

# Sacramento-San Joaquin Delta Regional Ecosystem Restoration Implementation Plan

## Ecosystem Conceptual Model

### Pyrethroid Insecticides

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## PREFACE

This Conceptual Model is part of a suite of conceptual models which collectively articulate the current scientific understanding of important aspects of the Sacramento-San Joaquin River Delta ecosystem. The conceptual models are designed to aid in the identification and evaluation of ecosystem restoration actions in the Delta. These models are designed to structure scientific information such that it can be used to inform sound public policy.

The Delta Conceptual Models include both ecosystem element models (including process, habitat, and stressor models); and species life history models. The models were prepared by teams of experts using common guidance documents developed to promote consistency in the format and terminology of the models  
[http://www.delta.dfg.ca.gov/erpdeltaplan/science\\_process.asp](http://www.delta.dfg.ca.gov/erpdeltaplan/science_process.asp) .

The Delta Conceptual Models are qualitative models which describe current understanding of how the system works. They are designed and intended to be used by experts to identify and evaluate potential restoration actions. They are not quantitative, numeric computer models that can be “run” to determine the effects of actions. Rather they are designed to facilitate informed discussions regarding expected outcomes resulting from restoration actions and the scientific basis for those expectations. The structure of many of the Delta Conceptual Models can serve as the basis for future development of quantitative models.

Each of the Delta Conceptual Models has been, or is currently being subject to a rigorous scientific peer review process. The peer review status of each model is indicated on the title page of the model.

The Delta Conceptual models will be updated and refined over time as new information is developed, and/or as the models are used and the need for further refinements or clarifications are identified.

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## 1. Objective

To illustrate the applicability of the general model outlined in Delta Chemical Stressors conceptual model Werner et al. (2008), we are providing an example of its implementation for a specific group of contaminants, synthetic pyrethroid insecticides. Although numerous different pyrethroids exist, the members of this group share many chemical and toxicological characteristics.

## 2. Background

The US EPA's decision to phase out certain uses of organophosphate insecticides because of their potential for causing toxicity in humans has led to their gradual replacement by pyrethroids, a class of synthetic insecticides applied in both urban and agricultural areas. They are applied in urban areas primarily for structural pest control, in agricultural areas on crops such as almonds, alfalfa, cotton, lettuce, pistachios, and peaches, and in the home in pet sprays and shampoos. In 2005, five pyrethroids were among the top 21 agricultural insecticides by acres treated in California: lambda-cyhalothrin (rank 7), permethrin (rank 9), esfenvalerate (rank 11), cypermethrin (rank 14) and cyfluthrin (rank 21) (California Department of Pesticide Regulation, Pesticide Use Reporting database: [www.cdpr.ca.gov](http://www.cdpr.ca.gov)).

Both winter storm runoff, as well as irrigation return water may be important routes of transport into aquatic systems. Pyrethroids at toxic concentrations have been detected in the majority of sediment samples collected from water bodies draining agricultural areas in the Central Valley (Weston et al., 2004; California Regional Water Quality Control Board Agricultural Waiver Program, 2007), as well as from urban creeks in the Bay/Delta region (Amweg et al., 2006; Woudneh and Oros, 2006 a, b). Pyrethroid concentrations toxic to aquatic life were detected in water samples from Central Valley agricultural drains and creeks (Central Valley Regional Water Quality Control Board, 2005; Bacey et al., 2005), and tributaries to San Francisco Bay (Woudneh and Oros, 2006 a, b).

Aquatic organisms, in particular insects, crustaceans and fish, are highly sensitive to pyrethroid insecticides (Oros and Werner, 2005). Acute toxicity to fish and aquatic invertebrates is generally observed at concentrations below 1 µg/L, and sublethal effects have been reported at low ng/L concentrations. Although it is difficult to model sublethal responses to toxicants and predict ecotoxicological impact or risk, measures of sublethal effects are likely to be as important, or more important, than the measures of acute or chronic lethal effects to accurately assess the consequences of contaminant exposure. All pyrethroids are potent neurotoxicants (Bradbury and Coats, 1989; Shafer and Meyer, 2004), can inhibit ATPases (Litchfield, 1985), and have immunosuppressive effects (Madsen et al., 1996; Clifford et al., 2005). In addition, these compounds and their breakdown products can disrupt hormone-related functions (Go et al., 1999; Tyler et al., 2000; Perry et al., 2006; Sun et al., 2007).

As pyrethroid concentrations in the Delta would be expected to peak during the winter/spring storm season (Werner et al. 2004, 2006), as well as after peak agricultural application in the summer and fall (Weston et al., 2004), early life-stages of important Delta fish species or their prey may be directly exposed to these contaminants. The storm season coincides with the spawning and rearing period of several important fish such as the delta smelt, which spawns from February to June (Moyle, 1976). Juvenile fish depend on planktonic crustaceans, small insect larvae, and mysid shrimp as their major food items (Moyle 1976), which are highly sensitive to pyrethroids. It has been suggested that urban and agricultural pesticide use in the Central Valley and Delta region might play a role in the pelagic organism declines observed in the upper estuary (Oros and Werner, 2005).

### 3. Conceptual Model

#### 3.1 Submodel 1: Transport and Fate - Exposure Assessment

Submodel 1 consists of 1) the modeling of transport and fate (→ *Hydrodynamic/SAV/FAV/ Organic C Models*), and 2) an estimation of the degree of contact with specific species and life-stages (→ *Species models*) that co-occur with the chemical(s).

The combined chemical load entering the Delta is a result of use patterns, climatic and hydrologic factors and the physical-chemical properties of pyrethroids. Habitat structure within the receiving water body and hydrodynamic factors such as flow and sediment load and transport, are important drivers of how pyrethroids partition between sediments, plants and water, where deposition and accumulation in the system will occur, and which species will be exposed and affected.

##### 3.1.1 Watershed Hydrology

The hydrology of the Sacramento-San Joaquin River Delta watershed is important to understanding the fate and transport patterns of chemical stressors in the Delta. Two aspects of the Delta's hydrology are crucial to the fate and transport submodel: 1) temporal and spatial patterns of precipitation and 2) freshwater flow. Information regarding when and where precipitation occurs can be combined with information regarding chemical use patterns to estimate wash-off loads of chemical stressors into small tributaries (i.e., stormwater runoff loads from urban lands to creeks and storm drains and wash-off loads from agricultural lands). Freshwater flows are important for estimating dilution and transit times of these loads to the Delta. Depending on the desired level of model sophistication, ancillary data regarding riparian area, watershed soils, slope, and land cover may also be important for determining chemical loads to the Delta.

### 3.1.2 Chemical Use Patterns

An average of 160,000 lbs/yr of pyrethroids were used in the Central Valley in 2000-2003. There are certain periods (temporal), locations (spatial), and activities (causal) that when combined into a single event (or use pattern) can increase the likelihood of a potential impact due to pyrethroid toxicity. Pyrethroids are applied as dormant sprays in agriculture during the winter season (primarily January-February), all year for structural pest control in urban areas, and in urban landscaping and field crop agriculture during spring, summer and fall. Guo et al. (2004) using regression modeling that related pesticide loading over time in the Sacramento River with the precipitation and pesticide use amounts in the Sacramento River watershed, showed that the amounts of precipitation and pesticide use were the two major environmental variables that dictated the dynamics of pesticide transport into surface water at the watershed level.

### 3.1.3 Sources

Input of pyrethroids into the Delta can occur from such non-point sources as agricultural and urban irrigation return water, stormwater runoff from agricultural and urban areas, chemical spills, and atmospheric input (drift from aerial or ground-based spraying, rain). More recently, due to the spread of West Nile Virus, direct deposition on water surfaces has become a potential source of these pesticides (Weston et al., 2006). Although there is presently no information, point sources such as effluents from municipal wastewater treatment plants and industrial facilities are less likely to contain high concentrations of pyrethroids. Likewise there is no information on potential off-site movement of pyrethroids from large animal operations (e.g. dairies, feedlots), where pyrethroids are used for pest control (flies, mosquitos, lice etc.). Sources can be outside the Delta, in which case chemicals are transported to the Delta via rivers and their tributaries, or they can be located directly within the Delta. Recent research findings suggest that pyrethroids are not transported far from the source (Amweg et al., 2006), thus sources within the Delta or immediately adjacent to the Delta are likely to be more important than upstream sources.

Several field studies have been conducted that have identified important transport pathways for pyrethroids. The critical transport pathways identified include agricultural stormwater runoff or irrigation return water, drift from aerial or ground-based spraying, and periodic release of agricultural return flows (tailwaters), which is a common practice in rice production (Oros and Werner, 2005). Bacey et al. (2005) reported that pyrethroids, particularly esfenvalerate and permethrin, were transported offsite into surface waters during winter rainstorm events occurring during February and March 2003. Their two sampling sites in Stanislaus and Sutter counties were selected because they were dominated by agricultural inputs and reflected areas with the heaviest historical applications of esfenvalerate and permethrin. Drift from aerial or ground-based spraying has also been implicated as a pathway for pesticide transport into the aquatic environment

primarily through aerosol transport and deposition that occurs immediately following spraying events (Tanner, 1996). Oros and Werner summarize their 2005 analysis of major pyrethroid sources as follows:

- a) Pyrethroids used in orchards during the winter dormant-spray season can potentially be transported off-site into adjacent surface waters as a result of rain storm events.
- b) In agricultural areas summer irrigation return-flows are a larger source of pyrethroids than are winter storm water flows.
- c) In rice fields the current holding times for releasing tailwaters are based on protecting biota against herbicide toxicity and thus have not determined if safe levels of pyrethroids are being released to surface waters when rice fields are drained.
- d) Urban area uses of pyrethroids make up nearly half of the total amount of pyrethroids used in the Central Valley, thus making storm and irrigation runoff from urban areas an important potential source of pyrethroids.

### **3.1.4 Factors Affecting Transport and Fate**

#### *3.1.4.1 Physical-Chemical Properties of Pyrethroids*

The fate and transport of organic compounds is controlled largely by the selective partitioning between water and sediment. Pyrethroids are hydrophobic and thus preferentially partition to sediment particles (both suspended and bedded) as well as other surfaces such as plants, phytoplankton and detritus. Sediment transport processes therefore are likely to determine the overall fate and transport of these contaminants in aquatic systems, making development of a sediment budget essential to predicting their ultimate fate.

The physical and chemical properties of several pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate (also fenvalerate), fenpropathrin, lambda-cyhalothrin, permethrin, and tralomethrin) have been reviewed by Laskowski (2002) and summarized by Oros and Werner (2005; see Table 1). Pyrethroids generally have low Henry's Law constants, which suggest they do not readily volatilize into the atmosphere. Solubility is generally low, and octanol-water partitioning coefficients are relatively high, suggesting that the majority of pyrethroid will partition to suspended particles, organic carbon and other surfaces. There is little information on how quickly (hours to days) and how extensively this occurs for different pyrethroids in the environment. It is to be expected that the partitioning process varies widely in different habitat types.

Pyrethroids are degraded in the environment by both chemical and biological processes, with typical degradation half-lives ranging from days to months. Pyrethroids in water solution tend to be stable at acid and neutral pH, but become increasingly

susceptible to hydrolysis at pH values above neutral. Exceptions at the higher pH are bifenthrin (stable), esfenvalerate (stable), and permethrin (half life = 240 days). Pyrethroids vary in their susceptibility to sunlight. Cyfluthrin and tralomethrin in water have half lives of 0.67 and 2.5 days; lambda-cyhalothrin, esfenvalerate, deltamethrin, permethrin, and cypermethrin are intermediate with a range of 17 to 110 days; and bifenthrin and fenpropathrin are the most stable with half lives of 400 and 600 days (Laskowski (2002). If deposited in sediments, pyrethroids may be far more stable than indicated above.

**Table 1. Physical and chemical properties of various pyrethroids** (from Oros and Werner, 2005).

Chemical	Log Kow <sup>1</sup>	Koc <sup>2</sup>	Solubility (mg/L) <sup>1</sup>	Vapor Pressure (mm Hg at 25°C) <sup>1</sup>	Henry's Law Constant (atm-m <sup>3</sup> /mol at 25°C) <sup>1</sup>	Soil Aerobic Half-life (days) <sup>2</sup>	Soil Anaerobic Half-life (days) <sup>2</sup>	Hydrolysis Half-life (days) <sup>2</sup>
Bifenthrin	6	237000	0.1	1.8x10 <sup>-4</sup>	<1.0x10 <sup>-3</sup>	96.3	425	>30
Cyfluthrin	5.9	124000	0.002	2.03x10 <sup>-9</sup>	9.5x10 <sup>-7</sup>	11.5	33.6	1.84-183
Lambda-Cyhalothrin	6.9	326000	0.003	1.5x10 <sup>-9</sup>	1.8x10 <sup>-7</sup>	42.6		8.66->30
Cypermethrin	6.6	310000	0.004	3.07x10 <sup>-9</sup>	4.2x10 <sup>-7</sup>	27.6	55	1.9-619
Deltamethrin	6.1		<0.002	1.5x10 <sup>-8</sup>	1.2x10 <sup>-4</sup>			
Esfenvalerate	4	251700	0.004 <sup>2</sup>	1.5x10 <sup>-9</sup>	4.1x10 <sup>-7</sup>	38.6	90.4	>30
Fenpropathrin	6		0.014	5.5x10 <sup>-6</sup>	1.8x10 <sup>-4</sup>			
Fluvalinate	4.3		0.002	5.7x10 <sup>-7</sup>	3.05x10 <sup>-5</sup>			
Permethrin	6.5	227000		2.2x10 <sup>-8</sup>	1.9x10 <sup>-6</sup>	39.5	197	>30-242
Resmethrin	5.4		-	1.13x10 <sup>-8</sup>	<8.9x10 <sup>-7</sup>			
Tralomethrin	7.6		0.08	3.6x10 <sup>-11</sup>	3.9x10 <sup>-15</sup>			

<sup>1</sup>Data are cited from USDHHS, 2003.  
<sup>2</sup>Data are cited from Laskowski, 2002.

### 3.1.4.2 Habitat Properties

The dominant properties of the aquatic habitat influencing fate and transport of pyrethroids are pH, temperature, amount and particle size distribution of deposited and suspended sediments (turbidity), presence of aquatic plants including phytoplankton, organic carbon (DOC, POC), and UV-light intensity. These directly influence sequestration, degradation and compartmentalization of pyrethroids within the system (Oros and Werner, 2005). Many of these factors are components or outcomes from other conceptual models (→ *Aquatic Plants, Hydrodynamics*).

The effects of aquatic plants on pyrethroid fate are relatively complex. While high temperature, high pH and UV-light decrease the half-life of pyrethroids, high turbidity and the presence of plants will reduce light penetration, and thus increase their half-lives by modifying photodegradation rates of chemicals. On the other hand, aquatic plants



could aid in the degradation of pyrethroids. Aquatic plants have been shown to absorb pyrethroids, and their microbial “Aufwuchs” communities may enhance pyrethroid degradation (Hand et al., 2001).

### 3.1.5 Hydrodynamics and Sediment Transport

To date, the fate of pyrethroids applied in the Central Valley is not well understood. Information on the movement of water and sediment within the Delta is key to determining the spatial and temporal distribution of pyrethroids within the aquatic system. Given that a majority of Central Valley runoff enters San Francisco Bay through the Sacramento – San Joaquin Delta, it is probable that a measurable amount of pyrethroids originating from the Central Valley will find their ultimate fate in the Delta and Bay. However, monitoring data for pyrethroids in water and sediment are scarce or do not exist, confounding attempts to estimate loads of pyrethroids transported to the Delta and Bay from the Central Valley. In an effort to fill this data gap, a first-order model of pyrethroid fate in Suisun Bay, the segment of San Francisco Bay directly connected to the Sacramento – San Joaquin Delta, was developed to estimate probable concentrations of pyrethroids in Bay surface sediments (Oros and Werner, 2005).

Using field data collected in agricultural return canals to estimate the concentration of pyrethroids on a particulate basis (~75 ng/g), literature values for average sediment washoff rates (~50,000 kg/km<sup>2</sup>-yr), and median values for pyrethroid degradation ( $t_{1/2}$ =175 days) it was estimated that 0.11% of the pyrethroids used in the Central Valley is available for transport through the Sacramento-San Joaquin Delta. Degradation accounted for ~6% of the pyrethroid mass while ~94% is thought to remain at the application site. Therefore, considering an annual application rate of 160,000 lbs of pyrethroids, the average use in the Central Valley for 2000-2003, approximately 160 lbs are available for transport.

### 3.1.6 Pyrethroid Distribution – Partitioning

Sediments in general are considered to be a “sink” for pyrethroids due to their hydrophobic properties, and the presence of aquatic macrophytes, phytoplankton and detritus can lead to adsorption of pyrethroids to plant surfaces. However, pyrethroids may remain in solution for hours to days before they sequester to suspended particles.

$$\% \text{ dissolved} = \frac{100}{1 + SSC \times Foc \times Koc}$$

Suspended sediment concentrations (SSC) at Mallard Island, considered the connection point of the Delta and the Bay, generally range from 20-120 mg/L. The fraction of organic carbon (Foc) on suspended particles in the Delta is not well quantified. The value generally used for in-Bay models is 0.03 (or 3%). A range of 0.01-0.03 (or 1-3%) was used for this analysis. From Table 1 partitioning coefficients (Koc) or pyrethroids range from  $1.24 \times 10^5$  (Cyfluthrin) to  $2.51 \times 10^5$  (Esfenvalerate). Using the

equation above and these ranges of SSC, Foc, and Koc yields a range of percent pyrethroid dissolved of 52-97%. This large range is an artifact of the wide ranges of SSC and Foc used in this analysis. Oros and Ross (2004) found the Foc of sediments in Suisun Bay, the bay region closest to the Delta, to be approximately 1%. Using this Foc reduces the range of percent dissolved to 77-97%.

It is evident from this rough analysis that the Delta water column can be dominated by the dissolved fraction of these pyrethroids, driven by low SSC and Foc. Still, given the relatively high Koc values, one would expect to see a large fraction of pyrethroids in the sediment and relatively low concentrations in the water column. This analysis only suggests that a high percentage of the low water column concentration can be in the dissolved fraction.

### **3.1.7 Intermediate Outcome 1: Exposure**

*[ → Data input from Species Life History Models ]*

Exposure signifies the degree of contact of an organism with a chemical. This takes into account the spatial and temporal distribution of a chemical within the Delta system, and whether the chemical is deposited in sediments, adsorbed to plant or detritus material, suspended sediments or remains in solution. The most significant factors related to exposure are the pathway, magnitude, duration, and frequency of exposure and the concentration of the chemical.

Pyrethroids are generally of very low water solubility and high lipophilicity, and therefore are rapidly adsorbed to particulate material and other surfaces. Adsorption occurs on the order of hours in sediment-laden solutions under ideal laboratory mixing conditions (Maund et al., 2002) or in systems like farm ponds that contain relatively large amounts of organic matter (Litchfield, 1985); however, in water bodies such as the Delta, where less ideal mixing conditions exist, adsorption may occur over a period of days rather than hours (Capel et al., 2001). Exposure of pelagic organisms to dissolved pyrethroids for several hours to days is therefore possible. The greatest known risk of pyrethroids to aquatic organisms is expected to be through exposure to contaminated sediments (both deposited and suspended), which means there is a substantial risk to benthic organisms, in particular sensitive crustacean and insect species. However, adsorption of pyrethroids to plant and detritus material may lead to dietary uptake by invertebrate species, in particular zooplankton and benthic crustaceans, but there is little information on the importance and magnitude of this uptake pathway.

Exposure of aquatic organisms to pyrethroids present in water, sediment, and/or food depends on the species, life stage, life history, trophic level, feeding strategy etc. It must therefore be determined which species and life-stages, and by what route organisms are exposed to a contaminant. Information on the temporal and spatial distribution of aquatic species of interest and their different life-stages can be derived from species models, and population monitoring data (CA Dept. of Fish and Game, CA Department of Water Resources). Land use and monitoring data are needed to identify where and when

pyrethroids may be present in the Delta. Results of recent monitoring studies are presented below.

### 3.1.7.1 Exposure of Benthic Species - Sediments

Weston et al. (2004) reported that pyrethroids were detectable in 75% of the sediment samples collected from water bodies in the Central Valley, with permethrin detected most frequently (66% of all samples) followed by esfenvalerate (32%) > bifenthrin (18%) > lambda-cyhalothrin (12%). Sediments from a pond that received tailwater from adjacent lettuce fields had the highest concentrations of pyrethroids: bifenthrin (29 ng/g), lambda-cyhalothrin (17 ng/g), and permethrin (459 ng/g). Permethrin was found at a median concentration of 2 ng/g, with highs of 129 ng/g in an irrigation canal; 55 and 120 ng/g in Root Creek adjacent to pistachio groves; and 47 ng/g in Del Puerto Creek, a small creek that passes through orchards and diverse row crops. Esfenvalerate highest concentrations were found in Little John Creek (30 ng/g), three irrigation canals (10-28 ng/g), Del Puerto Creek (18 ng/g) and in Morisson Slough (11 ng/g) in an area of peach and plum orchards. A bifenthrin maximum concentration of 21 ng/g was found in Del Puerto Creek and it was also found in two irrigation canal sites at 9 and 10 ng/g levels. Lambda-cyhalothrin maximum concentration of 8 ng/g was found in an irrigation canal from an alfalfa growing area. In addition, Weston et al. (2004) reported that pyrethroid concentrations were high enough to have contributed to the toxicity found in 40% of samples toxic to the midge *Chironomus tentans* and nearly 70% of samples toxic to the amphipod *Hyalella azteca*. *C. tentans* and *H. azteca* are both resident species within Central Valley water bodies. Weston et al. (2004) also reported that the observed pyrethroid concentrations in the sediment samples were greatest in the late summer and fall months (August and November), which is near the end of the irrigation season.

Of 33 sediment samples collected by the Agricultural Waiver Program in agricultural drains in the Central Valley, permethrin was detected in 24% of the sites with a maximum concentration of 4 ng/g. Lambda-cyhalothrin was detected in 15% of the sites with a maximum concentration of 6 ng/g in Orestimba Creek at Kilburn Road. Esfenvalerate was detected at 12% of the sites with a maximum concentration of 44 ng/g in a ditch along Bonetti Drive in San Joaquin County. Bifenthrin was detected in 9% of the sites with a maximum concentration of 41 ng/g in Hospital Creek at River Road. When compared to median LC50s for the freshwater amphipod *Hyalella azteca* developed by Amweg et al. (2006), it becomes apparent that the lambda-cyhalothrin, esfenvalerate, and bifenthrin maximum sediment concentrations reported were each enough (equal or greater than the median LC50 values) to cause acute toxicity to *H. azteca*.

Urban use of pyrethroid insecticides and subsequent transport into surface waters may be a significant contributor to the contamination of rivers with pyrethroids. A study on sediments in urban creeks in Sacramento (Weston, 2007) showed that all 28 sediment samples taken had measurable concentrations of pyrethroids. Six of seven creeks studied

and two thirds of samples taken contained concentrations high enough to be toxic to sensitive aquatic life. Bifenthrin, which is used in structural pest control and as an insecticide for lawns, was the compound most often associated with toxicity.

A one-box model of Suisun Bay, the segment of San Francisco Bay directly connected to the Delta, was developed to estimate the probable pyrethroid concentration in Bay sediments resulting from pyrethroid loads from the Central Valley. The one-box model is based on a model of polychlorinated biphenyls in San Francisco Bay (Davis, 2004) and includes the major processes governing contaminant fate in the Bay; external loads, sediment-water partitioning, volatilization, degradation, and tidal exchange with ocean waters. Using an estimated 160 kg/yr loading rate of pyrethroids, the one-box model predicts pyrethroid concentrations in Suisun Bay surface sediments in the 1-2 ng/g (ppb) range. To date, these estimates have not been corroborated by field samples. However, a recent presentation (Hladik et al., 2006) at the CALFED Science Conference reported a single grab sample taken at Mallard Island had particulate pyrethroid concentrations in the same range. Sediment grab samples and water samples taken from 10 sites throughout the Delta in June 2006 had no detectable concentrations of pyrethroids (CA Dept. of Pesticide Regulation).

#### *3.1.7.2 Exposure of Pelagic Species - Water Column*

Measurements of pyrethroids in surface water samples are relatively scarce. Bacey et al. (2005) investigated whether pyrethroids, particularly esfenvalerate and permethrin, were carried offsite into surface waters during winter storm events occurring during February and March 2003. Their sampling sites were dominated by agricultural inputs and reflected areas with the heaviest historical applications of esfenvalerate and permethrin. In February 2003 following a rain storm event, Wadsworth Canal in Sutter County, which flows into the Sacramento River, showed esfenvalerate at trace concentrations and permethrin at 94 ng/L. The estimated dissolved phase concentration range in the water samples was 7 ng/L to 32 ng/L. Peak runoff concentrations for pyrethroids were obtained at the time of peak discharge (55 cfs) and peak total suspended sediment (TSS) levels (3,114 mg/L). In March 2003, Del Puerto Creek in Stanislaus County, which flows into the San Joaquin River, showed esfenvalerate present in six whole water samples with concentrations ranging from trace level to 94 ng/L. Bifenthrin was also found in one sediment sample at a concentration of 24 ng/g dry wt. It should be noted that pyrethroid concentrations in stormwater were shown to be highest before peak discharge occurred, within the first 1-2 h of onset of rainfall, in a study by Brady et al. (2006).

Of 130 water samples collected in agricultural drains during the irrigation season bifenthrin was detected twice at a concentration of 12 ng/L in Orestimba Creek at Kilburn Road and 18 ng/L in Stevenson Lower Lateral at the intersection of Faith Home and Turner Roads (Central Valley Regional Water Quality Control Board, 2005a). In addition, the Irrigation Monitoring Phase II Agricultural Waiver Program collected 157 water samples from 15 sites in the Central Valley during the winter dormant-spraying season January through March 2004 (Central Valley Regional Water Quality Control

Board, 2005b). The Program reported detectable concentrations of the pyrethroids permethrin-1 and permethrin-2 in 6 samples. The median (range) concentrations for permethrin-1 was 10 (range 7-216 ng/L) and permethrin-2 was 23 (range 14-390 ng/L). The maximum concentrations of permethrin-1 and permethrin-2 were each found in a drain on Sarale Farms at Bonetti Drive in Merced County, which is primarily field crops such as tomatoes, cotton, vegetables, and grains. The reported concentrations were high enough to be acutely toxic to sensitive aquatic species.

Gill and Spurlock (2004) monitored esfenvalerate in storm water runoff following a dormant spray application of a prune orchard in Glenn County. The study was designed to examine the rainfall runoff potential of the dormant spray esfenvalerate in a prune orchard with managed floors during two rain events. The esfenvalerate application rate was 0.05 lb AI/acre. The results showed that esfenvalerate concentrations in whole water in-field runoff samples, where cover crops were located, were highly variable, ranging from below the reporting limit 50 ng/L to 5,390 ng/L. In an edge-of-field drainage ditch whole water runoff samples has esfenvalerate concentrations ranging from 424 to 3,060 ng/L, which were comparable to the esfenvalerate concentrations found in the in-field runoff samples. In a holding pond that received runoff from the orchard, esfenvalerate concentrations ranged from 73 to 473 ng/L. This study demonstrated the potential for surface water impact due to orchard runoff.

Starner et al. (2006) collected 100 water and bed sediment samples from creeks in agricultural regions of California in 2004/05. Pyrethroids were detected in 61% of samples, most of them in sediment samples. However, detection limits for water samples analyzed during the first part of the study were relatively high. Lambda-cyhalothrin was detected at 110-140 ng/L in water samples from the Northern San Joaquin Valley, and cypermethrin was detected at 55 ng/L in surface water of the Salinas Valley.

A sample collected from the Delta by the UC Davis Aquatic Toxicology Laboratory contained 5 ng/L cyfluthrin and 24 ng/L permethrin (unpublished data). Subsequent laboratory studies usinshowed that these concentrations were acutely toxic to the amphipod *Hyaella azteca*.

### *3.1.7.3 Contamination of Drinking Water – Human Exposure*

Contamination of drinking water for human consumption with pyrethroids is not considered to be a major concern, because of the chemicals' hydrophobic nature and relatively short half-lives. However, monitoring data for the Delta is lacking. A study performed in Poland (Badach et al., 2007) detected the pyrethroid alpha-cypermethrin in drinking water wells from an area of intensive agriculture at a concentration of 0.3 µg/L. Other pesticides including organophosphates, organochlorines (DDT) and triazines were detected far more frequently than pyrethroids. It was not clear from the study, whether this reflected lower use amounts or lower risk of groundwater contamination, especially since DDT is also highly hydrophobic. Bifenthrin (max. conc. 4.3 µg/L) and lambda-cyhalothrin (2.9 µg/L) were also detected in groundwater samples from shallow aquifers in an agricultural area in Pakistan (Tariq et al., 2004), and rainwater samples collected in

February, July and August 2002 in an agricultural area in India contained up to 0.8 µg/L deltamethrin, 0.9 µg/L fenvalerate and 1.09 µg/L cypermethrin (Kumari et al., 2007).

## **Limitations and Recommendations**

There is a lack of information on the temporal and spatial distribution, as well as concentrations of pyrethroids in the Delta. Estimates of the spatial distribution of pyrethroids in the Delta watershed can be made from land use and prethroid application/use data, and models could be used to estimate the effective delivery to and subsequent transport through the Delta. The inventory, or stock, of pyrethroids in the Delta is a key information gap at this time. One of the major limitations for obtaining data on the sources and quantities of pyrethroids in the environment, in particular in water samples, is the sensitivity of the existing analytical chemistry techniques. Because pyrethroids are toxic at such low concentrations (low to mid parts per trillion range) monitoring data which is based on insufficiently low detection limits is of little use. In fact, it can convey a false sense of safety with regard to the potential toxic effects of pyrethroid contamination on aquatic ecosystems. Overall, quantitative data for pyrethroids is limited to recent studies done in agricultural drains or small streams, some of them conducted with relatively high detection limits. Due to their relatively short half-lives and hydrophobic nature, pyrethroid concentrations in larger water bodies are expected to be generally ephemeral, especially in the water column. This further limits our ability to monitor large systems such as the Delta. Presently, the relative contribution of agricultural and residential irrigation return water (summer) versus stormwater (winter) is largely unknown, and information on their temporal distribution is scarce. Due to their higher toxicity as well as reduced degradation rates at low temperatures, pyrethroids may be a greater risk to aquatic life during the winter period. However, use of pyrethroids in agriculture and professional urban pest control has been reported to be higher in the summer.

### **3.2 Submodel 2: Bioavailability**

Chemicals may enter an organism through the body surface (dermal), the gills (respiratory) or via ingestion (dietary). In general, water-insoluble (lipophilic) chemicals such as pyrethroids are adsorbed to suspended particles, organic matter, phytoplankton, plants or sediments. However, lipophilic chemicals adsorbed to suspended particles or sediments may enter an organism when they are in direct contact with gills, body surfaces or intestinal membranes.

#### **3.2.1 Physical-Chemical Habitat Properties**

In their dissolved state, pyrethroids are readily bioavailable to aquatic organisms. In the adsorbed state their bioavailability to aquatic organisms is reduced. The extent to

which they are bioavailable after adsorption to these compartments is unclear and highly substrate and species-specific. Yang et al. (2006a) showed that the presence of suspended sediment (200 mg/L) reduced toxicity of pyrethroids to *Ceriodaphnia dubia* by a factor of 2.5-13. However, half-lives increase when pyrethroids are sequestered into sediments. The degradation of pyrethroids bound to sediment particles is considerably slower than in soil. For example, the half-life of bifenthrin is reported to be 8-17 months (20°C) in sediments (Gan et al., 2005), and 42-96 days in soil (Laskowski, 2002).

Weston et al. (2004) demonstrated that sediment-bound pyrethroids are bioavailable to benthic invertebrates and that environmental sediment concentrations adversely affect benthic and epibenthic organisms. Contaminant uptake from sediments is most closely associated with fine organic-rich deposits. Xue et al (2005) measured porewater and particle-bound pyrethroid concentrations in fine sediments of Beijing Buantin Reservoir. Sediments contained deltamethrin at 78.6-301 pg/g (mean: 81.4 pg/g; particle-bound) and ND-54.2 ng/L (mean: 31.8 ng/L) in pore water; fenvalerate at 45.4-148 pg/g (mean: 70.3 pg/g; particle-bound) and ND-26.3 ng/L (mean: 6.32 ng/L), and cypermethrin at ND-8.77 pg/g (mean: 3.48 pg/g, particle-bound) and ND-8.87 ng/L (mean 3.18 ng/L) in pore water.

In the water column, bioavailability of pyrethroids may be reduced due to adsorption to dissolved and particulate organic matter, suspended sediment particles and phytoplankton. Turbidity (suspended particles) and temperature are the dominant factors determining the bioavailability of pyrethroids in the water column. Yang et al. (2006 b) showed that dissolved organic matter (DOM) at a concentration of 10 mg/L reduced permethrin toxicity to *Ceriodaphnia dubia* as well as bioaccumulation by *Daphnia magna* by approximately a factor of 2. However, DOM (DOC) concentrations in the Delta are rarely above 2 mg/L (CA Dept. of Water Resources, unpublished data). Otherwise, there is little information on the bioavailability of pyrethroids bound to suspended sediments, detritus or phytoplankton, which may be absorbed dermally via gills or via the diet. It is also unknown to what extent commercial pesticide formulations might alter the environmental fate, bioavailability and toxicity of pyrethroids.

### **3.2.2 Biological Habitat Properties**

Microbial communities and their activity affect the breakdown of many organic contaminants. This can be an important factor to consider in habitat restoration. Pyrethroids also tend to adsorb to phytoplankton, detritus and submerged aquatic vegetation, where they can be taken up, broken down or ingested by aquatic planktivores and herbivores. Wetlands can therefore be beneficial where these biodegradable, hydrophobic contaminants are present (Hand et al., 2001 Moore et al. 2001, Bennett et al. 2005). In addition, the structure and activity of the animal community will affect how and where contaminants are sequestered, ingested and released. For example, mollusks (clams, snails etc.) are relatively insensitive to pyrethroids and tend to bioaccumulate these chemicals in their tissues. This is a potential pathway of how sediment-bound

pyrethroids could become available for uptake by bottom-feeders at higher trophic levels (ducks, sturgeon etc.), but no studies have been done to date.

### **3.2.3 Organism Properties I**

A species' trophic level, and associated feeding behavior, diet and digestive processes, are major factors contributing to bioavailability and uptake of contaminants. Benthic sediment feeders may take up larger amounts of pyrethroids than pelagic organisms. In addition, life-stage and gender specific behavior and other features need to be taken into account when assessing contaminant bioavailability and uptake. For example, Chinook salmon embryos have been shown to be less sensitive to the pyrethroid lambda-cyhalothrin than fry (Phillips et al. 2005), possibly due to the chorion's protective effect. In general, very little is known about the effects of these organism properties on the uptake of pyrethroids. Seasonal (reproductive) cycles and the overall physiological condition can also influence organism behavior, diet and disposition, which will in turn affect the uptake of contaminants. For the protection of a species, it is critical to link contaminant exposure to the most vulnerable life-stages exposed to the contaminants.

### **3.2.4 Intermediate Outcome 2: Bioavailable Concentration or Dose**

“Bioavailable Concentration” or “Dose” is the result of exposure and bioavailability and constitutes the concentration of contaminant that is transported through biological membranes of the gut (dietary), gills (respiratory) or skin and cell walls (dermal) into the organism. It is generally not directly quantified, but rather assessed on the basis of the observable toxic effects on the organism.

## **Limitations and Recommendations**

As is evident from the previous sections, the determination of how much pyrethroid is bioavailable to a given organism is limited by the lack of data on pyrethroid concentrations in the field. In spite of pyrethroids being considered “not bioavailable” once sequestered to sediment or soil, Weston et al. (2004) and Amweg et al. (2006) demonstrated that sediment-associated pyrethroids are, in fact, bioavailable and toxic to benthic organisms. Xue et al. (2005) measured sediment pore water concentrations of several pyrethroids that are high enough to cause mortality in benthic crustaceans. This is important for benthic communities, because the chemicals' half-lives in benthic habitats can be on the order of months to years. In the water column, available data shows that bioavailability of pyrethroids is significantly reduced by the presence of suspended sediments and DOM (Yang et al., 2006 a, b), but the effective suspended sediment and DOM concentration need to be compared to conditions in the Delta. An overwhelming lack of surface water monitoring data with sufficiently low detection limits currently prevents an estimation of the risk of pyrethroid contamination to pelagic organisms.



### 3.3 Submodel 3: Toxic Effects

#### 3.3.2 Organism Properties II

Species and organism properties such as life-stage, gender and size, as well as body temperature (reflecting the surrounding water temperature in ectothermic species) are the major factors determining whether a chemical is stored in tissues (bioaccumulation), excreted (transformation and elimination), or exerts toxicity (biologically effective concentration) after being taken up by an organism.

#### 3.3.2 Water Temperature

Water temperature is perhaps the most important factor affecting biochemical and physiological processes of individual organisms. It affects contaminant transformation and excretion rates. Temperature has been demonstrated to have an inverse effect on pyrethroid toxicity, which increases at lower temperatures (Motomura and Narahashi, 2000). This negative temperature dependence of pyrethroid action has in the past been ascribed to the slow metabolism of pyrethroids at low temperature. Recent studies showed that this effect is mostly due to the increased sodium current flow through (i.e., increased sensitivity of) nerve cell membranes at low temperature (Narahashi et al., 1998).

#### 3.3.3 Bioaccumulation

Bioaccumulation is the net accumulation of a contaminant in and on an organism from all sources (water, air, food, sediment, maternal transfer, suspended sediment, detritus). It is determined by the chemical properties of the contaminant, and the metabolism (enzymatic activity) of a species, and often dependent on gender, age, life-stage and physiological condition of the organism. Pyrethroids, despite their high lipophilicity (generally an indication of a chemical's bioaccumulation potential) have relatively low bioaccumulation potential due to being readily metabolized and eliminated by most species. In fish, reported 22-42 day bioaccumulation (bioconcentration) factors (BCF) range from 359 (fenpropathrin) to 6090 (bifenthrin; Laskowski 2002). Some of the reported BCFs are based on C14 studies, where corrections for metabolites were not made. In general, BCF values tend to be lower than expected from the highly nonpolar nature of pyrethroids because the bioconcentration studies show that fish can metabolize pyrethroids and keep accumulation in their bodies at low levels through the continuous turnover of chemical. Little information is available for bioaccumulation factors in invertebrates. For oysters, the bioconcentration factor (BCF) of fenvalerate is reported to be >4700 (Clark et al., 1989). This is of potential interest, because mollusks are relatively insensitive to pyrethroids, and may act as a vector for transfer of sediment-associated pyrethroids into the food chain.

Recent studies show that pyrethroids can accumulate in human breast milk. Bouwman et al. (2006) report mean concentrations (by wet weight) of 14.51 mg/L permethrin, 41.74 mg/L cyfluthrin, 4.24 mg/L cypermethrin, 8.39 mg/L deltamethrin in mothers from several villages in South Africa. Exposure pathways were not investigated in these studies. The pyrethroids are used in agriculture, domestic applications, and, in the case of deltamethrin, for malaria control, and exposure may have occurred via drinking water, food or direct contact. For example, a recent study indicates that table grapes can contain high concentrations of pyrethroids and other pesticides (Poulsen et al. 2007). Pyrethroids (permethrin, cyfluthrin, deltamethrin) were also detected in breast milk samples collected in Switzerland in 1998/99 (Zehringer and Herrman, 2001). In this study, the sum of 13 pyrethroids and pyrethrins reached from ~0.015 mg/kg fat to 0.45 mg/kg milk fat. Mainly allethrin, bifenthrin, cyfluthrin, l-cyhalothrin, fenpropathrin, fluvalinate, permethrin, and pyrethrins were detected, and permethrin and pyrethrins were the most prominent. The authors could not find any correlation between pyrethrins or, respectively, pyrethroid concentrations and the use of these insecticides in households. Even the milk of women who never use pyrethroids in their homes contained pyrethroids and pyrethrins. In Switzerland, tolerance values in cow's milk for several pyrethroids such as fenvalerate, bifenthrin, cyfluthrin, permethrin, range from 0.3 and 1.7 mg/kg fat. According to the authors, the maximum pyrethroid concentrations found in breast milk did not exceed the Swiss criteria for cows' milk.

### **3.3.4 Biologically Effective Concentration**

Toxicant effects begin by the interaction of contaminants with biomolecules. Effects then cascade through the biochemical, subcellular, cellular, tissue, organ, individual, population, community, ecosystem, landscape, and biosphere levels of organization. The chemical may be present at acutely toxic concentrations leading to significant mortality in individuals or it may exert sublethal effects potentially resulting in mortality and/or reduced reproductive success in a population. Continuous exposure to a chronic dose of a chemical stressor can also act as a selective force leading to stressor-resistant populations. Changes in population structure or abundance may lead to indirect effects of the contaminant on species at a higher or lower trophic level thus affecting community structure and ultimately leading to ecosystem changes (Newman and Unger, 2003; Rand, 1995).

### **3.3.5 Factors Affecting Toxicity**

#### *3.3.5.1 Organism Properties III*

The toxic effects of a given contaminant as well as the effective contaminant concentration are highly dependent on the susceptibility of the species, gender and life-

stage. However, information on life-stage or gender-specific susceptibility to pyrethroids is scarce. The available data suggests that smaller and/or younger organisms and life-stages are more sensitive than larger/adult organisms. For example, <24-h old *Daphnia magna* (Cladocera) were about 10 times more sensitive to cypermethrin than 6-d old adult cladocerans (CDFG, 2000). In a recent study on copepods, calanoid (*Acartia tonsa*), nauplii were 28 times more sensitive to cypermethrin than adults, with 96-h LC50s of 0.005 ppb and 0.142 ppb (measured concentrations) for nauplii and adults, respectively (Medina et al., 2002). Gender differences were also observed: During the first 24 h of exposure, male adult copepods were about twice as sensitive as female adults.

Fish embryos appear to be less sensitive to pyrethroids than larvae. A study on the sensitivity of embryos and larvae of Chinook salmon (*Onchorhynchus tshawytscha*) to lambda-cyhalothrin showed no effect on mortality, hatching success, or larval survival when embryos were exposed to nominal concentrations ranging from 0.3-5.0 ppb (nominal). The estimated 96-h LC50 for Chinook salmon fry was 0.15 ppb (nominal; Phillips and Werner, 2005), making fry at least 33 times more sensitive to lambda-cyhalothrin than embryos. The 48-h LC50 of deltamethrin for carp (*Cyprinus carpio*) embryos was 0.21 ppb, while the respective LC50 for carp larvae was 0.074 ppb (Koprucu and Aydin, 2004). Similarly, topsmelt (*Atherinops affinis*) embryos survived 30-d exposure to 3.2 ppb fenvalerate, while 0.82 ppb fenvalerate caused complete mortality of exposed topsmelt fry (Goodman et al, 1992).

The physiological condition of the exposed organism determines its ability to respond to contaminants and other stressors. For example, low nutritional status may result in increased susceptibility of organisms to pyrethroids. Barry et al. (1995) showed that esfenvalerate toxicity to *D. carinata* increased significantly with decreasing food concentration. Fenvalerate decreased survival and growth of *Daphnia magna* in the week following a 24-h pulse exposure at 1.0 ppb (Pieters et al., 2005). Age at first reproduction increased, with adverse effects on fecundity. Low food conditions exacerbated the effects of fenvalerate exposure on juvenile survival and growth during the first week, and reduced the significant effect concentration from 0.6 ppb (high food availability) to 0.3 ppb. No mortality occurred during the 24-h fenvalerate exposure, but complete mortality was observed at 3.2 ppb after a 6-d recovery period in control water.

Gender and reproductive stage will notably influence the effects of pyrethroids on the endocrine system, but little information is available at this point. An organism's size and trophic level will determine its susceptibility to predation after being negatively affected by neurotoxic chemicals such as pyrethroids, and behavioral characteristics (e.g. complex reproductive strategies) can modify the effects of endocrine disruptors as well as neurotoxicants on the individual.

### 3.3.5.2 Mechanism of Toxic Action

The mechanism of toxic action of a contaminant determines which species are most susceptible, but it is important to recognize that deleterious effects on non-target species and unwanted side-effects are common.

All synthetic pyrethroids are potent neurotoxicants that interfere with nerve cell function by interacting with voltage-dependent sodium channels as well as other ion channels, resulting in repetitive firing of neurons and eventually causing paralysis (Bradbury and Coats, 1989; Shafer and Meyer, 2004). Exposed organisms may exhibit symptoms of hyperexcitation, tremors, convulsions, followed by lethargy and paralysis. There are two groups of pyrethroids with distinctive poisoning symptoms (Type I and Type II). Type II pyrethroids are distinguished from type I pyrethroids by an alpha cyano group in their structure. While type I pyrethroids (e.g. permethrin, cismethrin) exert their neurotoxicity primarily through interference with sodium channel function in the central nervous system, type II pyrethroids (e.g. deltamethrin, esfenvalerate, cypermethrin, bifenthrin) can affect additional ion-channel targets such as chloride and calcium channels (Burr and Ray, 2004).

### 3.3.5.3 Exposure Regime

The exposure regime (magnitude (concentration), duration and frequency) is an important factor affecting toxicity. Multiple brief exposures within a given time period to a specific contaminant concentration may not have the same toxic effect as one continuous exposure over the same time period. High magnitude exposures of short duration may be enough to cause population level impacts, while low magnitude, long duration exposures may have no impact at all.

Forbes and Cold (2005) found that even very brief (1-h) exposures to environmentally realistic concentrations of esfenvalerate during early larval life-stages of the midge *Chironomus riparius* can have measurable population level effects on larval survival and development rates. For surviving organisms no lasting effects on fecundity or egg viability were observed. Brief (30 min) pulse exposures to lambda-cyhalothrin (nominal conc. 0.05-10 ppb; Heckmann and Friberg, 2005) in an in-stream mesocosm study demonstrated that macroinvertebrate drift increased significantly after each exposure. *Gammarus pulex*, Ephemeroptera and Simuliidae were predominantly affected. Structural change in the community was found at 5 and 10 ppb, and recovery occurred within approximately two weeks.

### 3.3.5.4 Multiple Stressors and Chemical Mixtures

Pre-exposure or simultaneous exposure to other contaminants, disease or stressful environmental conditions such as salinity and temperature may considerably alter the physiological condition and therefore susceptibility of the organism, as well as modify the toxicity of a given contaminant. Organisms in the environment often experience many

stressors simultaneously, including those of a physical, biological, and chemical nature (Lydy et al., 2004). Chemical analysis of surface water conducted by the U.S. Geological Survey under the National Water Quality Assessment Program indicates that pesticide mixtures are contaminating surface waters. More than 50% of all stream samples tested contained five or more pesticides (U.S. Geological Survey 1998). In addition, many other contaminants such as heavy metals, PAHs and PCBs are often present in aquatic environments. When large numbers of chemicals are included in the mixture experiments, an additive response is typically found (Lydy et al., 2004). It is therefore evident that we must consider mixtures to be the most common exposure scenario when evaluating the ecological effects of contaminants. Unfortunately, information on mixture effects is scarce.

*PBO:* The synergist piperonyl butoxide (PBO) is commonly added to pyrethroid and pyrethrin formulations to enhance the toxic effects of the active ingredient. PBO functions by inhibiting a group of enzymes (mixed-function oxidases), which are involved in pyrethroid detoxification. PBO can enhance the toxicity of pyrethroids by 10-150 times (Wheelock, 2004). Recently, 3-4-fold enhancement of pyrethroid toxicity to amphipods has been reported (Amweg et al., 2006). The 96-h LC50 of PBO for rainbow trout is 2.4 ppb (USEPA, 2002). PBO in concentrations less than 1 ppm can reduce fish egg hatchability and growth of juvenile fish.

*Pesticide formulations:* Inert ingredients of various pesticide formulations, such as emulsifiers, solvents and surfactants influence the environmental fate, mobility and potentially the toxicity of pyrethroids. Overall, water-insoluble pesticides applied in emulsion formulations have higher storm- and irrigation runoff potential than water-soluble pesticides (Moran, 2003). More information is needed on the effects of formulations on off-site movement as well as on the toxicity of pyrethroids.

*Pyrethroid-other insecticides:* Given that P450-activated OPs will inhibit esterases, thus decreasing an organism's ability to detoxify pyrethroids, greater than additive toxicity is to be expected. Denton et al. (2003) demonstrated that exposure to esfenvalerate and diazinon resulted in greater than additive toxicity in fathead minnow larvae. Synergistic toxic effects have also been observed in exposures to pyrethroids and carbamates. Permethrin and the carbamate propoxur elicited greater than additive toxicity in the mosquito *Culex quinquefasciatus* (Corbel et al., 2004). These greater than additive effects were attributed to the complementary modes of toxic action of these two insecticide classes, which act on different components of nerve impulse transmission.

*Pyrethroid-infectious agents:* Clifford et al. (2005) showed that susceptibility of juvenile Chinook salmon to Infectious Hematopoietic Necrosis Virus (IHNV) was significantly increased when 6-week old fish were exposed to a sublethal concentration of esfenvalerate (0.08 ppb). Of juveniles exposed to both esfenvalerate and to IHNV, 83% experienced highly significant ( $p < 0.001$ ) mortality ranging from 20% to 90% at 3 days post-viral exposure. This early mortality was not seen in any other treatment group. In addition, fish exposed to both esfenvalerate and IHNV died 2.4 to 7.7 days sooner than fish exposed to IHNV alone. Results from this study show that accepted levels of

pollutants may not cause acute toxicity in fish, but may be acting synergistically with pathogens to compromise survivorship of fish populations through immunologic or physiologic disruption.

### **3.3.6 Individual Toxic Effects**

A contaminant may exert acutely toxic effects leading to mortality or sublethal effects in individuals. Sublethal toxic effects can occur at exposure levels far below the concentrations that cause lethality, and can have severe consequences for the fitness, reproductive success and survival of aquatic organisms, ultimately leading to population-level effects (Carson, 1962). Sublethal biological responses include altered behavior, reduced growth, immune system effects, reproductive/endocrine effects, histopathological effects as well as genetic effects. Direct links of these responses to higher-level effects are often difficult to establish. Nevertheless, sublethal toxic effects can have far-reaching consequences in the aquatic environment, especially where organisms are exposed to many different stressors. Both simple and complex techniques exist for assessing biological responses to contaminant stressors and often the simplest techniques can reap substantial rewards. Careful development of portfolios of biological indicators can make investigations practical and cost effective

#### *3.3.6.1 Lethal Effects*

Most aquatic invertebrates and fish are highly susceptible to pyrethroid insecticides (Smith and Stratton, 1986, Clark et al. 1989, many others). Pyrethroids are several orders of magnitude more toxic to fish than the organophosphate pesticides they are replacing in many agricultural, commercial and residential applications. Yet overall, most aquatic invertebrates are more sensitive to pyrethroids than fish. Most pyrethroid 96-h LC50s (the concentration that causes 50% mortality in a group of organisms within 96 h) for fish, aquatic insects and crustaceans are well below 1 ppb ( $\mu\text{g/L}$ , Table 2). In contrast, molluscs are relatively insensitive to these chemicals (Clark et al. 1989). Information on the toxicity of individual pyrethroids to fish and aquatic invertebrate species occurring in the Sacramento-San Joaquin Delta is limited. The available data suggest that some species resident in the Sacramento-San Joaquin watershed and delta are more sensitive to these compounds than standard bioassay species.

**Table 2. Summary of aquatic toxicity data for selected pyrethroids (lowest values), [from Werner & Moran, in review]**

Test Species	Lambda-Cyhalothrin		Bifenthrin		Cyfluthrin		Cypermethrin		Deltamethrin		Esfenvalerate		Permethrin	
	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)
<b>Invertebrates</b>														
<i>Ceriodaphnia dubia</i>			48-h LC50	0.07	48-h LC50	0.14					96-h LC50 <sup>4</sup>	0.3	48-h LC50	0.55
<i>Daphnia magna</i>	48-h EC50 <sup>7</sup>	0.36	48-h LC50	0.32	48-h LC50	0.17	24-h LC50	0.53	24-h LC50	0.11	48-h LC50 <sup>1</sup>	0.24	48-h LC50 <sup>1</sup>	0.075
		0.002	48-h EC50	1.6	48-h EC50	0.025	48-h LC50	0.13	48-h LC50	0.037	48-h LC50 <sup>1</sup>	0.27	LC50 <sup>1</sup>	6.8
	21-d NOEC <sup>7</sup>						48-h LC50 <sup>3</sup>	1.00	96-h LC50	0.01	48-h LC50	0.15	72-h LC50	0.3
							48-h EC50		96-h EC50	0.003	LC50		LC50	0.039
<i>Daphnia pulex</i>											48-h EC50		96-h LC50	
											EC50		LC50	
													96-h EC50	
													LC50	
													3-h LC50	9,200
													48-h LC50	2.75
													LC50	0.08
													72-h LC50	
													LC50	

Copepod, <i>Cyclops</i> sp.	48-h EC50 <sup>7</sup>	0.3							
Mayfly, <i>Hexagenia</i> <i>bilineata</i>								96-h LC50 <sup>3</sup>	0.1
Mayfly, <i>Procladius</i> sp.			48-h LC50 <sup>9</sup>	0.084				48-h LC50 <sup>9</sup>	0.090
Mayfly, <i>Cloeon dipterum</i>	48-h EC50 <sup>7</sup>	0.038			72-h EC50 <sup>3</sup>	0.006 0.023 0.03		96-h LC50 <sup>3</sup>	
Isopod, <i>Asellus aquaticus</i>	48-h EC50 <sup>7</sup>	0.026			72-h LC50 <sup>3</sup>	0.008			
Midge, <i>Chironimus</i> <i>dilutus</i>			96-h LC50 <sup>9</sup>	26.15				96-h LC50 <sup>9</sup>	10.45
Midge, <i>Chironimus</i> <i>riparius</i>	48-h EC50 <sup>7</sup>	2.4			48-h LC50 <sup>3</sup>	0.007			
Midge, <i>Chironimus</i> <i>plumosus</i>								48-h EC50 <sup>3</sup>	0.56
Grass shrimp, <i>Palaemonetes</i> <i>pugio</i>					96-h LC50 <sup>3</sup>	0.016			
<i>Hyalella azteca</i>	48-h	0.0023	96-h	0.009	48-h	0.005	42-D	0.05	96-h 0.021



	EC50 <sup>7</sup>	LC50 <sup>9</sup>	LC50 <sup>3</sup>	LOEC 96-h LC50 <sup>6</sup>	0.008	LC50 <sup>9</sup>
<i>Gammarus pulex</i>	48-h EC50 <sup>7</sup> 0.5-h LC50 <sup>8</sup>	0.014 5.69				
<i>Gammarus daiberi</i>				96-h LC50 <sup>6</sup>	0.033	
<i>Gammarus pseudolimnaeus</i>						96-h LC50 <sup>3</sup> 0.17
Crayfish, <i>Orconectes immunis</i>						96-h LC50 <sup>10</sup> 0.08
Mysid shrimp (B) <i>Americamysis bahia</i>		96-h LC50 0.004	96-h LC50 0.0024 2 LC50	96-h LC50 <sup>3</sup>	0.005 96-h LC50 0.0017	96-h LC50 <sup>1</sup> 0.038 96-h LC50 <sup>3</sup> 0.02
Pink shrimp (S, juv.), <i>Penaeus duorarum</i>			96-h LC50 <sup>3</sup>	0.036		96-h LC50 <sup>3</sup> 0.22
Stone crab (S), <i>Menippe mercenaria</i>						96-h EC50 <sup>3</sup> 0.018
Fiddler crab (S), <i>Uca pugilator</i>						96-h LC50 <sup>3</sup> 2.39
<i>Penaeus sp.</i> (S)			96-h LC50	0.036		96-h LC50 0.17

Oyster, <i>Crassostrea</i> <i>virginica</i> (S, B)	48-h EC50 (embryo)	285	96-h EC50	2.69	96-h EC50	370	96-h EC50	8.2	48-h EC50	1000
Oyster, <i>Crassostrea gigas</i> (S, B)	48-h EC50 <sup>2</sup> (larvae)	590.00			48-h LC50	2,270			48-h EC50	1,050

<sup>9</sup>(120= Anderson et al., 2006

<sup>10</sup>(121=Paul & Simonin, 2006

**Table 2 (cont.). Summary of aquatic toxicity data for selected pyrethroids (lowest values).**

Test Species	Lambda-Cyhalothrin		Bifenthrin		Cyfluthrin		Cypermethrin		Deltamethrin		Esfenvalerate		Permethrin	
	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)	Test	Result (µg/L)
<b>Vertebrates</b>														
Fathead minnow	96-h LC50 <sup>7</sup>	0.70	96-h LC50 <sup>1</sup>	0.26	96-h LC50 <sup>1</sup>	2.49					24-h LC50	0.24	24-h LC50	5.4
<i>Pimephales promelas</i>											48-h LC50	0.22	96-h LC50 <sup>1</sup>	
Rainbow trout	96-h LC50 <sup>2</sup>	0.54	96-h LC50	0.15	48-h LC50	0.57	12-h LC50	2.5	24-h LC50	0.7	96-h LC50 <sup>1</sup>	0.26	24-h LC50	4.3
<i>Oncorhynchus mykiss</i>	96-h LC50 <sup>2</sup>	0.24			96-h LC50	0.3	24-h LC50	5	48-h LC50	0.25	96-h LC50	0.07	48-h LC50	0.62
							48-h LC50	0.39	96-h LC50				96-h LC50	
Carp, <i>Cyprinus</i>	96-h LC50 <sup>7</sup>	0.50					96-h LC50 <sup>3</sup>	0.9						

<i>carpio</i>														
Mosquitofish,	24-h	0.18												
<i>Gambusia</i>	LC50 <sup>2</sup>	0.08												
<i>affinis</i>	24-h													
	LC50 <sup>2</sup>													
Atlantic salmon <i>Salmo salar</i>												96-h LC50 <sup>3</sup>	17	
Chinook salmon, <i>Onchorynchus tshawytscha</i>												96-h LC50 <sup>5</sup>	0.1-1.0	
Coho salmon, <i>O. kisutch</i>												96-h LC50 <sup>3</sup>	3.2	
Brook trout, <i>Salvelinus fontinalis</i>												24-h LC50	4	
												96-h LC50 <sup>3</sup>	3.2	
Sacramento splittail, <i>Pogonichthys macrolepidotus</i>												96-h LC50 <sup>4</sup>	0.50	
Sheepshead minnow (S) <i>Cyprinodon variegatus</i>	28-d NOEC <sup>7</sup>	0.25	96-h LC50 <sup>3</sup>	17.8	96-h LC50	4.05	96-h LC50	0.73	96-h LC50	0.36	96-h LC50 <sup>1</sup>	430	96-h LC50	7.8
Atlantic silverside, (S)													96-h	2.2

<i>Menidia menidia</i>														LC50 <sup>3</sup>
Inland silverside, (S)														96-h LC50 27.5
<i>Menidia beryllina</i>														
Bluegill (S),	96-h	0.42	144-h	0.35	96-h	0.87	96-h	1.78	96-h	0.36	96-h	0.26	24-h	6.6
<i>Lepomis macrochirus</i>	LC50	0.21	LC50 <sup>3</sup>		LC50		LC50 <sup>3</sup>		LC50		LC50 <sup>1</sup>		LC50	2.5
	96-h												96-h	
	LC50												LC50 <sup>3</sup>	
<b>Plants</b>														
<i>Selenastrum capricornutum</i>	96-h	>1000												
	EC50 <sup>7</sup>													
<i>Skeletonema costatum</i>														

Source: All unmarked values from U.S. Environmental Protection Agency (USEPA), Ecotox (Acquire) database, 2005

<sup>1</sup> California Department of Pesticide Regulation, 2007

<sup>2</sup> PAN (Pesticide Action Network) Pesticides Database, 2007

<sup>3</sup> California Department of Fish and Game, 2000

<sup>4</sup> Werner et al., 2002a

<sup>5</sup> Eder et al., 2004

<sup>6</sup> Werner I., unpublished data

<sup>7</sup> Schroer et al., 2004

(S) saltwater species

(B) brackish water species

### 3.3.6.2 Sublethal Effects

Effects of environmental stress can be evaluated at several levels of biological organization, from molecular processes up to growth and reproduction that impact overall population size and community interactions (Table 3). Some physiological endpoints commonly tested include hematological and immunological ones (e.g., hematocrit, plasma cortisol concentrations), assessments of liver and gill structure and function (e.g., liver somatic index, mixed function oxidases [MFO] enzyme induction), energetics (e.g., RNA/DNA ratios, swimming performance, feeding and growth rates), and behavioral and nervous system function (e.g., temperature tolerance, swimming performance, altered predator-prey interactions).

*Biochemical and physiological effects:* The use of biochemical and physiological biomarkers is widespread in aquatic toxicology, partly because their induction is much more sensitive to stress than traditional indices such as growth inhibition (Feder and Hofmann, 1999; Huggett et al. 1992). Some of these sublethal stress responses divert an organism's energy away from normal metabolic functions and can result in "higher-level" effects such as growth inhibition or reduced reproductive success. For example, increased expression of cellular stress proteins (hsps), an indicator of cellular protein damage, has been linked to reduced scope-of-growth in bivalves (Sanders et al., 1991), and a reduction in cellular energy levels (Viant et al. 2004) in juvenile steelhead trout.

Biochemical and physiological effects of pyrethroids have been measured in juvenile Chinook salmon (0.01 ppb esfenvalerate; Eder et al., 2004), in Korean rockfish (*Sebastes schlegeli*; mean fish wt: 52 g) exposed to 0.041 ppb cypermethrin (Jee et al., 2005), and in Atlantic salmon exposed to 0.004 ppb (Moore and Waring, 2001).

*Tissue and organ damage:* Histopathological lesions in the liver were observed in Sacramento splittail (*Pogonichthys macrolepidotus*; Teh et al., 2005) shortly (1 wk) after a 96-h exposure to sublethal concentrations of organophosphate and pyrethroid insecticides. Fish recovered from these lesions, but showed high (delayed) mortality rates, grew slower and showed signs of cellular stress even after a 3 month recovery period. A significant reduction in liver glycogen levels of fathead minnow (*Pimephales promelas*, Denton, 2001) was observed after 96-h exposure to 0.20 ppb esfenvalerate. Likewise, Haya and Wainwood (1983) found a depletion of glycogen stores in liver and muscle for starving juvenile Atlantic salmon exposed to fenvalerate. The loss of glycogen (a secondary stress response) should be regarded as a nonspecific response signifying stress and has been linked to changes in cortisol during exposure to various stressors (Wedemeyer et al., 1990).

*Behavior:* Abnormal behaviors produced by contaminants include changes in preference or avoidance, activity level, feeding, performance, learning, predation, competition, reproduction and species-specific social interaction such as aggression. Such changes can have significant consequences for fitness, survival and reproductive success of an individual. For example, many neurotoxic compounds such as pyrethroids cause abnormal swimming behavior or compromise swimming ability in fish and other aquatic animals (U.S. EPA, 2005; Christensen et al., 2005; Heckmann et al., 2005). In the field, such changes can directly translate into increased vulnerability to predation or decreased food intake.

Sublethal effects of acute cypermethrin exposure on swimming performance were assessed in studies in rainbow trout and bluegill sunfish (USEPA, 2005). The sublethal signs

of toxicity included rapid and erratic swimming, partial/complete loss of equilibrium, jaw spasms, gulping respiration, lethargy, and darkened pigmentation. For the two studies, the acute NOEC values for sublethal effects were several orders of magnitude lower than the LC50 value; in rainbow trout, the acute NOEC and LC50 values were 0.00068 ppb and 0.8 ppb, respectively, and in bluegill sunfish, the acute NOEC and LC50 values were <0.0022 ppb and 2.2 ppb, respectively. Sublethal effects of acute cypermethrin exposure in estuarine/marine fish (loss of equilibrium and lethargy) were reported in two studies of sheepshead minnow (USEPA, 2005). Acute NOEC values for sublethal effects ranged from 0.84 ppb to 1.4 ppb and are approximately 2 to 3-fold lower than the corresponding LC50 values of 2.7 and 2.4 ppb, respectively.

In waterflea, the sublethal signs of pyrethroid toxicity include immobilization and decreased movement in response to stimulation. Acute NOEC values for the sublethal effects of cypermethrin range from 0.085 ppb to 0.14 ppb. Christensen et al. (2005) showed that environmentally relevant, brief (6 h) exposures to 0.1 ppb cypermethrin decreased feeding efficiency and swimming ability of *Daphnia magna*. Animals recovered after 3 days in clean water. A 30-min pulse exposure of *Gammarus pulex* to lambda-cyhalothrin (Heckmann et al. 2005) significantly impaired pair formation (pre-copula), with EC10 (30 min) and EC50 (30 min) values of 0.04 and 0.2 ppb. Significant mortality was observed at 0.3 ppb, with an LC50 (30 min) of 5.69 ppb. Sublethal effects (lethargy, erratic swimming behavior, loss of equilibrium, and surfacing) of cypermethrin in estuarine/marine invertebrates were also reported in two studies of mysid shrimp (USEPA 2005). Acute NOEC values for sublethal effects range from 1.7 to 2.3 ppt (ng/L) and are approximately 2 to 3-fold lower than the corresponding LC50 values of 5.5 and 5.9 ppt (ng/L), respectively.

*Reproductive toxicity and endocrine disruption:* Moore and Waring (2001) demonstrated that the pyrethroid cypermethrin reduced the fertilization success in Atlantic salmon after a 5-day exposure to 0.1 ppb. In a study on bluegill sunfish, Tanner and Knuth (1996) found delayed spawning and reduced larval survival after two applications of 1 ppb esfenvalerate. Results of a study performed by Werner et al. (2002b) suggest that dietary uptake of esfenvalerate (148 ppm) may lead to a decrease in fecundity in adult medaka (*Oryzias latipes*), and a decrease in the percentage of viable larvae.

Day (1989) showed that concentrations of <0.01 ppb permethrin and other pyrethroids reduced reproduction and rates of filtration of food by daphnids. A concentration of 0.05 ppb esfenvalerate led to a significant decrease in reproductive success (number of neonates) of *Daphnia carinata* (Barry et al., 1995). Reynaldi and Liess (2005) demonstrated that fenvalerate delayed the age at first reproduction in *Daphnia magna*, and reduced fecundity at a LOEC of 0.1 ppb (complete mortality occurred at 1 ppb). Population growth rate was inhibited at 0.6 ppb (24 h), and recovery occurred after 21 d. Results of chronic toxicity studies in mysid shrimp show that exposure to cypermethrin had adverse effects on reproductive parameters. For decreased number of young, a chronic NOEC value of 1.5 ppt (ng/L) was reported in two studies (USEPA, 2005).

*Growth:* Growth integrates a suite of biochemical and physiological effects into one endpoint that can often be associated with individual fitness. Results of chronic toxicity studies in mysid shrimp show that exposure to technical grade cypermethrin had adverse effects on growth parameters. For decreased growth and length, the chronic NOEC value reported is 0.781 ppt (ng/L). In a mesocosm study on bluegill sunfish, Tanner and Knuth (1996) found that young-of-the-year growth was reduced by 57, 62 and 86% after two

applications of 0.08, 0.2 and 1 ppb esfenvalerate, respectively.

*Immune system effects:* The immune response of fish and invertebrates plays a key role in the control of aquatic diseases, fitness and reproductive success. Pesticides are among those contaminants identified to cause immunosuppressive effects on fish (Banerjee, 1999; Austin, 1999), but few studies have established the correlation between pyrethroids and disease resistance. Zelikoff et al. (1998) found reduced disease resistance in fish exposed to the pyrethroid permethrin. The susceptibility of juvenile Chinook salmon and rainbow trout to infectious hematopoietic necrosis virus (IHNV) was dramatically increased in juvenile fish exposed to sublethal concentrations of esfenvalerate (Clifford et al. 2005). Eder et al. (2004) found that exposure to 0.08 ppb esfenvalerate for 96 h altered the transcription of immune-system messenger molecules (cytokines) in juvenile Chinook salmon (*Oncorhynchus tshawytscha*). Cytokines regulate the innate and adaptive immune systems and are produced in response to infection or an inflammatory insult.



**Table 3. Reported sublethal effects of several pyrethroids on aquatic species, [from Werner & Moran, in review]**

Pyrethroid	Species	Life-Stage/Test Duration	Effect	Effect Concentration (µg/L)	Source
Bifenthrin	Fathead minnow, <i>Pimephales promelas</i>	Life-cycle	LOEC NOEC	0.09 0.05	California Department of Fish and Game, 2000
Lambda-Cyhalothrin	<i>Gammarus pulex</i>	Adult/ 30 min	EC10 (Pair formation) EC50 (Pair formation)	0.04 0.20	Heckman et al., 2005
Cypermethrin	<i>Daphnia magna</i>	Adult/6 h	LOEC (Decrease in feeding efficiency and swimming ability)	0.1	Christensen et al., 2005
	Mysid shrimp, <i>Americamysis bahia</i>	28 d	LOEC (fecundity) NOEC (fecundity) LOEC (growth)	0.0028 0.0015 0.00078	US EPA, 2005
	Fathead minnow, <i>Pimephales promelas</i>	Larvae/30 d	LOEC NOEC	0.33 0.15	California Department of Fish and Game, 2000
	Rainbow trout, <i>O. mykiss</i>	-	LOEC (behavior)	0.68	US EPA, 2005
	Bluegill sunfish, <i>Lepomis macrochirus</i>	-	LOEC (behavior)	<2.2	US EPA, 2005
	Atlantic salmon, <i>Salmo salar</i>	Gamets/5 d Adult/5 d	LOEC (fertilization success) Impaired olfactory function	0.1 <0.004	Moore & Waring, 2001
	Korean rockfish, <i>Sebastes schlegeli</i>	52 g/8 wk	Changes in blood parameters	0.041	Jee et al., 2005
Esfenvalerate	<i>Daphnia carinata</i>	Adult	Reduced fecundity	0.05	Barry et al., 1995
	Midge, <i>Chironomus tentans</i>	Larvae/14-16 d	EC10 Mobility EC50 Mobility	0.078 0.21	Belden & Lydy, 2006
	Fathead minnow, <i>Pimephales promelas</i>	Larvae/96 h	Reduction in hepatic glycogen NOEC Swimming performance	0.20 0.13	Denton, 2001
	Fathead minnow, <i>Pimephales promelas</i>	Larvae/4 h	Swimming performance	0.7	Floyd et al., in review
	Bluegill, <i>Lepomis macrochirus</i>	Juvenile/90 d Young-of-the-Year Adult Embryos/Larvae	LOEC NOEC Growth Delayed spawning Reduced larval survival	0.025 0.010 0.08 1.0 1.0	CDFG, 2000 “ Tanner & Knuth, 1996
	Medaka, <i>Oryzias latipes</i>	Adult/7 d	Stress protein (hsp) increase	21 µg/g (diet)	Werner et al., 2002b
	Chinook salmon, <i>Oncorhynchus tshawytscha</i>	Juvenile/96 h	Alteration of immune response Stress protein (hsp) increase	0.08 0.01	Clifford et al., 2005 Eder et al., 2007
Permethrin	Daphnid	Adult	LOEC (fecundity)	<0.01	Day, 1989
	Sheepshead minnow, <i>Cyprinodon variegatus</i>	28 d	LOEC NOEC	22 10	CDFG, 2000

### 3.3.7 Population Level Effects

Toxic effects of pyrethroids leading to changes in population size and structure of Delta species can have far reaching effects on the food web, many of which are difficult to predict. If, for example, key invertebrate species are decimated, species at higher trophic levels may be affected due to reduced survival of highly specialized early life-stages leading to a reduction of surviving adults. This may, in turn, reduce predation pressure (or control) of other prey species, and so on, eventually altering the entire community structure.

Pyrethroids are generally of very low water solubility and high lipophilicity, and therefore are rapidly adsorbed to particulate material and other surfaces. Adsorption occurs on the order of hours in sediment-laden solutions under ideal laboratory mixing conditions (Maund et al., 2002) or in systems like farm ponds that contain relatively large amounts of organic matter (Litchfield, 1985); however, in typical streams, where less ideal mixing conditions exist, adsorption may occur over a period of days rather than hours (Capel et al., 2001). In the adsorbed state their bioavailability to aquatic organisms is reduced (Yang et al., 2006 a, b). Direct toxic effects may therefore be expected when animals are in direct contact with sediments, and/or when organisms are highly sensitive to pyrethroids, which is the case for aquatic insects and crustaceans. In the water column exposures of short duration or pulse exposure are believed to be more common than long-term chronic exposures. Below we summarize the results of short-term field and pulse studies.

Studies on the effects of cypermethrin on fish, where application rates ranged from 0.011 lb a.i./A (Davies and Cook, 1993) to 0.0623 lb a.i./A (Crossland et al., 1982), found no acute toxicity (mortality) on fish populations, but sublethal effects (including loss of equilibrium, lethargy, and muscle tetany) were reported following a single application of 0.011 lb a.i./A. In this study, sublethal pathological changes in fish were observed for 26 days following application and were attributed, to direct exposure to cypermethrin as well as to dietary exposure from ingestion of dead and dying invertebrates.

In field studies assessing the effects of cypermethrin on aquatic invertebrates and benthic populations, results show that exposure to cypermethrin at application rates to water surfaces ranging from 0.00025 lb a.i./A (Mulla et al., 1978) to 0.125 lb a.i./A (USEPA, 2005) causes significant decreases in abundance and diversity of aquatic invertebrate populations. Effects include catastrophic drift within 0-90 minutes after application of cypermethrin (Crossland, 1982; Farmer et al., 1995; Mohsen and Mulla, 1982), and decreased abundance and diversity of macroinvertebrates over a longer time-period (several weeks to several months; Farmer et al., 1995; Kedwards et al., 1999a, b; Mulla et al., 1978; Mulla et al., 1982). Plecoptera and ephemeroptera comprised 89-92% of the drift immediately after spraying (Davies and Cook, 1993). Soon after treatment, concentrations of cypermethrin associated with surface water and emergent vegetation were much greater than those associated with subsurface water and benthic sediment. Downward dispersion from surface to subsurface water was relatively limited. Only 8-16% of cypermethrin applied to the surface was subsequently found in subsurface water (Crossland, 1982).

Field studies on the effects of esfenvalerate also demonstrated detrimental effects on aquatic systems (2 ha pond) by reduction or elimination of many crustaceans, chironomids, juvenile bluegills and larval cyprinids at exposure levels of 1 ppb (Lozano et al., 1992, Tanner

and Knuth, 1996). Esfenvalerate exposures of 1 and 5 ppb resulted in drastic reductions or elimination of most crustaceans, chironomids, juvenile bluegills (*Lepomis macrochirus*), and larval cyprinids. Abundance of some copepod and insect genera declined at esfenvalerate concentrations of 0.08 to 0.2 ppb, and these effects were apparent up to 53 d. Some invertebrate communities were able to recover by day 25 in enclosures containing concentrations of less than or equal to 0.2 ppb esfenvalerate (Lozano et al. 1992).

Roessink et al. (2005) compared the fate and effects of the pyrethroid insecticide lambda-cyhalothrin in mesotrophic (macrophyte-dominated) and eutrophic (phytoplankton-dominated) ditch microcosms (0.5 m<sup>3</sup>). Lambda-cyhalothrin was applied three times at one-week intervals at concentrations of 10, 25, 50, 100, and 250 ng/L (part per trillion). The highest concentration was selected based on a 5% drift emission from a field application of 0.015 kg/ha of lambda-cyhalothrin (as "Karate" formulation) into a ditch with a depth of 0.3 m. The rate of dissipation of lambda-cyhalothrin in the water column of the two types of test systems was similar. After 24 h, 30% of the amount applied remained in the water phase. None of the lambda-cyhalothrin applied in the water column was recovered from sediment samples. Initial, direct effects were observed primarily on arthropod taxa. Threshold levels for slight and transient direct toxic effects were similar (10 ng/L) between the two mesotrophic and eutrophic test systems. At treatment levels of 25 ng/L and higher, apparent population and community responses occurred. At treatments of 100 and 250 ng/L, the rate of recovery of the macroinvertebrate community was lower in the macrophyte-dominated systems, primarily because of a prolonged decline of the amphipod *Gammarus pulex*. This species occurred at high densities only in the macrophyte-dominated enclosures. Indirect effects (e.g., increase of rotifers and microcrustaceans) were more pronounced in the plankton-dominated test systems, particularly at treatment levels of 25 ng/L and higher.

Hill et al. (1994) reviewed approximately 75 freshwater field studies with pyrethroid insecticides. The studies were carried out in natural/farm ponds, streams or rivers (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, fenvalerate and permethrin), rice paddies (cypermethrin, lambda-cyhalothrin and permethrin), ponds for farming fish and crayfish (fenvalerate and permethrin), lake limnocorral enclosures (fenvalerate and permethrin), pond littoral enclosures (cypermethrin, esfenvalerate and permethrin) and outdoor pond microcosms or mesocosms (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin and tralomethrin). The authors concluded that the spectrum of acute biological effects of these products in bodies of water, at application rates equivalent to a single "drift-entry" of 1-5% of the USA labeled maximum use-rate (applied as multiple treatments), is limited to the zooplankton and macroinvertebrate crustaceans and to some of the aquatic insects.

Van Wijngaarden et al. (2005) reviewed 18 microcosm and mesocosm studies on eight pyrethroids. The authors concluded that recovery of sensitive endpoints usually occurs within 2 months of the last application when peak pyrethroid concentrations remain lower than (0.1 x EC50) of the most sensitive standard test species. Amphipoda and Hydracarina were the taxa most sensitive to pyrethroid insecticides, followed by Trichoptera, Copepoda, Ephemeroptera and Hemiptera.

## Limitations and Recommendations

Critical data gaps on pyrethroids exist. To provide much needed information the following questions should be answered in future work:

- Which pyrethroids compounds and at what concentrations are present in key fish spawning areas of the Delta?
- Are pyrethroids found at biologically relevant concentrations that can cause toxicity to critical species and sensitive life stages?
- Which activities (agricultural and urban) are most likely responsible for transporting pyrethroids to sensitive spawning areas?
- Do chronic, low doses of pyrethroids cause direct (to resident fish) and indirect (to resident food supply species) toxicity?
- Do pyrethroids interact with each other or with other chemical contaminants to induce toxicity?

*Toxic effects on Delta species:* In general, little is known about the toxic effects of pyrethroids on resident Delta species. Even less is known about the sublethal toxic effects of these contaminants. Although it is difficult to model sublethal responses to toxicants and predict ecotoxicological impact or risk, measures of sublethal effects are likely to be as important, or more important, than the measures of acute or chronic lethal effects to accurately assess the consequences of contaminant exposure. The primary mechanism of toxic action is often not the only toxic effect a chemical can exert on target and non-target species. For example, neurotoxic pesticides may impair the immune system or exhibit hormonal effects, or can alter behavior with negative effects on predator avoidance or reproductive success (see above). Many of these chemical side effects are poorly understood or unknown.

*Effects of chemical mixtures and multiple stressors:* In the Delta, organisms are likely to be simultaneously exposed to multiple chemical stressors in addition to potential physical and biological stressors. To date, the effects of multiple stressors and chemical mixtures are poorly understood. Approaches to assess the effects of mixtures are discussed in the Delta Chemical Stressors conceptual model Werner et al. (2008).

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