. The sample extract was transferred to a 10-ml tube and was concentrated to dryness under a gentle stream of nitrogen. The sample was reconstituted in 1.0 ml hexane and subjected to the following Florisil clean up procedure.

For sample cleanup, a 32 × 1.2 cm glass column was packed with 10 g of deactivated Florisil and 1 g of anhydrous Na₂SO₄. Before use, the Florisil was precleaned with methanol, methylene chloride, and hexane in a sonication bath, activated by drying at 140°C overnight and deactivated with 6% (by volume) deionized water. The Florisil column was first rinsed with 40 ml of hexane and then the sample was loaded onto the column. The sample was eluted through the column with 50 ml of ethyl ether-hexane mixture (30:70, v/v) into a 250-ml pear-shaped flask, and the eluent was reduced to about 5 ml. To remove sulfur residues in the sample, a small amount (<1.5 g) of activated copper was added into the sample extract and mixed on a vortex for 20 s. Before use, the copper was activated with 20% nitric acid, neutralized with deionized water, washed with acetone and then dried under nitrogen. The sample extract was then passed through anhydrous Na₂SO₄ into a concentrator tube and was further condensed to 0.5 ml under a stream of nitrogen. The final sample was transferred to a 2-ml autosampler vial and reconstituted to 1.0 ml with n-hexane. An aliquot was used for analysis by gas-

chromatography (GC) coupled with an electron capture detector (ECD). The mean method recovery was 109% for bifenthrin, 89% for fenpropathrin, 91% for lambda-cyhalothrin, 111% for *cis*-permethrin, 98% for *trans*-permethrin, 98% for cyfluthrin, 95% for cypermethrin, 99% for esfenvalerate, and 85% for deltamethrin.

Analysis of Freely Dissolved Porewater Concentrations

The solution associated with the wet sediments was physically separated from the sediment phase and operationally defined as “porewater” in this study. The sediments were packed into a cylindrical funnel plugged with glass wool and the solution was collected into in a 20-ml glass centrifuge tube under vacuum. Dry sediment samples were excluded from this analysis. A 2-ml aliquot of the porewater sample was diluted to 20 ml with organic-free deionized water and analyzed for dissolved organic carbon (DOC) on an Apollo 9000 Carbon Analyzer (Teledyne Instruments, Mason, OH). A previously developed SPME method was used to determine the freely dissolved concentration in the sediment porewater (13). Briefly, a 10-ml aliquot of porewater was transferred to a 20-ml glass scintillation vial. A Supelco SPME sampling assembly with polydimethylsiloxane (PDMS, 30 μm)-coated fiber was used for the SPME sampling. The fiber exposure time was 15 min, and the fiber immersion depth was fixed at 2 cm from the surface. During sampling, a small Teflon-coated magnetic bar was used to stir the sample solution at 600 rpm. After sampling, the fiber was directly injected into a 6890 Agilent GC-ECD (Agilent, Palo Alto, CA) and kept in the inlet for 3.0 min to

thermally desorb the enriched pesticides into the capillary column to be eluted under the following conditions.

Analytical Conditions

A 6890 Agilent GC-ECD system coupled with a DB-5MS column (30 m × 0.25 mm × 0.32 μm) was employed for separation and analysis of all pyrethroid compounds. The inlet temperature was 260 °C, and the detector temperature was 320 °C. The column temperature program was as follows: initial temperature 160 °C held for 1 min, ramped to 290 °C at 3 °C min⁻¹, and held 20 minutes at 290 °C. The column flow rate was 1.5 ml min⁻¹ (helium). The sample was injected in a pulsed splitless mode with the pressure set at 25 psi for 0.5 min. The total splitless time was 1.0 min. For compounds with multiple peaks, the sum of all peak areas was used for calibration and quantification. Confirmation of pyrethroids were verified by running the same samples on a DB-1701 column (30 m × 0.25 mm × 0.25 μm) under the same conditions as described above. Calibration standards of pyrethroids for SPME analysis were prepared daily at five different concentrations (0.5, 0.2, 0.04, 0.02, and 0.01 μg l⁻¹) in 100 ml volumetric flasks by consecutive dilution and used for quantifying the freely dissolved concentration in pore water (C_{free}) with a unit of μg l⁻¹. Quality control was evaluated by running duplicate samples for every five samples and a blank for each set of samples. The 3σ standard deviation for the recovery of four sediments spiked with 5 μg kg⁻¹ pyrethroid standards was used as the method detection limit (MDL) for sediments. The respective MDLs were 0.03 μg kg⁻¹ for bifenthrin and cyhalothrin, 0.08 μg kg⁻¹ for permethrin and deltamethrin, 0.09 μg kg⁻¹ for

cyfluthrin, and $0.11 \mu\text{g kg}^{-1}$ for fenpropathrin. The MDLs were estimated at $1\text{-}5 \text{ ng l}^{-1}$ for SPME analysis of porewater samples.

RESULTS AND DISCUSSION

Sediment Concentrations

The total concentration of pyrethroids found in the sediments ranged from <0.02 to $560 \mu\text{g kg}^{-1}$ in the dry season sediments and from <0.02 to $142 \mu\text{g kg}^{-1}$ in the wet season sediments (Tables 3.1 and 3.2). Bifenthrin and fenpropathrin were detected most frequently in both sets of samples, while other pyrethroids were detected less frequently (Figures 3.2 and 3.3). Bifenthrin was detected in 95 to 100% of the samples, with the maximum concentration of $542 \mu\text{g kg}^{-1}$ for the dry season samples and $122 \mu\text{g kg}^{-1}$ for the wet season samples. Fenpropathrin was the second most frequently detected pyrethroid, found in 68% of the dry season samples and 90% of the wet season samples. Concentrations for fenpropathrin ranged from $14.9 \mu\text{g kg}^{-1}$ during the dry season to $19.35 \mu\text{g kg}^{-1}$ during the wet season. All other pyrethroids were detected less frequently and often at lower concentrations, with the highest concentrations at $< 4 \mu\text{g kg}^{-1}$ for cyhalothrin ($2.51 \mu\text{g kg}^{-1}$), permethrin ($3.09 \mu\text{g kg}^{-1}$), cyfluthrin ($2.48 \mu\text{g kg}^{-1}$), and deltamethrin ($1.73 \mu\text{g kg}^{-1}$). Esfenvalerate was detected in one sample at $10.45 \mu\text{g kg}^{-1}$.

Table 3.1. Dry season pyrethroid concentrations ($\mu\text{g kg}^{-1}$) in sediment.

Location	LUT [†]	TOC	Chemical			
			Bifen.	Cyflu.	λ -Cyhal.	Delta.
1	M	2.09	1.66	nd	nd	nd
2	M	0.43	nd	nd	nd	nd
3	M	0.69	0.51	nd	nd	nd
4	R	0.71	0.60	nd	nd	nd
5	A	0.32	0.29	nd	nd	nd
6	R	0.53	8.05	nd	nd	nd
7	R	0.33	0.20	nd	nd	0.01
8	M	0.31	0.16	nd	nd	nd
9	M	0.23	0.03	nd	nd	0.01
10	A	0.17	0.02	nd	nd	nd
11	A	2.27	542.4	nd	2.51	nd
12	A	1.71	249.8	nd	nd	nd
13	A	0.47	36.0	0.81	nd	nd
14	M	0.52	1.64	nd	0.01	nd
15	A	0.26	1.01	nd	nd	nd
16	R	2.65	10.87	nd	nd	nd
17	R	3.72	0.19	nd	nd	nd
18	R	6.84	17.21	nd	nd	nd
19	M	0.33	0.81	nd	0.01	nd
Location			Esfen.	Fenp.	Perm.	
1			nd	nd*	nd	
2			nd	nd	nd	
3			nd	0.42	nd	
4			0.02	0.86	nd	
5			nd	0.16	nd	
6			nd	2.86	nd	
7			nd	0.04	nd	
8			nd	0.10	nd	
9			nd	0.04	nd	
10			nd	0.07	nd	
11			nd	14.9	nd	
12			nd	nd	nd	
13			10.5	3.11	nd	
14			nd	2.52	nd	
15			nd	nd	nd	
16			nd	nd	nd	
17			nd	0.05	nd	
18			nd	nd	nd	
19			nd	0.28	nd	

* nd, not detected, dash, not collected,[†] LUT, land use type; A = agriculture, R = residential, M = mixed commercial/residential, Bifen.=bifenthrin, λ -Cyhal. = λ -cyhalothrin, Cyper.=cypermethrin, Esfen.= esfenvalerate, Perm.=permethrin

Table 3.2. Wet season pyrethroid concentrations ($\mu\text{g kg}^{-1}$) in sediment.

Location	LUT [†]	TOC	Chemical			
			Bifen.	λ -Cyhal.	Cyfluth.	Delta.
1	M	0.55	1.39	0.02	nd	0.05
2	M	0.32	0.88	0.03	nd	nd
3	M	0.32	0.73	0.01	nd	nd
4	R	0.60	0.33	nd	nd	nd
5	A	0.34	0.16	nd	nd	nd
6	R	0.57	3.91	0.09	0.29	0.12
7	R	0.30	1.03	0.01	nd	nd
8	M	0.33	1.61	0.03	0.50	nd
9	M	0.40	0.40	0.01	nd	nd
10	A	2.57	0.18	nd	1.74	nd
11	A	0.58	21.4	0.15	1.14	1.73
12	A	1.90	102.1	nd	2.48	0.05
13	A	1.24	122.4	nd	nd	nd
14	M	0.57	4.37	0.17	nd	nd
15	A	0.52	8.02	nd	nd	nd
16	R	-	-	-	-	-
17	R	0.90	0.54	nd	nd	nd
18	R	3.93	13.03	nd	nd	nd
19	M	0.49	2.58	0.02	0.60	0.53
Location			Esfen.	Fenp.	Perm.	
1			0.13	0.29	nd*	
2			nd	0.37	nd	
3			nd	0.23	nd	
4			nd	0.46	nd	
5			nd	nd	nd	
6			0.06	0.70	0.8	
7			0.02	0.18	nd	
8			0.15	1.01	5.01	
9			0.06	0.18	nd	
10			nd	nd	nd	
11			nd	9.62	nd	
12			nd	1.18	nd	
13			0.58	19.35	nd	
14			nd	5.09	nd	
15			nd	2.51	nd	
16			-	-	-	
17			nd	0.24	nd	
18			0.19	3.07	nd	
19			0.08	7.82	1.06	

* nd, not detected, dash, not collected, [†] LUT, land use type; A = agriculture, R = residential, M = mixed commercial/residential, Bifen. = bifenthrin, λ -Cyhal. = λ -cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin

Permethrin accounted for 88% of the total reported use of pyrethroids in Orange County in 2004 (<http://www.cdpr.ca.gov/docs/pur/purmain.htm>). However, permethrin was not detected in any of the dry season sediments and only 16% of the wet season samples. The total concentration of permethrin (sum of *cis* and *trans*-permethrin) ranged from <0.02 to 5.01 $\mu\text{g kg}^{-1}$. One potential explanation for the discrepancy between the low number of permethrin detections in this study and the high reported usage is the relatively short persistence of permethrin (half-life of 2 to 10 months at 20 °C) compared to pyrethroids such as bifenthrin (half-life of 12 to 16 months at 20 °C) in sediments, as shown in a recent study (7). Therefore, despite the fact that permethrin is used more widely, its relatively short persistence may have prevented it from appearing in downstream sediments.

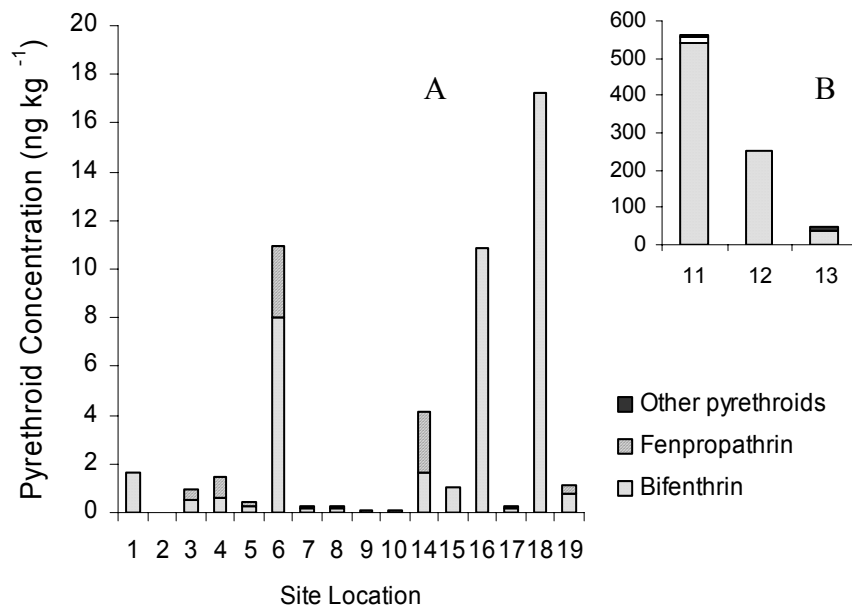


Figure 3.2. Compositions of pyrethroid concentrations ($\mu\text{g kg}^{-1}$) in dry season sediments. A) Study sample sites excluding nursery outlets; B) Nursery outlet sample sites.

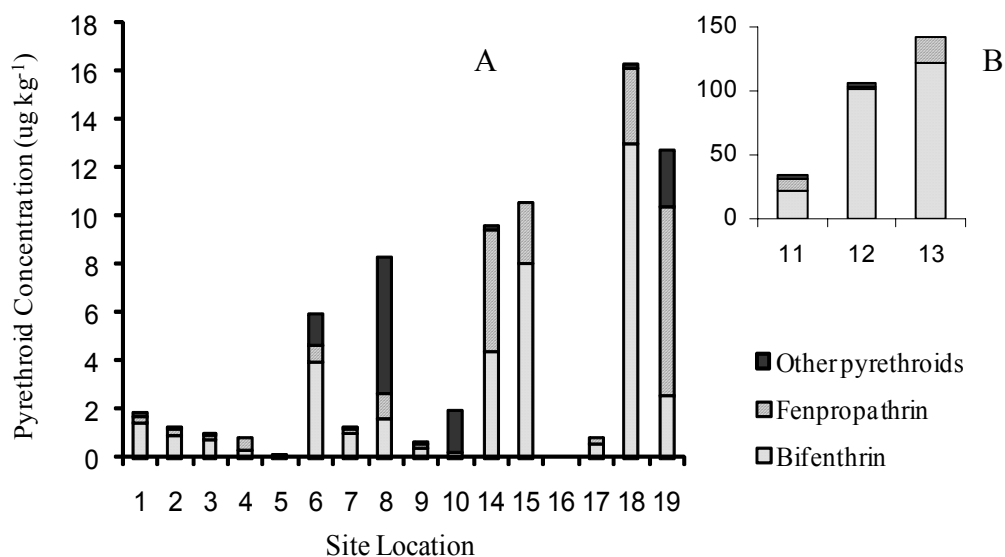


Figure 3.3. Compositions of pyrethroid concentrations ($\mu\text{g kg}^{-1}$) in wet season sediments. A) Study sample sites excluding nursery outlets; B) Nursery outlet sample sites. (Note: Site 16 was not collected during this sampling period).

Effect of Land Use

Land use has been shown to play an important role in contaminant loadings to surrounding waterways. Agriculture fields are a well documented source of pyrethroids into sediment beds. Weston et al. (2004) detected pyrethroids in 75% of sediment samples collected within the agriculture dominated Central Valley of California (2). In the current study, the highest concentrations of pyrethroids within the San Diego Creek-Newport Bay Watershed were detected in areas in close proximity to agricultural land use areas. In particular, those sites located near the outlets of commercial nurseries (sites 11, 12 and 13) contained the highest concentrations of bifenthrin, during both sampling events. Concentrations were also the highest for fenpropathrin ($20 \mu\text{g kg}^{-1}$) and

esfenvalerate ($10 \mu\text{g kg}^{-1}$) at site 13. Lambda-cyhalothrin, cyfluthrin and deltamethrin were detected sporadically near these agricultural sites at concentrations $< 3 \mu\text{g kg}^{-1}$. This observation is in agreement with findings from other studies in which the highest concentrations were found near storm outlets (3). Use of bifenthrin by commercial nurseries in Orange County is mandatory as part of the quarantine requirements for red and imported fire ant control (6). Products of bifenthrin such as the granular formulation Talstar are directly incorporated into potting mixes before seeding or transplanting. In previous studies, high concentrations of bifenthrin and permethrin were found in irrigation-induced runoff water and sediments inside a large nursery (6, 7). However, because many nurseries in this area capture and recycle irrigation runoff (6), the actual export under dry weather conditions should be small. In contrast, storm water runoff is essentially uncontrolled, and storm water runoff from the nursery sites can contribute significantly to loadings of pyrethroids into the San Diego Creek and potentially to the downstream Newport Bay.

Concentrations of pyrethroids were generally lower in the residential areas. The lower observed concentrations surrounding residential areas could be a result of use patterns (i.e., much lower application rates and scattered uses) and environmental conditions. Vegetative ground cover has been shown to be very effective in preventing pyrethroid transport during storm water runoff events (10). The sites surrounding residential areas were generally well vegetated with grasses and shrubs, which could be an important reason why pyrethroid residue concentrations were low at these sites.

Fenprothrin was detected at several sites designated as having primarily

residential inputs. However, fenpropathrin was only registered for agriculture or nursery use in California. Therefore, fenpropathrin detected within the residential areas most likely originated from agricultural/nursery sources through unknown pathways. To explore this finding further, we examined the relationship between bifenthrin and fenpropathrin and found a fairly high correlation between the concentrations of these two compounds ($r = 0.76$). This could be indicative of similar source inputs for these compounds. In 2004, over 3,600 lbs of bifenthrin was used in non-agriculture structural control, while only 300 lbs were registered for agricultural use. If bifenthrin and fenpropathrin indeed had the same source inputs (i.e., agricultural use), this might suggest that residential use was a less important contributor than agricultural use in mixed land use environments. The difference may be due to the diffused use pattern and the specific application methods and surface conditions (e.g., grassed lawns) in residential areas. This observation might also help explain the low number of permethrin detections in this study, despite the fact that 66,400 lbs of permethrin were applied for structural pest control in Orange County in 2004. However, this is fairly speculative in nature and more direct sampling of residential inputs is necessary to draw more concrete conclusions.

Although concentrations in samples located near residential or commercial areas were generally lower than the agricultural outlets, there was evidence for broad pyrethroid usage. Sites 4, 6, 7, 16, 17 and 18 were located in areas for which residential runoff was dominant. Pyrethroids were detected at each of these sites, with concentrations ranging from 0.78 to 16.29 $\mu\text{g kg}^{-1}$ in the wet season sediments, and 0.24 to 17.21 $\mu\text{g kg}^{-1}$ in the dry season sediments. Three of the sites (sites 6, 8 and 19) running

adjacent to residential or mixed land use contained all of the analyzed pyrethroids. While permethrin was not detected in any of the agricultural samples, it was detected from 0.8 to 5.01 $\mu\text{g kg}^{-1}$ at the three sites located within residential areas. This observation could be indicative of the recent shift in land use to the use of more diverse products by homeowners, with permethrin being the most common active ingredient in retail products for residential use (4).

While agricultural and commercial applications of pesticides in California are tracked and reported in California Department of Pesticide Regulation's Pesticide Use Reporting (PUR) databases, homeowner retail sales are excluded, making it difficult to estimate the total pyrethroid usage in residential areas. However, residential usage was attributed as the primary contributor of pyrethroids found in two separate monitoring studies of selected northern California urban streams (4, 15). Although samples near residential and mixed land use areas were detected with lower concentrations than those at agricultural sites in this study, our findings reaffirm the contribution of these land use areas to total pesticide loadings to urban surface waterbodies.

Effect of Seasonality

Pyrethroids adsorb strongly to solid surfaces and have been shown to move with loose sediment particles in runoff (7). Therefore, it was hypothesized that sediments collected immediately after the storm season would have higher concentrations than during the dry season. A quantitative and qualitative analysis was conducted to assess

differences in seasonal sediment concentrations of pyrethroids. The wet season sediments had a more diverse profile of detections than the dry season sediments (Tables 1 and 2). The frequency of sediments with a positive detection was consistently higher for the wet season sediments than the dry season sediments for fenprothrin (89 vs. 68%), cyhalothrin (56 vs. 16%), permethrin (17 vs. 0%), cyfluthrin (33 vs. 5 %), esfenvalerate (44 vs. 11%) and deltamethrin (28 vs. 11%). However, a signed pair test ($\alpha = 0.05$) found that individual and total pyrethroid residue concentrations were not statistically different between the wet season and dry season samples. A possible explanation for similar concentrations in both sampling periods could be due to the regional environmental conditions. The months (January-April) prior to the first sampling round had a cumulative precipitation of 380 mm, with several heavy rainfalls. Most of the agricultural sampling sites received only storm runoff, and were dry throughout the dry season lasting from April through October. Degradation and aerial drift were most likely the only factors that would cause changes in pesticide concentrations between sampling periods at these sites. Higher pyrethroid concentrations found during the dry season at the agriculture sites indicate high persistence of pyrethroids in the sediments, and the increases could be a result of spatial variability in sampling. However, although runoff and downstream transport of pyrethroids from the agricultural sites was likely negligible under dry weather conditions, sediments within these agricultural drainage paths represent temporary storage areas of sediments with high concentrations of pyrethroids that could be transported downstream during subsequent heavy storm events.

Bioavailability of Sediment-borne Pyrethroids

With the exception of bifenthrin, most of the pyrethroids were detected infrequently by the SPME method in this study (Table 3.3). The freely dissolved concentrations measured by SPME (C_{free}) and OC-normalized sediment concentrations for bifenthrin are plotted on logarithmic scales in Figure 3.4. Only those samples with SPME analysis were considered, and $\frac{1}{2}$ MDL was used for the non-detects. The OC-based sediment concentrations of bifenthrin showed poor correlation with the C_{free} values, with $R^2 = 0.25$ for the linear regression for all samples (Figure 4).

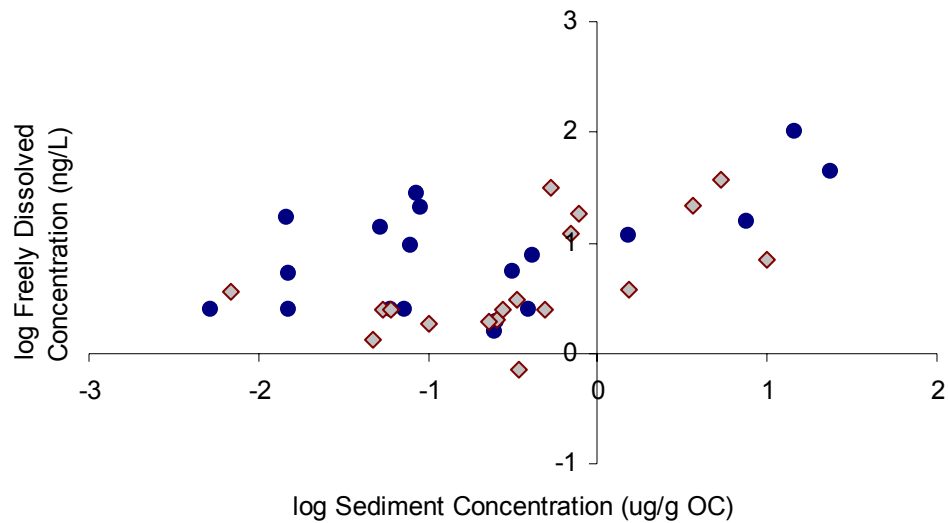


Figure 3.4. Bifenthrin organic carbon-normalized sediment concentration ($\mu\text{g kg}^{-1}$) versus the freely dissolved porewater concentration (C_{free} , ng l^{-1}) measured by solid phase microextraction (SPME) for dry and wet season sediments.

Table 3.3. Freely dissolved porewater concentrations detected by solid-phase microextraction (C_{free} , ng l^{-1}) and organic carbon-normalized sediment concentrations ($\mu\text{g g}^{-1}$) of bifenthrin in selected sediments.

Season	Sample Site	DOC*	C_{free}	TOC (%)*	OC Normalized
Dry	1	240.6	9.5	2.09	0.08
	2	19.9	5.3	0.43	nd
	3	27.2	nd [†]	0.69	0.07
	4	12.7	27.7	0.71	0.09
	5	- [§]	-	0.32	0.09
	6	9.2	11.6	0.53	1.52
	7	9.2	nd	0.33	0.06
	8	7.7	13.5	0.31	0.05
	9	6.0	nd	0.23	0.01
	10	-	-	0.17	0.01
	11	-	-	2.27	23.89
	12	-	-	1.71	14.61
	13	-	15.7	0.47	7.66
	14	15.7	5.4	0.52	0.32
	15	-	-	0.26	0.39
	16	34.1	7.7	2.65	0.41
	17	-	-	3.72	0.01
	18	15.0	1.9	6.84	0.25
	19	4.2	1.5	0.33	0.25
Wet	1	97.2	2.0	0.55	0.25
	2	27.1	nd	0.32	0.28
	3	30.7	1.9	0.32	0.23
	4	15.2	nd	0.60	0.05
	5	16.5	1.3	0.34	0.05
	6	76.0	12.0	0.57	0.69
	7	22.3	0.7	0.30	0.34
	8	28.4	nd	0.33	0.49
	9	67.8	1.9	0.40	0.10
	10	30.0	3.6	2.57	0.01
	11	23.6	21.9	0.58	3.68
	12	-	-	1.90	5.37
	13	-	-	1.24	9.87
	14	24.1	18.4	0.57	0.77
	15	19.9	3.8	0.52	1.54
	16	nc [‡]	nc	nc	nc
	17	24.5	nd	0.90	0.06
	18	13.5	3.0	3.93	0.33
	19	10.1	31.2	0.49	0.53

* DOC, dissolved organic carbon in porewater (mg l^{-1}); [†] nd, not detected; [‡] nc, sample not collected; [§] -, not enough porewater available for analysis.

Sediment toxicity or bioavailability is usually estimated from the OC-based sediment concentration, as evidenced in the application of the Equilibrium Partitioning Theory (16). Organic carbon-based sediment concentrations were recently used to calculate toxicity units of pyrethroids, from which the sediment toxicity was further predicted (3, 15). However, while the OC-based sediment concentration considers the importance of sediment OC, it does not account for the qualitative differences in the sediment organic matter from different sources. In contrast, novel sampling methods such as SPME have been shown to selectively detect the bioavailable concentration of hydrophobic compounds in sediments and soils (11- 12, 17 – 19). The poor relationship between OC-based sediment concentrations and C_{free} in this study suggests that not only the quantity, but also the quality or characteristics of sediment organic matter, among other factors, affect the phase distribution and thus the potential toxicity of pyrethroids in sediment (20 – 23). Therefore, selective methods such as SPME should be used over the whole sediment analysis when monitoring for pyrethroids.

CONCLUSIONS

Pyrethroids were detected at various concentrations and frequencies in bed sediments within the San Diego Creek-Newport Bay Watershed in southern California. Bifenthrin and fenprothrin were among the most frequently detected pyrethroids in sediments taken following the wet season and during the dry season. While agriculture land use was determined to have the greatest potential to contribute high concentrations

of pyrethroids in the runoff sediments, residential land use was noted to be a potential source for diffused loadings. The distribution patterns of pyrethroid residues were similar between the wet and dry seasons, suggesting that the lack of flow in the dry season rendered pyrethroid residues immobile in the watershed. Poor correlation was found between OC-based sediment concentrations and the freely dissolved porewater concentrations measured by SPME, implying that other factors, such as characteristics of sediment organic matter and aging, may significantly influence the bioavailability of sediment-borne pyrethroids. Selective sampling methods such as SPME are therefore more appropriate for predicting sediment toxicity from pyrethroid contamination. Further studies are needed to understand homeowners' use of pyrethroid products, persistence and offsite transport behaviors of pyrethroids in residential landscapes, and conditions that are conducive to movement of pyrethroids during surface runoff.

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Chapter 4

Efficacy of Constructed Wetlands in Pesticide Removal From Tailwaters in the Central Valley, California

ABSTRACT

Pollutants in agricultural irrigation return flow (tailwater) constitute a significant non-point source of pollution in intensive agricultural regions such as the Central Valley of California. Constructed wetlands (CWs) represent a feasible mitigation option to remove pollutants including pesticides in the tailwater. In this study, we evaluated two CWs in the Central Valley for their performance in removing pyrethroid and organophosphate insecticides under field-scale production conditions. Both CWs were found to be highly effective in reducing pyrethroid concentrations in the tailwater, with season-average concentration reductions ranging from 52 to 94%. The wetlands also reduced the flow volume by 68-87%, through percolation and evapotranspiration. When both concentration and volume reductions were considered, the season-average removal of pyrethroids ranged from 95 to 100%. The primary mechanism for pyrethroid removal was through sedimentation of pesticide-laden particles, which was influenced by hydraulic residence time and vegetation density. Temporal analysis indicates a potential efficiency threshold during high flow periods. The season-average removal of chlorpyrifos ranged 52-61%. The wetlands, however, were less effective at removing

diazinon, likely due to its limited sorption to sediment particles. Analysis of pesticide partitioning showed that pyrethroids were enriched on suspended particles in the tailwater. Monitoring of pesticide association with suspended solids and bed sediments suggested an increased affinity of pyrethroids for lighter particles with the potential to move further downstream before subject to sedimentation. Results from this study show that flow-through CWs, when properly designed, are an effective practice for mitigating hydrophobic pesticides in the irrigation tailwater.

INTRODUCTION

Pesticides have been detected in most surface water systems throughout the United States (1). The occurrence of insecticides such as organophosphates and pyrethroids is of particular importance due to their broad-spectrum aquatic toxicities (2, 3). Non-point sources including discharges from agricultural irrigation runoff have been identified as the most important contributor to pesticide contamination in surface waterways (4, 5).

The Central Valley contributes greatly to the production of many crops in the United States, while tailwater discharges from this region are a source of pollution for sensitive ecosystems including the San Francisco Bay Estuary. The region contains over 2.8 million hectares of irrigated land representing over 25,000 individual dischargers. During the irrigation season, almost all of the flow in certain stretches of the San Joaquin River (SJR), a main drainage channel to the San Francisco Bay, can originate from irrigation return flows (6). The extensive use of insecticides with concurring irrigation has clearly contributed to the ubiquitous occurrence of insecticides in the local waterways. For instance, pyrethroids were detected in 75% of the sediment samples collected from various surface water bodies throughout the Central Valley (5). A survey study within the San Joaquin watershed showed the presence of organophosphates at levels frequently above water quality standards (7). Additional studies further related toxicities to the occurrence of both classes of insecticides in the waterways (8-9).

Therefore, there is a critical need for management practices that may be used to improve water quality from irrigation tailwaters in this region.

The conversion of marginal agricultural land into constructed or restored wetlands is a growing land use practice throughout the Central Valley, especially along riparian corridors. Many constructed wetlands (CWs) in the Central Valley receive agricultural tailwater as the primary water supply during the growing season. This practice is promoted to enhance wildlife habitat in agricultural regions, but may also provide added ecosystem benefits through the wetlands' ability to filter polluted water originally destined for surface water bodies.

Given the vastness of the source area and the diffuse nature of contaminant loading, CWs represent a feasible and economical mitigation option for this region. A CW may cause the removal of a contaminant in runoff effluent via physical, chemical, and biological processes (10, 11). Several studies have shown the potential for CWs to remove pesticides from agricultural runoff (12-15). However, most studies have focused on organochlorine and organophosphate insecticides, rather than pyrethroids that are currently widely used and comprehensive studies under well characterized field conditions are rare. Cooper et al. (17) found that oxbow lakes were effective in removing the pyrethroids cyfluthrin and λ -cyhalothrin from the water column, while densely vegetated agricultural ditches were observed to be capable of removing bifenthrin and λ -cyhalothrin (16, 17). In another study, permethrin concentrations were reduced by 50% within 22 m of a vegetated agricultural ditch under simulated conditions (18). These and other studies show that the rate of inflow, water residence time in the wetland, and

availability of organic matter to bind contaminants are the most important factors affecting the water purification capacity of wetlands (19, 20).

The primary objective of this study was to evaluate the efficacy of flow-through CWs for mitigating prevalent insecticides, especially pyrethroids, in agricultural tailwater in California's Central Valley region, and to identify the most influential factors in the removal process.

MATERIALS AND METHODS

The Study Area

The CWs were located within Stanislaus County, California. Figure 1 is a schematic of CW1 and CW2 used in this study. The estimated surface areas of CW1 and CW2 were 2.3 and 2.5 ha, respectively, and received irrigation return flows from approximately 450 ha of irrigated agricultural land. The inlet into the wetlands was via an agricultural tailwater ditch, and therefore only received inflow during the irrigation season. Water from the tailwater ditch was diverted into a sediment settling basin before entering the CWs. CW1 consisted of two distinct segments. The first segment of CW1 had a shallow dendritic flow path that was dispersed into thick vegetation. The second segment was a wider, deeper stretch with slower moving water. Using Google Earth, the estimated flow path length of CW1 was 450 m. CW2 was densely vegetated during the study period and had consistent shallow depths (< 1 m). CW2 had a total length of flow path of 720 m. In both wetlands, vegetation biomass was observed to increase

dramatically through the irrigation season lasting typically from around May to September, with algal mats noted to proliferate toward the end of the irrigation season. The dominant species within the wetlands were knotgrass (*Paspalum distichum*), pale smartweed (*Polygonum lapathifolium*), and barnyardgrass (*Echinochloa crus-galli*). Water passing through both CWs flowed back into the tailwater ditch that discharged into SJR, making the two wetlands a semi-closed system and allowing for calculation of contaminant inputs and outputs. Water quality parameters were measured from weekly grab samples collected at input, middle, and output locations (Table 4.1).

Flow into each CW passed over adjustable weir boards, the height of which was controlled manually by a wetland manager. Water flow rates were calculated from pressure heads monitored 1-m upstream of the rectangular weirs at inlets and outlets of the wetlands using self logging pressure transducers.

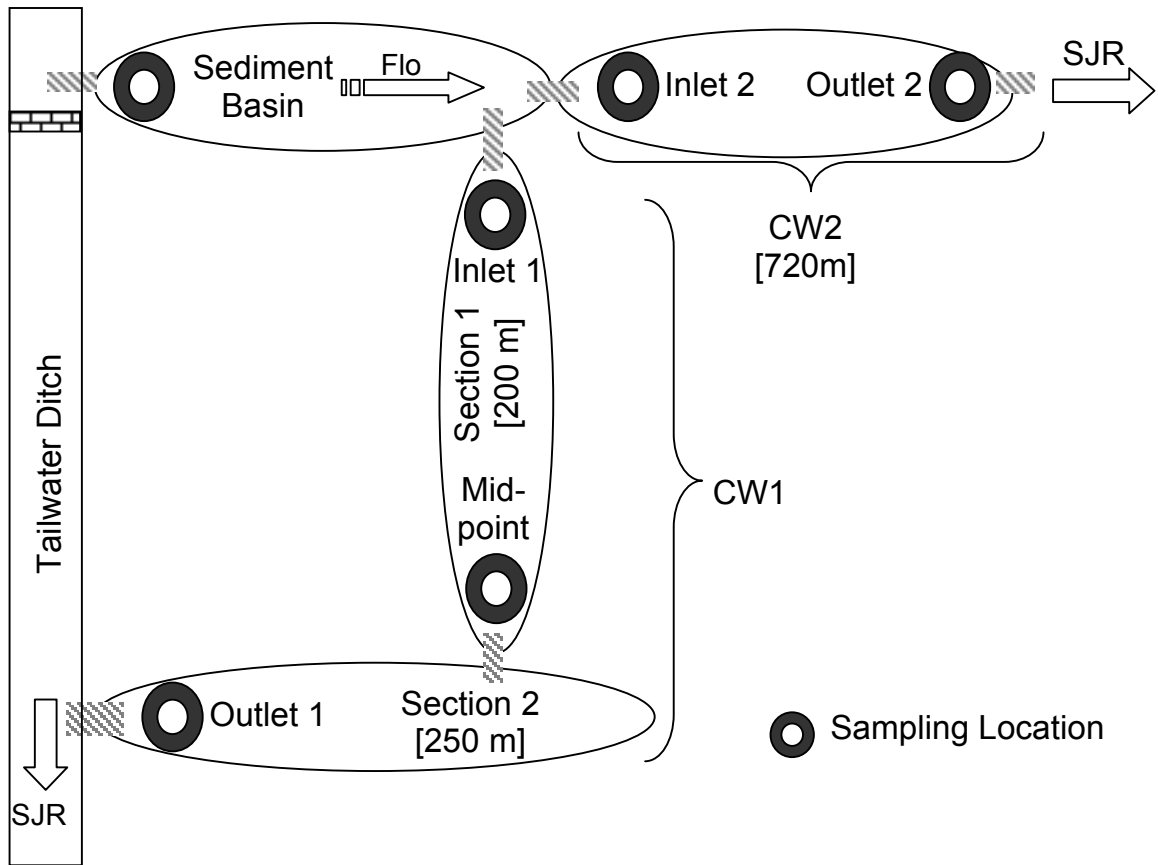


Figure 4.1. Schematics of the two flow-through constructed wetlands adjacent to the San Joaquin River (“SJR”) showing sampling locations.

Field Sample Collection

Two 1-L water samples were collected biweekly using 1-L amber glass bottles for the duration of the irrigation season (May 9 through August 20, 2007). Samples were collected at the inlet of the sediment basin, the inlets of CWs 1 and 2, the midpoint of CW1, and the outlets of both CWs (Figure 1). The bottle was rinsed with stream water before sample collection and was immersed in the opposite direction of the flow to

collect the water. Water samples were placed on ice during transport and stored at 4 °C until analysis, which was within 2 d of collection.

Sediment samples were collected into 1-L wide-mouth glass jars using a sediment trap configuration. The jars were placed upright in a 10-cm diameter PVC tubing that was embedded in the sediment floor to serve as a protective barrier. An advantage of using a passive collection method over grab sampling is that the time during which the sediment accumulated was clearly known, i.e., from the trap installment to trap removal. Sediment samples were collected on 5 dates (Jun 6 through Aug 20, 2007) throughout the irrigation season.

Chemicals

Standards of bifenthrin (2-Methyl-3-phenylphenyl)methyl (1*S*,3*S*)-3-[(*Z*)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate) (98.8%), permethrin (3-Phenoxybenzyl (1*RS*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate) (97.0%), and cypermethrin (Cyano(3-phenoxyphenyl)methyl (+/-)-*cis*/*trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate) (95.1%) were obtained from FMC (Princeton, PA). Deltamethrin ([cyano-(3-phenoxyphenyl)-methyl] 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropane-1-carboxylate) (99.4%) was obtained from Bayer CropScience (Stilwell, KS). Esfenvalerate ((*RS*)-*alpha*-Cyano-3-phenoxybenzyl (*RS*)-2-(4-chlorophenyl)-3-methylbutyrate) (98%), λ -cyhalothrin (3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-cyano(3-phenoxyphenyl)methyl cyclopropanecarboxylate) (98.7%), and

fenpropathrin (alpha-Cyano-3-phenoxybenzyl-2,2,3,3-tetramethyl cyclopropanecarboxylate) (99.7%) were obtained from Chem Service (West Chester, PA), Syngenta (Bracknell, Berks, UK), and Valent (Walnut Creek, CA), respectively. An organophosphate mixture containing chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) and diazinon (Diethoxy-[(2-isopropyl-6-methyl-4-pyrimidinyl)oxy]-thioxophosphorane) was purchased from Chem Service (West Chester, PA). Surrogate mixture 8080 (2000 $\mu\text{g mL}^{-1}$) containing decachlorobiphenyl was also obtained from Chem Service. Florisil (60-100 mesh) was purchased from Supelco (Bellefonte, PA). Before use, Florisil was pre-cleaned with methanol, methylene chloride, and hexane in a sonication bath, activated by drying at 140 °C overnight and deactivated with 6% deionized water (by volume). Laboratory grade copper powder was purchased from Fisher Scientific (West Chester, PA), and was activated by washing with 10% nitric acid, neutralizing with deionized water, washing with acetone, and then drying under nitrogen. All glassware and sodium sulfate were baked at 400 °C for 4 h before use to remove water and to prevent carryover contamination of pyrethroid residues.

Hydraulics Evaluation

Two tracer studies were conducted to estimate the residence time of the wetland systems. Potassium bromide slugs were injected at the inlets of CW1 (35 kg) and CW2 (50 kg). Samples were collected at the respective outlets and measured for bromide concentrations by ion chromatography (Dionex, Sunnyvale, CA). The hydraulic

residence time was estimated by the time for which half of the bromide mass was recovered at the outlet monitoring site.

Analysis of Water and Sediment Samples

Whole water samples were analyzed using modified EPA method 3510 for liquid-liquid extraction (1). Analysis by this method resulted in the total pesticide concentration, which included the fraction adsorbed to suspended particles and dissolved organic matter (DOM). Briefly, water samples were extracted three consecutive times with methylene chloride (50 mL each time) in a 2-L glass separatory funnel. The extract was passed through 40 g anhydrous sodium sulfate, concentrated to dryness, and reconstituted in 1 mL hexane. The extract was further cleaned by loading onto a 1.0-g Florisil cartridge (PrepSep SPE, Fisher Scientific) and eluting with 9 mL acetone/hexane (10:90 v/v). The samples were concentrated to approximately 0.5 mL under nitrogen and reconstituted to a final volume of 1.0 mL in hexane for analysis. An aliquot of the water sample was taken for measurement of dissolved organic carbon (DOC), total organic carbon (TOC) and total suspended solid (TSS). The DOC was determined from the filtrate passed through a 0.45 μm glass filter. The DOC and TOC analyses were carried out on an Apollo 9000 Carbon Analyzer (Teledyne Instruments, Mason, OH). The TSS level was measured using modified EPA method 160.2 (2, 3).

Pesticide concentrations in sediment samples were analyzed using modified EPA method 3550 for extraction, method 3620 for Florisil cleanup, and method 3660B for removing sulfur interference (1). Briefly, 5 g of wet sediment was mixed with enough

sodium sulfate to achieve dryness and placed into 250 mL beakers. The sediments were extracted with 50 mL of acetone/methylene chloride (1:1 v/v) solution using a model 550 Sonic Dismembrator (Fisher Scientific). Each sample was sonicated three times with 50 mL of fresh acetone/methylene chloride (1:1 v/v) solution on high frequency for 5 min, under a 3s on/ 1s off cycle. The extract was passed through 5 g anhydrous sodium sulfate, concentrated to dryness and reconstituted with 1 mL n-hexane. For sample cleanup, a 31.5 cm (length) × 1.2 cm (diameter) glass column was packed with 10 g of deactivated Florisil and 1 g of anhydrous sodium sulfate. The Florisil column was rinsed with 40 mL of n-hexane and then the sample extract was loaded onto the column. The sample was eluted through the column with 50 mL of ethyl ether-n-hexane mixture (30:70, v/v) into a 250-mL pear-shaped flask, and the eluent was reduced to approximately 5 mL on a vacuum rotary evaporator. To remove sulfur residues in the sample, a small amount (<1.5 g) of activated copper was added into the sample extract and mixed on a vortex for 20 s. The sample extract was then passed through anhydrous sodium sulfate into a concentrator tube and further condensed to 0.5 mL under a stream of nitrogen. The final sample was transferred to a 2-mL autosampler vial and reconstituted to 1.0 mL with n-hexane for analysis.

Chromatographic Analysis

A 6890 Agilent gas chromatograph coupled with a micro-electron capture detector and dual columns (DB-5MS, 30 m × 0.25 mm × 0.32 μm, and DB-1701, 30 m × 0.25 mm × 0.25 μm) was employed for separation and analysis of all pyrethroid and

organophosphate compounds. The following instrument conditions were used. The inlet temperature was 260 °C, and the detector temperature was 320 °C. The column temperature program was as follows: initial temperature 50 °C held for 1 min, ramped to 180 °C at 20 °C min⁻¹, then ramped to 250 °C at 7 °C min⁻¹ and held 7 min, then ramped to 300 °C at 2 °C min⁻¹ and held for 3 min. The column flow rate was 1.0 mL min⁻¹ (helium). The sample was injected in a pulsed splitless mode with the pressure set at 50 psi for 0.8 min. The total splitless time was 1.0 min. For compounds with multiple peaks (i.e., cypermethrin, cyfluthrin), the sum of all peak areas was used for calibration and quantification. Quantification was made with response from the DB-5MS column, with confirmation of analytes made using the DB-1701 column.

Quality Assurance

Various steps were used to assure the accuracy and reproducibility of sample analysis. Confirmation of analytes was achieved through the use of dual columns with differing polarities. Extraction efficiencies of pyrethroids and organophosphates from water and sediment samples were estimated for each sample set by spiking, before extraction, with 1.0 mL of 20 µg L⁻¹ decachlorobiphenyl (in acetone), and of 50 µg L⁻¹ carbophenothion (in acetone), respectively. Calibration standards for pyrethroids (200, 50, 10, 2, and 0.5 µg L⁻¹) and organophosphates (160, 60, 20, 8, and 4 µg L⁻¹) were run at the beginning of each batch to establish the instrument response factor. Further quality control was achieved by running a blank for each set of samples. The average surrogate recovery for water samples was 80% (32-129%), with all but three samples having >60%

recovery. The instrument detection limit (IDL) was estimated by running ten replicates of 0.5 ppb standard. The IDL for bifenthrin, fenpropathrin, λ -cyhalothrin, *cis*-permethrin, *trans*-permethrin, esfenvalerate, and deltamethrin were 0.15, 0.17, 0.10, 0.08, 0.17, 0.14, 0.17, and 0.11 ppb, respectively. The method detection limit (MDL) was calculated for each compound using the EPA method (4), by multiplying the standard deviation of eight spiked (1 mL 2 ppb pyrethroid and 1 mL ppb organophosphate standards) water samples with a one tailed *t* critical value $t_{df=7,p=0.01}$. The method detection limits estimated for bifenthrin, fenpropathrin, λ -cyhalothrin, *cis*-permethrin, *trans*-permethrin, esfenvalerate, and deltamethrin were 0.9, 0.8, 0.6, 2.6, 2.3, 0.7, 0.6 ng L⁻¹, respectively for water samples. Cypermethrin had a MDL of >2 ng L⁻¹. The MDLs for diazinon and chlorpyrifos were 2.3 and 6.9 ng L⁻¹, respectively. Because the actual detection limits were influenced by sample matrix, there were instances where positive detections were made under these MDLs. These positive detections were carefully verified and included in the calculation. The average surrogate recovery for sediment samples was 80% (59-112%). Organophosphate recovery in sediments was relatively poor using the ultrasonic extraction method and therefore the data was not evaluated herein.

Data Analysis

Pyrethroid concentrations in water collected at the inlet and outlet on the same day were compared for each CW using the paired nonparametric Wilcoxon Signed Rank test. Pesticide concentration reduction, R(%), was calculated as the relative decrease of

outlet (or midpoint) concentration (C_{Outlet}) to the inlet concentration (C_{Inlet}) for each CW on the same day using the following equation:

$$R(\%) = \left[1 - \frac{C_{Outlet}}{C_{Inlet}} \right] \times 100 \quad (1)$$

For the purpose of calculating R(%), a non-detect (nd) was treated as zero. The sediment basin R(%) was determined using the daily mean concentrations of both wetland inlets. The seasonal R(%) was the average of all daily R(%) values. To obtain an estimate of daily pesticide loadings at the various locations of the wetlands, pesticide concentrations between sampling dates were interpolated and then multiplied by the corresponding daily flow rate. Seasonal load (mg) for a given location was calculated from the integral sum of all the daily load estimates. The pyrethroid partitioning ratio of suspended solids (SS) to the total water concentration was calculated using the formula:

$$PR(\%) = \left[\frac{C_{SS}}{C_{SS} + C_{Dis}} \right] \times 100 \quad (2)$$

The Wilcoxon Signed Rank Test was conducted by ranking the absolute differences between paired inlet and outlet concentrations. The sum of the directional (+/-) rankings were then compared with z critical numbers for a one directional test at the 0.01 level.

RESULTS AND DISCUSSION

Insecticide Concentrations in Source Water

Water entering the wetlands at the entrance to the sediment basin (Figure 4.1) was analyzed a total of 7 times for pyrethroids, and 5 times for organophosphate pesticides. In general, pesticide levels in the input flow varied erratically over time, and no apparent pattern could be discerned for the detected pyrethroids (Figure 4.2). Permethrin was detected in all 7 samples, with concentrations from 30 to 470 ng L⁻¹ (mean = 203 ng L⁻¹). Both bifenthrin and λ-cyhalothrin were detected in 6 out of the 7 samples, with levels ranging from 0.2 to 7.9 ng L⁻¹ (mean = 3.1 ng L⁻¹) for bifenthrin and from nd to 17.1 ng L⁻¹ (mean = 6.6 ng L⁻¹) for λ-cyhalothrin. Cypermethrin concentrations ranged from nd to 43.4 ng L⁻¹ (mean = 12.0 ng L⁻¹) and esfenvalerate from nd to 1.41 ng L⁻¹ (mean = 0.4 ng L⁻¹), each detected in 5 out of the 7 samples. Therefore, relative high levels of a suite of pyrethroids were present in the tailwater throughout the irrigation season, thereby justifying the necessity for mitigation of this class of insecticides. In contrast, diazinon was not detected at any time in the input tailwater, while chlorpyrifos was detected in 2 samples with a maximum level of 5.8 ng L⁻¹ (mean = 5.5 ng L⁻¹).

The levels of pyrethroids in the source flow appeared to vary greatly on a temporal scale. The pesticide use records showed that there is a high degree of variation in pesticide usage in this region, and the peak pesticide application (May to July) overlaps with most of the study duration. The tailwater ditch at the study site drained about 450 ha of agricultural land, used for cultivating various crops including melons, alfalfa, and row crops. The high temporal variation in pesticide concentrations in the input tailwater was most likely a response to the timing of pesticide application, as well as changes of irrigation patterns over time.

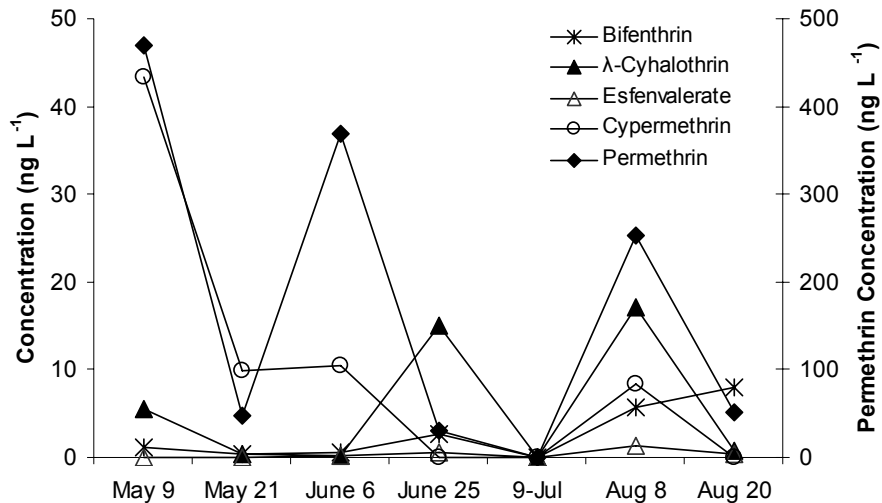


Figure 4.2. Whole-water concentrations of pyrethroid insecticides (ng L^{-1}) in the agricultural tailwater before entering the constructed wetlands.

Reductions in Pyrethroid Concentrations

Concentrations in the outlet flow were found to be significantly smaller than those in the inlet flow for both CWs for permethrin, cypermethrin, bifenthrin, and λ -cyhalothrin (Wilcoxon Signed Rank test, $p \leq 0.025$). Esfenvalerate concentrations were significantly lower at the outlet than at the inlet for CW2 ($p < 0.05$), although the difference was not significant for CW1 (Table 4.1).

The average R(%) for the sediment basin was estimated to be 6% for bifenthrin, -34% for λ -cyhalothrin, 2% for cypermethrin, 15% for esfenvalerate, and 17% for permethrin. Overall, the sediment basin had little effect on the pyrethroid concentration levels in the passing tailwater. The lack of pesticide reduction was likely due to the fact that gravity-induced sedimentation in the sediment basin predominantly caused heavy

(i.e., sand) particles to settle out of the flow and was less effective at retaining lighter particles. This notion was supported by a textural analysis of sediment samples. While sediments from the sediment basin contained 43% sand on the average, the sand fraction was only 19% in the sediments at the inlets of the CWs. This observation was similar to the finding of Smith et al. (24), who showed that under high flow conditions, pesticides were not found in the sediment from a retention basin, although they were detected downstream. Gan et al. (25) observed that in a drainage ditch, the sand fraction of the sediment deposit decreased from 87% at the start of the channel to 21% at 145 m downstream, while the clay fraction increased concurrently from 5% to 23%, and organic matter content from 0.65% to 6.37%. This observation also suggests that pyrethroids in the input tailwater were likely associated predominantly with low-density or fine particles that traveled un-retained through the sediment basin into the wetlands.

For CW1, the seasonal average R(%) was 69% for bifenthrin, 71% for λ -cyhalothrin, 52% for cypermethrin, 87% for esfenvalerate, and 90% for permethrin. Although the flow path lengths were similar for both segments of CW1 (200 m and 250 m, respectively), the majority of concentration reduction occurred in the second segment of CW1. The hydrologic and hydraulic properties of wetlands are known to have a dramatic effect on the transport of contaminants through the system (26). Section 1 of CW1 was designed with a dendritic flow pattern lined with dense vegetation within the finger channels. However, the main channel of the first segment of CW1 was almost barren of vegetation throughout the course of the study. A bromide tracer study

conducted in the middle of the irrigation season showed that the median retention time for this segment was only about 1 h (Figure 4.3a). This was much shorter than the 5 h

Table 4.1. Constructed wetland 1 (CW1) and 2 (CW2) pesticide concentrations (ng L⁻¹) and ranges in water samples with percent reduction (R%) in concentration from inlet to outlet, Central Valley, Calif., 2007.

Sediment Basin		CW1			
Compound		Inlet 1	Midpoint	Outlet 1	R (%)
Bifenthrin	3.1 (0.4–7.9)	2.0 (nd-9.0)	1.6 (nd-6.8)	0.2 (nd-0.4) ^b	69
Cyhalothrin	6.6 (0.2–17.1)	1.8 (nd-5.9)	1.1 (nd–3.5)	0.26 (nd–0.9) ^b	71
Cypermethrin	12.0 (nd-43.4)	16.2 (1.7–	14.2 (1.3–	4.3 (nd–12.4) ^b	52
Esfenvalerate	0.39 (nd–1.4)	1.1 (nd-6.5)	1.2 (nd–7.8)	0.04 (nd-0.2)	87
Permethrin	203 (29.5–	88 (13.8–	37 (14.1–56.8)	5.1 (nd–14.5) ^b	90
Chlorpyrifos	5.5 (5.1–5.8)	3.9 (1.2–7.3)	2.7 (1.2–4.3)	1.6 (0.4–2.2)	61
Diazinon	Nd	8.2 (6.6–9.8)	11.0 (7.2–	16.0 (4.4–	-168
Diazinon ^a	Nd	9.1 (8.3–9.8)	11.2 (7.2–	7.1 (4.4–10.2)	22
Sediment Basin		CW2			
Compound		Inlet		Outlet	R (%)
Bifenthrin	3.1 (0.4–7.9)	2.6 (nd – 11.6)		0.21 (nd –	84
Cyhalothrin	6.6 (0.2–17.1)	3.3 (nd – 12.9)		0.17 (nd –	90
Cypermethrin	12.0 (nd-43.4)	20.5 (1.50 –		3.6 (nd -	64
Esfenvalerate	0.39 (nd–1.4)	0.89 (nd - 5.2)		0.03 (nd –	77
Permethrin	203 (29.5–	77 (14.2 –		5.8 (nd - 15.9) ^b	94
Chlorpyrifos	5.5 (5.1–5.8)	3.0 (1.26 –		1.6 (0.57 –	52
Diazinon	Nd	17.0 (nd –		61.4 (nd –	-710
Diazinon ^a	Nd	19.5 (nd –		3.7 (nd – 7.4)	82

^a An unusually high concentration at the outlet was excluded from calculation; ^b Significantly different from inlet concentration at $\alpha = 0.025$; ^c Significantly different from inlet concentration at $\alpha = 0.05$

estimated using a plug flow model with mean volumes and flow rates, suggesting that flow short-cutting occurred in this segment. The suspended solid and turbidity values were consistently higher at the midpoint than at the inlet in CW1 (Table 4.2), suggesting re-suspension of sediments and scouring of the bed layer. In comparison, TSS and turbidity values were significantly lower at the outlet than at the midpoint or the inlet, suggesting that the second segment of CW1 was more effective at removing suspended particles. As mentioned earlier, the second section of CW1 was much deeper, with very slow flow. A tracer study did not yield the residence time for the second segment of CW1 due to dilution of the tracer below detection limits. Pesticide removal efficiency was previously shown to decrease quickly with increasing flow through wetlands (27).

Table 4.2. Seasonal average water quality measurements (mean \pm standard deviation) at the constructed wetlands, Central Valley, California (May-August, 2007).

Location	pH	DOC (mg L ⁻¹)	TSS (mg L ⁻¹)	Turbidity	Chlorophyll a (ppb)
	8.58	4.4 \pm 1.3	242.3 \pm 330.4	106.9 \pm 168.2	55.0
			<u>Sediment basin</u>		
			<u>Constructed wetland 1</u>		
Inlet	8.61	4.3 \pm 1.0	28.5 \pm 21.0	21.7 \pm 23.0	50.8
Midpoint	8.54	4.5 \pm 2.0	48.0 \pm 60.2	45.6 \pm 84.1	56.3
Outlet	8.40	4.2 \pm 1.1	19.9 \pm 19.1	13.7 \pm 17.2	32.1
			<u>Constructed wetland 2</u>		
Inlet	8.65	4.1 \pm 1.0	31.2 \pm 20.6	37.8 \pm 87.3	53.5
Outlet	8.69	5.0 \pm 1.8	14.7 \pm 11.5	11.1 \pm 11.6	30.7

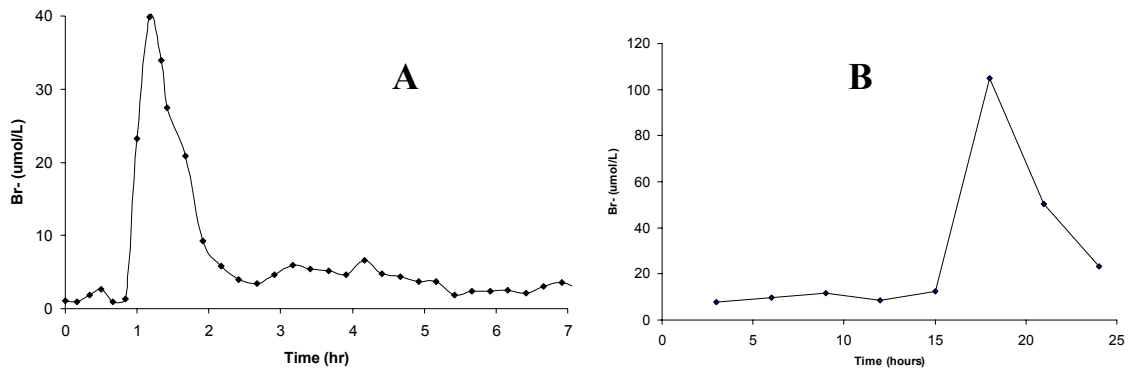


Figure 4.3. Bromide tracer study for segment 1 of constructed wetland 1 (A) and constructed wetland 2 (B).

CW2 was slightly more efficient at reducing pyrethroid levels from the tailwater than CW1. The average seasonal R(%) for CW2 was 84% for bifenthrin, 90% for λ -cyhalothrin, 64% for cypermethrin, 77% for esfenvalerate, and 94% for permethrin. CW2 had a long flow route (about 720 m), with dense vegetation running the entire course of the wetland. CW2 had an estimated residence time of 18 h (Figure 4.3b). Compared to the inlet, the suspended solid and turbidity levels at the outlet of CW2 decreased by 53% and 71%, respectively, and the decreases were greater than those for CW1 (30% and 37%, respectively). Therefore, the longer flow path and denser vegetation in CW2 appeared to have contributed to a more effective retention of particles carrying pyrethroids, leading to improved removal efficiency. Bennett et al. (16) found bifenthrin and λ -cyhalothrin levels were reduced to <0.1 % of the initial concentration over a 280-m densely vegetated ditch with 88% grass coverage. In comparison to an un-vegetated ditch, the presence of vegetation promoted particle settling and decreased the distance necessary to reduce initial permethrin concentrations by 50% from 55 m to 21 m. Therefore, vegetation in a wetland plays a critical role in retaining hydrophobic pollutants

such as pyrethroids. The retention may be due to adsorption of these compounds to live and decayed plant materials, and/or physical trapping of particles that are enriched with contaminants. Unfortunately, due to the heterogeneous nature of vegetation biomass both spatially and temporally within our wetlands, a quantitative evaluation of the role of vegetation in pesticide removal was not feasible.

Reductions in Organophosphate Concentrations

Chlorpyrifos was detected at all sampling locations within CW1 and CW2 throughout the study. On average, CW1 and CW2 showed 61% and 52% reductions, respectively, of the whole water concentration of chlorpyrifos. The outlet chlorpyrifos concentrations were significantly lower ($p < 0.05$) than the inlet concentrations for CW1 but not for CW2. The reduction of chlorpyrifos in our wetland system was comparable to that in Schulz and Peall (14), who observed that 55% of the total organophosphate loads were retained in a 134-m long CW.

Diazinon was also detected in most of the water samples in both wetlands at mostly low levels (Tables 1 and 2). A statistical analysis was not performed on diazinon due to the small sample size ($n = 4$) with detectable diazinon concentrations. It was noted that the average diazinon concentrations at the outlets of CW1 and CW2 were greatly influenced by one time point, in which the outlet concentration was more than an order of magnitude higher than the average diazinon concentration. While the exact cause for this exception was unknown, factors such as spray drift could have led to the observed concentration reversal. After excluding the unusual concentrations for that date, the

average reduction in diazinon concentrations increased to 22% for CW1 and 82% for CW2. The relatively smaller reductions for chlorpyrifos and diazinon by the wetlands may be attributed to their much lower K_{OC} values (1000 for diazinon and 6000 for chlorpyrifos) (28) than those for pyrethroids ($0.5-4.4 \times 10^6$) (29).

Pesticide Removal by Wetlands

Water flow rates at the outlet of CW1 or CW2 were much smaller than those at the inlet (Figure 4.4). On average there was an 87% decrease from $0.071 \text{ m}^3 \text{ s}^{-1}$ at the inlet to $0.009 \text{ m}^3 \text{ s}^{-1}$ at the outlet for CW1, and a 68% loss from $0.016 \text{ m}^3/\text{s}$ at the inlet to $0.005 \text{ m}^3 \text{ s}^{-1}$ at the outlet for CW2. According to the recorded weather data at an adjacent station, the average daily maximum temperature was $36.1 \text{ }^\circ\text{C}$ and the daily relative humidity was 46%, resulting in an average 0.68 cm d^{-1} loss due to evapotranspiration. It was estimated that the overwhelming loss in flow through the CWs was due to underground seepage. The active underground seepage is due to the porous underlying bed layer that is common for this area. Soils are highly permeable in the vicinity of the study site, where soil types such as Columbia, Dinuba, Hilmar and Elsalado are common. To verify that pesticides were not being transported downward with the aqueous phase, one set of water samples were collected from 3 piezometers at the 100 cm depth along the main channel of CW1. No pyrethroids were observed within any piezometer water sample. Trace levels of diazinon ($0.14 - 0.35 \text{ ng L}^{-1}$) and chlorpyrifos ($0.14 - 1.55 \text{ ng L}^{-1}$) were detected in all samples. Although the concentrations followed a decreasing trend in concentrations along the flow path, further

investigation of the potential for vertical transport of these and other pesticides is warranted.

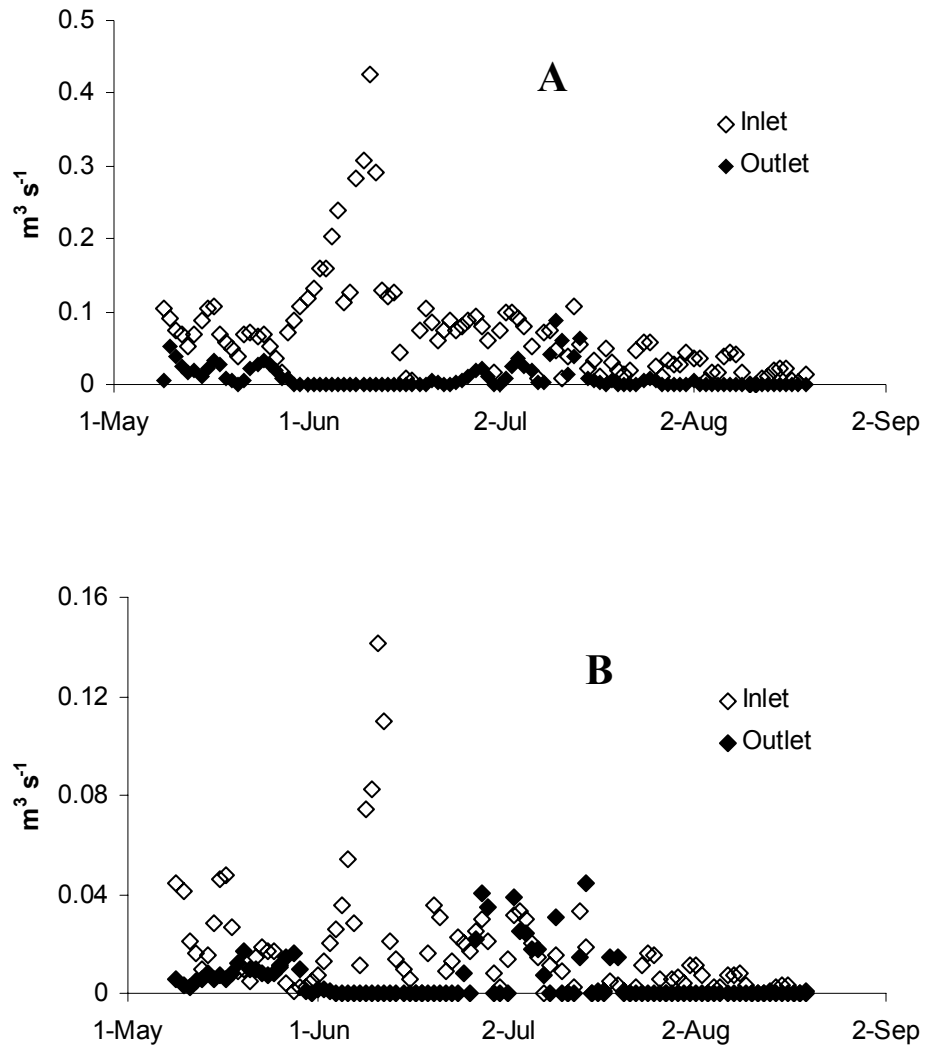


Figure 4.4. Flow rates recorded at the inlet and outlet of constructed wetlands. (A) Constructed wetland 1; and (B) Constructed wetland 2.

Seasonal loads were calculated from May 9 to Aug 20, 2007 for pyrethroids, while organophosphate loads were estimated from June 6 to Aug 20, 2007 (Table 4.3).

The amounts of individual pyrethroids entering CW1 over the irrigation season were substantially greater than those entering CW2. For CW1, pesticide loading into the wetland ranged from 633 mg for bifenthrin to over 91,000 mg for permethrin, while loading into CW 2 ranged from 159 mg for bifenthrin to about 12,000 mg for permethrin. The primary mechanism for the disparity in pesticide loading between the wetlands is the difference in flow rates, with the average flow rate into CW1 ($0.07 \text{ m}^3\text{s}^{-1}$) more than double that into CW2 ($0.02 \text{ m}^3\text{s}^{-1}$). Removal rates calculated from the difference between loads at the outlet and the inlet were from 95 to near 100% for pyrethroids, and 68 to 99% for diazinon and chlorpyrifos. Therefore, when taking the flow volume reductions into consideration, both CWs were extremely efficient at removing pyrethroids and chlorpyrifos, and moderately efficient at removing diazinon, from the tailwater. After passing through each wetland, only a very small portion of the initial amount of pyrethroids (0-5%) was not removed before returning to the tailwater ditch.

Table 4.3. Seasonal pesticide load estimates (mg) and percent reduction by the constructed wetlands CW1 and CW2, between May 9 and August 20, 2007.

Chemical	Wetland 1			Wetland 2		
	Inlet	Outlet	Reduction (%)	Inlet	Outlet	Reduction (%)
Bifenthrin	633	12	98	159	8	95
Cyhalothrin	1155	18	98	582	5	99
Cypermethrin	12291	318	97	3252	152	95
Esfenvalerate	1046	3	100	185	2	99
Permethrin	91596	308	100	12415	148	99
Chlorpyrifos	1828	34	98	322	23	93
Diazinon	2865	242	92	1442	458	68

Role of Sedimentation in Pyrethroid Removal

Analysis of suspended solids and filtrate showed that a predominant fraction (62-93%) of pyrethroids in the whole water was associated with the suspended solids. Such phase partitioning pattern appeared to be prevalent throughout the CWs. After averaging across all pyrethroid compounds and sampling points, the fraction associated with suspended solids ranged from 64 to 86% for the different locations. It must be noted that the pore size of the filter paper was 0.7 μm . Therefore the filtrate might still contain fine particles $< 0.7 \mu\text{m}$ as well as DOM.

Sedimentation rates were estimated for each segment from discrete daily flow rates and TSS values. The average sedimentation rate was 2322 kg d^{-1} (80% of the input mass) for the sediment basin, 444 kg d^{-1} (15% of the input mass) for CW1, and 144 kg d^{-1} (5% of the input mass) for CW2. Depositional rates based on suspended solid concentrations and TSS indicate the sediment basin as being the largest sink for pesticides. Pesticide concentrations associated with suspended solids (on dry mass basis) however were found to be higher on average at the wetland inlets than within the sediment basin for bifenthrin (elevated by 66%), λ -cyhalothrin (29%), cypermethrin (43%), esfenvalerate (59%), and permethrin (10%) (Table 4.4). Also, pyrethroid concentrations in sediments collected at the wetland inlets were found to be higher on average than those in the sediment basin on a dry weight basis. The season-average increase was about 18-fold for bifenthrin, 3.6-fold for λ -cyhalothrin, 1.5-fold for cypermethrin, 1.2-fold for esfenvalerate, and 1.9-fold for permethrin. These findings

indicate that pyrethroids had an increased affinity for lighter or finer suspended solids that passed through the sediment basin unrestrained.

Table 4.4. Average daily (mg d^{-1}) and seasonal total loading (mg) of pyrethroids associated with TSS in sediment basin and constructed wetland 1 (CW1) and constructed wetland 2 (CW2).

Segment	Bifen.	Cyhal.	Perm.	Cyper.	Esfen.
Sediment	13				
Basin	(1329)	95 (9844)	2220 (230909)	128 (13277)	6 (675)
Wetland 1	6 (1461)	14 (1461)	1308 (136051)	44 (4552)	2 (230)
Wetland 2	2 (243)	10 (1051)	291 (30233)	23 (2407)	1 (99)

Bifen. = bifenthrin, λ -Cyhal. = λ -cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin

Removal of pesticides through sedimentation suggests transfer of pesticide residues from water column to the wetland bed sediment. Compared to the inlet of CW1, pyrethroid concentrations in the sediment consistently decreased at the midpoint (except for esfenvalerate) and further at the outlet (Figure 4.5). The season-average decrease in sediment concentrations between the inlet and outlet of CW1 was 86% for bifenthrin, 99% for cyhalothrin, about 100% for cypermethrin, 60% for esfenvalerate, and 98% for permethrin. The greatest reduction in sediment concentrations again occurred within the second segment of CW1. This is particularly evident for the sampling period between June 6 and June 25, with bifenthrin (-21%), cypermethrin (-70%), and esfenvalerate (-40%) concentrations higher at the midpoint in relation to the inlet. Midpoint R% values were the lowest observed for permethrin (51%) during this time period as well. The peak daily flow (Figure S1) into wetland 1 occurred on June 11 ($0.43 \text{ m}^3 \text{ s}^{-1}$), which was an order of magnitude higher than the seasonal average flow of $0.07 \text{ m}^3 \text{ s}^{-1}$. This corresponded with the highest TSS value (251 mg l^{-1}) recorded at the midpoint. During

this period of high flow, it is likely that there was more active transport of pyrethroid-laden sediment through the un-vegetated first segment of CW1. This observation could be indicative of a threshold of which mitigation capacity of the wetlands was reduced at greater flow rates. The efficacy of the wetlands under high flow regimes such as a storm event should be evaluated in the future.

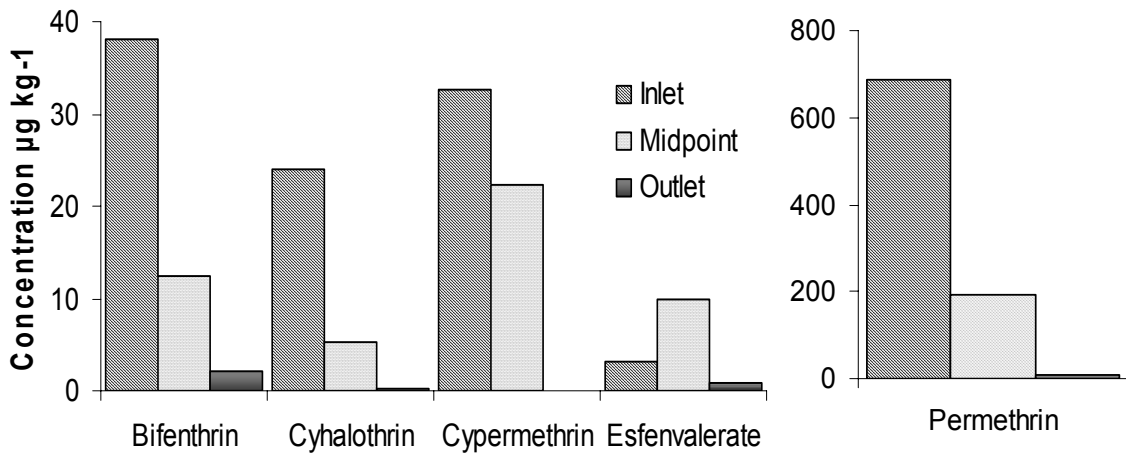


Figure 4.5. Mean pyrethroid concentrations ($\mu\text{g kg}^{-1}$) in sediment samples within the constructed wetland 1 (CW1).

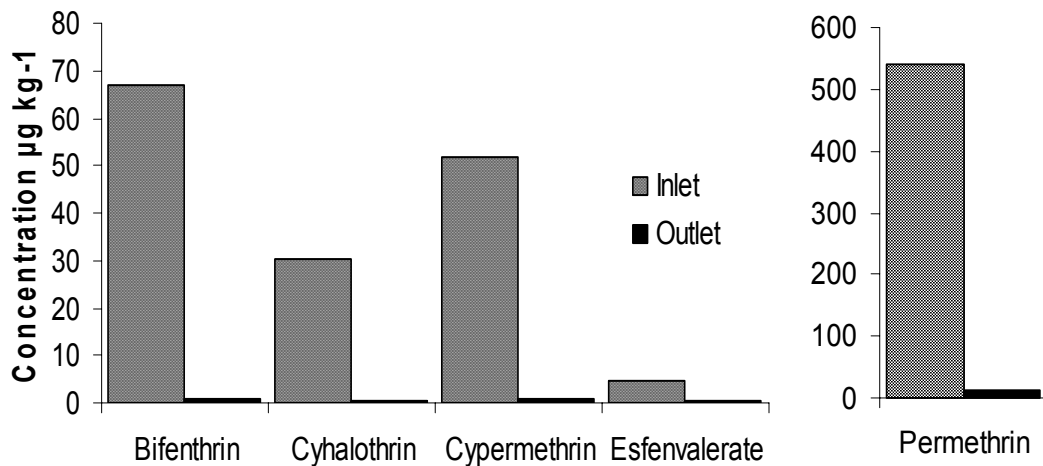


Figure 4.6. Mean pyrethroid concentrations ($\mu\text{g kg}^{-1}$) in sediment samples within the constructed wetland 2 (CW2).

A similar trend in sediment deposition was observed for CW2 (Figure 4.6). The seasonal average reduction in sediment pyrethroid concentrations between the inlet and outlet of CW2 was 96% for bifenthrin, 99% for λ -cyhalothrin, 97% for cypermethrin, 87% for esfenvalerate, and 98% for permethrin. Decreases in sediment concentrations of pyrethroids clearly suggested that the wetlands were efficient at trapping particles with adsorbed pyrethroids after the tailwater passed through the sediment basin. The fact that little pyrethroids were found in the sediment at the outlets showed that the suspended particles reaching the outlets were relatively free of pyrethroids, and were likely a result of re-suspension of clean sediment in the last section of the wetlands.

Amweg et al. (3) obtained OC normalized LC50 values for several pyrethroids using *Hyallela azteca*, a benthic invertebrate. The sediments used in the toxicity test were also from the Central Valley region, which allows a brief discussion of the potential toxicity reductions by the wetlands. Texture and organic carbon analysis was performed on sediment samples with enough sample material after extraction for pesticides, and the corresponding sediment concentrations were normalized to OC content. Out of the 9 inlet sediment samples, 4 samples showed bifenthrin concentrations greater than the LC50 ($0.52 \mu\text{g g}^{-1} \text{OC}$), 7 showed λ -cyhalothrin concentrations greater than the LC50 ($0.45 \mu\text{g g}^{-1} \text{OC}$), and 8 displayed permethrin concentrations greater than the LC50 ($10.83 \mu\text{g g}^{-1} \text{OC}$). In comparison, none of the 5 outlet samples had concentrations above the LC50 values for any of the pyrethroids. Therefore, under the study conditions, both CWs

significantly reduced the potential toxicity attributable to pyrethroids in the runoff returned into the tailwater ditch after passing through the wetlands.

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Chapter 5

Partitioning and Persistence of Pesticides within Constructed Wetlands

ABSTRACT

Constructed wetlands have proven to be an effective mitigation strategy to remove pyrethroid and organophosphate pesticides from agricultural tailwaters. However, little is known about the fate and transport of these chemicals in wetlands under field conditions. In this study we investigated the behavior of several pyrethroid and organophosphate pesticides in wetlands. In agricultural tailwater, pyrethroids were found to partition overwhelmingly to suspended solids. The suspended solid partitioning ratios (62 – 93%) did not vary considerably throughout the wetland systems, which was attributed to the relatively constant organic carbon content in water. Sediment fractionation analysis revealed a biphasic relationship around the 53- μm size fraction with a clear sorption tendency for sediment organic carbon. The tendency for pyrethroids to sorb to both the clay fraction and larger aggregated organic matter increased the potential for downstream chemical transport, which may explain the ineffectiveness of sediment traps for retaining pesticides. Varying flow during the irrigation season caused changes in the depositional rate within the system. The estimated effective length of one test system ($L_{1/2}$) for most pyrethroids were below 117 m under low flow conditions, but increased up to 267 m under high flow regimes. The degradation experiments revealed that most of the test pyrethroids degraded at a moderate rate under anaerobic conditions ($T_{1/2}$ 133-376 d),

while the half-life of the organophosphate chlorpyrifos was slightly faster at 106 d.

However, bifenthrin was found to be virtually non-degradable under both aerobic and anaerobic conditions, indicating its potential for persistence and accumulation within the wetlands.

INTRODUCTION

Agricultural tailwater is a stressor to freshwater systems, typically delivering an overabundance of nutrients and pesticides through irrigation ditches. This is especially true in the Central Valley of California, where almost all of certain stretches of the San Joaquin River is comprised of agricultural return flow during the irrigation season (1). Organophosphate and pyrethroid insecticides have been detected in both water and sediment samples within the watershed at the levels that are above toxicity thresholds (2, 3). There has been an increasing interest in utilizing constructed wetlands as a mitigation strategy to reduce water quality contaminants before the effluent reaches larger freshwater systems such as rivers, lakes, and estuaries.

Several studies have considered the potential for utilizing constructed wetlands (CWs) to remove pesticides from agricultural tailwater. Budd et al. (2009) found that over the course of an irrigation season, whole-water pyrethroid concentrations were reduced 52 – 94% after passing through wetlands (4). Moore et al. (2009) estimated that lambda-cyhalothrin and cyfluthrin concentrations would fall below toxicity endpoints after flowing through a 215-m wetland (5). Constructed wetlands have also been shown to be effective at reducing the organophosphate chlorpyrifos and herbicide azinphos-methyl concentrations in the water column (6-8).

Although CWs have proven to be effective for removing pesticides from agricultural tailwater, there is a lack of knowledge concerning the fate and transport of pesticides within these systems. Phase partitioning controls both transport and transformation processes. While the dissolved phase may be transported with the passing

water, sorption to the bed sediment increases the probability of reductive dechlorination mediated by sediment anaerobic bacteria (9). Partitioning of chemicals between aqueous and sorbent phases is typically determined in the laboratory using freshly spiked samples (10-12). However, these values may differ significantly from field occurrences as environmental conditions such as pH, temperature, and dissolved organic carbon content (DOC) can all affect a chemical's equilibrium partition (13). A literature search showed no studies characterizing phase partitioning within the water column utilizing measured suspended solid concentrations. Knowing chemical distribution within a wetland can guide the design of constructed wetlands to maximize contaminant removal.

Sediment basins are a common design component of constructed wetlands. Although effective at trapping heavier particles, several studies have shown sediment traps to be ineffective at retaining pesticides (4, 5, 14). This observation appears to contradict with the assumption that sedimentation is the primary removal mechanism for hydrophobic compounds (4). If pesticide concentrations were homogenous across particle fractions, chemical deposition rates may be predicted from Stokes law. The fact that pesticide removal is not related to sedimentation rate in sediment traps suggests an inequality meriting mechanistic investigation.

Once deposited in the wetland, concern arises that pesticides have the potential to persist and accumulate in the system. If accumulation occurs due to prolonged persistence, pesticides remaining on the surface layer of a wetland may be flushed out of the system under high flow conditions. Also, chemical concentrations could increase to levels that are detrimental to wildlife that utilize the wetlands as habitat.

Pyrethroids monitored in this study have been observed to degrade quickly (0.5 – 31 d) in other aquatic systems under controlled conditions (15). However, several environmental factors could affect the rate of degradation, including the prevalent redox potential, moisture content, microbial activity, and sorption (32). The persistence of four organophosphate insecticides increased dramatically under anaerobic conditions (16), while several herbicides have been found to degrade more rapidly under strongly reduced conditions in wetland sediments (17). Degradation of hydrophobic pesticides has also been documented to be hindered by strong adsorption to organic matter (18). It was reported that less than 6% of permethrin and cypermethrin were found to remain in mineral soils after 8 weeks, while approximately 16% of both chemicals were still detected in an organic sediment (28). It is believed that once adsorbed to sediment, aging further decreases the bioavailability of the sorbed chemical to the microbial community, therefore slowing the degradation process (19). Ahmad et al. (2004) found that up to 33% of carbaryl remained unavailable to degradation due to sequestration into soil nanopores (20). However, the above parameters and processes are often site specific and vary spatially and temporally in field settings, and should be evaluated under field conditions.

The primary objectives of this study were to evaluate the phase distribution of pesticides in the water column as irrigation tailwater passes through a wetland, determine the preferential sorption sediment fractions, and understand if pesticides persist and accumulate in the bed sediment under variable environmental conditions. These objectives will improve our current knowledge of pesticide behavior in constructed

wetlands and may be used to maximize pesticide removal while minimizing the adverse effects of this practice.

MATERIALS and METHODS

Study Sites

A detailed description of the study sites used in this study is provided in Chapter 4. The CWs were located within Stanislaus County, California. Water from the tailwater ditch was diverted into a sediment settling basin before entering the CWs. The flow path length of CW1 was approximately 450 m while CW2 had a flow path of 720 m. Water quality parameters were measured from weekly grab samples. As with many of the CWs in the area, these CWs receive water only during the summer irrigation months, and are virtually dry during the winter months. This has important implications for the fate of the chemicals, as the surface bed will experience both aerobic and anaerobic conditions during the course of a year. In addition to the sampling locations used for the 2007 monitoring season, two locations were added along the transect of CW1 in 2008. These two sites were located before and after a strand of bulrush (*Schoenolplectus californicus*) as described in Chapter 6.

Analysis of Partitioning in Whole Water

One liter water samples were collected biweekly in 1-L amber glass bottles for the duration of the irrigation season (May through August, 2007). Samples were collected at the inlet of the sediment basin, the inlets of CWs 1 and 2, the midpoint of CW1, and the

outlets of both CWs. Water samples were placed on ice during transport and stored at 4 °C until analysis, typically within two days.

Water samples were first filtered through Whatman GF/B filter paper (0.7µm) to obtain the suspended solid (C_{SS}) and filtered water (C_{Dis}) fractions. Filtered water samples were analyzed for pesticides using modified EPA method 3510 for liquid-liquid extraction (22). Pesticide concentrations associated with suspended particles were analyzed using modified EPA method 3550. A detailed description of extraction methods used for water, suspended solid, and sediment samples may be found in Chapter 4. The filter was placed in 250 mL beaker and air dried for 24 h before extraction by sonication. The final sample was transferred to a 2-mL autosampler vial and reconstituted in 1.0 mL n-hexane for analysis. The total suspended solid (TSS) level of water samples was measured using modified EPA method 160.2 (23, 24). To estimate the freely dissolved concentration (C_{Free}), the filtrate fractions for samples from two sampling dates were analyzed using solid phase micro-extraction (SPME), as described in Bondarenko et al. (2007) (10).

Sediment Fractionation

Sediment samples for fractionation analysis were collected in 1-L wide-mouth glass jars placed upright into a 10-cm diameter PVC tubing that was embedded in the sediment floor. Suspended particles passively dropped out of the water column into the pre-installed jars and were collected on two dates during the irrigation season. One set of sediment samples were used to obtain “bulk” scale fractionation and a second set of

samples were used to determine fractionation on a finer scale. For the bulk scale analysis, approximately 50 g (wet) sediment was wet sieved (in order) through 1000 μm , 500 μm , 250 μm , 106 μm , 53 μm sieves and 0.7 μm filter paper. For the finer scale analysis, approximately 10 g (wet) sediment was wet sieved through 1000 μm , 53 μm , 2 μm sieves and 0.7 μm filter paper. For the purpose of this study, particles $\geq 53 \mu\text{m}$ are classified as sand, 2 – 53 μm as silt, and $< 2 \mu\text{m}$ as clay. The samples were wet sieved using tap water under low pressure. The isolated fractions were air dried and then extracted using the sonication method as described above. An aliquot of the final filter water was also analyzed for the dissolved chemical fraction.

Sediment Depositional Experiment

Sediment core samples were extruded from the wetland bed using 6-cm wide PVC pipes. Cores were collected at the sediment basin, inlets to both CWs, before and after the bulrush, midpoint of CW 1, and both CW outlets. Cores were collected after the irrigation season, and most of the sampling locations had no free standing water at the time of sampling. The sediment basin and the inlet to CW2 were still receiving small amounts of tailwater flow at the time of sample collection. The cores were transported on ice to the laboratory and stored at 4 °C until analysis. The sediment cores were cut with a saw into four sections according to the depth: 0-5, 5-10, 10-15, and below 15 cm. The sediment from each increment was homogenized and extracted using the sonication method described above. In addition, the extracts were cleaned through 1 g of Florisil using a method described in Chapter 4.

Degradation Experiments

Three degradation experiments were carried out using field-contaminated sediment samples. Two laboratory degradation experiments were conducted by incubating the field contaminated sediment samples under anaerobic conditions. Sediments for the first anaerobic degradation experiment were collected in the summer of 2007 and stored at 4 °C for about 10 months before use. For sample collection, a 1-L Mason jar was filled by grab sampling from the irrigation ditch and the middle sections of both wetlands. All sediment samples were thoroughly homogenized and approximately 50 g of each sample (wet weight) was placed in a 125 mL glass container, followed by saturation with de-ionized water to form a 3 cm overlaying water layer. One set of samples from CW1 (CW1^a) was sterilized by addition of 0.005 mmol sodium azide to inhibit microbial activity. To achieve anaerobic conditions, the sample jars were purged with nitrogen and the sealed containers were stored in inflatable glove chamber under nitrogen. Three replicates were removed and extracted on 0, 7, 14, 28, 58, 147, and 274 d of incubation.

A second anaerobic degradation experiment was conducted using sediment samples collected from the irrigation ditch and CW1 in the summer of 2008. The primary difference of this experiment from the previous anaerobic incubation experiment was that the sediments were used immediately without storage to infer the potential effect of aging. The second set of samples were analyzed after 0, 28, 56, 112, 148, 182, 215, and 270 d of incubation.

In addition, an *in situ* experiment was completed to follow pesticide dissipation in the field with predominantly aerobic conditions. For the *in situ* experiment, three 1 × 1 m frames were inserted into the bed sediment immediately following the irrigation season. Two sampling frames were installed halfway between the inlet and midpoint of CW1 and the third installed in the middle of CW2. Sediment from the top 5 cm of the irrigation ditch was transferred to one of the boxes within CW1 to achieve an approximate 10 cm depth. A four-point composite sample was collected from each box after various time intervals from the top 2 cm utilizing a brass ring, and transferred on ice to the laboratory. All sediment samples were homogenized in the laboratory and extracted using the sonication method described above. Three replicates per sample were used for the analysis of pesticides.

Chromatographic Analysis

A 6890 Agilent gas chromatograph (GC) coupled with a micro-electron capture detector and dual columns (DB-5MS, 30 m × 0.25 mm × 0.32 μm, and DB-1701, 30 m × 0.25 mm × 0.25 μm) was employed for separation and analysis of all pyrethroid and organophosphate compounds in the samples from the phase distribution and sediment fractionation experiments. Details of the analytical conditions can be found in Chapter 4.

Analysis of degradation samples was carried out on a Varian 3800 GC (Varian Instruments, Sunnyvale, CA) coupled with a Varian 1200 triple-quadrupole mass spectrometer and a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland) and a

DB-5 MS column (30 m x 0.25 mm x 0.25 μ m) was used for separation. The final sample (0.5 mL) was spiked with 50 μ L of ^{13}C -*cis*-permethrin (1000 ppb) as an internal standard for quantitation (2009). A pulsed splitless mode was used for injection, with the pulse pressure of 45 psi for 0.8 min. The inlet temperature was 260 $^{\circ}\text{C}$. The initial column temperature was 80 $^{\circ}\text{C}$ for 1 min., ramped to 160 $^{\circ}\text{C}$ at 25 min^{-1} , then ramped to 300 $^{\circ}\text{C}$ at 5 min^{-1} , and held at 300 $^{\circ}\text{C}$ for 7 min. Helium (99.9999%) was used as the carrier gas at a flow rate of 1.0 mL min^{-1} . Details of the instrument configurations including the selected ions for detection are provided in Table 5.1.

Table 5.1. Conditions used in the mass spectrometry detection of two organophosphate and nine pyrethroid compounds.

	Precursor (m/z)	Product ion (m/z)	Collision Energy (eV)
Diazinon	304	179	8
Chlorpyrifos	314	258	10
	317	261	10
Bifenthrin	181	166	10
Fenpropathrin	181	152	20
λ -Cyhalothrin	181	152	20
<i>cis</i> -Permethrin	183	153	12
^{13}C - <i>cis</i> -Permethrin	189	174	14
<i>trans</i> -Permethrin	183	153	12
Cyfluthrin	163	127	7
Cypermethrin	163	127	7
Esfenvalerate	167	125	10
	181	152	25
Deltamethrin	252	93	20
	252	172	10

Data Analysis

The non-parametric Wilcoxon signed rank test was employed to determine differences in mean concentrations on all sample sets with $n \geq 5$. Apparent partition coefficient (K_{da}) and free concentration-based partition coefficient (K_{df}) were estimated using the formula:

$$K_{da} = \frac{C_{TSS}}{C_{Dis}} \quad \text{or} \quad K_{df} = \frac{C_{TSS}}{C_{Free}} \quad (5.1)$$

where C_{TSS} is the pesticide concentration associated with the suspended solid fraction, C_{Dis} is the concentration associated with the filtrate fraction, and C_{Free} is the freely dissolved concentration analyzed by SPME. K_d values were only calculated for samples in which both phase concentrations were above detection limits. The K_{DOC} values were estimated by the formula:

$$K_{DOC} = \frac{(C_{Tot} - C_{Free})/[DOC]}{C_{Free}} \quad (5.2)$$

where C_{Tot} is the total water concentration and $[DOC]$ is the concentration of dissolved organic carbon (mg/L). Pesticide dissipation as a function of time in the degradation experiments was fitted to the first-order decay model to derive the first-order rate constant k (d^{-1}) and half-life ($T_{1/2}$) from the formula:

$$C_t = C_0 e^{-kt} \quad (5.3)$$

where C_t is the pesticide concentration at time (t) and C_0 is the initial concentration. For the purpose of this study half-life is the time necessary for 50% dissipation of initial concentration.

RESULTS AND DISCUSSION

Phase Distribution in Whole Water

The whole water samples were filtered and analyzed for pesticides associated with suspended solid (C_{TSS}) and dissolved (C_{Dis}) concentrations. Throughout the irrigation season, the apparent dissolved concentrations were nd – 4.8 ng L⁻¹ for bifenthrin, nd – 1.5 ng L⁻¹ for cyhalothrin, nd – 35 ng L⁻¹ for permethrin, nd – 16.3 ng L⁻¹ for cypermethrin, and nd – 0.6 ng L⁻¹ for esfenvalerate. C_{TSS} values were generally orders of magnitude higher than the C_{Dis} values, with ranges of nd – 1.0×10^6 ng kg⁻¹ for bifenthrin, nd – 1.6×10^5 ng kg⁻¹ for cyhalothrin, nd – 6.8×10^6 ng kg⁻¹ for permethrin, nd – 5.9×10^5 ng kg⁻¹ for cypermethrin, and nd – 3.3×10^4 ng kg⁻¹ for esfenvalerate. Based on mass per volume (ng L⁻¹) in the water column, on average, the fraction of pesticides on suspended particles accounted for 62% for bifenthrin, 79% for cyhalothrin, 93% for esfenvalerate, and 73% permethrin (Figure 5.1). Cypermethrin (39%) was the only chemical with the sorbed fraction below 50%. This observation further illustrates the importance of sedimentation in the removal of pyrethroid insecticides within the wetlands as reported in Chapter 4.

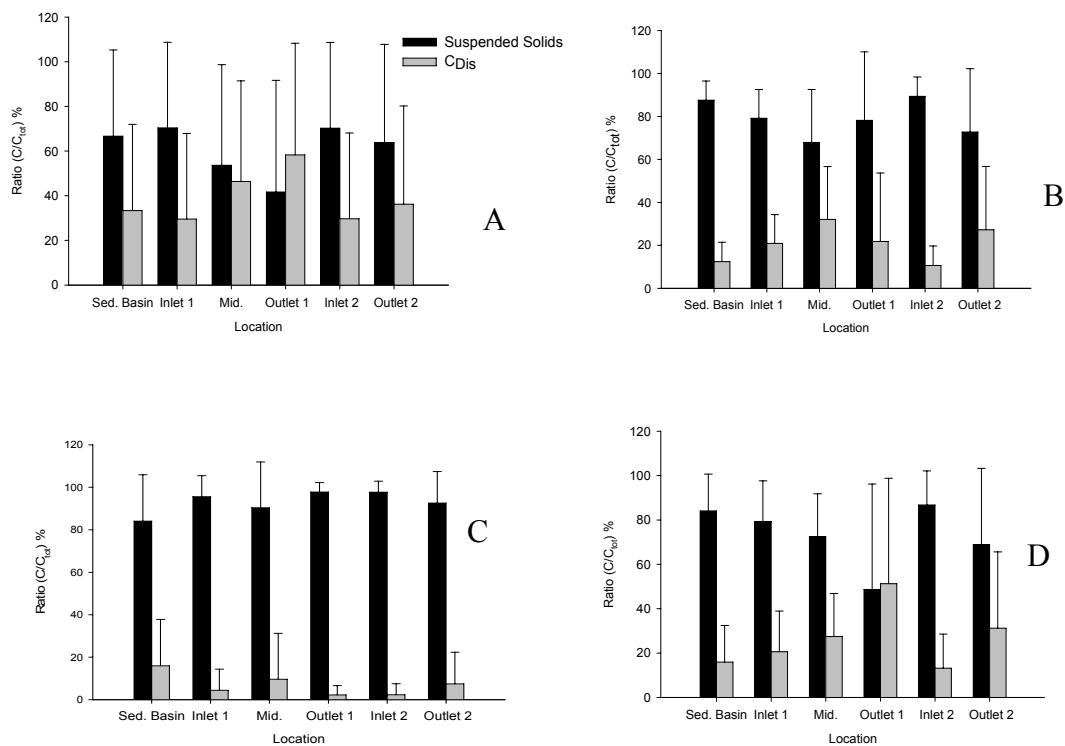


Figure 5.1. Ratios of (A) bifenthrin, (B) cyhalothrin, (C) esfenvalerate, and (D) permethrin associated with suspended particles (C_{TSS}) ($> 0.7 \mu\text{m}$) and aqueous phase ($C_{Dis} = C_{DOM} + C_{free}$) fractions water samples collected within wetlands.

Values of apparent K_{da} were estimated from the ratio of C_{TSS}/C_{Dis} (Table 5.2). The season-averaged K_{da} was 1.35×10^5 for bifenthrin, 1.87×10^5 for λ -cyhalothrin, 1.94×10^4 for cypermethrin, 7.29×10^4 for esfenvalerate, and 3.08×10^5 for permethrin, clearly indicating the strong preference of pyrethroids for suspended particles $> 0.7 \mu\text{m}$ within the water column. These values are slightly lower than those reported by Liu et al. (2004), who found the partition coefficient of stream water to be 2.1×10^6 for bifenthrin and 1.1 to 1.6×10^6 for permethrin (11), but slightly higher than those calculated by Lee et al. (2003) for nursery runoff sediments ranging from 3.6×10^3 for bifenthrin and 1.7 to 2.6×10^3 for permethrin (12). These discrepancies are most likely due to differences in the chemical properties of the sorbent. Zhou et al. (1995) showed that both the quantity and the quality of the organic matter present will affect the sorption process of pyrethroids in solution, observing increased partitioning with increasing aromaticity and decreasing polarity of the organic matter (21, 42). Unfortunately the mass of suspended solids collected in this study was too limited to do a comprehensive analysis of organic carbon composition.

A single set of samples were collected separately and analyzed using GC-MS for chlorpyrifos. The derived average K_{da} for chlorpyrifos (1.46×10^4) was considerably smaller than any of the pyrethroids, which was consistent with its higher water solubility (1.4 mg L^{-1}) compared to that of pyrethroids (1.0×10^{-3} to $6.0 \times 10^{-3} \text{ mg L}^{-1}$) (7, 34).

Since the suspended fraction only included those particles greater than $0.7 \mu\text{m}$, the filtrate fraction contained finer particles, colloids, and dissolved organic matter. The

freely dissolved concentration C_{Free} was determined by SPME on one sampling date, and the $K_{d\text{a}}$ and $K_{d\text{f}}$ were estimated from the ratio of C_{TSS} , C_{DIS} , and C_{free} (Table 5.3).

Table 5.2. Apparent adsorption coefficient K_{da} values (C_{TSS}/C_{dis}) [$L\ kg^{-1}$] derived from water passing through the wetlands.

Location	DOC (mg L ⁻¹)	TSS (mg L ⁻¹)	Bifen.	λ-Cyhal.	Cyper.
<i>N</i>			14	31	22
Sed. Basin	12.69	242.32	1.25×10^4	6.19×10^4	1.35×10^4
CW1 Inlet	8.33	28.54	1.15×10^5	1.76×10^5	1.88×10^4
CW1 MP	8.60	48.01	2.24×10^5	1.92×10^5	2.34×10^4
CW1 Outlet	8.51	19.89	2.87×10^5	7.77×10^4	6.04×10^3
CW2 Inlet	6.05	31.24	2.06×10^5	4.37×10^5	3.92×10^4
CW2 Outlet	10.66	14.68	7.53×10^4	9.24×10^4	1.00×10^4
Average			1.35×10^5	1.87×10^5	1.94×10^4
Location	DOC (mg L ⁻¹)	TSS (mg L ⁻¹)	Esfen.	Perm.	Chlor.
<i>N</i>			7	36	1
Sed. Basin	12.69	242.32	1.17×10^4	1.39×10^5	8.1×10^3
CW1 Inlet	8.33	28.54	3.70×10^4	2.40×10^5	1.1×10^4
CW1 MP	8.60	48.01	3.14×10^4	1.89×10^5	1.3×10^4
CW1 Outlet	8.51	19.89	7.18×10^4	2.15×10^5	2.7×10^4
CW2 Inlet	6.05	31.24	2.42×10^5	4.76×10^5	-
CW2 Outlet	10.66	14.68	1.04×10^5	6.23×10^5	-
Average			7.29×10^4	3.08×10^5	1.46×10^4

Bifen. = bifenthrin, λ-Cyhal. = λ-cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos, MP = midpoint, Sed. Basin = sediment basin

Table 5.3. Permethrin C_{free} concentrations ($ng\ L^{-1}$) with estimated C_{free}/C_{Tot} ratios, K_{da} and K_{df} values.

Location	DOC (mg L ⁻¹)	C_{free} (ng L ⁻¹)	C_{free} (%)	K_{da}	K_{df}
Sediment Basin	2.68	2.34	25	$2.7E \times 10^5$	$1.4E \times 10^5$
W2 Inlet	3.17	1.42	16	$3.6E \times 10^5$	$1.8E \times 10^5$
W2 Midpoint	4.06	0.98	19	$1.4E \times 10^5$	$6.6E \times 10^4$
W2 Outlet	10.38	0.47	39	$1.5E \times 10^5$	$6.8E \times 10^4$

Only permethrin was detected in all three phases. Like the whole water concentrations presented in Chapter 4, the C_{Free} concentrations decreased along the system transect, from 2.34 ng L^{-1} in the sediment basin, to 1.42 ng L^{-1} in the wetland inlet, 0.98 ng L^{-1} at the midpoint, and 0.47 ng L^{-1} at the outlet. The decreasing lateral trend confirms the system's efficiency at reducing both total and freely dissolved concentrations in return flows. In a previous study, Liu et al. (2004) found that 22 – 27% of permethrin and bifenthrin at the inlet and 10-14% at the outlet of a nursery drainage channel were in the freely dissolved phase (11). In our system C_{Free} accounted for 16 – 39% of the total permethrin concentrations. Interestingly, the estimated $K_{\text{d f}}$ was consistently slightly lower than the $K_{\text{d a}}$. Partition coefficient estimations using SPME analysis has the potential for underestimation due to attachment of very fine particles to the fiber, therefore overestimating the C_{Free} concentration (41).

To further illustrate the importance of partitioning to dissolved organic matter in the passing flow, the apparent K_{DOC} values were calculated using equation 5.2 (Table 5.4). The average apparent K_{DOC} values ranged from 8.4×10^4 for esfenvalerate to 1.0×10^6 for λ -cyhalothrin. This calculation again included fractions that associated with particles $< 0.7 \mu\text{m}$ and dissolved organic matter. However, the $K_{\text{DOC f}}$ estimated using C_{Free} as measured by SPME was 9.9×10^5 for permethrin. The $K_{\text{DOC f}}$ values are in fairly good agreement with those reported by Bondarenko et al. (2007) for permethrin (0.69 - 6.07×10^5) (10). Agreement between K_{DOC} estimates using both filtrate and SPME concentrations gives confidence that the filtration method provides a good estimate for

partitioning coefficients in systems with low dissolved organic carbon contents (<20 mg L⁻¹).

Table 5.4. Apparent partition coefficient $K_{\text{DOC a}}$ values estimated from water passing through the wetlands.

Location	Bifen.	λ -Cyhal.	Cyperm.	Esfen.	Perm.	Perm.*
Sed. Basin	6.5×10^5	2.5×10^6	2.8×10^5		1.3×10^6	1.1×10^6
CW1 Inlet	2.7×10^5	8.7×10^5	9.3×10^4		6.3×10^5	1.7×10^6
CW1 MP	2.1×10^5	4.8×10^5	1.7×10^5	8.4×10^4	4.0×10^5	1.0×10^6
CW1 Outlet		5.7×10^4	8.4×10^4		4.8×10^4	1.5×10^5
CW2 Inlet	2.5×10^5	8.2×10^5	3.0×10^5		9.7×10^5	
CW2 Outlet		3.4×10^4	9.4×10^3		1.0×10^5	
Average	3.46×10^5	1.03×10^6	1.62×10^5	8.38×10^4	6.31×10^5	9.9×10^5

Perm* estimated from C_{Free} and DOC associated concentrations; Bifen. = bifenthrin, λ -Cyhal. = λ -cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos, MP= midpoint, Sed. Basin = Sediment Basin

Pesticide Distribution in Deposited Sediments

The deposited sediments from each location were separated into various size ranges and the different fractions were analyzed for pesticide concentrations (Figure 5.2). An inverse relationship between sediment size and concentration was expected. A positive relationship was found, however, between particle size and pesticide concentration for sizes greater than 53 μm , with a negative linear correlation coefficient $r^2 > 0.95$ for bifenthrin, cyhalothrin, and permethrin, and $r^2 > 0.70$ for cypermethrin and esfenvalerate. The sample size was too small to perform statistical analysis on individual chemicals. The sum of all pyrethroids showed a significant ($p = 0.0005$) concentration decrease between 1000 μm and 53 μm size fractions. The organic carbon contents (OC) in these fractions generally mimicked the changes in pesticide concentration, with the highest OC content found in the larger size fractions (>53 μm), thus reaffirming affinity

of pyrethroids for organic matter. Upon visual inspection of soil cores, it was noted that the top layers (0 – 5 cm) contained deposits of large non-decomposed plant materials and aggregated organic matter, suggesting the introduction of mulch-like plant materials likely from plant residues. Pyrethroids have been found to preferentially bind to organic matter that is at an earlier stage of decomposition compared with field sediments (12). Adsorption of λ -cyhalothrin to aquatic macrophytes has been found to be both rapid and virtually irreversible (35). It is likely that sorption to these particles occurred in the field. This observation may have serious implications for wetland management, as such plant matter are lower in density and are less prone to gravitational sedimentation. Such particles and aggregates therefore have a greater potential for downstream transport. However, the partitioning toward larger particles may reduce overall bioavailability for selective benthic organisms who feed on smaller organic rich particles (36).

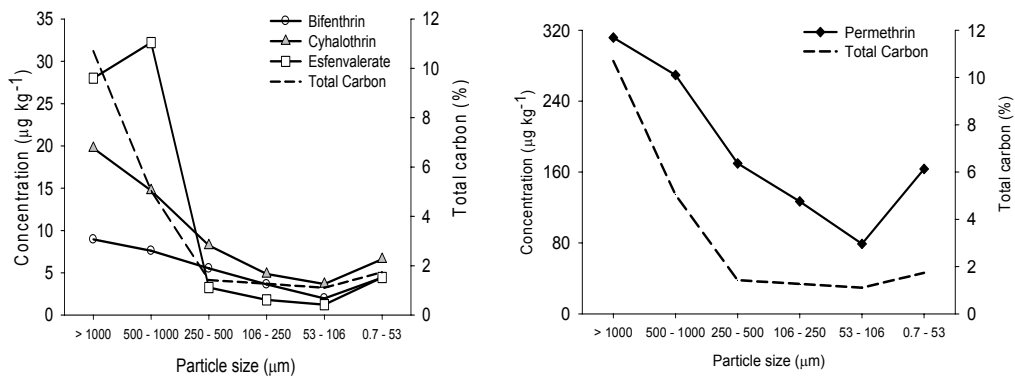


Figure 5.2. Fractionation (bulk scale) of pyrethroid concentrations ($\mu\text{g kg}^{-1}$) and total carbon as function of particle size.

Concentrations of all chemicals and organic carbon were significantly higher in the 0.7 - 53 μm fraction than the 53 - 106 μm ($p = 0.005$), indicating a reverse of the positive trend in concentrations within this range. To better understand pesticide distribution in the fractions $< 53 \mu\text{m}$, an additional fractionation experiment covering the finer scale was completed. The highest concentrations were observed in the clay fraction, with 48-72% of the total concentrations associated with the $< 2 \mu\text{m}$ particle size (Figure 5.3). The chemical concentrations were not statistically different between the sand ($> 53 \mu\text{m}$) and silt (2-53 μm) fractions, however, the clay fraction was found to be significantly higher than both the sand and silt fractions ($p = 0.0005$). This increase validated the reversal of pesticide dependence on particle size toward the end of the size range as observed in the coarse fractionation experiment, and suggested that for finer particles, OC content likely increased with decreasing particle sizes or increasing particle surface areas, resulting in a relative pesticide enrichment on fine particles. These observations are in agreement with previous observations. A linear partition relationship with organic carbon in both water and sediment phases has been noted for non-polar hydrophobic organic contaminants (HOCs) (36), and a fractionation batch experiment conducted by de Jonge et al. (2000) found prochloraz sorption to the clay and silt fractions both faster and more pronounced on a mass basis than sand particles (37).

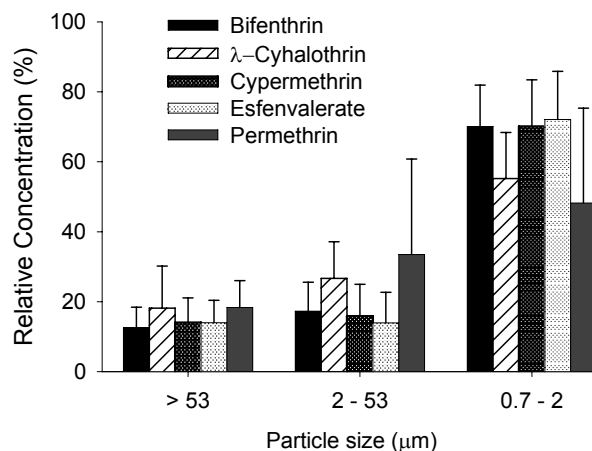


Figure 5.3. Fractionation of pyrethroid concentrations (fine scale) per sieve size.

Sand (>53 μm) made up the majority of the mass (68%) within the sediment basin. However, within the wetlands silt was the dominant size fraction, ranging from 81-84% at the inlets to 68 – 80% at the outlets. About 71% of the total pyrethroid mass was associated with the silt fraction due to the large silt deposits in the area (Table 5.5). This enrichment of pyrethroids on finer particles was similar to Gan et al. (2005), who found that the clay content of deposited sediment and pyrethroid levels increased along a transect away from the source (25).

Table 5.5. Average mass distribution (%) of pyrethroids from the finer scale fractionation experiment.

Fraction	Bifen.	λ-Cyhal.	Cyper.	Esfen.	Perm.	Average
> 53 μm	18	17	24	27	17	20
2 - 53 μm	67	80	67	63	75	71
0.7 - 2 μm	4	3	6	5	3	4
< 0.7 μm	11	1	3	4	6	5

Bifen. = bifenthrin, λ-Cyhal. = λ-cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos

In summary, pesticide association with sediment particles displayed a “V” shape trend driven by organic carbon content, with enhanced affinity for both large particles that were made of plant debris and decomposed aggregates, and very fine colloids of large surface areas and OC content. This particular pattern helps explain why sediment basins are often not effective at reducing pesticide loads, while still capable of reducing the level of suspended solid in the passing water. This finding suggests that caution must be used in predicting contaminant removal by wetlands or similar systems solely based on sedimentation estimations. The makeup of suspended particles in the runoff flow, along with contaminant distribution, should also be considered. From a management perspective, however, the removal of large masses of suspended solids by a sediment trap is essential for avoiding rapid buildup of sediments within a wetland, and the sediment in a sediment trap is also more easily cleaned and moved.

Pesticide Deposition

Sediment cores were collected in October 2008 and then February 2009 following the end of the 2008 irrigation season. The October sediment cores were taken within a month of irrigation water ceasing to flow into the wetlands and represented the depositional composition of the 2008 irrigation season. The latter date was used as a check and estimation of *in situ* dissipation. Surprisingly, as shown in Table 5.6 and Table 5.7 below, the majority of pesticide mass was retained within the sediment basin for λ -cyhalothrin (77%), cypermethrin (68%), esfenvalerate (94%), permethrin (94%), and chlorpyrifos (63%). This contrasted the finding from the 2007 irrigation season (Chapter

4) in which relatively little pesticides were retained within the sediment basin. This was likely caused by the significant difference in environmental conditions between the 2007 and 2008 irrigation seasons. The 2008 irrigation season was extremely dry, and water rations to local farmers were reduced below the 2007 levels. This resulted in average flow into the wetlands for 2008 ($0.03 \text{ m}^3 \text{ s}^{-1}$) approximately half that of the 2007 season ($0.07 \text{ m}^3 \text{ s}^{-1}$). The slower flow likely caused an increased settling of pesticide-laden particles earlier along the wetland transect. The maximum seasonal flow rate ($0.43 \text{ m}^3 \text{ s}^{-1}$) in 2007 was considerably greater than that during the 2008 season ($0.16 \text{ m}^3 \text{ s}^{-1}$). In addition, unlike 2007, the reduction due to sedimentation during the 2008 season at the midpoint of CW1 compared to the inlet was significant for bifenthrin (59%), λ -cyhalothrin (96%), cypermethrin (73%), esfenvalerate (97%), permethrin (78%), and

Table 5.6. Average sediment core concentrations ($\mu\text{g kg}^{-1}$) of pesticides in sediment samples collected from CW1 and CW2 in October 2008 (% of total concentration in parenthesis).

Location	Chemical		
	Bifenthrin	λ -Cyhalothrin	Cypermethrin
Sediment Basin	38.60 (34)	17.51 (70)	17.74 (66)
Inlet 1	9.03 (8)	3.29 (13)	0.54 (2)
Before Vegetation	50.94 (45)	2.16 (9)	6.37 (24)
After Vegetation	11.27 (10)	1.55 (6)	1.74 (6)
Midpoint	0.69 (<1)	0.11 (<1)	0.07 (<1)
Outlet 1	0.82 (<1)	0.18 (<1)	0.12 (<1)
Inlet 2	0.74 (<1)	0.17 (<1)	0.19 (<1)
Outlet 2	0.10 (<1)	0.11 (<1)	0.05 (<1)
	Esfenvalerate	Permethrin	Chlorpyrifos
Sediment Basin	11.51 (48)	230.33 (92)	9.65 (57)
Inlet 1	3.81 (16)	2.13 (<1)	2.16 (13)
Before Vegetation	6.75 (28)	8.47 (3)	1.80 (11)
After Vegetation	1.79 (7)	6.77 (3)	1.90 (11)
Midpoint	0.08 (<1)	0.21 (<1)	0.25 (1)
Outlet 1	nd (0)	nd (0)	0.21 (1)
Inlet 2	0.13 (<1)	1.16 (<1)	0.20 (1)
Outlet 2	nd (0)	nd (0)	0.82 (5)

Table 5.7. Average sediment core concentrations ($\mu\text{g kg}^{-1}$) of pesticides in sediment samples collected from CW1 and CW2 in February 2009 (% of total).

Location	Bifenthrin	λ -Cyhalothrin	Cypermethrin
Sediment Basin	2.15 (13)	2.11 (58)	2.09 (38)
Inlet 1	6.15 (37)	1.11 (31)	0.67 (12)
Before Vegetation	4.06 (24)	nd (0)	1.36 (25)
After Vegetation	2.13 (13)	nd (0)	0.16 (3)
Midpoint	0.40 (2)	nd (0)	0.03 (<1)
Outlet 1	0.34 (2)	nd (0)	0.03 (<1)
Inlet 2	1.56 (9)	0.39 (11)	1.14 (21)
Outlet 2	0.02 (<1)	nd (0)	0.02 (<1)
	Esfenvalerate	Permethrin	Chlorpyrifos
Sediment Basin	0.95 (26)	25.83 (68)	0.78 (13)
Inlet 1	1.89 (52)	5.38 (14)	2.75 (46)
Before Vegetation	0.48 (13)	1.33 (4)	0.32 (5)
After Vegetation	0.12 (3)	0.54 (1)	0.17 (3)
Midpoint	0.03 (<1)	0.08 (<1)	0.06 (1)
Outlet 1	nd (0)	0.07 (<1)	0.08 (1)
Inlet 2	0.20 (6)	4.21 (11)	1.38 (23)
Outlet 2	nd (0)	0.52 (1)	0.44 (7)

chlorpyrifos (96%). This observation suggested that efficacy of a given mechanism (e.g., sedimentation) in removing contaminants greatly depends on the prevalent flow conditions that are influenced by other factors such as climate conditions and agricultural practices, and may not be generalized.

Vertical distribution patterns of a pesticide in a sediment core provide a snapshot of pesticide deposition history as well as leaching potential. In the high depositional areas such as the sediment basin and wetland inlets, there was a more diverse vertical dispersion of concentrations (Figure 5.4). Along the flow path in CW1, after the inlet, less than 3% of the deposited pyrethroids was found in the >15 cm segment, while <10%

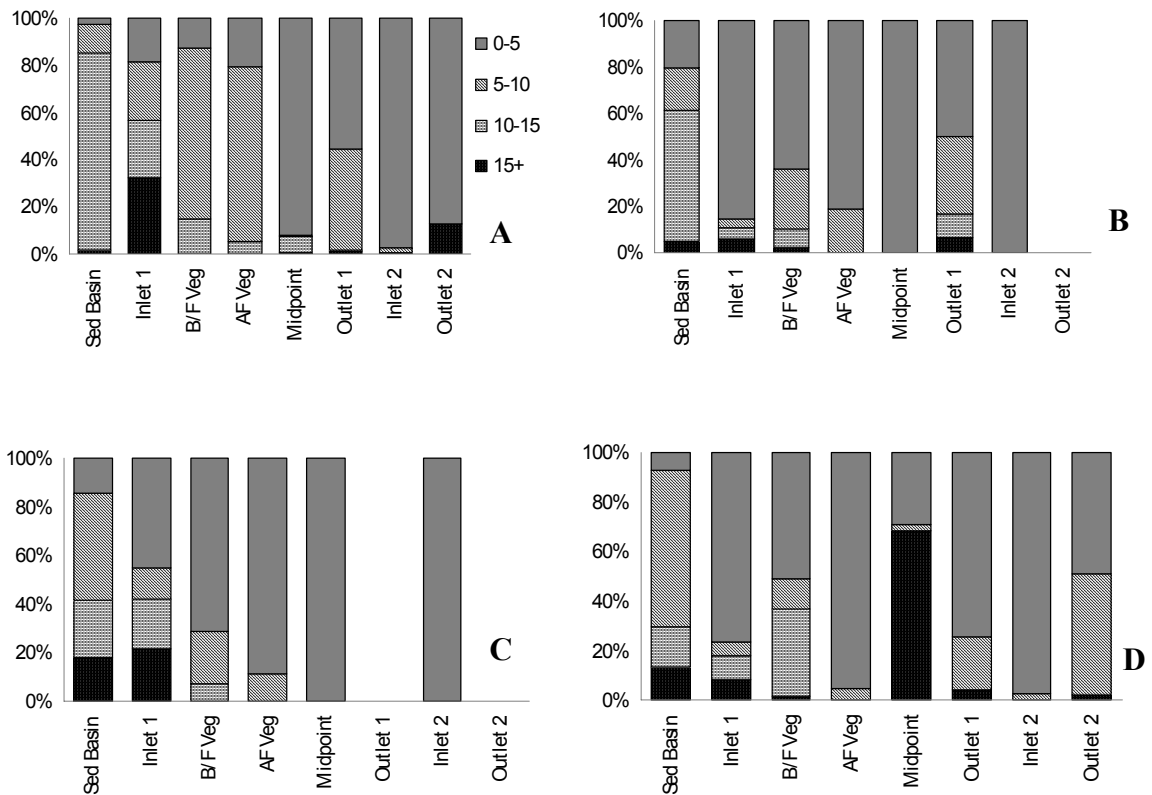


Figure 5.4. Vertical distribution (% of total) of pesticides in sediment cores at different locations. (A) bifenthrin, (B) cyhalothrin, (C) permethrin, and (D) chlorpyrifos.

was present in the 10 – 15 cm range. In comparison, 18% of the total chlorpyrifos was detected at depths >15 cm, indicating a relatively greater potential of chlorpyrifos for downward leaching.

Table 5.8. Mass distribution (μg , (% of total)) of pesticides as a function of depth (cm) in sediment cores taken in October 2008.

Depth	Bifen.	λ-Cyhal.	Cyperm.	Esfen.	Perm.	Chlor.
Ave 0-5	1.3 (46)	0.7 (71)	1.1 (61)	0.6 (58)	4.2 (64)	0.4 (55)
Ave 5-10	4.7 (26)	0.3 (10)	0.8 (24)	0.5 (14)	8.6 (13)	0.6 (14)
Ave 10-15	4.3 (17)	1.0 (11)	0.5 (5)	0.9 (16)	5.7 (8)	0.3 (11)
Ave 15+	0.7 (11)	0.2 (8)	0.3 (10)	0.3 (11)	8.7 (15)	0.3 (20)

Bifen. = bifenthrin, λ -Cyhal. = λ -cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos

One important parameter for wetland design is the flow length necessary to achieve the desired removal. For the purpose of this study the effective length ($L_{1/2}$) was defined as the distance necessary to achieve 50% reduction in pesticide concentrations. To estimate pesticide depositional rate within the test systems, pesticide concentrations within the 0 – 5 cm layer along the transect of CW1 were plotted against distance from source (Figure 5.5). Sample location distances were estimated using Google Earth. The 0 – 5 cm layer represented the most recently deposited pesticide residues. The distances relative to the sediment basin (0 m) were 140, 225, 240, 320, and 600 m for wetland inlet, before bulrush, after bulrush, midpoint, and the outlet, respectively. The pesticide concentrations along the flow transect within CW1 is presented in Figure 5.4. A first order model was used to fit the data, from which the pesticide deposition rate (s) ($\mu\text{g kg}^{-1} \text{m}^{-1}$) was estimated. Due to heavy deposits of plant material within the top layer of the

inlet, the data for inlet was discarded from $L_{1/2}$ estimations. The estimated half-distances ($L_{1/2}$) are presented in Table 5.9.

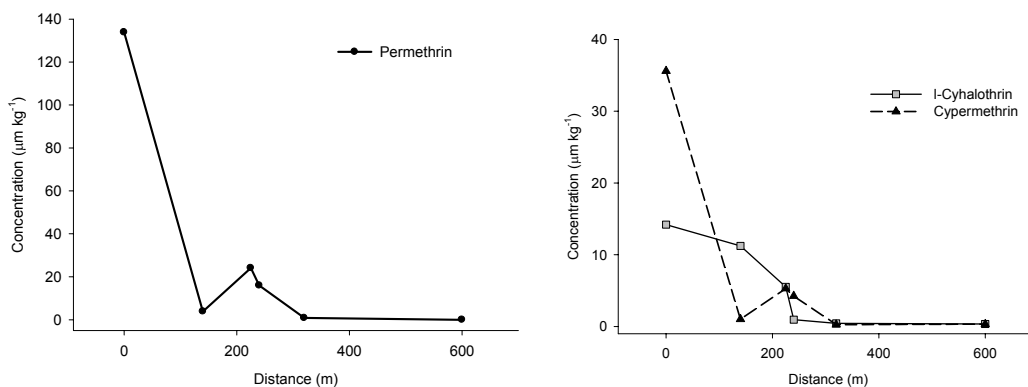


Figure 5.5. Concentrations ($\mu\text{g kg}^{-1}$) from the 0 – 5 cm depth along the transect of CW1.

Chemical concentrations fell below 50% within 100 m of wetland length for λ -cyhalothrin (100 m), cypermethrin (76 m), and permethrin (80 m). It must be stressed that these estimates are valid only under the prevalent environmental conditions, with an average flow rate of $0.03 \text{ m}^3\text{s}^{-1}$. A comparison to high flow conditions ($0.07 \text{ m}^3\text{s}^{-1}$) was made using the average seasonal pesticide concentrations in the freshly deposited sediment at the four sampling locations along the transect during the 2007 irrigation season. As previously noted, the concentrations for bifenthrin and esfenvalerate were higher within the wetland compared to sediment basin and inlet concentrations, therefore effective length calculation was not possible for these compounds. As expected, the estimated effective lengths increased under high flow conditions for λ -cyhalothrin (267 m, $r^2 = 0.54$), cypermethrin (100 m, $r^2 = 0.97$), and permethrin (178 m, $r^2 = 0.93$).

Table 5.9. Estimated effective wetland lengths ($L_{1/2}$, m) to achieve 50% reductions in pesticide concentrations.

Chemical	2007		2008	
	$L_{1/2}$	r^2	$L_{1/2}$	r^2
λ -Cyhalothrin	267	0.54	100	0.92
Cypermethrin	100	0.97	76	1.0
Permethrin	178	0.93	80	0.99

Pesticide Degradation in Wetland Sediments

Pesticide persistence in wetland sediments was evaluated under different conditions to understand pesticide fate after their accumulation on the wetland floor. The estimated half lives ($T_{1/2}$) from the different treatments are presented in Table 5.10, with the initial concentrations presented in Table 5.12. The sediment samples were not

Table 5.10. Average half-life ($T_{1/2}$ [d]) of selected pyrethroid and organophosphate insecticides in sediments from constructed wetlands in the Central Valley, CA, under anaerobic conditions.

	Bifen.		λ -Cyhal.		Cyper.		Esfen.		Perm.		Chlor.	
	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
2007 Sediment												
Ditch	1733	0.62	178	0.96	198	0.88	315	0.76	154	0.95	nd	
W2	S		67	0.95	21	0.75	116	0.83	347	0.90	nd	
W2 ^a	S		63	0.89	102	0.48	65	0.72	495	0.61	nd	
W3	S		nd		154	0.72	nd		330	0.90	nd	
2008 Sediment												
Ditch	S		169	0.96	139	0.93	151	0.68	239	0.83	144	0.90
W2	S		210	0.67	182	0.47	182	0.50	693	0.56	68	0.96
Ave.	S		137±68		133±64		166±94		376±193		106 ±54	

S = Stable, W2^a = CW1 microbial inhibited soil, Bifen. = bifenthrin, λ -Cyhal. = λ -cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos

laboratory spiked, and thus represented environmental concentrations that had undergone some degree of aging. Even with very low initial concentrations, good regression of the dissipation trends was derived for several chemicals. The average $T_{1/2}$ values in all

sediments under anaerobic conditions were < 1 yr for λ -cyhalothrin (137 ± 68 d), cypermethrin (133 ± 64 d), esfenvalerate (166 ± 94 d), and the organophosphate chlorpyrifos (106 ± 54 d). Permethrin was found to degrade at a slightly slower rate (376 ± 193 d) (Figure 5.6).

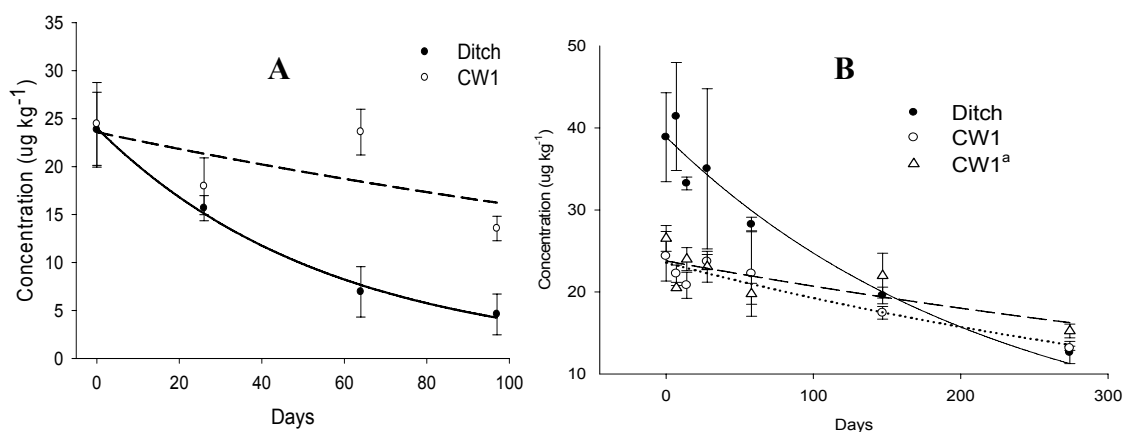


Figure 5.6. Dissipation of permethrin in sediment from the irrigation ditch, constructed wetland 1 (CW1) and the sterilized sediment (CW1^a) under (A) *in situ* aerobic conditions and (B) laboratory anaerobic conditions.

A meaningful degradation rate constant could not be determined for the wetland sediment under *in situ* conditions for most of the chemicals due a lack of appreciable dissipation, while detectable degradation occurred for cyhalothrin and permethrin in the ditch sediment (Table 5.11). The wetland sediment had a higher organic carbon content (1.57%) than the ditch sediment (0.4%) (Table 5.12), and it is likely that the difference in sorption of pyrethroids to the soil organic matter contributed to the different persistence for some of the pyrethroids. Comparisons under the two redox conditions were variable. However, the moderate to long persistence as observed for pyrethroids under both

anaerobic and in situ aerobic conditions suggests a possibility for accumulation of pyrethroids in the wetland.

Table 5.11. Average half-life ($T_{1/2}$ [d]) of selected pyrethroid and organophosphate insecticides in sediment from constructed wetlands in the Central Valley, CA, under *in situ* aerobic conditions.

	Bifen.		λ-Cyhal.		Cyper.		Esfen.		Perm.		Chlor.	
	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2	$t_{1/2}$	r^2
Ditch	S		122	0.91	S		S		39	1.00	58	0.73
W2	S		S		S		S		178	0.41	nd	
Ave.									109		58	

S = Stable, Bifen. = bifenthrin, λ-Cyhal. = λ-cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos

Chapman et al. (1981) found that five pyrethroids degraded much slower in a sterilized soil, indicating the importance of microbial enhancement of dissipation (28). In a previous study biodegradation of bifenthrin and permethrin increased dramatically in the aqueous phase in the presence of pyrethroid degrading bacteria (18). In this study, microbial degradation appeared to have the most significant effect for cypermethrin and permethrin, for which the half lives increased by 81 and 148 d, respectively after sterilization. Esfenvalerate persisted longer in the presence of microbes, however this is most likely a result of variance due to the low initial concentrations (< 1 ppb). Also, microbial activity is often hindered by the high affinity of HOCs for sediment, a concept which is amplified with increased contact time (18, 20).

Comparisons between ditch and wetland sediments were inconclusive. While cyhalothrin, cypermethrin, and esfenvalerate degraded faster in ditch sediments in the

aged samples, the reverse was true for the second study. However, permethrin degraded slower in wetland sediment (347 – 693 d) than ditch sediment (154 – 239 d) in both experiments. Chlorpyrifos concentrations were below detection limits in the aged sediments, but degraded more rapidly in the wetland sediments in the 2008 sediments.

There are most likely competing forces in the degradation process. Although the microbial populations were not evaluated in this study, it is reasonable to expect that they were more prolific in the organic rich wetland sediments than the irrigation ditch.

Table 5.12. Initial concentrations ($\mu\text{g kg}^{-1}$) of pesticides and organic carbon content (%) in field contaminated sediments used for the degradation experiments.

	OC	Bifen.	λ-Cyhal.	Cyper.	Esfen.	Perm.	Chlor.
1st Anaerobic Sediments							
Ditch	0.38	0.72	4.43	1.45	3.22	38.86	nd
W2	1.71	5.77	2.80	4.56	0.38	24.36	nd
W2 ^a	1.70	6.11	2.56	4.07	0.36	26.52	nd
W3	2.92	0.97	nd	0.40	nd	1.70	nd
2nd Anaerobic Sediments							
Ditch	0.72	2.0	4.1	8.9	1.1	101.1	2.0
W2	1.19	3.7	1.1	2.6	1.2	12.5	3.1
<i>In situ</i> (aerobic) Sediments							
Ditch	0.40	1.78	1.29	1.25	1.86	23.84	0.55
W2	1.57	4.82	1.02	9.60	0.83	24.44	0.40
W3	2.26	1.04	nd	0.10	0.27	1.55	nd

W2^a = W2 sediment inhibited, Anaer. = anaerobic conditions, OC = Organic carbon, Bifen. = bifenthrin, λ -Cyhal. = λ -cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos; nd = not detected

However, the higher binding capacity of the organic matter within the wetlands may have reduced the availability of pyrethroids to microbial action (25).

Bifenthrin was found to be stable under both anaerobic and aerobic conditions and therefore deserves special attention. A degradation rate was not attainable in the

field, and estimated half lives were greater than 6 yr under anaerobic conditions ($r^2 < 0.6$). This is similar to results from Baskaran et al. (1999) who found bifenthrin to be stable ($t_{1/2} = 1332 - 1410$ d) in three sandy soils with similar organic carbon contents (0.1 – 1.2 %) as our sediments (29), but differs from findings by Lee et al. (2004) who found bifenthrin to degrade more rapidly (36 – 163 d) in a field sediment (18). Gan et al. (2005) found bifenthrin to be stable under aerobic conditions ($T_{1/2} > 1$ yr), with moderate to long persistence (251 – 498 d) under anaerobic conditions (25). Bifenthrin has been found to be stable to abiotic hydrolysis at pH 5, 7, and 9, suggesting that that primary degradation pathway for bifenthrin may differ from other similar chemicals in that ester cleavage is not the primary route of dissipation (30, 31). Our findings display the potential for bifenthrin to persist within the CWs under wet and dry season conditions.

In this study we compared four treatments: ditch vs. wetland sediments, aerobic vs. anaerobic conditions, and the effects of sediment aging and microbial populations on the rates of degradation. Overall, the results were variable among different compounds and treatments. Several researchers have reported that pesticide dissipation behavior may follow a two-compartment model, with an initial quick dissipation followed by a slower period in which pesticides may persist at low levels for long periods (18, 29, 38). Our assumption of first-order kinetics may be an over-simplification, especially for chemicals with low initial concentrations (Table 5.12). For example, the initial concentrations of permethrin were typically an order of magnitude greater than other chemicals. Permethrin dissipation rates were consistent with organic carbon content and microbial activity in each sediment, indicating that a first order model adequately described the

degradation. Although a first-order model resulted in good correlations for cypermethrin, esfenvalerate, and λ -cyhalothrin, the variability in the degradation rates between treatments suggests that the model did not adequately describe dissipation for these chemicals at the field concentrations. Also, pesticide sorption depends not only on the quantity, but also the quality of the organic matter (12, 40). For instance, pyrethroids partition more favorably to organic matter high in humic acids than those containing fulvic acids (21). This is related to the source and age of decomposition of the organic material. The contributing agricultural area surrounding the wetlands in this study included a variety of crops that were irrigated and then harvested at various times throughout the season. Differences in the nature of the organic carbon has been noted between different land-use practices with similar soil structural properties (39). The source, and therefore the composition of organic matter entering the system would likely change throughout and between seasons which could have affected the sorption capacity of the pesticides.

Although variability existed between conditions, by pooling the six treatments together led to confidence of average pesticide dissipation behavior within the test system. Most of the pyrethroids tended to degrade within 166 d under anaerobic conditions, with permethrin appearing more stable. The irrigation season typically lasts from approximately April through September (6 months). Depending on when the pesticides are deposited, transformation during the irrigation season is possible. However, due to the lack of appreciable degradation during the dry season, there is a potential for persistence between seasons, which could lead to accumulation over long

time periods. This is especially true for bifenthrin which appears stable under all field conditions. Therefore, the long-term implications of pesticides accumulated within such wetlands must be understood before this practice is promoted for wide adoption.

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Chapter 6

Evaluation of Seasonal and System Variations

ABSTRACT

A second-year follow-up study was undertaken to increase the scope of evaluation on the wetland performance observed during the previous irrigation season. Two constructed wetlands with larger volumes and flow rates were monitored in addition to the two previously monitored wetlands. All four wetlands were effective in reducing both pyrethroid and organophosphate concentrations in water samples (12 – 100%) within the system. A noted increase in chlorpyrifos concentrations at the outlet of one wetland was likely attributable to spray drift or direct field runoff. While a striking decrease in concentrations entering the wetland were noted for most chemicals in the 2008 season than the 2007 season, chlorpyrifos and esfenvalerate were detected at higher concentrations in 2008, indicating a shift in pesticide usage from local growers. The sediment basin was ineffective at reducing pesticide concentrations in water samples, although a greater deposition of sediments was observed at the beginning of the system. A significant increase in removal efficiency in the first section of CW1 during the second monitoring season was attributed to the decrease in flow and an increase in vegetation biomass between seasons. Observations before and after a strand of bulrush in CW1 did not show a noted decrease in pesticide concentrations in the water samples, however deposited sediments before the strand indicate an area of higher sedimentation. In addition, there was no notable vertical transport of pyrethroids, but chlorpyrifos was

observed down to the 100 cm depth, with a 90% loss of initial concentration within 56 cm.

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INTRODUCTION

Observations of constructed wetland performance reported in Chapter 4 prompted the expansion of the scope of work by considering year-to-year variations and including more wetland systems. A second year of monitoring at the CWs monitored in 2007 was conducted during the 2008 irrigation season, as well as the inclusion of two separate CWs with different environmental characteristics. Although sediment basins are an integral and necessary component of wetland design, they have been reported as being ineffective at removing pesticides in the water column (1). This was also observed in our system during the 2007 season. To further test this assumption, the performance of sediment basins was re-evaluated in 2008 under different flow conditions.

Vegetation plays an important role in pesticide removal in wetlands (2, 3). Vegetation can directly sequester a pesticide through root uptake, or indirectly influence transport by providing sorption sites and increasing sedimentation of chemicals bound to suspended particles by decreasing flow velocities (4 -6). The direct measurement of the role of vegetation in pesticide removal was not considered in the previous season, but was investigated in the second year study.

Vertical transport of pesticides in a wetland is another important parameter of consideration, as significant leaching may lead to the contamination of local aquifers. Even pesticides with high soil sorption potentials have been shown to move vertically. Permethrin has been found to diffuse in pore water to a depth of 30 mm (7). Vinten et al. (1983) found that 18% of DDT previously sorbed to suspended solids leached greater than 9 cm in a sandy loam (8). The preliminary findings of vertical transport of

pesticides discussed in Chapter 4 were inconclusive, and a more detailed evaluation was warranted.

The primary objectives of this study were to: 1) determine if wetland removal efficiencies remained consistent from year to year, 2) compare the efficiencies of the same CWs under different flow conditions, 3) evaluate the role of a common wetland vegetation species in pesticide removal, and 4) further evaluate the potential vertical transport of pesticides within CWs.

MATERIALS AND METHODS

The Study Area

Constructed wetlands 1 (CW1) and 2 (CW2) are the same systems as described in Chapter 4 for the 2007 study. Wetlands 3 (CW3) and 4 (CW4) were chosen as comparison wetlands that received larger volumes of tailwater from larger contributing irrigation areas. All wetlands were adjacent to the San Joaquin River with outlets leading to the river downstream. CW1 and CW2 occupied a relatively small area (2.5 and 1.5 ha, respectively) compared to CW3 (7.3 ha) and CW4 (150 ha). The former also drained a comparatively smaller area (~300 ha.), while the latter had a larger input potential (~1500 ha and 2000 ha respectively). The seasonal average flow (March 28 – Sept 1, 2008) into CW1 was $0.031 \text{ m}^3\text{s}^{-1}$ and CW2 was $0.015 \text{ m}^3\text{s}^{-1}$. CW3 was monitored between March 28 – July 14th, 2008 and had an average flow of $0.11 \text{ m}^3\text{s}^{-1}$. A weir board was not present at the inlet to CW4, but based on velocity and channel width measurements the average

seasonal inflow was estimated to be about $0.3 \text{ m}^3\text{s}^{-1}$. The estimated total volumes flowing into the wetlands over the 153 d irrigation period were $4.1 \times 10^5 \text{ m}^3$, $2.0 \times 10^5 \text{ m}^3$, $1.5 \times 10^6 \text{ m}^3$ and $4.0 \times 10^6 \text{ m}^3$ for CW1, CW2, CW3 and CW4, respectively. Water quality parameters were measured from samples collected at the inlet and outlets of each wetland (Table 6.3).

Sample Collection and Analysis

Water samples were collected biweekly in 1 L amber bottles throughout the 2008 irrigation season at the inlet and outlets of CW1, CW2, CW3, and CW4. In addition, water samples were collected within the sediment basin on four dates, and at the midpoint of CW1 on 3 dates. A strand of bulrush (*Schoenoplectus californicus*) within CW1 was chosen to directly evaluate the effect of emergent vegetation on pesticide concentrations in the water column. The strand was chosen due to a lack other species and fairly consistent biomass (~16 m long, 533 – 632 g m²). Water samples were collected on three dates directly before the strand (BV) and after the strand (AV) in the flow path. To evaluate the potential vertical transport of pesticides, samples were collected from two piezometer nests of depths 10 cm, 50 cm, and 100 cm using a handheld jackrabbit pump into 1 L amber bottles. Wells were purged once prior to sample collection. Nest one (N1) was located approximately 110 m downstream from the inlet of CW1, and nest two (N2) was located at the midpoint of CW1. Sediment samples were collected at the inlets and outlets of CW1 and CW2. In addition, sediment samples were collected at the midpoint and outlet of CW1 on three dates in the passive samplers as described in

Chapter 4. Only one sediment sample was collected at the inlet of CW1 due to damage to the sampler.

The methods used for extracting and analyzing water and sediment samples were described in detail in Chapter 4. For most samples the lowest reported value was 0.5 ng L⁻¹, however, values were reported for some samples below reporting limit when a positive detection was confirmed. For the purposes of calculating seasonal means, all non-detects were assigned a zero value. Due to the large number of non-detects throughout the 2008 season, statistical evaluation of mean pesticide concentrations were conducted by pooling all chemical data for each treatment (i.e., inlet vs. outlet). The pooled data was then subjected to the nonparametric Wilcoxon Rank Sum test for determining differences in mean concentrations.

RESULTS AND DISCUSSION

Wetland Efficacies

Pesticide whole water concentrations and reduction efficiencies (% R) for the constructed wetlands (CW1 – CW4) are presented in Table 6.1. Comparing the data for CW1 and CW2, there was a general decrease in concentrations from the 2007 season to the 2008 irrigation season (Tables 4.2 and Table 6.1). There was a decrease in average water concentrations entering the system between the 2007 and 2008 seasons for bifenthrin (63%), λ -cyhalothrin (90%), cypermethrin (72%), and permethrin (84%). Interestingly the average inlet concentrations for both chlorpyrifos and esfenvalerate were

more than an order of magnitude greater during the 2008 season. This could indicate a shift in pesticide use patterns between seasons and changes in the needs or available products for pest control. Unfortunately, the 2008 pesticide usage data was not available at the time of data analysis so a detailed analysis was not feasible. Also, as discussed in Chapter 5, local growers were subject to water restrictions from the 2007 allowances, as apparent by the decrease (45%) in the average seasonal flow. Flow could also explain a decrease in pyrethroid concentrations entering the wetlands, as pesticide-laden sediments might not be transported off fields under low flow conditions. Retention of suspended solids has been shown to decrease with increasing flow rates (9). Unlike the previous season, inlet concentrations for all pesticides had a positive correlation with flow (Figure 6.1).

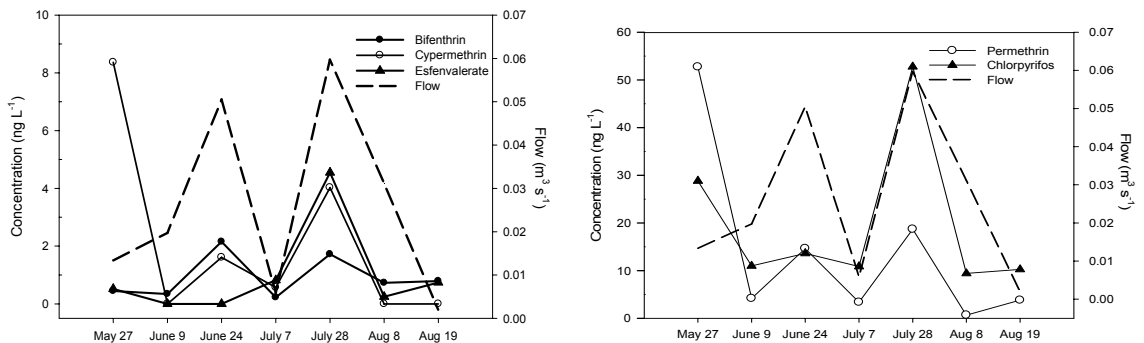


Figure 6.1. Pesticide concentrations (ng L⁻¹) and flow data (m³ s⁻¹) in the inlet of constructed wetland 1 (CW1) during the 2008 irrigation season.

All the wetlands were effective at reducing λ -cyhalothrin (60 – 100%), cypermethrin (100%), esfenvalerate (83 – 100%), and permethrin (80 – 100%). Bifenthrin was more variable, with %R ranging from 12 – 60%. As bifenthrin has been

noted as having a greater potential for persistence in our systems (Chapter 5), the low bifenthrin concentration (near detection limit) observed at the outlets could be re-suspended particles of residual pesticides from previous seasons. Overall, pesticide concentrations were statistically higher at the inlet than at the outlet for CW1, CW2 and CW3 ($p \leq 0.0005$). The inlet concentrations were not significantly higher within CW4 due to the large number of non-detects. The reductions in pyrethroid concentrations were in good agreement with the %R estimates for the 2007 season, indicating that overall the systems were efficient at removing pyrethroids from irrigation water under two different flow regimes. The similarity in reductions between wetlands further indicated the potential of CWs as a best management practice for reducing pesticide loads into the San Joaquin River.

The removal results for chlorpyrifos were somewhat inconsistent. While the removal of chlorpyrifos was fairly consistent with the CW1 (75%), CW3 (51%) and CW4 (49%) systems throughout the season, CW2 had an overall increase in concentrations (-73%) at the outlet. The magnitude of the increase was dominated by one date in which the concentration of chlorpyrifos was 8 times higher at the outlet compared with the inlet. However, the reduction in concentrations were only greater than 50% on one sampling date during the season. This is surprising since the average flow was slower in CW2 ($0.015 \text{ m}^3 \text{ s}^{-1}$) compared with CW1 ($0.031 \text{ m}^3 \text{ s}^{-1}$). The discrepancy in chlorpyrifos reductions was further validated by analysis of the deposited sediments (Table 6.2). Only one sediment sample was collected at the inlet of CW1, therefore midpoint sediment concentrations were used to evaluate the overall CW1 wetland efficiency. Sedimentation

was effective at retaining pyrethroids (87 – 100%) in both wetlands. While there was an 85% reduction in sediment chlorpyrifos concentrations within CW1, a much smaller reduction was observed within CW2 (-14%). Since both wetlands shared the same inlet source water, it is likely that a secondary source such as spray drift or runoff from adjacent fields contributed chlorpyrifos loading directly into CW2. Previous studies have found spray drift capable of transporting pesticides more than 500 m from the source (10).

Table 6.1. Seasonal pesticide concentrations (ng L⁻¹) and ranges in water samples collected within constructed wetlands 1 – 4 (CW1 – CW4) during 2008 with percent reduction (R%) in concentration from inlet to outlet (C_{Out}/C_{In}).

Chemical	W1 In	W1 Out	W1 %R
Bifenthrin	0.8 (nd – 2.2)	nd	100
λ-Cyhalothrin	0.2 (nd – 0.6)	nd	100
Cypermethrin	2.1 (nd – 8.4)	0.1 (nd – 0.8)	60
Esfenvalerate	0.9 (nd – 4.5)	0.1 (nd – 1.0)	100
Permethrin	12.3 (0.7 – 52.7)	0.1 (nd – 0.8)	97
Chlorpyrifos	51.0 (1.2 – 214.5)	2.5 (nd – 7.1)	75
Diazinon	nd	nd	-
Chemical	W2 In	W2 Out	W2 %R
Bifenthrin	0.8 (nd – 3.4)	0.4 (nd – 1.6)	25
λ-Cyhalothrin	nd	nd	-
Cypermethrin	8.7 (nd – 43.1)	nd	100
Esfenvalerate	0.3 (nd – 1.7)	nd	100
Permethrin	13.9 (1.5 – 39.6)	0.6 (nd – 3.3)	80
Chlorpyrifos	72.4 (2.5 – 222.2)	64.7 (1.78 – 428.6)	-73
Diazinon	nd	nd	-
Chemical	W3 In	W3 Out	W3 % R
Bifenthrin	8.4 (nd – 46.9)	0.8 (nd – 2.0)	83
λ-Cyhalothrin	6.6 (nd – 43.2)	2.5 (nd – 15.6)	71
Cypermethrin	nd	nd	-
Esfenvalerate	0.6 (nd – 2.0)	nd	100
Permethrin	0.1 (nd – 0.6)	nd	100
Chlorpyrifos	19.9 (1.1 – 45.7)	8.6 (0.8 – 26.8)	51
Diazinon	0.1 (nd -0.7)	0.1 (nd – 0.8)	-19
Chemical	W4 In	W4 Out	W4 % R
Bifenthrin	0.4 (nd – 1.2)	nd	100
λ-Cyhalothrin	6.5 (nd – 37.2)	2.9 (nd – 20.4)	100
Cypermethrin	nd	nd	-
Esfenvalerate	0.1 (nd – 0.5)	nd	100
Permethrin	nd	nd	-
Chlorpyrifos	1.9 (nd – 7.4)	0.6 (nd – 1.1)	52
Diazinon	0.1 (nd – 0.6)	0.1 (nd – 0.6)	7

Table 6.2. Seasonal pesticide concentrations ($\mu\text{g kg}^{-1}$) and ranges in sediment samples collected within constructed wetlands 1 and 2 (CW1 and CW2) during 2008 with percent reduction (%R) in concentration from inlet to outlet ($C_{\text{Out}}/C_{\text{In}}$).

Chemical	CW1 In	CW1 Midpoint	CW1 Outlet	W1 %R
Bifenthrin	4.5	8.0 (2.5 – 13.8)	1.0 (0.8 – 1.4)	87
λ -Cyhalothrin	4.5	2.6 (0.4 – 5.1)	nd	100
Cypermethrin	13.3	1.9 (1.2 – 3.1)	0.1 (nd – 0.2)	97
Esfenvalerate	5.6	4.2 (0.3 – 8.5)	nd	100
Permethrin	198.8	31.5 (10.7 – 71.5)	0.7 (0.5 – 1.0)	97
Chlorpyrifos	42.2	18.7 (11.8 – 29.2)	2.6 (2.3 – 2.8)	85
Chemical	CW2 Inlet		CW2 Outlet	W2 %R
Bifenthrin	9.7 (4.8 – 15.8)		0.4 (0.3 – 0.6)	95
λ -Cyhalothrin	4.6 (3.2 – 7.2)		0.1 (nd – 0.3)	96
Cypermethrin	15.8 (8.2 – 25.5)		1.4 (0.4 – 3.1)	93
Esfenvalerate	11.2 (3.2 – 22.1)		nd	100
Permethrin	112.1 (37.7 – 221.0)		9.3 (0.6 – 26.8)	95
Chlorpyrifos	19.8 (7.9 – 41.6)		29.8 (5.8 – 75.6)	-14

^aCW1 Inlet only collected on 1 date, nd = not detected

Table 6.3. Seasonal water quality measurements taken from constructed wetlands 1 – 4 (CW1 – CW4).

Wetland	pH	TSS (mg L^{-1})		DOC (mg L^{-1})		Chlorophyll a ($\mu\text{g L}^{-1}$)	
		Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
CW1	8.50	165.01*	40.94	4.24	5.86	57.81	41.46
CW2	8.28	31.95	18.41	3.74	5.59	52.82	43.82
CW3	7.91	283.06	77.51	6.20	5.48	3.85	89.98
CW4	7.97	368.53	56.90	4.27	7.10	65.03	66.21

* Collected within the sediment basin, CW = constructed wetland

Sediment Basin

Water samples were collected within the sediment basin on four dates throughout the 2008 season (Table 6.4). Similar to the 2007 season, whole water concentrations indicated that the sediment basin was not effective at retaining pesticides from the tailwater. The difference in concentrations between the sediment basin and inlets were not significant however. Also, the average seasonal water concentrations were higher in the sediment basin than at the inlet for bifenthrin (28%), cyhalothrin (86%), esfenvalerate (83%), permethrin (60%), and chlorpyrifos (13%) (Tables 6.1 and 6.4). Cypermethrin was the only chemical with seasonal concentrations higher at the inlets (-62%). The negative %R values might be an artifact of the very low input concentrations and the relatively smaller residence time within the basin. A positive correlation was noted for permethrin concentrations when plotted against removal efficiency ($r^2 = 0.92$) and flow ($r^2 = 0.97$) (Figure 6.2). However, this relationship broke down at lower input concentrations, indicating chemicals with lower input concentrations were subject to higher variability in wetland response. The positive relationship between flow and %R indicated that heavier particles laden with permethrin were transported downstream during high flows and subsequently deposited within the sediment basin. This hypothesis was supported by the sediment core data, which found higher concentrations in the top 5 cm of the sediment basin compared to the inlets for λ -cyhalothrin (21%), cypermethrin (97%), and permethrin (97%).

Table 6.4. Seasonal pesticide concentrations (ng L^{-1}) and ranges in water samples collected within the sediment basin during 2008 with percent reduction (R%) in concentration from sediment basin to wetland inlets ($C_{\text{In}}/C_{\text{SB}}$).

Sample	2007		2008	
	Concentration	%R	Concentration	%R
Bifenthrin	3.1 (nd – 7.9)	6	1.1 (nd – 3.4)	-70
λ -Cyhalothrin	6.6 (nd – 17.1)	-34	0.7 (nd – 1.5)	81
Cypermethrin	12.0 (nd – 43.4)	2	3.3 (nd – 6.7)	-173
Esfenvalerate	0.4 (nd – 1.4)	15	3.7 (nd – 14.8)	-5
Permethrin	203.4 (29.5 – 469.6)	17	32.5 (1.2 – 61.7)	-18
Chlorpyrifos	5.5 (5.1 – 5.9)	12	71.2 (5.5 – 213.6)	-27
Diazinon	nd	-	nd	-

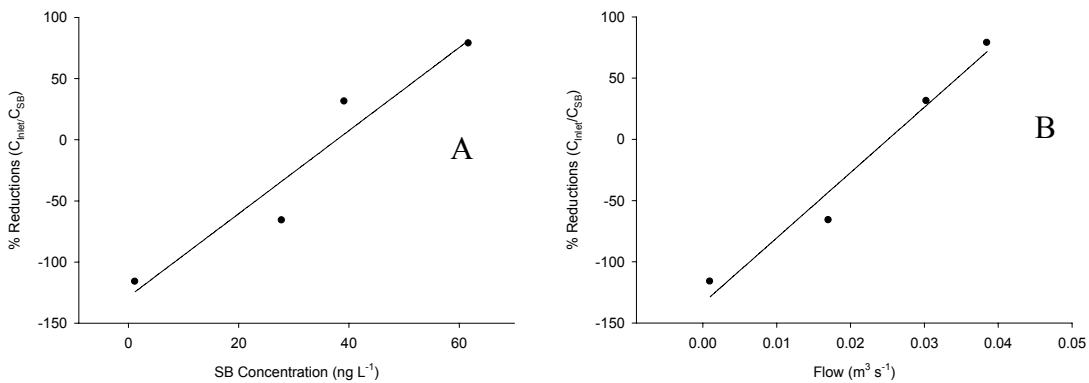


Figure 6.2. Reductions in permethrin concentrations within the sediment basin (SB) plotted against (A) input concentrations (ng L^{-1}) and (B) flow ($\text{m}^3 \text{s}^{-1}$).

Wetland Midpoint

Water samples were taken at the midpoint of CW1 on three dates during the 2008 irrigation season to evaluate changes in pesticide removal efficiency within the front section of CW1 between seasons. There was a marked increase in %R at the midpoint compared with the 2007 season (Table 6.5), with CW1 inlet concentrations significantly

($p \leq 0.005$) higher than at the midpoint. Surface (0 – 5 cm) sediment cores taken at the end of the irrigation season confirmed that reductions in deposited pesticides between wetland inlet and midpoint increased for bifenthrin by 47%, cyhalothrin (24%), cypermethrin (79%), esfenvalerate (100%), and permethrin (17%) for the 2008 season (Figure 5.5). This marked change in reduction was most likely due to variations in environmental conditions. As noted previously, the flow was considerably slower for the 2008 season, facilitating settling of suspended particles. Although not quantified, a visual survey suggested that vegetation density increased dramatically within this section between the 2007 and 2008 seasons.

Table 6.5. Seasonal pesticide concentrations (ng L^{-1}) and ranges in water samples collected at the midpoint during 2008 with percent reduction (R%) in concentration from the inlet to midpoint ($C_{\text{MP}}/C_{\text{In}}$).

Sample	2007		2008	
	Concentration	%R	Concentration	%R
Bifenthrin	1.6 (nd – 6.8)	4	0.6 (0.5 – 0.8)	50
λ -Cyhalothrin	1.0 (nd – 3.5)	0.36	nd	100
Cypermethrin	14.2 (1.3 – 57.2)	18	0.7 (nd – 1.4)	48
Esfenvalerate	1.2 (nd – 7.8)	-3	0.2 (nd – 0.7)	92
Permethrin	36.9 (14.1 – 56.8)	25	4.5 (nd – 11.6)	70
Chlorpyrifos	2.7 (1.2 – 4.3)	15	37.8 (1.3 – 84.1)	36
Diazinon	11.0 (7.2 – 17.9)	-12	nd	-

Effect of Vegetation

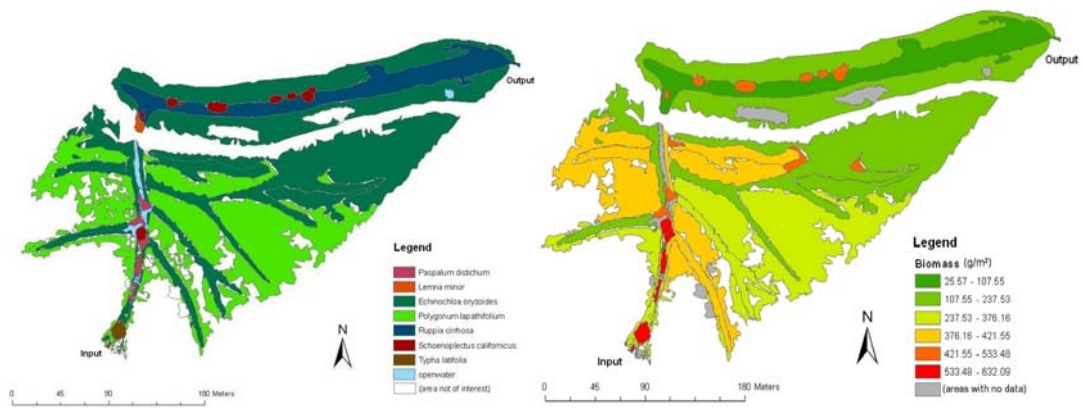
The diversity in vegetation species and biomass within the studied wetlands were profound (Figure 6.3). Although numerous studies have indicated vegetation as an important component in pesticide removal, direct evaluation of the role of vegetation

within our CWs was difficult because of great seasonal variability. A strand of bulrush (*Schoenoplectus californicus*) located halfway through the front section of CW1 was chosen to evaluate the potential effect of vegetation on pesticide removal by CWs. Miglioranza et al. (2004) found the stems of *S. californicus* to be effective at sorbing DDT and chlordane. Species of bulrush (*S. validus*) has been found to be very effective at removing metalochlor and simazine in subsurface flow wetlands (6,11).

The pesticide concentrations and reduction estimates in water samples taken before and after the bulrush strand are presented in Table 6.6. The bulrush appeared to not have any significant effect on reducing pesticide water concentrations. Surprisingly, the water concentrations were statistically higher ($p \leq 0.025$) after the bulrush. However, sediment cores taken after the irrigation season indicated that there was a higher rate of pesticide deposition in the top 5 cm before the vegetation for bifenthrin (63%), cyhalothrin (60%), cypermethrin (47%), esfenvalerate (82%), permethrin (60%), chlorpyrifos (1%), and diazinon (10%) than after the vegetation strip. The noted increase in water pesticide concentrations might be a result of sampling error due to the limited numbers of samples. Samples were collected before the vegetation strand first. It is possible that sediment before the bulrush was disturbed during sampling, which was then collected in the downstream sample.

Table 6.6. Seasonal pesticide concentrations (ng L^{-1}) and ranges in water samples collected during 2008 with percent reduction (R%) in concentration from before (BV) to after (AV) bulrush (C_{AV}/C_{BV}).

	Before Vegetation	After Vegetation	%R
Bifenthrin	0.2 (nd -0.5)	0.5 (nd – 1.0)	-104
λ -Cyhalothrin	nd	nd	-
Cypermethrin	2.0 (0.9 – 3.7)	2.5 (1.0 – 5.2)	-20
Esefenvalerate	0.3 (nd – 0.9)	0.3 (nd – 0.8)	7
Permethrin	11.4 (4.2 – 19.2)	13.4 (3.6 – 23.7)	-9
Chlorpyrifos	58.4 (29.5 – 77.3)	64.3 (31.3 – 96.3)	-9
Diazinon	nd	nd	-12.6



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Figure 6.3. Vegetation species (A) and biomass within constructed wetland 1 (CW1).

Vertical Distribution of Pesticides in Wetland Floor

Water samples were collected from two piezometer nests (N1 and N2) on April 20, 2009 at the surface and at 10 cm, 50 cm, and 100 cm depth to assess the potential for groundwater contamination. Nests N1 – 10 and N2 – 50 were damaged during sampling, and therefore samples were not collected. Pesticide concentrations as a function of depth from the surface are presented in Table 6.7. Except for bifenthrin, no other pyrethroids were detected at depths below the surface layer, further validating that vertical transport of these chemicals is generally limited. However, residue of bifenthrin was detected in water samples from the 50 and 100-cm depths. The presence of bifenthrin in the deep sediment layers could be from older sediment deposits. The great stability of bifenthrin as observed in the previous degradation experiments further suggested the likelihood of contribution from sediment that was buried earlier in time.

Chlorpyrifos was detected at all depths from the surface to 100 cm in both N1 (17 – 173 ng L⁻¹) and N2 (14 – 223 ng L⁻¹). Chlorpyrifos concentrations, however, decreased quickly with depth, and the concentration found at the 100-cm depth being only 6-11% of those found near the surface. Given the relatively short persistence of chlorpyrifos as compared to pyrethroids, the presence of chlorpyrifos in the deep sediment layers suggested probable vertical downward movement of this compound. The soil structures in this region are known for active water infiltration, and within these CWs, water loss through infiltration was found to be 87%. The active water infiltration, along with the relatively low sorption of chlorpyrifos to soil (as compared to pyrethroids), together may have resulted in the occurrence of chlorpyrifos in the lower subsurface layers.

Table 6.7. Pesticide concentrations (ng L⁻¹) within the piezometer nests taken on April 20, 2009

Sample	Bifen.	λ-Cyhal.	Cyper.	Esfen.	Perm.	Diaz.	Chlor.
N1 Surf	0.89	nd	0.43	0.44	6.4	0.12	172.7
N1 50	0.82	nd	nd	nd	nd	0.22	17.7
N1 100	0.73	nd	nd	nd	nd	0.23	19.1
N2 Surf	0.48	nd	nd	nd	2.3	0.19	222.9
N2 10	0.28	nd	nd	nd	nd	0.27	48.6
N2 100	0.22	nd	nd	nd	nd	0.14	13.6

Bifen. = bifenthrin, λ-Cyhal. = λ-cyhalothrin, Cyper. = cypermethrin, Esfen. = esfenvalerate, Perm. = permethrin, Chlor. = chlorpyrifos, Surf = surface, N1 = nest 1, N2 = Nest 2

CONCLUSIONS

There were dramatic differences in environmental conditions of the wetlands between the 2007 and 2008 irrigation seasons. However, pesticide removal efficiencies remained relatively unchanged, indicating overall wetland performance was consistent under both high and low flow regimes. Also, two wetlands with larger surface areas and contributing irrigated land was found to have similar removal efficiencies. The consistent results between seasons and across wetlands further indicate the potential of constructed wetlands to remove pesticides from return flow. Although the sediment basin does not appear effective at removing pesticides, the retention of particles in this section is a benefit to water quality measurements. From observations made from the front section of CW1 we infer the importance of having a dense biomass and to minimize channeling within the main streamline. Although none of the pyrethroids were found to

be transported vertically, chlorpyrifos was found at the deepest sampling interval, creating concern over its potential to contaminate local aquifers.

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Chapter 7

General Summary and Conclusions

Pyrethroid and organophosphate pesticides have been found in numerous waterways throughout the United States. Our observations within the San Diego Creek watershed in Orange County, California, confirmed that runoff from agricultural fields are a primary contributor to pesticide loads within these waterways. The development of best management practices such as constructed wetlands is necessary to improve water quality in agricultural return flows or tailwaters.

Two constructed wetlands located in the Central Valley of California were monitored over two consecutive irrigation seasons in 2007 and 2008. These wetlands were heterogeneous in design, with sections that had shallow dendritic flow patterns, as well as deep, wide sections. Both wetlands were found to be very effective at reducing pyrethroid concentrations (52-94%) and moderately effective at reducing chlorpyrifos concentrations (52-61%) under relatively high flow conditions. Under low flow conditions, with the exception of bifenthrin, the seasonal reductions for all pyrethroids increased to 80 – 100%. When taking into consideration of reductions in flow rates due largely to high water infiltration into the wetland floor, pyrethroid loading was reduced 95 – 100% in outgoing water. Vertical transport of pyrethroids were found to be negligible in general. However, low concentrations of chlorpyrifos were found in the sediment porewater at 100 cm from the surface, suggesting a likelihood for less

hydrophobic pesticides to contaminate shallow aquifers through the use of constructed wetlands.

Variability in environmental parameters showed a marked effect on wetland performance. During the first year of monitoring there was minimal reduction in water concentrations (<25%) within the first section of wetland 1, likely due to a lack of vegetation in the main channel. There was a significant increase in pesticide removal efficiency (36 – 92 %) in water samples during the second year of monitoring, which was attributable to slower flow rates and a substantial increase in vegetation density.

The transport mechanisms were evaluated by evaluating the partitioning of pesticides in the water column. Pyrethroids overwhelmingly sorbed to suspended solids greater than 0.7 μm (62 – 93%) based on mass, with resulting apparent partitioning coefficients (K_{da}) ranging from 1.9×10^4 to 3.1×10^5 . The freely dissolved concentration of permethrin represented 26 – 39% of the total chemical mass in water samples. Only 19% of the initial C_{Free} remained at the outlet, suggesting that wetlands had proportional reduction effects on the pesticide distributed in different phases.

Organic carbon was found to be the controlling parameter in pesticide transport. Pesticide concentrations were analyzed after the deposited sediments were fractionated into various particle sizes. Pesticide concentrations mimicked organic carbon contents of the fractions, with a positive correlation with particle size above 53 μm , and a negative correlation below 53 μm . The larger particles represented aggregates of organic material, while the smaller particles (< 53 μm) were most likely organic matter coated clay particles. Both fraction sizes are problematic as they represent lighter particles that are

less susceptible to sedimentation and are therefore capable of transporting pesticides further downstream. This observation helps explain why the sediment basin was not effective at removing pesticides from tailwater, especially during high flow periods.

Wetland lengths are an important parameter for wetland design, as space is often limited in agriculture dominated areas. The wetland lengths necessary to reduce pesticide concentrations to below 50% ($L_{1/2}$) were estimated from changes in pesticide concentrations in the top 0 – 5 cm sediment layer and from seasonal deposited sediment data. The calculated $L_{1/2}$ was less than 100 m for cyhalothrin, cypermethrin and permethrin under low flow conditions (ave. = $0.03 \text{ m}^3\text{s}^{-1}$), with $L_{1/2}$ estimates almost doubling under high flow conditions (ave. = $0.07 \text{ m}^3 \text{ s}^{-1}$).

The laboratory and *in situ* degradation studies indicated that the monitored pesticides had potential for persisting within the system between irrigation seasons, suggesting a possibility for accumulation, especially for bifenthrin. Under laboratory anaerobic conditions, the half-dissipation times for λ -cyhalothrin, cypermethrin, and esfenvalerate were less than 6 months. The half-dissipation time increased to slightly over 1 yr for permethrin. However, appreciable dissipation was not observed for most chemicals *in situ*. In particular, bifenthrin at low concentrations was found to be virtually non-degradable, indicating a potential for prolonged persistence and hence accumulation over time in the constructed wetlands.

Findings from our field experiments clearly suggest that sedimentation of suspended particles is to be the key to the removal of hydrophobic compounds such as pyrethroid insecticides by wetlands. Therefore, processes and conditions that promote on-

site settling of suspended particles should be considered and included to maximize the efficiency of wetlands. Vegetation patterns and flow paths should be optimized. The residence time should also consider high flow conditions to accommodate changes in environmental conditions or agricultural practices in the fields charging the wetland. In addition, sediment basins, although relatively ineffective at removing pesticides, serve the role of settling large particles and removing the majority of suspended solids by mass. Sediment basins are therefore a crucial component of a sustainable wetland design.

Based on our observations, the following two aspects should be further considered in the evaluation of flow-through wetlands as a management practice to mitigate non-point source pesticide runoff. First, the fate of pesticides in the wetland should be studied over a longer term. It is likely that certain pesticides may accumulate over time on the wetland floor. Under high flow conditions, e.g., storm runoff or increased irrigation runoff, the accumulated pesticide residues may be flushed out of the wetland and transported downstream. Excessive accumulation of pesticides within wetlands may also pose risks to non-target organisms, including wildlife, that use the wetlands as habitats. The other aspect that merits additional attention is the potential for groundwater contamination by pesticides through water exchanges within wetlands. The limited data on chlorpyrifos suggests that downward movement of pesticides is likely for less hydrophobic compounds. Additional pesticides, including herbicides and fungicides that are in general less hydrophobic than the insecticides considered in this research, should be considered in this further investigation.