Pyrethroid Insecticides: An Analysis of Use Patterns, Distributions, Potential Toxicity and Fate in the Sacramento-San Joaquin Delta and Central Valley

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1. Introduction

1.1. Objective

The objective of this white paper is to summarize our current knowledge of the potential role of pyrethroid insecticides in the pelagic organism decline in the upper San Francisco estuary (Suisun Bay and the Sacramento-San Joaquin Delta). Included in this white paper is a discussion on pyrethroid use patterns, transport and fate, regional monitoring results, uses of special concern such as orchard dormant season and urban area applications, analytical testing methods, and toxicity to critical species focusing on aqueous exposure since the concern here is pelagic species. Information and data gaps are identified and recommendations for immediate and future work on pyrethroids are made. To facilitate the reading bullets are presented at the beginning of each chapter to highlight the important points that are discussed. The intent here is to present information in a weight of evidence approach that can be used to help address several key questions:

- *What are the major use patterns, activities, and events that can contribute pyrethroids to the Delta watershed?*
- *Where are pyrethroids found?*
- *Are concentrations high enough to cause toxicity to species of concern?*
- *Are there periods when the potential for pyrethroid exposure is greatest and are species of concern present during those periods?*
- *Is there a link between pyrethroid use and the declining pelagic organism populations in the Delta?*

1.2. Problem Statement

In 2005, the Interagency Ecological Program (IEP) reported that pelagic fish populations in the upper San Francisco Estuary have declined over the last few years. The 2002-2004 Fall Midwater Trawl survey (MWT) abundance indices indicated record lows for delta smelt and age-0 striped bass and near-record lows for longfin smelt and threadfin shad (Bryant and Souza, 2004). The Summer Townet Survey (TNS) abundance indices were also among the lowest in the 45-year record of field monitoring. A recent study in the San Francisco estuary showed that there were no significant declines in its catches of marine/lower estuary species (Hieb et al., 2004), thus the fish decline problem appeared to be limited to fishes in the upper estuary only. In addition, the IEP further reported that zooplankton were also showing declining abundance trends especially calanoid copepods, which are the primary food for larval pelagic fishes in the upper estuary (IEP, 1987; Meng and Orsi, 1991; Nobriga, 2002) and older life stage of planktivorous species such as delta smelt (Lott, 1998). It has been suggested that pesticide use in the Central Valley and Delta region might play an important role in pelagic organism declines in the upper estuary. Agricultural field runoff of pesticides has been implicated as a potential cause of aquatic biota toxicity in the Delta's receiving waters.

The pesticides of concern in this white paper are the pyrethroid insecticides, which are the replacements for the organophosphate (OP) insecticides. Pyrethroid concentrations in the Delta would be expected to peak during periods of peak agricultural application, which are in the spring and summer months. Unfortunately, this application period is noted to coincide with the spawning period of several important fish such as the delta smelt, which spawns from February to June (Moyle, 1976). Juvenile delta smelt prey on planktonic crustaceans, small insect larvae, and mysid shrimp as their major food items (Moyle, 1976). These prey items are prone to pyrethroid toxicity. Pyrethroids are designed to act as insecticides so their potential impact in aquatic environments is largely on arthropods and is much greater than other species such as fish.

1.3. Background

The U.S. EPA's decision to phase out/eliminate certain uses of the OP insecticides because of their potential for causing toxicity in humans, especially children, has led to their gradual replacement with another class of insecticides, pyrethroids. Pyrethroids are synthetic derivatives of pyrethrins, which are natural insecticides that are produced by certain species of chrysanthemum. Pyrethroids are neurotoxins and target insects' central nervous system.

The pyrethroids of greatest interest to water quality include bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lamba-cyhalothrin, and permethrin. These insecticides are applied in urban areas primarily for structural pest control, in agricultural areas on row crops (e.g., alfalfa, cotton, and lettuce) and orchards (e.g., almonds, pistachios, and peaches), and are used in the home in pet sprays and shampoos. In 2003, permethrin was ranked the 43rd most used pesticide in California: 443,676 pounds applied over 755,978 acres (California Department of Pesticide Regulation, Pesticide Use Reporting database: www.cdpr.ca.gov). Some of the new pyrethroids such as cypermethrin, which is used in much lower amounts, could be up to 20 times more toxic than permethrin. For instance, 1 kg of cypermethrin has about the same toxic potency as 18 kg of permethrin (Amweg et al., 2005). Pyrethroids are not very toxic to mammals, but laboratory tests have shown that they are extremely toxic to fish such as fathead minnow, rainbow trout, brook trout, bluegill, and sheepshead minnow (TDC, 2003).

Pyrethroid peak agricultural application periods are in the spring and summer months. This application period coincides with the spawning period of several important fish species such as the Delta smelt, which spawns from February to June (Moyle, 1976). Juvenile delta smelt prey on planktonic crustaceans, small insect larvae, and mysid shrimp as their major food items (Moyle, 1976). In a worst case situation, these prey items can be impacted due to pyrethroid toxicity especially during the periods of peak agricultural and urban runoff discharge.

2. Pyrethroid Use Patterns

Important Points:

- *Permethrin and cypermethrin use amounts continue to dominate over other pyrethroids composing 32% and 27% of the total pyrethroids used in 2003, respectively.*
- *Pyrethroid use amounts (lbs) for the period 2000-2003 were 1.6 to 2 times higher than during the period 1991-1995.*
- *Pyrethroid use in the San Joaquin Valley composed 62% of the total pyrethroid amounts used in 2003, while the Sacramento Valley was 38% of the total.*
- *Agricultural uses continue to dominate over other non-agricultural uses especially during the summer months May through August, with peak use occurring in July.*
- *Pyrethroid average application rates (lbs/acre) for the Central Valley were 0.134 lbs/acre during the period 1991-1995, 0.170 lbs/acre for 1996-1999, and 0.177 lbs/acre for 2000-2003, an overall increase of 32% since the 1991-1995 period.*

Pyrethroid use patterns are presented to evaluate the potential for impacts due to pyrethroid off-site losses from agricultural and non-agricultural (other uses) source areas where pyrethroids are applied. The pyrethroid use data were accessed from the California Department of Pesticide Regulation's, Pesticide Use Reporting (PUR) database: www.cdpr.ca.gov. Emphasis was placed on analyzing pyrethroid use patterns in the Sacramento Valley and San Joaquin Valley drainage areas over the period 1991-2003, since these are the data that were available. Data from both valleys were combined, hereafter referred to as the Central Valley, to show pyrethroid use patterns for the Delta's watershed.

2.1. Agricultural and Non-Agricultural Applications

The total pyrethroid use amounts (lbs) for the Central Valley watershed, which is the sum of the use amounts for the Sacramento and San Joaquin Valleys, during 1991-2003 are shown in Table 1 and are also plotted in Figure 1. Pyrethroid use in the Central Valley has steadily increased since 1991, peaked in 2002 at ~186,000 lbs and declined to ~178,000 lbs in 2003. Further analysis of the data show that pyrethroid use amounts in the Sacramento Valley (total sum of nine counties) and San Joaquin Valley (total sum of five counties) grew at a similar rate up through 1998 and thereafter San Joaquin Valley use amounts significantly exceeded those in the Sacramento Valley. In 2000, the pyrethroid use amounts in the San Joaquin Valley reached ~120,000 lbs, which was two times higher than that of the Sacramento Valley for the same year. The amount of use in the San Joaquin Valley has since gradually declined to its 2003 level of ~110,000, which is 62% of the total pyrethroids used (~178,000 lb) in that year. On average, the county that used the most pyrethroids over the period 1991-2003 was Stanislaus (~24,000 lbs/year), followed by Merced (~18,000 lbs/yr) and Sacramento and San Joaquin (both with ~17,000 lbs/yr) counties.

Table 1. Pyrethroid use amounts (lbs) by county 1991-2003.

Sacramento Valley													
County	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Butte	2,262	3,761	5,543	6,907	5,757	7,621	8,989	7,631	8,941	6,175	6,348	4,726	4,774
Colusa	1,411	2,296	2,258	3,092	3,277	2,247	2,835	9,347	3,559	2,210	2,636	2,727	3,096
Glenn	2,371	2,778	4,211	4,726	4,494	4,457	5,413	3,677	3,410	4,307	3,794	4,653	3,485
Sacramento	2,834	3,365	4,675	6,719	9,362	17,849	13,551	16,013	20,360	20,071	24,235	28,899	25,568
Solano	3,401	2,123	7,801	3,255	4,477	3,733	4,212	5,034	4,307	3,985	2,987	3,251	4,827
Sutter	4,991	6,366	6,110	7,725	6,855	8,497	12,701	9,173	7,588	9,600	7,842	7,686	7,525
Tehama	576	745	1,098	916	1,278	1,263	1,464	1,498	962	876	937	1,143	1,103
Yolo	5,018	4,724	4,616	7,098	8,459	7,705	7,752	9,019	7,503	6,646	4,689	4,937	4,694
Yuba	2,006	2,883	3,114	3,591	3,857	3,741	3,258	3,617	2,673	2,853	2,951	2,408	2,824
Total	24,867	29,041	39,427	44,029	47,817	57,112	60,173	65,009	59,303	56,723	56,418	60,430	57,896
San Joaquin Valley													
County	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
San Joaquin	6,034	11,773	9,462	10,461	10,118	14,647	14,643	17,544	18,092	21,276	16,034	19,732	22,744
Merced	3,770	8,320	8,788	9,031	10,934	10,301	12,642	28,847	27,231	30,165	22,528	17,512	16,443
Madera	3,115	5,534	5,570	7,366	6,007	7,202	9,775	9,112	9,110	13,791	11,800	14,418	12,733
Fresno*	6,400	11,619	9,212	7,507	9,781	8,572	8,936	11,621	8,676	8,563	7,925	9,226	9,981
Stanislaus	6,177	7,204	9,293	12,010	12,438	13,693	17,186	18,660	21,957	40,309	47,667	40,762	29,742
Total	25,497	44,448	42,324	46,374	49,278	54,415	63,181	85,783	85,066	114,103	105,954	101,649	91,642
Central Valley[1]	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Total	50,364	73,489	81,751	90,403	97,094	111,527	123,354	150,792	144,369	170,826	162,372	162,079	149,537

*Multiplied by 0.25 factor since only 25% of Fresno County drains into the San Joaquin River.
[1]Central Valley is the sum of the use amounts for Sacramento and San Joaquin Valley counties.
PUR database county codes are provided.

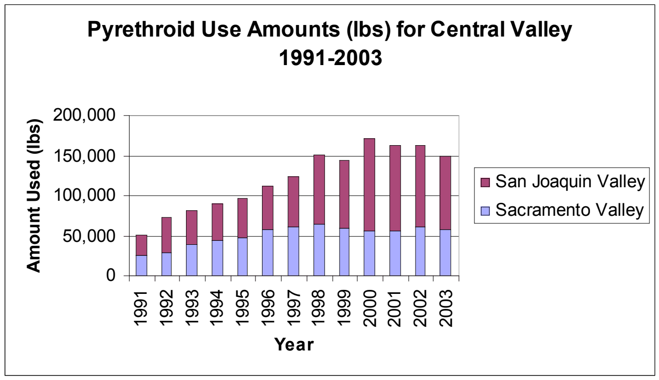


Figure 1. Bar plot showing pyrethroid use amounts (lbs) for the Central Valley 1991-2003. Central Valley is the sum of the use amounts for the Sacramento and San Joaquin Valleys.

Monthly pyrethroid use amounts for the period covering 2001-2003 for the Central Valley watershed, and the Sacramento and San Joaquin Valleys are shown in Figures 2, 3, and 4, respectively. Agricultural uses were slightly higher than other non-agricultural uses (e.g., structural pest control, landscape, right-of-way, and public health pest control), especially during the months May through August. Agricultural use begins to increase in May, peaks in July, and tapers down by October. In January pyrethroid use increases again, decreases in February, and increases again in March. These three winter months coincide with nut tree and stone fruit orchard dormant season applications, which begin around late December and continue through February. Other non-agricultural applications (e.g., structural pest control, landscape, right of way, and public health pest control, etc.) generally peak from May through October. Pyrethroid use in November and December was predominantly from other non-agricultural applications. The Sacramento Valley and San Joaquin Valley monthly pyrethroid use trends for agricultural and other non-agricultural uses are similar.

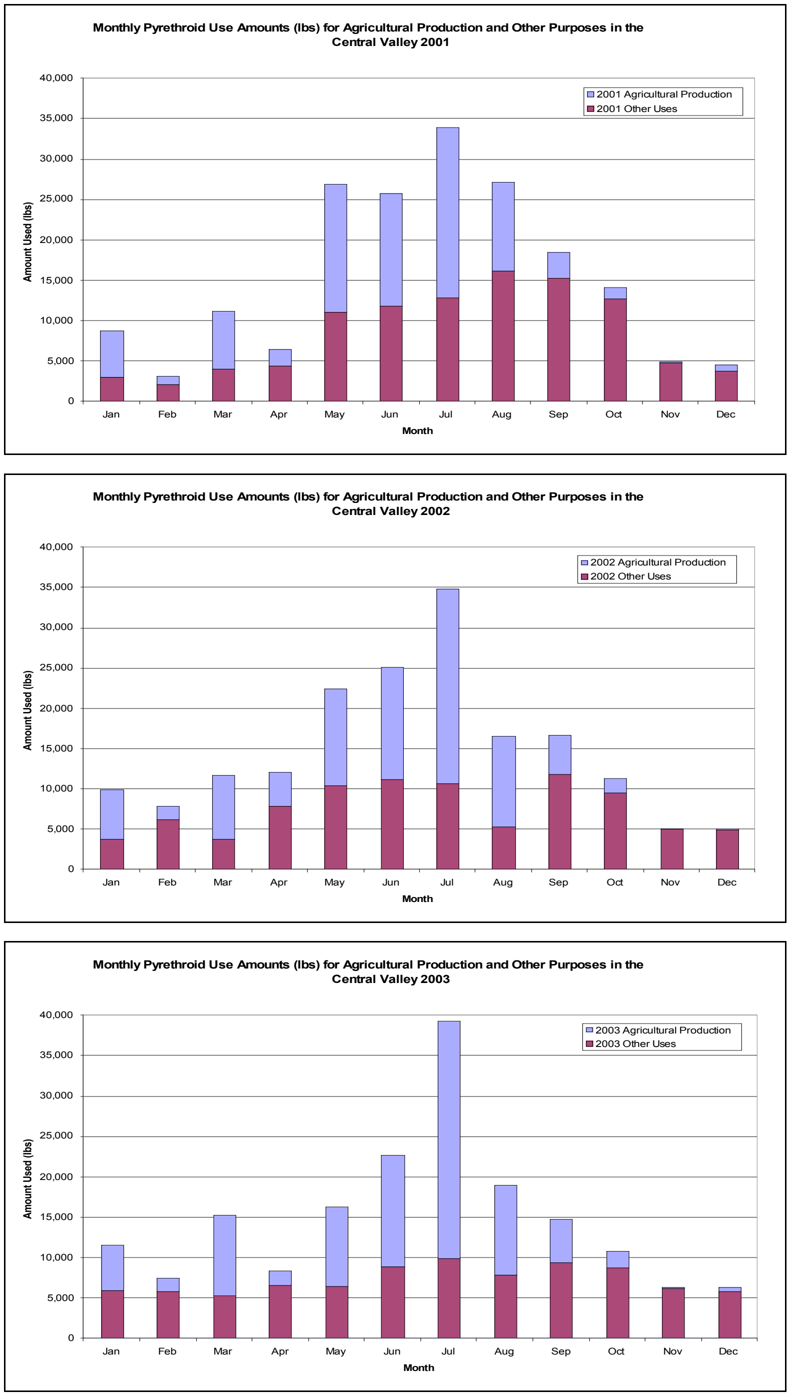


Figure 2. Bar plot showing monthly pyrethroid use amounts (lbs) for agricultural and other purposes in the Central Valley 2001-2003.

Data were derived from CDPR PUR database. Non-agricultural uses include structural pest control, landscape, right of way, and public health pest control Counties include Butte, Colusa, Glenn, Sacramento, Solano, Sutter, Tehama, Yolo, and Yuba in the Sacramento Valley, and 0.25*(Fresno), Madera, Merced, Stanislaus, and San Joaquin in the San Joaquin Valley. Pyrethroids included were bifenthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, permethrin, deltamethrin, cyfluthrin, resmethrin, tralomethrin, pyrethrin, fenpropathrin, fenvalerate, tau-fluvinate, and zeta-cypermethrin.

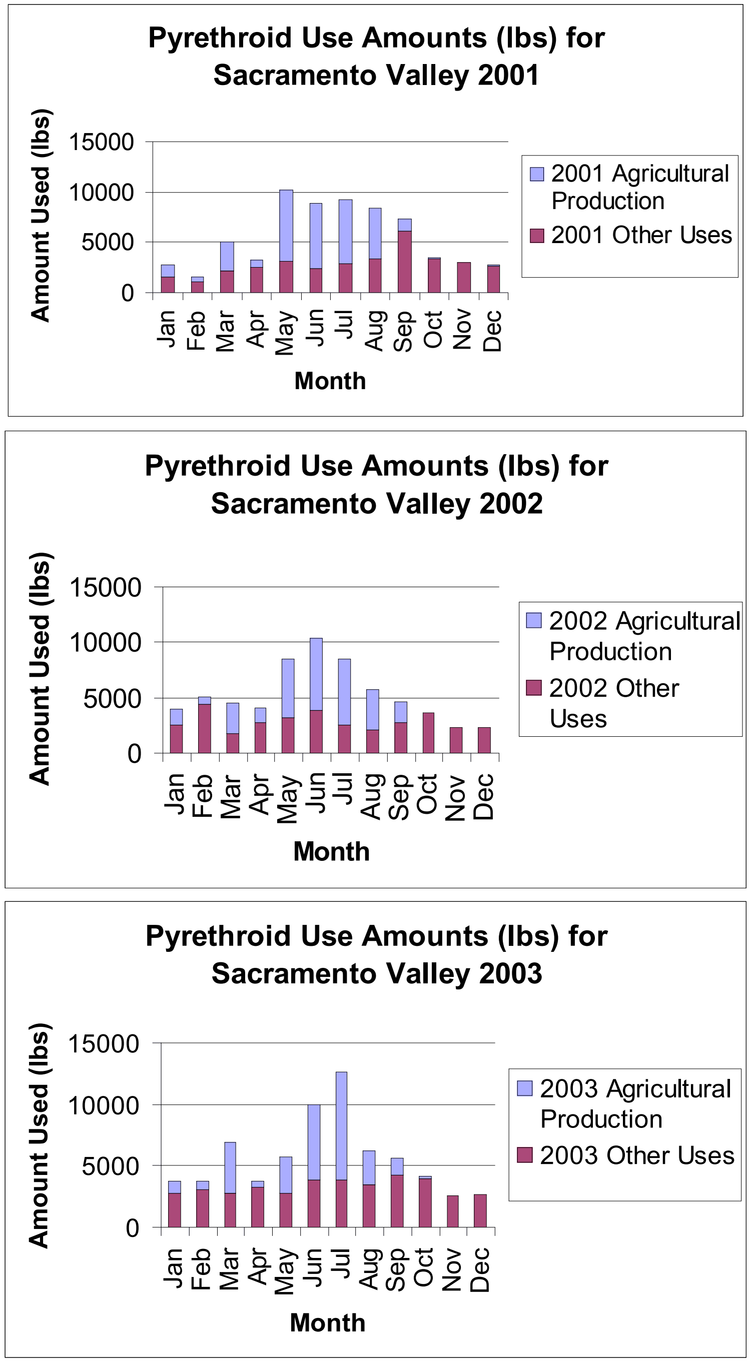


Figure 3. Bar plot showing monthly pyrethroid use amounts (lbs) for agricultural and other purposes in the Sacramento Valley 2001-2003.

Data were derived from CDPR PUR database. Counties queried include Butte, Colusa, Glenn, Sacramento, Solano, Sutter, Tehama, Yolo, and Yuba in the Sacramento Valley. Pyrethroids included were bifenthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, permethrin, deltamethrin, cyfluthrin, resmethrin, tralomethrin, pyrethrin, fenpropathrin, fenvalerate, tau-fluvinate, and zeta-cypermethrin.

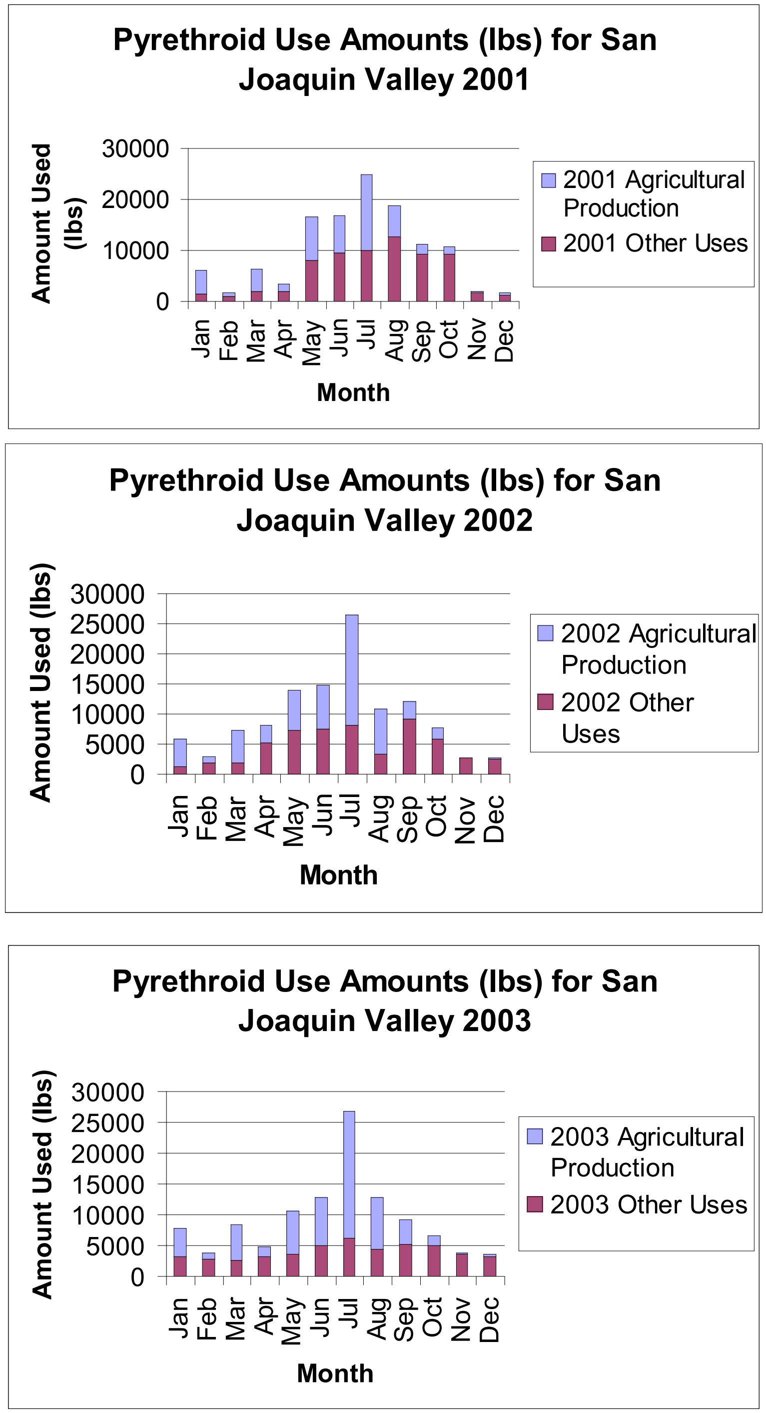


Figure 4. Bar plot showing monthly pyrethroid use amounts (lbs) for agricultural and other purposes in the San Joaquin Valley 2001-2003.

Data were derived from CDPR PUR database. Counties queried include 0.25*(Fresno), Madera, Merced, Stanislaus, and San Joaquin in the San Joaquin Valley. Pyrethroids included were bifenthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, permethrin, deltamethrin, cyfluthrin, resmethrin, tralomethrin, pyrethrin, fenpropathrin, fenvalerate, tau-fluvinate, and zeta-cypermethrin.

2.2. Pyrethroid Application Patterns

The pyrethroid use amounts for the Central Valley, which is the sum of the use amounts for the Sacramento and San Joaquin Valleys during the period 1991 to 2003, are shown in Table 2. The pyrethroids that were used most in the Central Valley include permethrin, cypermethrin, esfenvalerate, bifenthrin, and cyfluthrin. Lambda-cyhalothrin has also been used in high amounts but only since 1998. The top 5 pyrethroids, which are focused on here because of their increasing use amounts during the most recent application period of concern 1999-2003, are plotted in Figure 5. Permethrin use continued to dominate over other pyrethroids comprising 32% of the total amount used (177,659 lbs) in 2003, while cypermethrin composed 27%. In the San Joaquin Valley, permethrin use decreased and cypermethrin use increased, while in the San Joaquin Valley permethrin use increased while cypermethrin use decreased. Bifenthrin use increased rapidly and it more than tripled in use from 2001-2003 peaking in 2003 at ~19,000 lbs.

The pyrethroid use amounts, acres applied, and application rates for the Central, Sacramento, and San Joaquin Valleys are shown in Table 3. The Central Valley use amount is the sum of the use amounts for the Sacramento and San Joaquin Valleys. These data are also plotted in Figure 6. Pyrethroid use amounts and acres treated have increased proportionally. Greater than 1 million acres of the Central Valley are now treated with pyrethroids.

Pyrethroid application rates (lbs/acre) for the Sacramento Valley were higher than those for the San Joaquin Valley during the period 1991-1998 and from 1998-2002 pyrethroid application rates for the Sacramento Valley were higher. The overall trend for the Central Valley is that pyrethroid application rates are increasing. The average application rate was 0.134 lbs/acre for the period 1991-1995, 0.170 lbs/acres for 1996-1999, and 0.177 lbs/acre for 2000-2003, which is an overall increase of 32% between the first and most recent period (Table 4). Between the 1991-1995 and 1996-1999 periods the average application rate increased rapidly by 26%, while between the 1996-1999 and 2000-2003 periods the average application rate increased by on 6%. Also in 2000-2003 the average application rate for the San Joaquin Valley was 22% higher than that of the Sacramento Valley (Table 4 and Figure 7). Application rates for pyrethroids can vary due to differences in their efficacy; however, for the Central Valley application rates are weighted heavily on the levels of permethrin and cypermethrin since these are the pyrethroids of highest use for both agricultural and other non-agricultural purposes.

Table 2. Total pyrethroid use amounts (lbs) in Central, Sacramento, and San Joaquin Valleys 1991-2003.

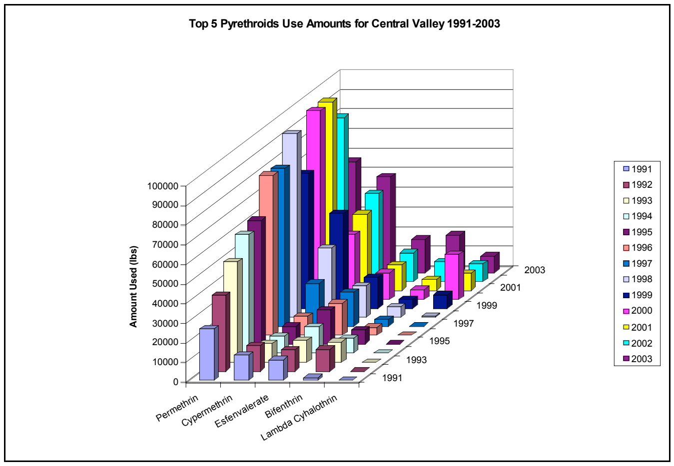
Sacramento Valley **Chemical**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Permethrin	14,511	17,890	28,741	31,261	32,579	42,643	37,335	35,013	29,068	24,525	17,726	18,323	18,259
Cypermethrin	5,049	4,532	4,326	4,172	3,916	4,623	12,208	19,771	16,375	16,007	24,540	27,864	26,084
Esfenvalerate	5,307	4,601	4,351	6,468	9,401	7,847	8,689	7,819	7,366	5,970	6,058	5,406	5,636
Bifenthrin	0	2,019	2,010	2,129	1,921	1,999	1,942	2,136	2,145	2,320	2,902	3,391	3,129
Lambda-Cyhalothrin	0	0	0	0	0	0	0	271	4,349	7,903	5,192	5,446	4,788
Deltamethrin	0	0	0	0	0	0	0	21	294	894	631	797	711
Cyfluthrin	741	879	1,031	1,541	1,715	3,053	1,942	1,575	1,380	1,829	3,226	8,045	4,097
Resmethrin	502	457	258	18	14	6	12	80	197	215	169	11	11
Tralomethrin	0	0	0	0	0	5	63	264	166	43	44	13	11
Pyrethrin	479	595	1,291	876	1,178	609	946	757	659	455	890	610	538
Fenpropathrin	0	0	0	0	0	1	10	3	1	0	651	2,299	2,892
Fenvalerate	1,814	2,054	3,913	2,762	3,396	2,861	2,362	380	2	1	0	0	0
Tau-Fluvalinate	115	310	107	56	50	200	61	88	145	122	249	251	90
Zeta-Cypermethrin	0	0	0	0	0	0	0	0	0	0	0	1	1,137

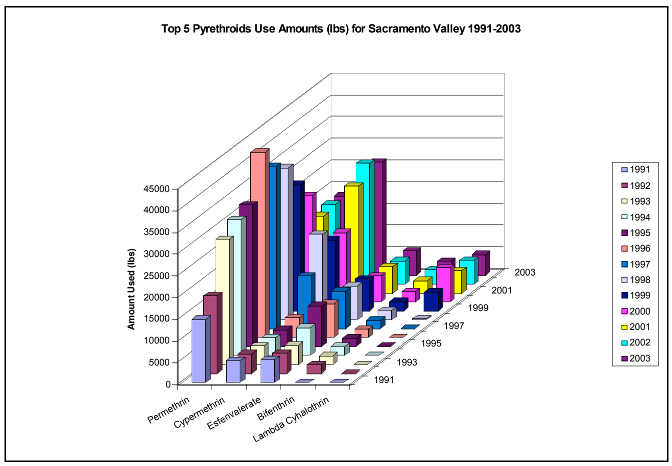
San Joaquin Valley* **Chemical**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Permethrin	11,547	20,774	22,337	29,236	30,623	38,776	43,049	58,303	39,685	71,521	78,407	65,254	38,271
Cypermethrin	7,677	8,376	5,053	4,511	5,301	5,175	9,712	15,510	32,089	17,108	14,359	16,925	22,574
Esfenvalerate	4,968	6,197	6,674	7,083	7,923	8,473	8,763	8,245	8,228	7,689	6,839	9,267	11,277
Bifenthrin	1,304	9,102	8,261	5,544	5,431	1,991	1,657	3,375	2,452	2,756	2,801	6,650	15,877
Lambda-Cyhalothrin	0	0	0	0	0	0	0	350	2,612	15,028	3,549	3,553	3,643
Deltamethrin	0	0	0	0	0	0	0	24	191	689	616	503	441
Cyfluthrin	517	1,293	2,419	3,538	3,554	4,536	7,918	6,498	5,016	3,439	7,084	4,828	9,098
Resmethrin	336	195	233	170	129	30	44	69	59	62	28	28	19
Tralomethrin	0	0	0	0	0	0	58	56	90	30	32	12	2
Pyrethrin	1,020	1,147	3,029	5,791	988	987	1,045	682	907	1,095	1,164	1,184	1,310
Fenpropathrin	0	0	0	5	0	64	37	26	9	7	1,885	5,020	6,947
Fenvalerate	1,248	358	952	180	304	207	173	23	0	0	1	1	0
Tau-Fluvalinate	580	816	724	994	535	613	76	143	881	62	15	60	62
Zeta-Cypermethrin	0	0	0	627	879	464	393	1,481	673	671	379	383	756

Table 2. (Continued) Total pyrethroid use amounts (lbs) in Central, Sacramento, and San Joaquin Valleys 1991-2003.

Central Valley[1] Chemical	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Permethrin	26,058	38,663	51,077	60,496	63,202	81,419	80,384	93,315	68,753	96,045	96,133	83,576	56,530
Cypermethrin	12,727	12,907	9,379	8,683	9,217	9,798	21,920	35,280	48,464	33,115	38,899	44,789	48,658
Esfenvalerate	10,275	10,798	11,024	13,551	17,324	16,320	17,452	16,065	15,594	13,659	12,898	14,673	16,912
Bifenthrin	1,304	11,120	10,271	7,673	7,352	3,990	3,599	5,511	4,597	5,076	5,703	10,041	19,006
Lambda-Cyhalothrin	0	0	0	0	0	0	0	621	6,961	22,931	8,740	8,999	8,432
Deltamethrin	0	0	0	0	0	0	0	44	485	1,583	1,247	1,300	1,152
Cyfluthrin	1,259	2,172	3,450	5,079	5,269	7,588	9,860	8,073	6,396	5,268	10,309	12,873	13,195
Resmethrin	838	652	490	189	143	36	56	149	256	277	197	39	30
Tralomethrin	0	0	0	0	0	6	122	320	256	73	76	25	13
Pyrethrin	1,499	1,741	4,319	6,667	2,165	1,596	1,991	1,439	1,566	1,549	2,055	1,794	1,847
Fenpropathrin	0	0	0	5	0	64	47	28	10	7	2,536	7,319	9,838
Fenvalerate	3,062	2,413	4,864	2,943	3,700	3,068	2,535	403	2	1	2	1	0
Tau-Fluvalinate	695	1,126	831	1,049	584	813	137	231	1,027	184	263	311	152
Zeta-Cypermethrin	0	0	0	627	879	464	393	1,482	673	671	379	384	1,893

*Multiplied by 0.25 factor since only 25% of Fresno County drains into the San Joaquin River.
[1]Central Valley is the sum of the use amounts for the Sacramento and San Joaquin Valleys.





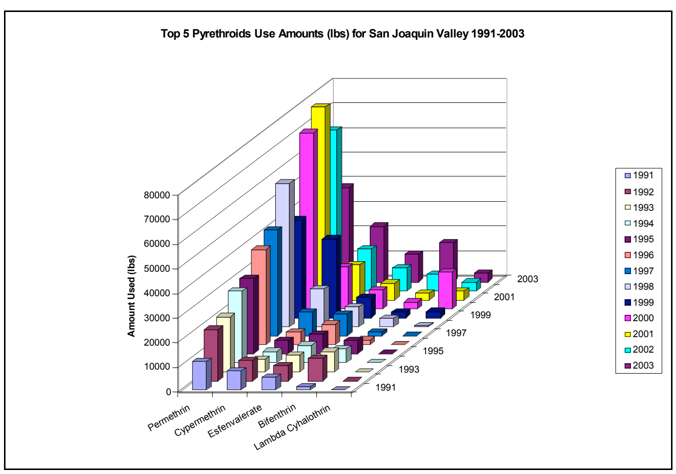


Figure 5. Bar plot showing top 5 pyrethroids use amounts (lbs) for the Central, Sacramento, and San Joaquin Valleys 1991-2003.

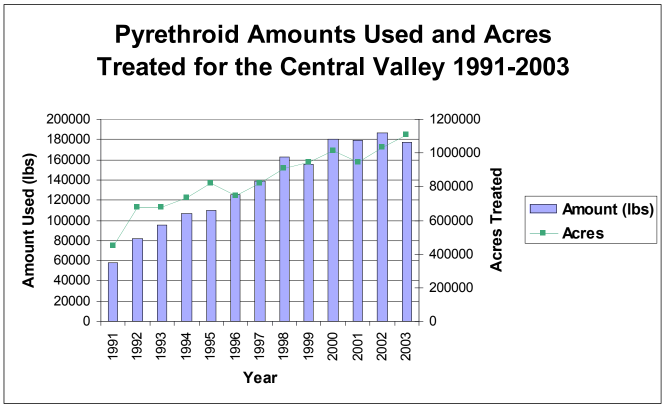
Table 3. Pyrethroid use amounts, acres applied, and application rates for Central, San Joaquin, and Sacramento Valleys 1991-2003.

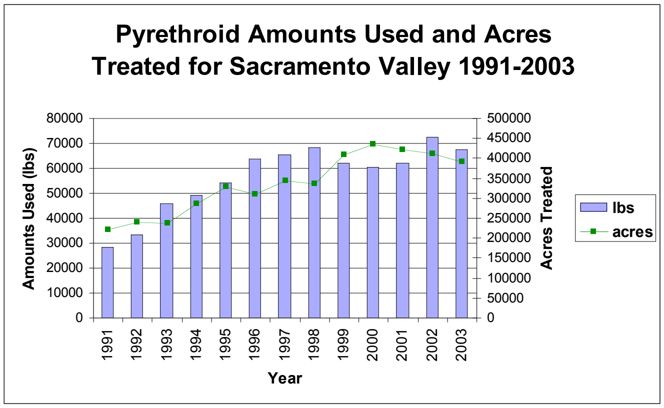
	Central Valley[1]			Sacramento Valley			San Joaquin Valley		
Year	Amount (lbs)	Acres	Application Rate (lbs/acre)	Amount (lbs)	Acres	Application Rate (lbs/acre)	Amount (lbs)	Acres	Application Rate (lbs/acre)
1991	57,717	450,626	0.128	28,519	220,597	0.129	29,198	230,029	0.127
1992	81,593	679,013	0.120	33,336	239,805	0.139	48,257	439,208	0.110
1993	95,706	676,217	0.142	46,026	235,693	0.195	49,680	440,524	0.113
1994	106,961	733,060	0.146	49,282	286,872	0.172	57,679	446,188	0.129
1995	109,834	821,741	0.134	54,169	327,681	0.165	55,665	494,060	0.113
1996	125,163	744,337	0.168	63,847	309,393	0.206	61,316	434,944	0.141
1997	138,495	818,384	0.169	65,569	344,415	0.190	72,926	473,969	0.154
1998	162,962	907,062	0.180	68,176	334,678	0.204	94,786	572,385	0.166
1999	155,039	947,338	0.164	62,147	410,041	0.152	92,892	537,297	0.173
2000	180,437	1,013,874	0.178	60,281	435,741	0.138	120,156	578,133	0.208
2001	179,435	944,707	0.190	62,277	421,693	0.148	117,158	523,015	0.224
2002	186,125	1,029,739	0.181	72,457	411,905	0.176	113,669	617,834	0.184
2003	177,659	1,106,476	0.161	67,382	391,623	0.172	110,276	714,853	0.154

[1]Central Valley use amount is the sum of use amounts for Sacramento and San Joaquin Valleys.

Table 4. Average pyrethroid application rates for various periodic blocks.

Year	Central Valley	Sacramento Valley	San Joaquin Valley
1991-1995	0.134	0.160	0.118
1996-1999	0.170	0.188	0.158
2000-2003	0.177	0.158	0.193





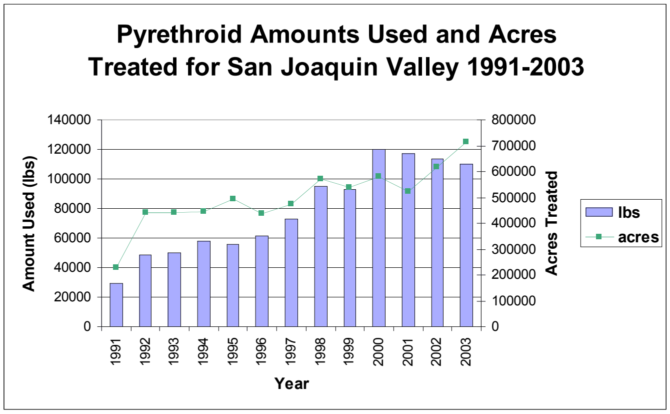


Figure 6. Box plot showing pyrethroid use amounts and acres treated 1991-2003.

Central Valley is the sum of the use amounts in the Sacramento and San Joaquin Valleys.

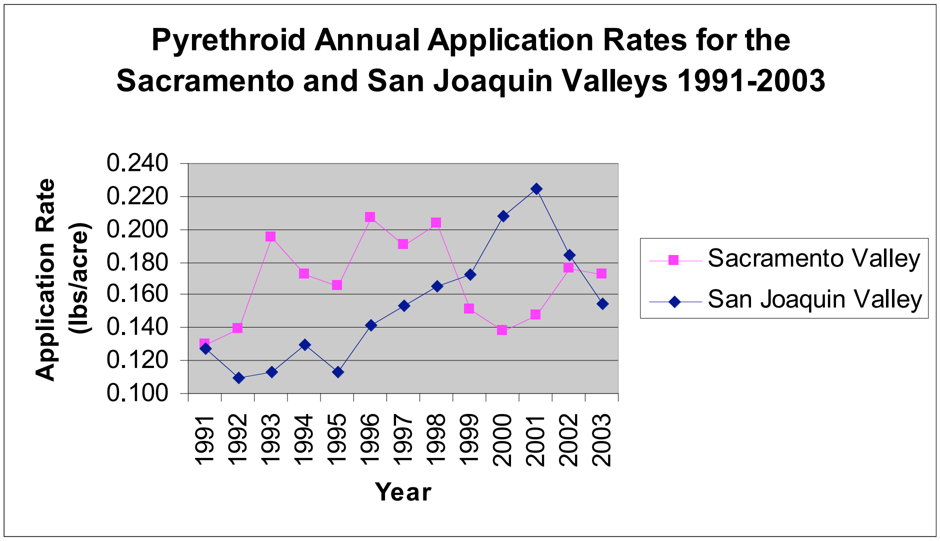


Figure 7. Line plot showing pyrethroid annual application rates for the Sacramento and San Joaquin Valleys 1991-2003.

3. Transport and Fate in Water

Important Points:

- *Pyrethroids are strongly hydrophobic and have a strong tendency to adsorb to particulate matter or bedded sediments rather than remain dissolved in the water column but short-term aqueous exposures may impact pelagic organisms.*
- *Pyrethroids transport pathways include agricultural runoff from rain storms, drift from aerial or ground-based spraying, and release of agricultural tailwaters.*
- *Pyrethroid use amounts and precipitation are the two major environmental variables that dictate the dynamics of pesticide transport into surface waters.*
- *Modeling results indicate that <1% of total pyrethroids applied to Central Valley agricultural fields is available for transport through the Sacramento-San Joaquin Delta to San Francisco Bay. Such loads are capable of producing pyrethroid concentrations in Suisun Bay surface sediments in the low ppb range, concentrations that are potentially toxic to benthic organisms.*

3.1. Pyrethroid Physical and Chemical Properties

The physical and chemical properties of a chemical can be used to determine its behavior and potential fate in the aquatic environment. Information on the physical and chemical properties of several pyrethroids that are used in high amounts is shown in Table 5. Pyrethroids generally have low vapor pressures and Henry's Law constants which suggest that they are not easily volatilized into the atmosphere. They have high octanol/water partition coefficients (Kow) so they tend to partition into lipids. They also have very high water/organic carbon (Koc) partition coefficients, which suggests that the greatest risk to aquatic organisms would be through exposure to pyrethroid contaminated sediments. Although pyrethroids may bioconcentrate, depuration is also rapid and bioaccumulation through the food web is not a significant route of exposure (Hill, 1985). They have a tendency to adsorb to surfaces so they can readily bind to suspended particulate materials in the water column including clay, soils, sediment particles, and organic matter, which act as primary vectors for pyrethroid transport through aquatic systems. Sorption to sediments has been suggested as a method to mitigate acute toxicity of pyrethroids by reducing their short term bioavailability in the water column.

Pyrethroids can be degraded by both chemical and biological processes with chemical degradation generally occurring in the atmosphere and in water. Their hydrolysis half-life in aquatic environments is typically on the order of days to weeks so pyrethroids can remain for some time in the water column but nevertheless they do react with water to form hydrolysis products. Their aerobic half-life in soils is on average 30-100 days for most pyrethroids, which suggests that aquatic organisms can have extended exposure to them. Overall, pyrethroids have similar physical-chemical properties and as a result they show similar behavior with respect to their movement and fate in the environment.

A variety of field studies have been conducted that have identified important transport pathways for pyrethroids. The critical transport pathways identified include agricultural runoff during rain storm events, drift from aerial or ground-based spraying, and intentional release of agricultural tailwaters, which is a common practice in rice production but releases are regulated and usually controlled (see Chapter 5). 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. Tanner (1996) showed that drift from aerial or ground-based spraying was also a pathway for pesticide transport into the aquatic environment primarily through aerosol transport and deposition that occurs immediately following spraying events. 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. USDA (1985) reported that fenvalerate and permethrin were present in runoff water at extremely low levels, except on several rare occasions when they were applied while irrigation water was on the field. For example, permethrin was found at 0.10 percent of total amount applied. The amounts of insecticides in runoff water varied over a wide range depending upon the pesticide, the crop to which it was applied, and the canopy coverage at the time of aerial application. The amount of insecticides in runoff appeared to be highly dependent upon the persistence of the insecticide at the soil surface.

Table 5. Physical and chemical properties of various pyrethroids.

Chemical	Log Kow[1]	Log Koc[2]	Solubility (mg/L)[1]	Vapor Pressure (mm Hg at 25°C)[1]	Henry's Law Constant (atm-m^3/mol at 25°C)[1]	Soil Aerobic Half-life (days)[2]	Soil Anaerobic Half-life (days)[2]	Hydrolysis Half-life (days)[2]
Bifenthrin	6	5.4	0.1	1.8×10^{-4}	$<1.0 \times 10^{-3}$	96.3	425	>30
Cyfluthrin	5.9	5.1	0.002	2.03×10^{-9}	9.5×10^{-7}	11.5	33.6	1.84-183
Cyhalothrin	6.9	5.5	0.003	1.5×10^{-9}	1.8×10^{-7}	42.6		8.66->30
Cypermethrin	6.6	5.5	0.004	3.07×10^{-9}	4.2×10^{-7}	27.6	55	1.9-619
Deltamethrin	6.1		<0.002	1.5×10^{-8}	1.2×10^{-4}			
Esfenvalerate	4	5.4	0.0002	1.5×10^{-9}	4.1×10^{-7}	38.6	90.4	>30
Fenpropathrin	6		0.014	5.5×10^{-6}	1.8×10^{-4}			
Fluvalinate	4.3		0.002	5.7×10^{-7}	3.05×10^{-5}			
Permethrin	6.5	5.4		2.2×10^{-8}	1.9×10^{-6}	39.5	197	>30-242
Resmethrin	5.4		-	1.13×10^{-8}	$<8.9 \times 10^{-7}$			
Tralomethrin	7.6		0.08	3.6×10^{-11}	3.9×10^{-15}			

[1]Data are cited from USDHHS, 2003.
[2]Data are cited from Laskowski, 2002.

3.2. Modeling Pyrethroid Fate in Suisun Bay

The ultimate fate of pyrethroids applied to Central Valley agricultural fields is not well understood. 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 the pyrethroids applied to Central Valley fields will find their ultimate fate in the Bay. Monitoring data for pyrethroids in Bay water and sediment do not exist, which confounds attempts to estimate loads of pyrethroids transported to the Bay from the Central Valley. In an effort to fill this data gap, a simple fate model of agricultural runoff was integrated with a one-box model of Suisun Bay.

A number of first-order calculations were made to estimate the near-field fate of pyrethroids applied to Central Valley fields, which used field data presented in Chapter 4 (Section 4.2), mean chemical and physical properties of pyrethroids presented in Table 5, and Central Valley pyrethroid use data presented in Table 1. Results indicate that for a pyrethroid application of 150,000 lbs/yr (~70,000 kg/yr), approximately 9,000 lbs/yr (~4,200 kg/yr) are lost to degradation in the field, 160 lbs/yr (~75 kg/yr) are washed off the field and available for off-site transport to neighboring water bodies, and the remaining 140,000 lbs/yr (~65,000 kg/yr) will remain on the field. Thus, 0.11% of the pyrethroids applied to Central Valley fields in any given year are available for transport through the Delta to San Francisco Bay.

A one-box model of Suisun Bay was developed to estimate probable pyrethroid concentrations in Bay sediments resulting from pyrethroid loads from Central Valley runoff. The one-box model is based on a model of polychlorinated biphenyls (PCBs) 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. The model was altered for this study to represent Suisun Bay, the north-eastern-most sub-embayment of San Francisco Bay and the direct link with the Sacramento-San Joaquin Delta. Three model scenarios were simulated, with each simulation representing a load of pyrethroids to the Bay equal to 0.11% of a given total application to Central Valley fields; 110 lbs/yr = 0.11% of 100,000 lbs/yr, 165 lbs/yr = 0.11% of 150,000 lbs/yr, and 220 lbs/yr = 0.11% of 200,000 lbs/yr. Model results indicate that surface sediment concentrations in the 1-2 ng/g dry wt range are probable in Suisun Bay under these loading scenarios (Figure 8). The model also allows for the quantification of individual loss pathways (Figure 8). Results indicate that a majority of the mass entering Suisun Bay from the Delta exits as outflow to San Pablo Bay (~250 kg after 5 years). Degradation is the second most important loss pathway, accounting for ~110 kg after 5 years. A key result of this model is that roughly 15 times the mass that remains in Suisun Bay (~15 kg) is exported as outflow to San Pablo Bay. Exported mass has the potential to accumulate in San Pablo Bay and the various other sub-embayments of San Francisco Bay.

The model results presented here are preliminary and represent our best first-order approximations of the potential fate of pyrethroids in San Francisco Bay. Much uncertainty surrounds these preliminary estimates, owing to the lack of adequate field data and information on the chemical and physical properties of pyrethroids in the aquatic environment. However, the preliminary model results, which are based on Central Valley use amounts, do indicate that low ppb range concentrations of pyrethroids are likely to be found in Suisun Bay surface sediments, concentrations that are potentially toxic to benthic organisms such as *H. azteca* (Weston et al., 2004). It is important to mention that pyrethroid sediment concentrations can be even higher due to pyrethroid use in the Delta and unreported uses (gardens and pest control) by consumers.

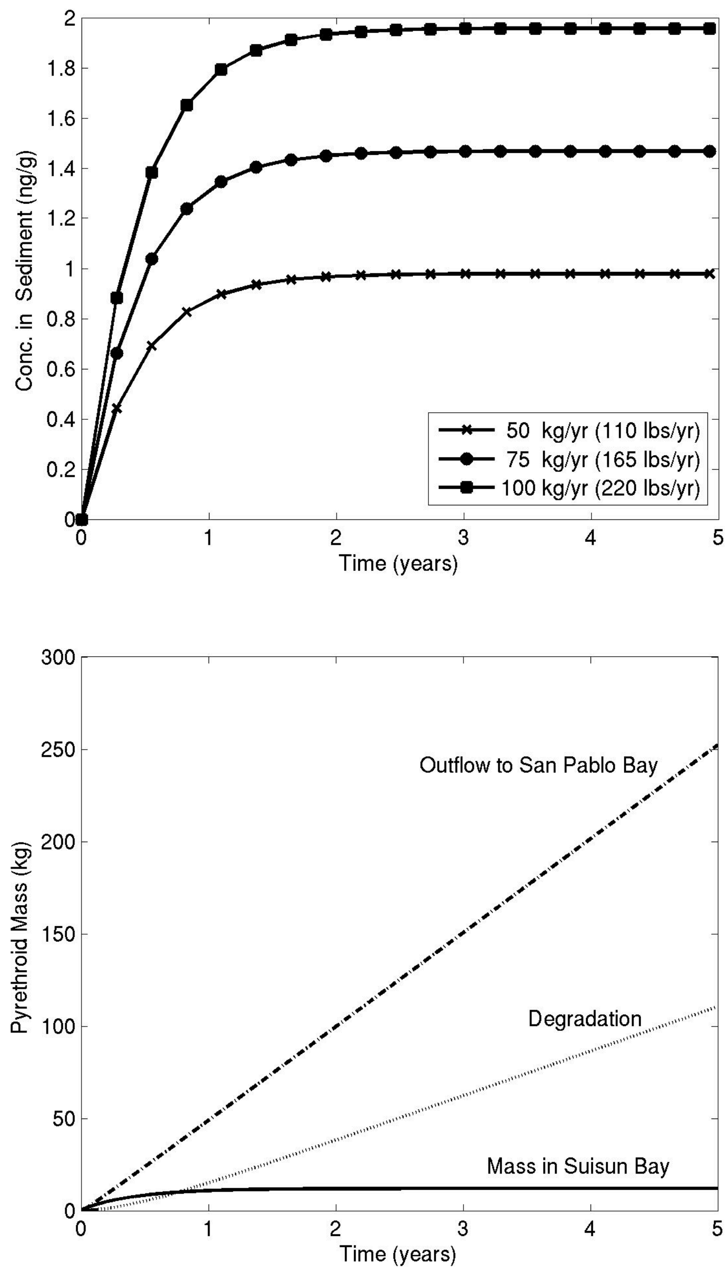


Figure 8. Model results for pyrethroids in Suisun Bay.

The upper panel shows results of a simple one-box model of Suisun Bay used to estimate possible surface sediment pyrethroid concentrations resulting from pyrethroid use in Central Valley agricultural fields. The model estimates surface sediment pyrethroid concentrations in the 1-2 ng/g range are possible in Suisun Bay, depending on the total load of pyrethroids delivered to the Bay in any given year. The lower panel shows a simplified mass budget of pyrethroids in Suisun Bay, which indicates that a majority of the pyrethroid mass entering Suisun Bay from the Delta exits the Bay as outflow to San Pablo Bay. Degradation is also a critical loss pathway. The mass that remains in Suisun Bay reaches steady-state value of approximately 15 kg. Curves represent the cumulative mass in each pathway for a 5 year model simulation with a total load of 75 kg/yr (165 lbs/yr). Modeling conducted by Dr. John Oram (SFEI).

4. Regional Monitoring Results

Important Points:

- *Pyrethroids are detectable in sediments from Central Valley agriculturally-dominated water bodies: permethrin was detected most frequently followed by esfenvalerate > bifenthrin > lambda-cyhalothrin.*
- *Pyrethroid concentrations in Central Valley sediment and water samples from agriculturally dominated water bodies were high enough to have contributed to toxicity to sensitive aquatic species.*
- *Pyrethroid concentrations in sediments are greatest shortly after their peak use (July-November) rather than in the winter following heavy winter rains (March-April).*
- *Pyrethroids tend to strongly bind to particulate matter, which is a primary means of transport and perhaps is more critical to toxicity than dissolved water concentrations.*
- *Pyrethroids can be transported offsite by irrigation return-flow, which peaks in the summer months, and by rain induced storm water runoff, which peaks in the winter season.*

Published field data for pyrethroids especially for agricultural areas are limited. The approach here is to discuss several relevant case studies where pyrethroids were monitored in and around the Delta region and its watershed the Central Valley.

4.1. Case 1: Pyrethroids in Central Valley Sediments

Weston et al. (2004) set out to determine the concentrations of pyrethroids and other hydrophobic pesticides in sediments of agriculture-dominated water bodies of the Central Valley and to determine whether toxicity to aquatic life was associated with these sediments. Their study focused on areas with high pyrethroid use (determined from the PUR database) and sampling in water bodies was conducted where water quality degradation was suspected to occur. A total of 70 sediment samples were collected over a 10 county area in the Central Valley during periods of peak use (July through November 2002) and in the winter following heavy rains (March 2002). Most sites were located in irrigation canals and small creeks dominated by agricultural return flow. Sediments were analyzed for 5 pyrethroids including other pesticides such organophosphates (OPs) and organochlorines (OCs). Pyrethroid detection limits in sediments were 1 ng/g dry wt.

Weston et al. (2004) reported that pyrethroids were detectable in 75% of the sediment samples, 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 (reported on a dry wt basis) 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 shortly after their use rather than in winter after heavy winter rains. This is in agreement with their peak months of use in the summer (also shown in this report in Section 2.1), which coincides with peak irrigation return-flows and spray drift from aerial and ground-based applications. Weston et al. (2004) also showed that 65% of the sediment sampling stations that had measurable pyrethroids had highest concentrations in the late summer and fall months (August and November), which is near the end of the irrigation season, and at only 35% of the sites were concentrations greatest in March and April, which is the end of the rainy season.

This study showed a prevalence of sediment toxicity in Central Valley agriculture-dominated water bodies and provided evidence that pyrethroids were likely responsible for much of the observed toxicity. It further demonstrated the need for greater awareness of the risks posed by particle-associated pyrethroids. There is a substantial risk to benthic organisms. Pyrethroids are toxic at sediment concentrations in the very low ng/g (ppb) range. Finally, the study showed that current method detection limits (MDLs) for pyrethroid analysis in sediments (1 ng/g dry wt) would need to be improved since some pyrethroid LC50s are just slightly above the MDL.

4.2. Case 2: Pyrethroid in Central Valley Waters

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. Pyrethroid concentrations in whole water samples (water plus suspended sediment) were reported. The reporting limit for pyrethroids was 50 ng/L.

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, which was the 10 to 90 percentile range. 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. The estimated dissolved phase concentrations of esfenvalerate in Del Puerto Creek whole water samples ranged from 4 ng/L to 37 ng/L. Peak runoff concentrations were obtained at the time of peak discharge (range 5-20 cfs) and peak TSS (range 452-2,708 mg/L) levels. Bifenthrin was also found in one sediment sample at a concentration of 24 ng/g dry wt.

Bacey et al. (2005) showed that pyrethroids are able to be transported offsite during rain induced runoff events. Furthermore, they specifically noted that due to the physical characteristics of pyrethroids, their tendency to adsorb to suspended sediment (organic carbon), and the low concentrations detected, that it was probable that measurable (detectable) concentrations may not be found in large river systems such as the Sacramento and San Joaquin Rivers, but this remains to be tested.

4.3. Case 3: Agricultural Waiver Program Monitoring

The Irrigation Monitoring Phase II Agricultural Waiver Program collected 130 water and 33 sediment samples from 31 sites in the Central Valley during the irrigation season July through September 2004 (CVRWQCB, 2005a). Details on the monitoring sites can be found on the State Water Board website: http://www.waterboards.ca.gov/centralvalley/. Sites were selected based on certain criteria: a drainage dominated by agricultural irrigation return-flow, land use patterns surrounding the sampling site were predominated by agricultural activities, and site was located near where agricultural drainage water is discharged into a creek or river. The pyrethroids monitored included *cis*- and *trans*-permethrin, bifenthrin, esfenvalerate, lambda-cyhalothrin, cypermethrin, cyfluthrin, and deltamethrin. Pyrethroid MDLs for water and sediment samples using EPA Method 1660 Modified with GC-ECD/GC-MS ranged from 2-10 ng/L and 1 ng/g dry wt, respectively. Sediment samples were analyzed for toxicity.

Of the 130 water samples collected 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. Both sites are located in the Northern San Joaquin Valley. No other pyrethroids were detected in water samples. When compared to bifenthrin 5^{th} (<3.8 ng/L) and 10^{th} (15 ng/L) percentile lethal concentrations (LC50s) for sensitive aquatic species developed by Solomon et al. (2001), it becomes apparent that the two bifenthrin sediment concentrations reported by the Agricultural Waiver Program's Phase II monitoring were high enough to be acutely toxic to sensitive aquatic species.

Of the 33 sediment samples analyzed concentrations were reported for four pyrethroids. 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. (2005), it becomes apparent that the lamba-cyhalothrin, esfenvalerate, and bifenthrin maximum sediment concentrations reported by the Agricultural Waiver Program's Phase II monitoring were each high enough (equal or greater than the median LC50 values) to cause acute toxicity to *H. azteca*.

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 (CVRWQCB, 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. When compared to permethrin 5th (<35 ng/L), 10th (76 ng/L), and 20th (200 ng/L) percentile lethal concentrations (LC50s) for arthropods developed by Solomon et al. (2001), it becomes apparent that both maximum permethrin water concentrations reported by the Agricultural Waiver Program's Phase II monitoring were high enough to be acutely toxic to arthropods. Sediment sampling and toxicity measurements were not conducted in this part of the program, which is unfortunate since winter storm water runoff is an ideal condition for transporting suspended sediment associated pesticides off-site from where they are being applied.

4.4. Case 4: Department of Pesticide Regulation Monitoring

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.

Kelley and Starner (2004) collected water and bedded sediment samples from creeks in the Salinas and San Joaquin Valleys (Stanislaus County) between June and September 2003, which is the summer growing season, and analyzed them for OP pesticides and pyrethroids (only Stanislaus County results for pyrethroids are reported here). Pyrethroids were found in several creeks: Westport Drain (water – esfenvalerate 57 ng/L; sediment – permethrin 32 ng/g), Pomelo Ag Drain (water – bifenthrin maximum of 20 ng/l, esfenvalerate maximum 142 ng/L; sediment – esfenvalerate maximum of 17 ng/g, permethrin at trace amounts), Orestimba Creek (water – bifenthrin at trace amounts; sediment – esfenvalerate maximum of 23 ng/g), Del Puerto Creek (water – bifenthrin maximum of 55 ng/L, esfenvalerate maximum of 166 ng/L, permethrin at trace amounts; sediment – esfenvalerate maximum of 12 ng/g, permethrin maximum of 14 ng/g). The pyrethroids lambda-cyhalothrin, cyfluthrin, and cypermethrin were not detectable.

4.5. Case 5: University of California at Davis Orchard Monitoring

Werner et al. (2004) demonstrated the potential for off-site movement of dormant season sprayed pesticides from orchards during winter rainfall events. They monitored esfenvalerate and diazinon in storm water runoff following a dormant spray application of a French prune orchard in Glenn County during winter 2000/2001. They determined the mitigating effect of three ground cover crops on insecticide loading and acute toxicity in esfenvalerate and diazinon sprayed orchard rows. Acute toxicity testing was conducted on two species of fish and three aquatic invertebrates. Results showed that runoff from the orchard section treated with esfenvalerate was less toxic to the waterflea (*C. dubia*) than runoff from a diazinon sprayed section. Runoff from the esfenvalerate sprayed orchard section was also highly toxic to fish larvae (100% fish mortality) with esfenvalerate concentrations ranging from 280 to 720 ng/L and diazinon concentrations ranging from 207 to 340 ug/L. One month later, runoff samples collected from both sections were not toxic to fish (0% mortality), but remained highly toxic to invertebrates due to residual diazinon (range 1-20 ug/L). The ground cover crops reduced total pesticide loading in runoff by approximately 50% in comparison to bare soil, however there were no differences between the types of vegetation used as ground covers.

5. Pyrethroid Use Patterns of Special Concern

Important Points:

- *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.*
- *Summer irrigation return-flows are a larger source of pyrethroid than are winter storm water flows.*
- *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.*
- *Urban area uses of pyrethroids make up nearly half of the total pyrethroids used in the Central Valley, which supports the need for implementing best management practices to prevent pyrethroids from entering urban storm water drains.*

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. Three examples of such events are the following: 1) agricultural runoff from orchards following the dormant season spraying period, 2) releases of irrigation tailwaters from rice fields during the spring and summer seasons, and 3) storm water runoff from urban areas following structural application. Details of each of these use patterns and their potential to impact the aquatic environment are described below.

5.1. Orchard Dormant Season Applications

Several monitoring studies have reported that orchard dormant season pesticides such as organophosphates (OPs) and pyrethoids are frequently detected in water samples during the winter season (Domagalski et al, 1997; Kratzer, 1998; Dileanis et al. 2002; Weston et al., 2004). Pesticides are applied to orchards of nut trees and stone fruit between late December and February when trees are dormant (Bacey et al., 2005), which is also the rainy season in California, thus runoff from rain storm events can mobilize insecticides off-site into adjacent water bodies. The use of OPs during the dormant-spray season has been gradually decreasing, and they are being replaced with pyrethroids (Epstein et al., 2000).

5.1.1. Organophosphate Pesticide Use Patterns

The use of OPs during the dormant spray season has been steadily decreasing and they are now being gradually replaced with pyrethroids (Epstein et al., 2000). The amounts (lbs) of OPs and pyrethroids that were applied to orchards of almond and stone fruit in the Central Valley from the period 1991 to 2003 are shown in Table 6 and plotted in Figure 9. OP pesticide use peaked in 1993 at ~523,110 lbs and has since decreased gradually where in 2003 ~247,985 lbs were applied in orchards.

Table 6. Pesticide annual use amounts (lbs) applied to orchards of almond and stone fruit in the Central Valley 1991-2003.

Year	Pyrethroids	Organophosphates
1991	11,055	346,338
1992	17,228	537,068
1993	23,500	523,110
1994	21,976	446,523
1995	20,398	330,001
1996	26,688	342,632
1997	31,110	313,068
1998	31,774	320,230
1999	28,628	261,261
2000	27,517	244,958
2001	29,061	208,977
2002	30,224	205,436
2003	28,768	247,985

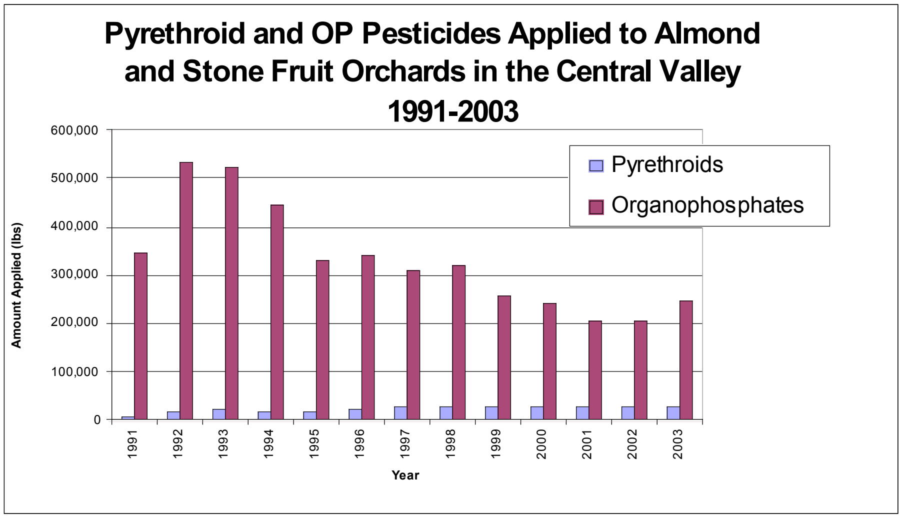


Figure 9. Bar plot showing annual amounts (lbs) of pyrethroid and organophosphate (OP) pesticides applied to almond and stone fruit orchards in the Central Valley 1991-2003.

Central Valley data include use data from both Sacramento and San Joaquin Valleys. Pyrethroid use data are for esfenvalerate and permethrin, while OP data are for diazinon and chlorpyrifos. Stone fruit include apricots, cherries, nectarines, peaches, plums, and prunes. Data were collected from the Department of Pesticide Regulation (DPR) Pesticide Use Reporting (PUR) database: www.cdpr.ca.gov.

The decision to phase out OP pesticides has resulted in major changes in their use patterns (Figure 10) in the San Joaquin and Sacramento Valleys. In the San Joaquin Valley diazinon use peaked in 1993 at ~514,000 lbs and since then their use has gradually declined to levels that are now lower than chlorpyrifos use. On the other hand, chlorpyrifos use exceeded 300,000 lbs in 1997, 1998, and 2000 and has since then dropped to historical use amounts ~200,000 lbs from 2001 to 2003. Much higher amounts of OPs are used in orchards in the San Joaquin Valley than in the Sacramento Valley. In the Sacramento Valley, diazinon use in orchards has always been much greater than those of chlorpyrifos. Diazinon use has been gradually decreasing since it peaked in 1992 at ~150,000 lbs and in 2003 its use amount was about three times lower at ~56,000 lbs. In 1992 the amount of chlorpyrifos used was ~14,000 lbs and its use has since more than doubled to ~32,000 lbs being applied in 2003. Although OP pesticides (specifically diazinon) are gradually being phased out and replaced by pyrethroids, they continue to be applied to Central Valley orchards especially in the San Joaquin Valley at high amounts (~400,000 lbs per year), which are still 10 times higher than pyrethroid use amounts.

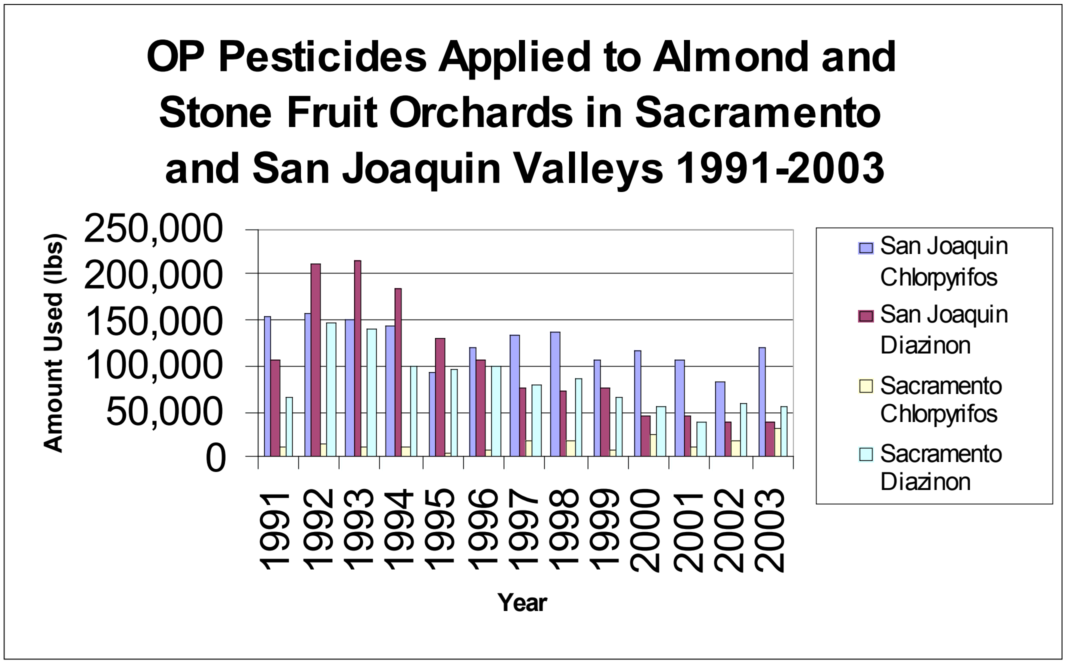


Figure 10. Bar plot showing annual amounts (lbs) of organophosphates (OPs) applied to orchards of almond and stone fruit in the Sacramento and San Joaquin Valleys 1991-2003.

Central Valley data include use data from both Sacramento and San Joaquin Valleys. OP data are for diazinon and chlorpyrifos. Stone fruit include apricots, cherries, nectarines, peaches, plums, and prunes. Data were collected from the Department of Pesticide Regulation (DPR) Pesticide Use Reporting (PUR) database: www.cdpr.ca.gov.

5.1.2. Pyrethroid Use Patterns

Pyrethroids use in orchards has gradually increased since 1991 (Figure 11). In 1996 the amount of pyrethroids used in the Central Valley reached 30,000 lbs, it increased to peak in 2002 at ~47,000 lbs, and in 2003 the amount decreased to ~39,000 lbs. Over the last 7 years (1997-2003) the use amount in Central Valley orchards has remained relatively constant at ~40,000 lbs per year, which are 2-4 times higher than pre-1996 amounts.

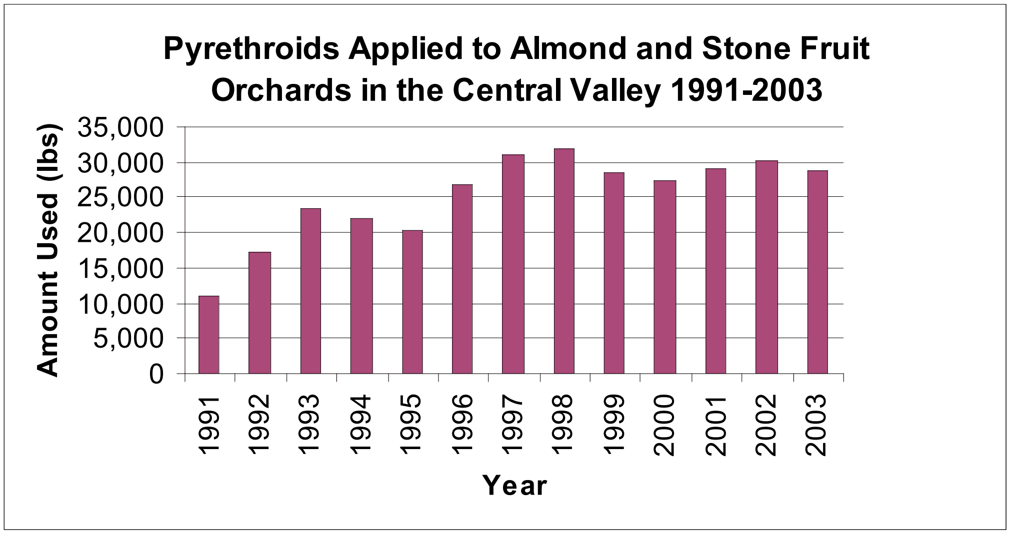


Figure 11. Bar plot showing amounts (lbs) of pyrethroids applied annually to orchards of almond and stone fruit in the Central Valley 1991-2003.

Central Valley data include use data from both Sacramento and San Joaquin Valleys. Pyrethroid use data are for esfenvalerate and permethrin. Stone fruit include apricots, cherries, nectarines, peaches, plums, and prunes. Data were collected from the Department of Pesticide Regulation (DPR) Pesticide Use Reporting (PUR) database: www.cdpr.ca.gov.

The amounts (lbs) of pyrethroids applied annually to orchards of almond and stone fruit in the Sacramento and San Joaquin Valleys over the period 1991-2003 are shown in Table 7 and are plotted in Figure 12. The amounts of pyrethroid used in the San Joaquin Valley are on average two times higher than the amounts used in the Sacramento Valley (see Figure 13). San Joaquin Valley permethrin use has increased sharply since 1991 and it has remained near 15,000 lbs since 1996. Esfenvalerate has increased gradually in use since 1991 reaching a peak use amount of ~6,900 lbs in 2003. In the Sacramento Valley, esfenvalerate use gradually increased since 1991 peaking in 2002 at ~3,400 lbs. Permethrin use reached a peak in 1993 at ~10,200 lbs and its use gradually declined over time down to ~3900 lbs in 2003. Based on the amounts of pyrethroids applied in orchards of almond and stone fruit, the San Joaquin Valley is at much greater risk than the Sacramento Valley for problems associated with pesticide transport off-site and into surrounding water bodies.

Table 7. Pyrethroid use amounts (lbs) for orchards in the Central, Sacramento, and San Joaquin Valleys 1991-2003.

Site	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Sacramento Valley													
Esfenvalerate	51	146	264	720	993	1,964	2,712	2,431	2,846	2,953	3,126	3,385	3,133
Permethrin	6,721	9,156	10,248	7,933	6,306	7,583	8,519	6,932	5,476	6,490	6,309	5,301	3,923
Total	6,772	9,302	10,512	8,654	7,299	9,547	11,231	9,363	8,321	9,444	9,435	8,685	7,056
San Joaquin Valley													
Esfenvalerate	1,263	2,194	3,047	2,956	2,421	3,102	3,415	4,187	4,537	4,208	4,479	5,617	6,872
Permethrin	3,020	5,732	9,941	10,366	10,678	14,039	16,464	18,223	15,770	13,865	15,147	15,921	14,840
Total	4,283	7,926	12,988	13,323	13,099	17,141	19,879	22,411	20,307	18,073	19,626	21,538	21,712
Central Valley[1]													
Esfenvalerate	1,315	2,339	3,311	3,677	3,414	5,066	6,127	6,619	7,383	7,162	7,605	9,002	10,005
Permethrin	9,740	14,888	20,189	18,300	16,984	21,622	24,983	25,155	21,246	20,355	21,456	21,222	18,763
Total	11,055	17,228	23,500	21,976	20,398	26,688	31,110	31,774	28,628	27,517	29,061	30,224	28,768

[1]Central Valley is the total of use amounts for the Sacramento and San Joaquin Valleys.

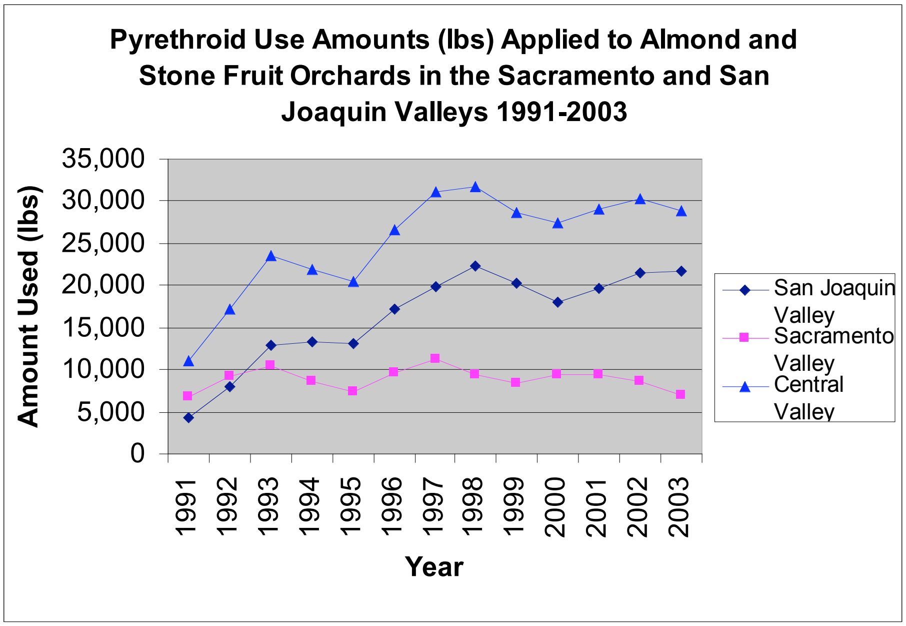


Figure 12. Line plot showing pyrethroid use amounts (lbs) in the Central, Sacramento, and San Joaquin Valleys 1991-2003.

Central Valley trend line in the sum of use amounts for Sacramento and San Joaquin Valleys.

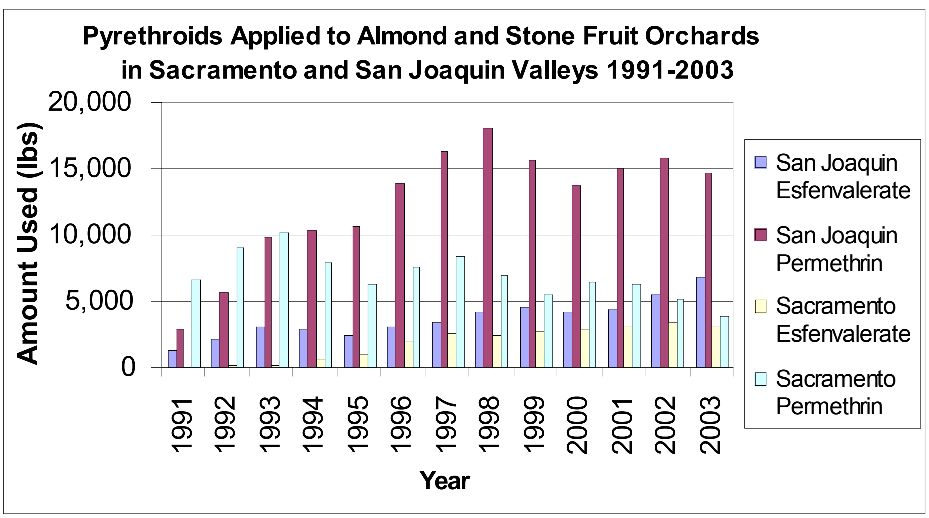


Figure 13. Bar plot showing annual amounts (lbs) of pyrethroids applied to orchards of almond and stone fruit in the Sacramento and San Joaquin Valleys 1991-2003.

Pyrethroid use data are for esfenvalerate and permethrin. Stone fruit include apricots, cherries, nectarines, peaches, plums, and prunes. Data were collected from the Department of Pesticide Regulation (DPR) Pesticide Use Reporting (PUR) database: www.cdpr.ca.gov.

5.2. Rice Production Use Patterns

In the 1990's, performance goals for surface waters were established and improved farming practices were implemented to control historical water toxicity problems that were attributed to the rice field pesticides found in agricultural tailwaters. Briefly, holding times for rice field water were mandated in order to decrease the concentrations of pesticide active ingredients that were causing toxicity problems. Unfortunately, these performance goals were not designed to control potential toxic releases of pyrethroid insecticides that are now being used in rice fields. In addition, the county agricultural commissioner may authorize the emergency release of tailwater if it is demonstrated that the rice crop is suffering because of the water management requirements. Under an emergency release variance, tailwater may be released only to the extent necessary to mitigate the documented problem. Hence, the volume of tailwater released is dependent on the severity of the water management requirements. The consequence of shortening the holding periods for water in rice fields is a much higher pesticide concentration in tailwaters because the in-field degradation period is also decreased. This will affect the levels of all pesticides (herbicides, fungicides, and insecticides) used in rice production. The amount and frequency of emergency releases is not covered in this white paper, but emergency releases of rice irrigation water prior to completion of holding times need to be included in risk assessments.

The Sacramento Valley contains more than 95% of the state's rice acreage with the leading rice producing counties being Colusa, Sutter, Butte, Glenn and Yolo (DPR, 2003). Pyrethroid insecticides are generally applied to rice fields prior to field flooding or within the initial stages of stand establishment. The pyrethroids that have been used in rice field production include lamba-cyhalothrin, permethrin, cypermethrin, and zeta-cypermethrin.

Table 8 shows the amounts (lbs) of the individual pyrethroids that were applied to rice for the entire Central Valley (sum of 10 counties) from 1998 to 2003. There is no record of pyrethroid use for rice in the PUR database prior to 1998. These data are also shown in a bar plot (Figure 14). Pyrethroid use jumped in 1999 (679 lbs), peaked in 2000 (4,191 lbs) and from 2001 to 2003 the amount used was maintained at an average of ~1,900 lbs/year. Lamba-cyhalothrin was the most abundantly used pyrethroid. Its use in rice peaked in 2000 at 4,189 lbs and from 2001 to 2003 its average use amount was ~1,900 lbs/year. Lambda-cyhalothrin is used primarily for rice water weevil control and secondarily for armyworm control.

In 2003, zeta-cypermethrin was registered for use in California rice and in its first year 175 lbs was applied to rice in Sutter (115 lbs), Yolo (41 lbs), and Yuba (19 lbs) counties. The application rate (lbs of active ingredient/acre treated) was the same for all counties 0.04. There are only two years on record for permethrin use in rice production. In 1998 permethrin use peaked (8 lbs) and it was applied only once more in 2000 (1 lb) for the last time on record.

Table 8. Pyrethroid use amounts (lbs) for rice in the Central Valley 1998-2003.

Active Ingredient	1998	1999	2000	2001	2002	2003
Cyhalothrin, lambda	0	679	4,189	1,856	2,242	1,591
Permethrin	8	0	1	0	0	0
Cypermethrin	0	0	0	0	0	13
Cypermethrin, zeta	0	0	0	0	0	175
Total	8	679	4,191	1,856	2,242	1,778

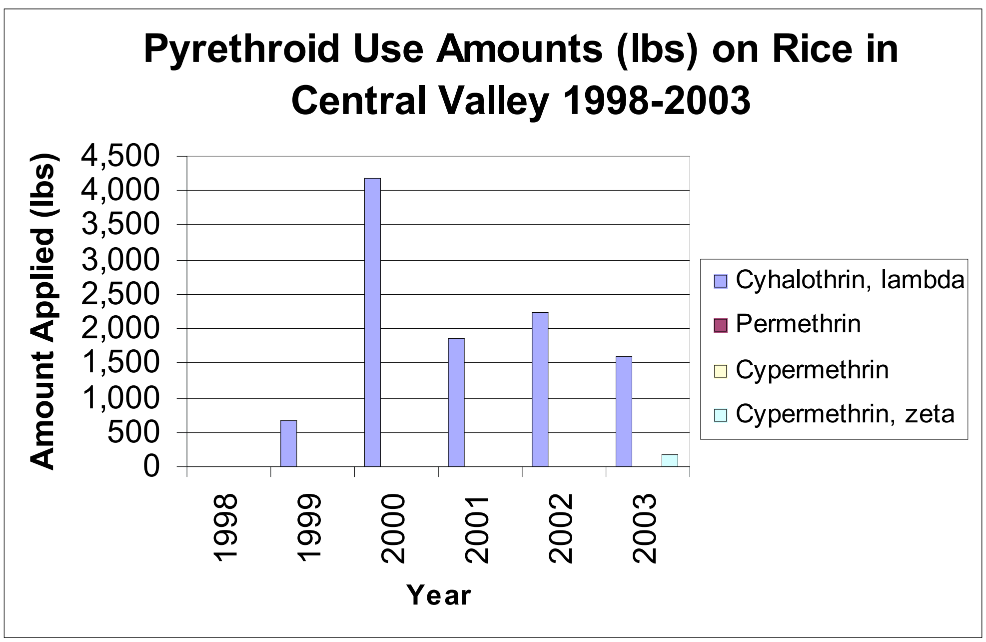


Figure 14. Bar plot showing the amounts (lbs) of pyrethroids applied to rice fields in the Central Valley 1998-2003.

Data were collected from the Department of Pesticide Regulation (DPR) Pesticide Use Reporting (PUR) database: www.cdpr.ca.gov. The PUR database has no record of pyrethroid use in rice fields prior to 1998.

Table 9 shows the amounts (lbs) of total pyrethroids that have been applied in each county from 1998 to 2003. The counties with the highest historical use of pyrethroids include Sutter (30% to total pyrethroids used), Glenn (22%), Butte (21%), and Colusa (14%) (see Figure 15). The most highly used pyrethroid was lambda-cyhalothrin (10,556 lbs or 98% of total pyrethroids), which began application to rice in 1999, followed by much lower amounts of zeta-cypermethrin (175 lbs), cypermethrin (13 lbs) and permethrin (9 lbs). The application rate was the same for all counties 0.03 lbs/acre.

Table 9. Pyrethroid use amounts (lbs) for rice by county 1998-2003.

County	Cyhalothrin, lambda	Cypermethrin, zeta	Cypermethrin	Permethrin	Amount (lbs)	% of Total
Sutter	3,101	115		8	3,224	30
Glenn	2,318		3	1	2,322	22
Butte	2,225				2,225	21
Colusa	1,514				1,514	14
Yuba	749	19			768	7
Sacramento	259				259	2
Yolo	126	41			167	2
San Joaquin	112		10		122	1
Merced	90				90	1
Stanislaus	62				62	1
Total	10,556	175	13	9	10,753	100

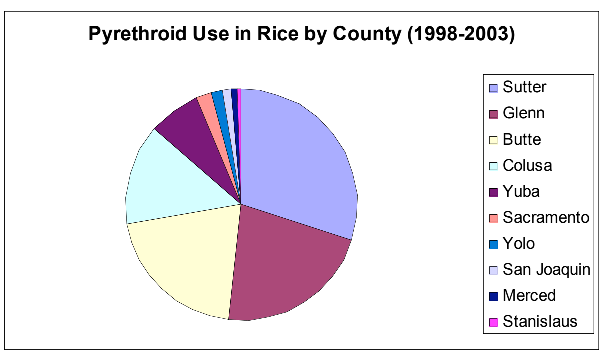


Figure 15. Pie chart showing pyrethroid use amounts (lbs) by county as a percentage of the total amount used 1998-2003.

Table 10 shows the amounts (lbs) of total acreage that were treated with pyrethroids by county from 1998 to 2003. The counties with the highest historical use of pyrethroids include Sutter (29% to total pyrethroids used), Butte (23%), Colusa (17%), and Glenn (16%)(also see

Figure 16). The most highly used pyrethroid was lambda-cyhalothrin (applied on 321,467 acres or 97% of total acreage) followed by much lower amounts of zeta-cypermethrin (applied on 4,232 acres), cypermethrin (272 acres) and permethrin (60 acres).

Table 10. Total acreage treated with pyrethroids by county 1998-2003.

County	Cyhalothrin, lambda	Cypermethrin, zeta	Cypermethrin	Permethrin	Amount (acres)	% of Total
Sutter	92,400	2,806		35	95,241	29
Glenn	50,565		64	25	50,654	16
Butte	75,680				75,680	23
Colusa	55,769				55,769	17
Yuba	25,308	504			25,812	8
Sacramento	9,067				9,067	3
Yolo	4,266	922			5,188	2
San Joaquin	3,757		208		3,965	1
Merced	2,559				2,559	1
Stanislaus	2,096				2,096	1
Total	321,467	4,232	272	60	326,031	100

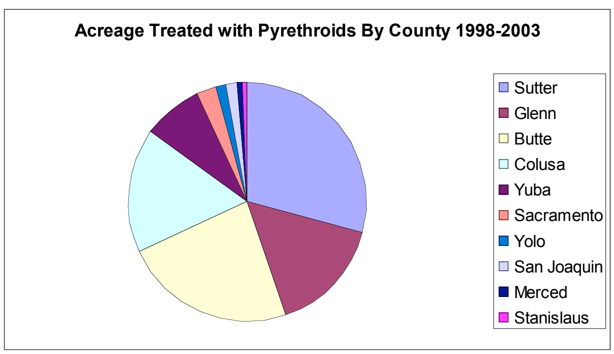


Figure 16. Pie chart showing the acreage treated with pyrethroids by county as a percentage of the total acreage treated 1998-2003.

5.2.1. Pyrethroid Use in Rice and Potential Impact on POD

Because zeta-cypermethrin was recently registered for use in California in 2003, it cannot have not have been a significant contributor to the observed POD in the Delta. Cypermethrin was also only used in 2003 and at a very low amount (13 lbs), so like zeta-cypermethrin it too could not have been a significant contributor. Permethrin was last used in 2000 (1 lb) and its total lifetime level of use in rice (9 lbs) was also much too low to consider it a significant contributor. On the other hand, lambda-cyhalothrin has been used for rice in much higher amounts more than any other pyrethroid (see Table 8). Its use in rice peaked in 2000 at 4,189 lbs and from 2001 to 2003 its average use amount was ~1,900 lbs/year. Lambda-cyhalothrin is replacement for the carbamate pesticide carbofuran.

Drainage of water from rice fields in Sutter, Glenn, Butte and Colusa counties is controlled and occurs during the spring and summer months (March-August) primarily into the Colusa Basin Drain, Butte Slough, and Sacramento Slough areas. The Department of Pesticide Regulation has tested water samples for the presence of lambda-cyhalothrin in the Colusa Basin Drain. Figure 17 shows the results of a field test from May 2000, which was conducted during a period of high use (>1,300 lbs) in the Glenn-Colusa study area. The analysis showed that lambda-cyhalothrin concentration was not detected or below the method detection limit (10 ng/L) in the water samples. The physical-chemical properties of lambda-cyhalothrin suggest that this compound, as well as other pyrethroids, has a strong tendency to adsorb to surfaces. Therefore, it is most likely to be bound to bedded sediments, suspended sediments, organic matter, or even bioaccumulated in biological tissue, rather than remain dissolved in the water column (Log Kow = 6.9; Log Koc = 5.5), which supports why it may not have been detectable in water samples from the Colusa Basin Drain.

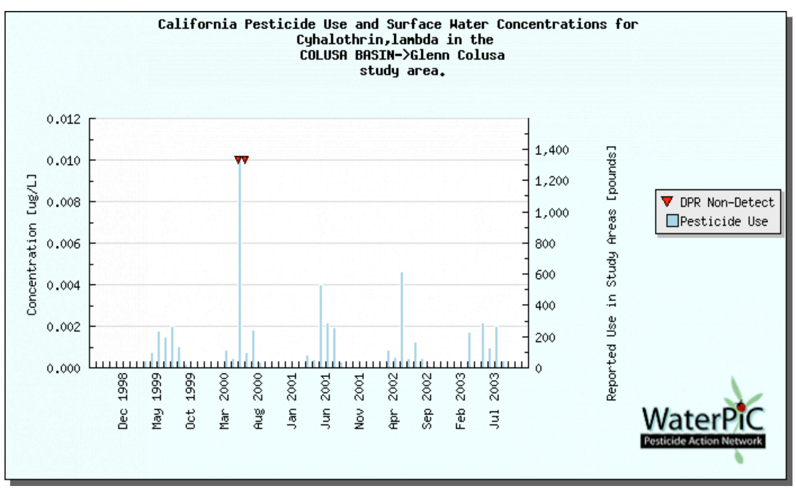


Figure 17. Plot of surface water concentrations of lambda-cyhalothrin in the Colusa Basin.

Data are from the Pesticide Action Network, North America, Water and Pesticides Information Center (WaterPIC, 2005) Map Server website http://www.pesticideinfo.org/waterpic/step1.jsp. Accessed September, 2005.

5.3. Urban Area Use Patterns

Pyrethroids are replacing the organophosphate (OP) pesticides (mainly diazinon and chlorpyrifos) in the urban use market. The primary uses for pyrethroids in urban areas include structural pest control, landscape maintenance, rights of way, and public health pest control, which are uses that are recorded in the DPR's PUR database. Commercial pesticide applicators are required to report pyrethroid use amounts to the DPR, while consumers that use pyrethroids for mainly home and garden use are not mandated to report use amounts to the DPR and thus, their use amounts are not included in the PUR database. Hence, pyrethroid total use amounts in any given year and possibly area are actually higher than what is kept on record with the DPR. A variety of pyrethroids are common active ingredients in commercial brands that are labeled for outdoor use. Many of these products such as *Ortho*, *Spectracide*, *Bayer* and *Scotts* can be purchased at many retail chain stores such as the Home Depot.

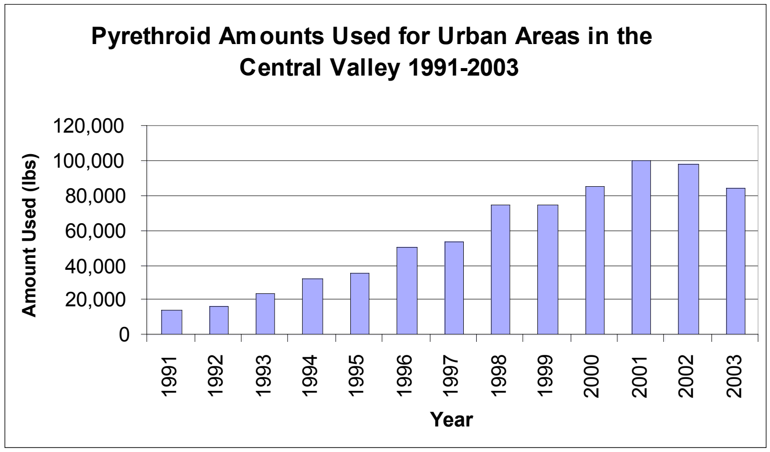
The urban applications with the greatest potential to release pesticides to surface water are applications to surface waters (directly), storm drains, outdoor impervious surfaces, other outdoor locations, sewers, spill cleanup, and washing of treated items (e.g., clothing, pets, and skin)(TDC, 2005). Flint (2003) conducted a telephone survey of residents in the Bay Area and in selected watersheds of Sacramento and Stockton and found that ant control was the primary reason for using pesticides around the home and that outdoor hard surfaces (e.g., sidewalks and building walls) were mostly treated with pesticides.

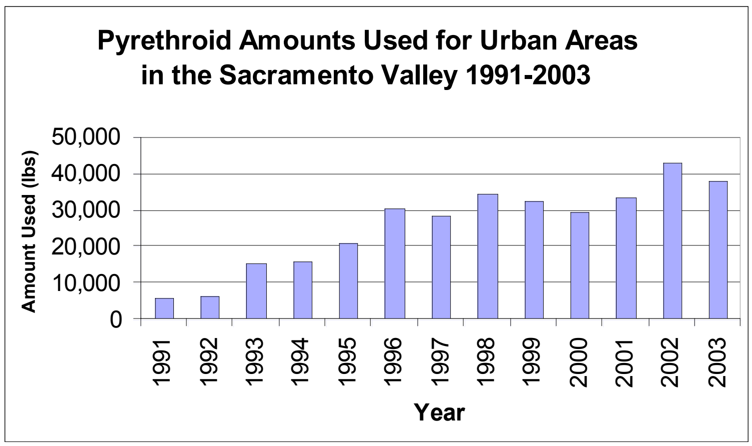
The pyrethroid use amounts for urban area applications in the Central Valley from 1991 to 2003 are shown in Table 11 and are plotted in Figure 18. The four major urban area uses in 2001 include structural pest control (96% of total pyrethroids used in urban areas), landscape maintenance (1.3%), public health pest control (2.4%), and rights of way (0.01%). More pyrethroids are used for urban areas in the San Joaquin Valley than in the Sacramento Valley (Table 11). Of the total amount (177,659 lbs) of pyrethroid used in the Central Valley during 2003, 82,211 (46%) were used in urban area applications. This demonstrates the importance of urban uses and strong need for implementing best management practices to prevent pyrethroids from entering water bodies through storm water drainage. Cypermethrin was the most abundantly used pyrethroid in the Central Valley urban areas, followed by bifenthrin and permethrin and their uses were primarily for structural pest control (Table 12).

Table 11. Pyrethroids use amounts (lbs) for urban areas in the Central Valley 1991-2003.

Sacramento Valley Urban Use	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Structural	5,633	5,653	14,141	14,642	18,699	29,378	25,832	33,442	30,974	28,447	31,342	41,398	36,896
Landscaping/Rights-of-Way	103	78	191	300	596	449	1,420	136	510	316	653	497	317
Public Health	339	712	1,364	959	1,624	651	1,211	855	864	755	1,394	1,089	1,034
Total	6,076	6,443	15,696	15,901	20,919	30,479	28,463	34,432	32,348	29,518	33,389	42,984	38,247
San Joaquin Valley **Urban Use**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Structural	6,710	9,473	6,289	11,160	13,946	19,135	24,547	40,312	41,644	55,051	65,654	53,613	44,980
Landscaping/Rights of Way	1,037	36	31	31	69	258	434	249	291	195	315	872	829
Public Health	485	668	1,992	5,192	563	659	881	446	700	822	902	853	997
Total	8,233	10,178	8,312	16,383	14,578	20,051	25,862	41,007	42,634	56,068	66,871	55,339	46,805
Central Valley[1] **Urban Use**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Structural	12,343	15,126	20,430	25,802	32,645	48,513	50,379	73,753	72,618	83,498	96,996	95,011	81,876
Landscaping/Rights-of-Way	1,140	114	222	332	665	707	1,853	385	800	511	968	1,369	1,145
Public Health	824	1,380	3,356	6,150	2,188	1,310	2,092	1,301	1,565	1,577	2,296	1,942	2,031
Total	14,308	16,621	24,008	32,283	35,498	50,530	54,325	75,439	74,982	85,586	100,260	98,323	85,052

[1]Central Valley is the sum of urban use amounts in Sacramento and San Joaquin Valleys.
Pyrethroids included in totals were bifenthrin, cypermethrin, lambda-cyhalothrin, permethrin, cyfluthrin, tralomethrin, and pyrethrin.





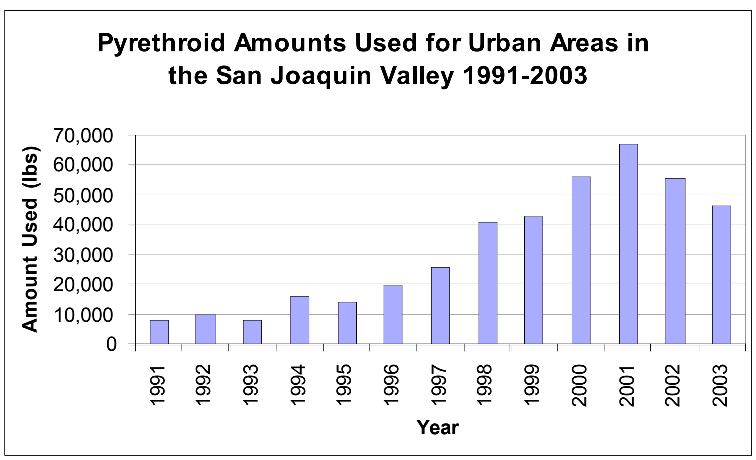


Figure 18. Pyrethroid use amounts (lbs) for urban areas of the Central, Sacramento, and San Joaquin Valleys 1991-2003.

Table 12. Pyrethroid use amounts for specific urban area applications in 2003.

Sacramento Valley

Pyrethroid	Total	Structural	Landscaping	Public Health	Rights-of-Way
Bifenthrin	1,637	1,577	60	0	0.1
Cyfluthrin	3,373	3,331	42	0	0.2
Cypermethrin	26,080	26,067	12	0	0.4
Lambda-cyhalothrin	296	294	2	0	0
Permethrin	6,383	5,547	187	642	7
Pyrethrin	467	69	5	393	0.7
Tralomethrin	11	11	0	0	0
Total	38,247	36,896	309	1,034	8

San Joaquin Valley

Pyrethroid	Total	Structural	Landscaping	Public Health	Rights-of-Way
Bifenthrin	12,242	12,223	18	0	0
Cyfluthrin	5,673	5,569	103	0	0.6
Cypermethrin	21,495	21,130	366	0	0
Lambda-cyhalothrin	400	393	7	0	0
Permethrin	5,797	5,465	330	1	1
Pyrethrin	1,197	199	3	995	0.02
Tralomethrin	1	1	0	0	0
Total	46,806	44,981	827	997	2

Central Valley[1]

Pyrethroid	Total	Structural	Landscaping	Public Health	Rights-of-Way
Bifenthrin	13,879	13,801	78	0	0.1
Cyfluthrin	9,046	8,900	145	0	0.7
Cypermethrin	47,575	47,197	378	0	0.4
Lambda-cyhalothrin	696	687	9	0	0
Permethrin	12,180	11,012	517	643	8
Pyrethrin	1,665	268	8	1,388	0.7
Tralomethrin	12	12	0.1	0	0
Total	85,053	81,877	1,135	2,031	10

[1]Central Valley is the total of use amounts for Sacramento and San Joaquin Valleys.

6. Linking Pyrethroid Use and Toxicity

Important Points:

- *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 (µg/L).*
- *Most sublethal effect concentrations of pyrethoids are in the low to medium part per trillion (ng/L) range.*
- *Although pyrethroids are relatively insoluble in water, all are sufficiently soluble to cause adverse biological effects.*
- *Amphipods and copepods are among the taxa most sensitive to pyrethroid insecticides.*
- *For the majority of these pesticides, the available toxicological data are inadequate for a scientific determination of the risks they pose for Delta fish species.*
- *Recently developed TIE methods use PBO addition (enhancement of pyrethroid toxicity) as well as carboxylesterase addition (decrease of pyrethroid toxicity) to identify pyrethroid-associated toxicity in water samples.*
- *There are extensive data gaps for these compounds, and sublethal as well as synergistic or additive toxic effects may occur at concentrations far below the levels presently used as adverse effect thresholds.*
- *Pyrethroid toxicity increases with decreasing water temperature, and is enhanced by food deprivation.*

6.1. Modes of Toxic Action

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). Due to the lipophilic nature of pyrethroids, biological membranes and tissues readily take up pyrethroids. Exposed organisms may exhibit symptoms of hyperexcitation, tremors, convulsions, followed by lethary and paralysis. Pyrethroids occur mostly as mixtures of stereoisomeric forms, and the toxicity of individual isomers can vary (Liu et al., 2005). 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). Pyrethroids also modulate the release of acetylcholinesterase in the brain's hippocampus region (Hossain et al., 2004), and can inhibit ATPases (Litchfield, 1985). In addition, pyrethroids can disrupt hormone-related functions (Go et al., 1999). In mammals, pyrethroids decrease progesterone and estradiol production (Chen et al., 2005), eliciting estrogenic effects in females and anti-androgenic effects in males (Kim et al., 2005). Furthermore, pyrethroids have been shown to inhibit cell cycle progress (Agarwal et al., 1994), cause cell stress (Kale et al., 1999), and have immunosuppressive effects (Madsen et al., 1996; Clifford et al., 2005). Additional long-term effects may be caused by damage to respiratory surfaces, and interference with renal ion regulation (Bradbury and Coats, 1989).

6.2. Acute and Sublethal Toxicity Endpoints

6.2.1. Acute Toxicity

Most aquatic invertebrates and fish are highly susceptible to pyrethroid insecticides (Smith and Stratton, 1986; Clark et al., 1989, among 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 (µg/L, see Table 13). 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 13). Among some of the dominant pyrethroids used in the Central Valley region, toxicity decreases roughly in the following order:

□-cyhalothrin> cyfluthrin > bifenthrin > cypermethrin > esfenvalerate > permethrin

6.2.2. Critical Life Stages/Groups

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 tsahwytscha*) 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).

Table 13. Summary of aquatic toxicity data for selected pyrethroids (lowest values).

Test Species	Lambda-Cyhalothrin		Bifenthrin		Cyfluthrin		Cypermethrin	
			Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)
Invertebrates								
Ceriodaphnia dubia			48-h LC50	0.07	48-h LC50	0.14		
Daphnia magna	48-h EC50[7] 21-d NOEC[7]	0.36 0.002	48-h LC50 48-h EC50	0.32 1.6	48-h LC50 48-h EC50	0.17 0.025	24-h LC50 48-h LC50[3] 24-h EC50 48-h EC50	0.53 0.13 2 1
Daphnia pulex								
Copepod, *Cyclops* sp.	48-h EC50[7]	0.3						
Mayfly, *Cloeon dipterum*	48-h EC50[7]	0.038					72-h EC50[3] 96-h LC50[3]	0.006-0.023 0.03
Isopod, *Asellus aquaticus*	48-h EC50[7]	0.026					72-h LC50[3]	0.008
Midge, *Chironimus riparius*	48-h EC50[7]	2.4					48-h LC50[3]	0.007
Grass shrimp, *Palaemonetes pugio*							96-h LC50[3]	0.016
Hyalella azteca	48-h EC50[7]	0.0023					48-h LC50[3]	0.005
Gammarus pulex	48-h EC50[7] 0.5-h LC50[8]	0.014 5.69						
Gammarus lacustris								
Gammarus fasciatus								
Mysid shrimp (B) *Americamysis bahia**			96-h LC50	0.004	96-h LC50	0.00242	96-h LC50	0.005
Pink shrimp (S, juv), *Penaeus duorarum*							96-h LC50[3]	0.036
Penaeus sp. (S)							96-h LC50	0.036
Crassostrea virginica (S, B)			48-h EC50 (embryo)	285	96-h EC50	2.69	96-h EC50	370
Crassostrea gigas (S, B)	48-h EC50[2] (larvae)	590.00					48-h LC50	2,270

Table 13 (Continued)
Aquatic toxicity data for selected pyrethroids (lowest values).

Test Species	Deltamethrin Test	Deltamethrin Result (ppb)	Esfenvalerate Test	Esfenvalerate Result (ppb)	Permethrin Test	Permethrin Result (ppb)
Invertebrates						
Ceriodaphnia dubia			96-h LC50[4]	0.3	48-h LC50	0.55
Daphnia magna	24-h LC50 48-h LC50 96-h LC50 24-h EC50 48-h EC50 96-h EC50	0.11 0.037 0.01 0.113 0.029 0.003	48-h LC50[1] 48-h LC50 48-h EC50	0.24 0.27 0.15	48-h LC50[1] 72-h LC50 96-h LC50 48-h EC50 96-h EC50	0.075 6.8 0.3 0.112 0.039
Daphnia pulex					3-h LC50 48-h LC50 72-h LC50	9,200 2.75 0.08
Hyalella azteca			42-D LOEC 96-h LC50[6]	0.05 0.008		
Midge, *Chironomus plumosus*					48-h EC50[3]	0.56
Mayfly, *Hexagenia bilineata*					96-h LC50[3]	0.1
Gammarus pseudolimnaeus					96-h LC50[3]	0.17
Gammarus lacustris						
Gammarus daiberi			96-h LC50[6]	0.033		
Gammarus fasciatus						
Mysid shrimp (B) *Americamysis bahia*	96-h LC50	0.0017	96-h LC50[1]	0.038	96-h LC50[3]	0.02
Stone crab (S), *Menippe mercenaria*					96-h EC50[3]	0.018
Fiddler crab, *Uca pugilator* (S)					96-h LC50[3]	2.39
Pink shrimp (S), *Penaeus duorarum*					96-h LC50[3]	0.22
Penaeus sp (S).					96-h LC50	0.17
Crassostrea virginica (B, S)	96-h EC50	8.2			48-h EC50 96-h EC50	1000 40.7
Crassostrea gigas (B, S)					48-h EC50	1,050

Tables based on Moran (2003), with kind permission of Kelly Moran.
Source: All unmarked values from USEPA Ecotox (Acquire) database (USEPA, 2002)
[1] from the DPR Ecotox database (DPR, 2002).
[2] from the PAN Aquatic Ecotoxicology Database
[3] State of California, Department of Fish and Game (2000)
[4] Werner et al., 2002
[5] Eder et al., 2004
[6] Werner et al., unpublished data
[7] Maund et al., 1998
[8] Heckmann et al. 2005
(S) saltwater species
(B) brackish water species

Table 13 (Continued)
Aquatic toxicity data for selected pyrethroids (lowest values).

Test Species	Lambda-Cyhalothrin		Bifenthrin		Cyfluthrin		Cypermethrin	
	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)	Test	Result (ppb)
Vertebrates								
Pimephales promelas	96-h LC50[7]	0.70	96-h LC50[1]	0.26	96-h LC50[1]	2.49		
Oncorhynchus mykiss	96-h LC50[2] 96-h LC50[2]	0.54 0.24	96-h LC50	0.15	48-h LC50 96-h LC50	0.57 0.3	12-h LC50 24-h LC50 48-h LC50 96-h LC50	2.5 5 5 0.39
Carp, *Cyprinus carpio*	96-h LC50[7]	0.50					96-h LC50[3]	0.9
Mosquitofish, *Gambusia affinis*	24-h LC50[2] 24-h LC50[2]	0.18 0.08						
Sheepshead minnow (S) *Cyprinodon variegatus*	28-d NOEC[7]	0.25	96-h LC50[3]	17.8	96-h LC50	4.05	96-h LC50	0.73
Inland silverside, (S) *Menidia beryllina*								
Bluegill (S), *Lepomis macrochirus*	96-h LC50 96-h LC50	0.42 0.21	144-h LC50[3]	0.35	96-h LC50	0.87	96-h LC50[3]	1.78
Plants								
Selenastrum capricornutum	96-h EC50[7]	>1000						
Skeletonema costatum								

Tables based on Moran (2003), with kind permission of Kelly Moran.
Source: All unmarked values from USEPA Ecotox (Acquire) database (U.S. EPA, 2002)
[1] from the DPR Ecotox database (DPR, 2002).
[2] from the PAN Aquatic Ecotoxicology Database
[3] State of California, Department of Fish and Game (2000)
[4] Werner et al., 2002
[5] Eder et al., 2004
[6] Werner et al., unpublished data
[7] Maund et al., 1998
(S) saltwater species
(B) brackish water species

Table 13 (Continued)
Aquatic toxicity data for selected pyrethroids (lowest values).

Test Species	Deltamethrin		Esfenvalerate		Permethrin	
			Test	Result (ppb)	Test	Result (ppb)
Vertebrates						
Fathead minnow, *Pimephales promelas*			24-h LC50 48-h LC50 96-h LC50	0.24 0.24 0.22	24-h LC50 96-h LC50[1]	5.4 2
Rainbow trout, *Oncorhynchus mykiss*	24-h LC50 48-h LC50 96-h LC50	0.7 0.5 0.25	96-h LC50[1] 96-h LC50	0.26 0.07	24-h LC50 48-h LC50 96-h LC50	4.3 6 0.62
Atlantic salmon, *Salmo salar*					96-h LC50[3]	17
Chinook salmon, juvenile (*Onchorynchus tshawytscha)*			96-h LC50[5]	0.1-1.0		
Coho salmon, *O. kisutch*					96-h LC50[3]	3.2
Brook trout, *Salvelinus fontinalis*					24-h LC50 96-h LC50[3]	4 3.2
Sacramento splittail *Pogonichthys macrolepidotus*			96-h LC50	0.50		
Sheepshead minnow (S), *Cyprinodon variegatus*	96-h LC50	0.36	96-h LC50[1]	430	96-h LC50	7.8
Atlantic silverside (S), *Menidia menidia*					96-h LC50[3]	2.2
Inland silverside, (S) *Menidia beryllina*					96-h LC50	27.5
Bluegill (S), *Lepomis macrochirus*	96-h LC50	0.36	96-h LC50[1]	0.26	24-h LC50 96-h LC50[3]	6.6 2.5
Plants						
Selenastrum capricornutum						
Skeletonema costatum						

Tables based on Moran (2003), with kind permission of Kelly Moran.
Source: All unmarked values from USEPA Ecotox (Acquire) database (USEPA, 2002)
[1] from the DPR Ecotox database (DPR, 2002).
[2] from the PAN Aquatic Ecotoxicology Database
[3] State of California, Department of Fish and Game (2000)
[4] Werner et al., 2002
[5] Eder et al., 2004
[6] Werner et al., unpublished data
[7] Maund et al., 1998
(S) saltwater species
(B) brackish water species

6.2.3. Sublethal Toxicity

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 biochemical responses. However, 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. Sublethal toxicity data for various pyrethroids and test species are shown in Table 14.

Growth: 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 part per trillion (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.

Behavior: Sublethal effects of acute cypermethrin exposure 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 pptrillion (ng/L) and are approximately 2 to 3-fold lower than the corresponding LC_{50} values of 5.5 and 5.9 part per trillion (ng/L), respectively.

Reproductive toxicity/endocrine disruption: Moore and Waring (2001) demonstrated that the pyrethroid cypermethrin reduced the fertilization success in Atlantic salmon after a 5-day exposure to concentrations of 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. (2002) show that dietary uptake of esfenvalerate (148 ppm) led 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 pptrillion (ng/L) was reported in two studies (USEPA, 2005).

Table 14. Sublethal toxicity data for several pyrethroids.

Species	Life-Stage/Test Duration	Effect	Effect Concentration (ppb)	Reference
Sublethal Toxicity Data for Bifenthrin				
Fathead minnow, *Pimephales promelas*	Life-cycle	LOEC NOEC	0.09 0.05	CDFG, 2000
Sublethal Toxicity Data for Lambda-Cyhalothrin				
Gammarus pulex	Adult/ 30 min	EC10 (Pair formation) EC50 (Pair formation)	0.04 0.20	Heckmann et al., 2005 "
Sublethal Toxicity Data for Cypermethrin				
Daphnia magna	Adult/6 h	LOEC (Decrease in feeding efficiency and swimming ability)	0.1	Christensen et al., 2005
Mysid shrimp, *Americamysis bahia*	28 d	LOEC (fecundity) NOEC (fecundity) LOEC (growth)	0.0028 0.0015 0.00078	US EPA, 2005 " "
Fathead minnow, *Pimephales promelas*	Larvae/30 d	LOEC NOEC	0.33 0.15	CDFG, 2000 "
Rainbow trout, *O. mykiss*	-	LOEC (behavior)	0.00068	US EPA, 2005
Bluegill sunfish, *Lepomis macrochirus*	-	LOEC (behavior)	0.0022	US EPA, 2005
Sheepshead minnow, *Cyprinodon variegatus*	-	LOEC (behavior)	0.84	US EPA, 2005
Atlantic salmon, *Salmo salar*	Gamets/5 d Adult/5 d	LOEC (fertilization success) Impaired olfactory function	0.1 <0.004	Moore & Waring, 2001 "
Korean rockfish, *Sebastes schlegeli*	52 g/8 wk	Changes in blood parameters	0.041	Jee et al., 2005
Sublethal Toxicity Data for Esfenvalerate				
Daphnia carinata	Adult	Reduced fecundity	0.05	Barry et al., 1995
Fathead minnow, *Pimephales promelas*	Larvae/96 h	Reduction in hepatic glycogen NOEC Swimming performance	0.20 0.13	Denton, 2001 "
Bluegill, *Lepomis macrochirus*	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, *Oryzias latipes*	Adult/7 d	Decreased fecundity/larval survival Stress protein (hsp) increase	148 ppm (diet) 21 ppm (diet)	Werner et al. 2002 "
Chinook salmon, *Oncorhynchus tshawytscha*	Juvenile/96 h	Alteration of immune response Stress protein (hsp) increase	0.08 0.01	Eder et al. 2004 Clifford et al., 2005 Eder et al. submitted
Sublethal Toxicity Data for Permethrin				
Daphnid	Adult	LOEC (fecundity)	<0.01	Day, 1989
Sheepshead minnow, *Cyprinodon variegatus*	28 d	LOEC NOEC	22 10	CDFG, 2000 "

Immune system effects: Toxicological assessments have identified the immune system as a frequent target of xenobiotic compounds (Luster et al., 1988, 1993; Arkoosh et al., 1991, 1998 a, b, 2001; Zelikoff, 1994). 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. Eder et al. (2004, submitted) 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. The susceptibility of juvenile Chinook salmon to Infectious Hematopoietic Necrosis Virus (IHNV) was dramatically increased in juvenile fish exposed to 0.08 ppb esfenvalerate (Clifford et al., 2005).

Biochemical and physiological effects: Increased expression of cellular stress proteins (hsps) was detected in juvenile Chinook salmon following exposure to sublethal concentrations of esfenvalerate (Eder et al., 2004; submitted; Teh et al., 2005). A nominal concentration of 0.01 ppb led to a significant increase of hsps in liver tissue. A study by Werner et al. (2002) detected induction of hsps in medaka after dietary exposure to esfenvalerate at concentrations, which also caused reduced fecundity and impaired larval survival. Hsps indicate the occurrence of significant protein damage in cells and tissues. The use of these 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). Increased expression of these proteins has been linked to abnormal development in larval sturgeon (Werner et al., in press), as well as an increase in energy expenditure in juvenile steelhead trout (Viant et al., 2004).

An eight-week exposure of Korean rockfish (*Sebastes schlegeli*; mean fish wt: 52 g) to cypermethrin had significant effects on a number of blood parameters (Jee et al., 2005). Red blood cell count, hemoglobin and hematocrit were significantly reduced after exposure to 0.041 ppb cypermethrin. The activity of several enzymes and serum osmolality were also altered. Reduced levels of serum total protein, albumin, cholesterol, lysozyme activity and significantly higher serum concentrations of glucose, bilirubin and malondialdehyde were attributed to an increased demand for energy by fish under stress.

Moore and Waring (2001) demonstrated that the pyrethroid cypermethrin impaired olfactory function in Atlantic salmon after a 5-day exposure to <0.004 ppb.

Histopathological effects: Histopathological lesions in the liver were observed in Sacramento splittail (*Pogonichthys macrolepidotus*; Teh et al., 2005) shortly (1 wk) after 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 Waiwood (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).

Swimming performance and behavorial effects: In an excellent overview of fish physiological measurements, Heath (1998) outlined measurements critical to successful assessment and integration of the impact of multiple stresses (e.g., chemicals, physical and/or chemical condition limitations) on aquatic ecosystems. 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. 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). Because esfenvalerate is a neurotoxin, a physiological endpoint pertinent to this study needed to be an integrator of the pesticide's energetic and neural effects on the whole organism. Swimming performance in the laboratory can be directly related to real world behavior: How well does the fish swim, and thereby capture food and avoid predators?

Swimming performance can be separated into two components and evaluated according to swimming activity (e.g., frequency and duration of movements, position in water column) or swimming capacity (e.g., orientation to water flow, physical capacity to swim against the flow). Both components are important integrated endpoint assessments that should be examined to evaluate the metabolic and behavioral effects of toxic chemicals. Little and Finger (1990) describe swimming behavior of fish exposed to a variety of contaminants ranging from pesticides (e.g., DDT, carbaryl, methyl parathion) to metals (e.g., zinc, copper, cadmium), and found that changes in swimming behavior were detected at exposures as low as 0.7 to 5% of the chemical's LC50 values. Little and Finger (1990) concluded that swimming performance and behavioral effects should be incorporated as methods for assessing additional sublethal endpoints to expand upon the range of sensitivity of the traditional endpoints such as survival and growth. An advantage of such endpoints is they are non-destructive, thereby allowing for repeated measurements essential for pulsed exposure studies. Swimming performance was chosen because it is an integrative measure of metabolic and energetic processes (Heath et al., 1997). Denton (2001) found that swimming performance tests made at no-observable-effect concentrations (swimming NOECs) revealed fathead minnows were impaired at or below the same effect level when compared to results from survival NOEC tests for esfenvalerate.

6.3. Toxic Effects on Aquatic Communities: Pulse Exposures and Their Effects on Fish and Invertebrates

Pyrethroids are generally of very low water solubility and high lipophilicity, and therefore are rapidly and strongly adsorbed to particulate material and other surfaces. In the adsorbed state their bioavailability to aquatic organisms is reduced. Therefore, brief field experiments and pulse exposure experiments are believed to be more environmentally realistic than LC50 data. Below we summarize the results of such field and pulse studies.

Field studies: Field 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 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 is 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; Moshen 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^3). 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 mesotropohic 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 Hydacarina were the taxa most sensitive to pyrethroid insecticides, followed by Trichoptera, Copepoda, Ephemeroptera and Hemiptera (Table 15).

Table 15. Reported negative effects on various taxonomic groups as a result of repeated application of pyrethroids in aquatic microcosms and mesocosms.

Taxon	TU			
	0.001-0.01 % Loss (n)	**0.01-0.1 % Loss (n)**	**0.1-1 % Loss (n)**	**1-10 % Loss (n)**
Amphipoda	-	100% (1)	100% (11)	100% (7)
Isopoda	-	-	80% 5)	100% (2)
Copepoda	0% (1)	60% (5)	56% (16)	73% (11)
Cladocera	0% (1)	0% (2)	50% 10)	86% (7)
Ostracoda	0% (1)	0% (1)	50% (2)	-
Trichoptera	0% (1)	67% (3)	86% (7)	83% (6)
Ephemeroptera	0% (1)	50% (6)	82% (17)	85% (13)
Diptera	0% (1)	33% (6)	82% (17)	100% (13)
Hemiptera	0% (1)	50% (2)	67% (6)	100% (2)
Odonata	0% (1)	33% (3)	36% (11)	50% (10)
Coleoptera	0% (1)	0% (2)	64% (11)	60% (10)
Hydracarina	0% (1)	100% (1)	100% (1)	-
Fish	0% (1)	0% (5)	33% (6)	83% (6)
Rotifera	0% (1)	0% (3)	0% (13)	0% (11)
Mollusca	0% (1)	0% (3)	0% (12)	0% (10)
Annelida	0% (1)	0% (2)	0% (11)	0% (6)
Turbellaria	0% (1)	0% (1)	0% (7)	0% (3)
Plants	0% (1)	0% (5)	0% (13)	8% (12)

* The effects are arranged according to toxic units and expressed as a percentage of the cases (n) in which a reduction in numbers or biomass of one or more taxa within a taxonomic group was reported. Data are cited from Van Wijngaarden et al. (2005). TU=toxic units= pyrethroid concentration divided by the EC50 of the most sensitive standard test species *(Daphnia magna, Pimephales promelas, Onchorynchus mykiss).**

Laboratory pulse exposures: 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.

6.4. Toxicity Identification Evaluation Approaches

Toxicity identification evaluation (TIE) methods have been applied broadly to identify the causes of toxicity in multiple aquatic matrices. TIE testing routinely has identified organophosphate (OP) insecticides, including diazinon and chlorpyrifos, as causes of toxicity in municipal effluents and surface waters in northern California, USA (Bailey et al., 2000; Werner et al., 2000; De Vlaming et al., 2000). New TIE methods using the enzyme carboxylesterase to identify pyrethroid toxicity were recently developed by Wheelock et al. (2004). Addition of the pyrethroid synergist piperonyl butoxide (PBO) increases pyrethroid-associated toxicity. However, this effect may be masked and therefore difficult to interpret in the presence of organophosphate (OP) insecticides, because OP toxicity is reduced by the addition of PBO. Carboxylesterase is an enzyme that rapidly degrades both type I and type II pyrethroids. This class of enzymes has proven effective in reducing pyrethroid-associated toxicity in water samples. Carboxylesterase activity removes pyrethroid associated toxicity in water samples in a dose-dependent manner and does not alter OP toxicity, suggesting that carboxylesterase treatment will not interfere with TIE methods aimed at detecting OP toxicity. In recent years, the addition of carboxylesterase as a TIE method to identify pyrethroid-caused toxicity has been successfully applied at the UC Davis Aquatic Toxicology Laboratory (UCD ATL). Generally, UCD ATL uses both PBO addition (enhancement of pyrethroid toxicity) as well as carboxylesterase addition (decrease of pyrethroid toxicity) to identify pyrethroid-associated toxicity in water samples.

6.5. Joint Interactions with Other Chemicals and Stressors

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). 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 and may "reactivate" pyrethroids already present in the environment. In a study on juvenile (90 d old) striped bass (*Morone saxitalis*) Rebach (1999) determined 24-h and 96-h LC50s of 32.9 and 16.4 ppb for a 1:1 mixture of PBO and permethrin. Unfortunately, no LC50 information for this species is available for permethrin alone.

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.

6.6. Environmental Conditions and Pyrethroid Toxicity Relationship

Temperature: 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).

Food: 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.

Turbidity/Discharge: Dabrowski et al. (2005) conducted artificial stream microcosm trials by exposing mayfly nymphs (*Baetis harrisoni*) to 1 ppb of cypermethrin. Results demonstrated that exposure to cypermethrin increased mayfly drift significantly under high turbidity (suspended particles) or high flow conditions, but in the presence of both increased flow and suspended particles drift was reduced. The authors concluded that mayflies are more likely to be affected by spray-drift exposure than by runoff exposure to cypermethrin.

6.7. Cases of Pyrethroid Toxicity in Regional Water Bodies

The available information on pyrethroids detected in water and sediment samples and pyrethroid-caused toxicity in sediment samples from the Delta and its tributaries is presented in Chapter 4 of this white paper. The information on sublethal effects of pyrethroids to fish is limited, thus it is evident that the concentrations of esfenvalerate, bifenthrin and permethrin detected in water samples from tributaries of the Sacramento and San Joaquin Rivers are high enough to cause acute toxicity to invertebrates as well as sublethal toxicity to fish (see Tables 13 and 14).

7. Other Chemical Contaminants of Concern

Important Points:

- *There are a wide variety of biologically active chemicals that enter into water bodies primarily through discharge of wastewater effluents.*
- *The potential toxic effects of individual chemicals and complex mixtures of chemicals on aquatic biota are mostly unknown, which is problematic.*
- *Endocrine system disrupting chemicals are a potential threat to aquatic biota because they are known to cause reproductive defects or diseases, thyroid dysfunctions, and infertility in some species.*

There are a variety of chemicals, other than pyrethroids, that are now emerging as potential problematic contaminants in the environment and these should not be ignored. Appendix 1 provides brief overviews of some individual chemicals and groups of chemicals that should be of concern due to their potential to cause harm to the aquatic ecosystem. The major source of these chemicals into the environment is through human input primarily by discharges from wastewater effluents and secondarily by urban and agricultural runoff. Recent evidence suggests that some of these synthetic compounds and their metabolites can potentially induce toxicity, act as endocrine system disruptors, and even accumulate in marine biota (fish, crabs, and bivalves) and in higher food chain consumers (birds, marine mammals, and humans). Information on their toxic effects on aquatic species is limited but the information determined for other species suggests that there is a high potential for harming the aquatic ecosystem.

7.1. Endocrine System Disrupting Chemicals

Of major concern now to aquatic system managers are endocrine system disrupting chemicals (EDCs). The endocrine system is responsible for maintaining natural bodily functions such as metabolism, growth, reproduction, and development. Their modes of toxic action of EDCs might include mimicking endogenous hormones such as estrogen, interfering with hormone function, interfering with uptake into target cells, and degrading hormones. Some EDCs include industrial waste products such as polychlorinated dibenzo dioxins (TCDDs) and furans, industrial chemicals such as polychlorinated biphenyls (PCBs) and organometals, pesticides such as organochlorines (e.g., DDT) and their degradation products, surfactants such as nonylphenol polyethoxylates and their transformation product (p-nonylphenol) used in pesticide formulations, phthalates in plastic products, and steroidal hormones used by humans and in animals. The aquatic concentrations of these EDCs generally fall below U.S. EPA established water quality criteria that are designed to protect humans and marine life from cancer (U.S. EPA, 2000); however, there are no water or sediment quality criteria for protecting humans and marine life against endocrine system disruption and its related effects, which can include reproductive defects or diseases, thyroid dysfunctions, and infertility.

7.2. Pharmaceuticals

It is now well established that some effluents from wastewater treatment plants and storm water runoff from agricultural and urban areas could contain pharmaceuticals and other personal care products that could potentially threaten water quality of domestic drinking water supply, surface water, and ground water (Daughton and Ternes, 1999; Kolpin et al., 2002). When pharmaceuticals (drugs) are detected in surface waters their concentrations range from ng/L (ppt) to μg/L (ppb) (Daughton and Ternes, 1999).

Human pharmaceuticals such as antibiotics, analgesics, antiinflammatories, antidepressants, antihypertensives, anticancers, and steroidal hormones are used to treat illness, disease, and medical conditions. The primary transport pathway of human pharmaceuticals into the environment is human ingestion followed by subsequent excretion into the municipal sewage system, while the secondary pathway is by disposal of unused and outdated medications directly into the sewage system. These biologically active compounds and their metabolites are not completely removed by current wastewater treatment plant technologies and are often common components in effluents. Wastewater treatment plants discharge billions of gallons of effluents into California's surface waters each year, and this could represent a significant loading of pharmaceuticals and their active metabolites into the aquatic environment especially in small water bodies such as creeks and rivers.

Veterinary pharmaceuticals, which are used primarily in food animals and pets, include vaccines and prophylactic medications to prevent or minimize infection, antibiotics to treat active infection, parasites, or prevent disease, and hormones for production enhancement, growth promotion, and improved feed efficiency. Veterinary pharmaceuticals can enter the environment through the application of biosolid waste products (manure) in agricultural fields followed by their transport in runoff into surface waters, and seepage into ground water.

Pharmaceuticals are continuously infused into the aquatic environment as complex mixtures in effluents. The continual discharge of effluents into aquatic systems can create a situation where aquatic biota exposure to these highly biologically active agents is chronic, depending on the discharge frequency, volume, and residence time that an effluent remains in any given area. In addition, pharmaceuticals are structurally very polar and nonvolatile, thus they tend to remain in the water column. The combined toxic effects of pharmaceuticals should be of major concern because at times more than one drug could target the same biological receptor, thus a low level concentration for one agent might not necessarily signify that toxic effects are not possible or even occurring. Pharmaceuticals are not currently monitored in the Delta and its tributaries and there are only limited published data available on the acute and chronic toxicological effects of pharmaceuticals on aquatic species.

7.3. Complex Chemical Mixtures

Another major concern is the occurrence of complex mixtures of chemicals in environmental samples. Waters and sediments of the Sacramento and San Joaquin Rivers generally contain complex mixtures of chemicals (stressors) derived from various sources and transport pathways including urban runoff, agricultural return-flows, municipal wastewater treatment plant effluents, and atmospheric deposition. Because each complex mixture has a unique toxicology due to their complexity, the potential biological effects cannot always be related back to a single causal agent. Although a single chemical can be measured at a concentration below its No Observable Adverse Effects Level (NOAEL) in an environmental sample it does not entirely exclude it from contributing to an observed toxic effect given that interactions among individual chemicals can possibly result in either additive, synergistic, potentiation, or antagonistic toxic effects. However, if each chemical in a mixture is below its NOAEL, then the toxicity of the mixture is often below its NOAEL. Lydy et al. (2004) provides an extensive literature summary of pesticide mixture studies and describes the challenges in regulating pesticide mixtures. Such is the case with agricultural return-flows that often contain complex mixture of pesticides including herbicides, insecticides, rodenticides, and fungicides. The combined effects of pesticides within the same class can be predicted fairly well based on our understanding of the mechanism of toxic action of these pesticides (i.e., diazinon in combination with chlorpyrifos is additive (Bailey et al., 1997)). However, the effects of across-class mixtures of pesticides, such as triazine herbicides and organophosphate insecticides, are more difficult to predict and to understand (Lydy et al., 2004). Ambient toxicity testing can be used within a watershed to examine the potential of pesticide to pesticide interactions (additive, greater than additive, etc.) and this approach has been successful as demonstrated by de Vlaming et al. (2000). At sites where toxicity is demonstrated, the use of EPA's Toxicity Identification Evaluation protocols are then used to identify the causative toxicant(s) (see section 8.2). Therefore, the approach of toxicity testing, along with understanding the geographic landscape to identify the possible pesticides in runoff, in conjunction with TIE analysis can assess the pesticide interaction potential (Lydy et al., 2004). In this case, toxicity equivalent methods could be applied. Complex chemical mixtures are definitely present in the aquatic environment and because not much is known about them there is a tendency to overlook their importance as causes of aquatic toxicity.

8. Analytical Methods

There is a strong need to develop chemical methods, dose-response, and toxicity identification evaluations (TIEs) for determining pyrethroid concentrations, efficacy, and toxicity in the aquatic environment. This section is a brief overview of several analytical and toxicological methods that are currently available or are being developed by scientists in the region to advance our knowledge of pyrethroids. Information on additional work efforts by scientists and government agencies in the region are described briefly in Appendix 2-Tables 1 and 2.

8.1. Chemical Methods

Several analytical methods that are used by local laboratories for measuring pyrethroids in water and sediments are described briefly in Table 16. The instruments used and methods detection limits that are achievable are shown. Currently, there are no U.S. EPA approved chemical methods for measuring pyrethroids at the low concentrations (ppt levels) that are necessary for these compounds in environmental matrices. U.S. EPA Method 1660 does not provide the sensitivity needed to determine concentrations that are toxicologically relevant to aquatic biota.

Liquid chromatography (LC) and gas chromatography (GC) based methods are the ones that are most commonly used for measuring pesticides in water and sediment samples. LC and GC instruments are coupled with a variety of detector choices including a mass selective detector (GC-MSD), electron capture detector (GC-ECD), or an electrolytic conductivity detector (GC-ELCD). In current efforts, there is a joint venture between three government laboratories, the CA Department of Fish and Game's Water Pollution Control Laboratory, CA Department of Food and Agriculture, and the U.S. Geological Survey's Organic Chemistry Laboratory to develop routine analytical methods for measuring pyrethroids in water, sediments, and biota at the very low ppt levels that are expected in the Delta. The development of these methods will allow local researchers to detect and confirm the presence of pyrethroids in environmental samples and establish baseline measurements for tracking any changes in concentrations in the region.

Table 16. Pyrethroid chemical methods.

Method	Matrix	MDL	Information Source
HPLC	Water	1-2 ug/L	U.S. EPA Method 1660
GC-ECD	Water	2-10 ng/L	CA Dept. of Fish and Game, Water Pollution Control Laboratory, Rancho Cordova, CA
GC/MS	Water	3-6 ng/L	Caltest Analytical Laboratory, Napa, CA
GC/MS (ion trap)	Water	0.5-5 ng/L	USGS, Organic Chemistry Laboratory, Sacramento, CA
GC/MS	Sediment	0.04-0.11 ng/g wet wt	Caltest Analytical Laboratory, Napa, CA
GC/MS (ion trap)	Suspended and Bed Sediments	1-6 ng/g	USGS, Organic Chemistry Laboratory, Sacramento, CA
GC/MSMS	Water	0.2-0.5 ng/L	CA Dept. of Fish and Game, Water Pollution Control Laboratory, Rancho Cordova, CA
GC/HRMS	Water (XAD extracted)	1-6 ng/sample[1]	AXYS Analytical Services Ltd., Sidney, BC, Canada
GC/MSD	Water	2.2-56 ng/L	CA Dept. of Food and Agriculture, Center for Analytical Chemistry, Sacramento, CA
GC-ECD	Sediment	0.5-1.0 ng/g	You et al. (2004) Archives of Environmental Contamination and Toxicology 47:141-147.
GC-ECD with GC/MS	Sediment	1-3 ng/g	CA Dept. of Fish and Game, Water Pollution Control Laboratory, Rancho Cordova, CA
GC-ECD with GC/MSD	Sediment	1 ng/g	CA Dept. of Food and Agriculture, Center for Analytical Chemistry, Sacramento, CA
GC/MSMS	Sediment	0.2-0.5 ng/g	CA Dept. of Fish and Game, Water Pollution Control Laboratory, Rancho Cordova, CA

[1]Based on total volume of water collected using XAD. For example: if 1L of water is collected then the MDL is 1-6 ng/L, if 10 L (0.1-0.6 ng/L), if 100 L (0.01-0.06 ng/L).

Abbreviations:
GC/HRMS: gas chromatography with high resolution mass spectrometry.
GC/MS: gas chromatography with mass spectrometry
GC-MSD: gas chromatography with mass selective detection
GC/MSMS: gas chromatography with tandem mass spectrometry
GC-ECD: gas chromatography with electron capture detection
HPLC: high pressure liquid chromatography
All sediment MDLs are in dry weight unless otherwise noted

8.2. Dose-Response and Toxicity Identification Evaluations

Scientist from the San Francisco Estuary Institute (SFEI) and UC Davis are currently developing dose-response information (LC50) for standard U.S. EPA sediment toxicity testing species, and ecologically relevant species to the San Francisco Bay for three pyrethroids that include bifenthrin, cypermethrin, and permethrin. The species to be evaluated include the amphipods *Eohaustorius estuarius* and *Ampelisca abdita*. In addition, these two institutions along with UC Berkeley are currently developing and validating toxicity identification evaluation (TIE) procedures for sediment toxicity tests targeting toxicity caused by pyrethroids. TIES are laboratory tests that try to identify the possible chemicals in environmental samples such as water and sediments that are causing toxicity to test organisms. TIEs can often determine a class of contaminants, such as pyrethroids, as causative agents of toxicity but often cannot distinguish the individual contaminants.

9. Conclusions

Relevant conclusions about pyrethroids are drawn based on what is currently known and on what has been identified as information needs and data gaps. Some progress has been made on understanding pyrethroid use patterns and major activities of use in the region, their modes of transport in the environment, and temporal (seasonal) periods that can influence their transport through the aquatic environment. Still, there are a variety of information needs and critical data gaps on pyrethroids that remain to be filled. Laboratory and field studies should be planned for filling data gaps and answering any new questions that might result from future investigations.

9.1. What We Do Know

9.1.1. Pyrethroid Use Patterns

Questions posed:

- *What are the major use patterns and activities that can contribute pyrethroids to the Delta watershed?*
- *Are there periods when the potential for pyrethroid exposure is greatest and are species of concern present during those periods?*

There are certain use patterns and activities, time periods, locations (spatial), and activities (causal) that when combined into a single event (or use pattern) can increase the risk for a potential impact on aquatic species due to pyrethroid off-site transport and toxicity. Several of the major pyrethroid use patterns have been described earlier. These uses of concern and their critical time periods include the following: 1) irrigation return-flows from row and orchard crops during the summer months; 2) spraying of orchards during the winter dormant season; 3) releasing agricultural tailwaters from rice fields during the late spring through early summer months; and 4) urban areas applications on hard surfaces that occur year around. Agricultural return-flows during the spring through summer months and storm water discharges during the wet season are the primary modes of pyrethroid transport off-site into surface waters, with sites nearest to release and discharge points being at a higher risk for potential toxic effects. Several studies have shown that aquatic and benthic species of concern are present during these events.

9.1.2. Field Measurements

Question posed:

- *Where are pyrethroids found?*

Several reports have shown that pyrethroids can be found in surface water samples collected from agriculturally-dominated areas at concentrations that are generally in the very low ppt range, while in sediments their concentrations are in the ppt-ppb range. There are no urban storm water data to report on for the upper San Francisco estuary and the Central Valley. Various studies have shown that pyrethroids can bind strongly to surfaces including suspended sediments so measuring pyrethroids in water samples alone, which has been done in most field studies, and by not including sediment measurements does not provide the best representation of pyrethroid distributions in aquatic systems. Field measurements need to include both water and sediment samples.

In addition, method detection limits (MDLs) for measuring pyrethroids in water samples are often much higher than the environmentally relevant low ppt concentrations that are expected in water bodies. Recently, very low MDLs for pyrethroids obtained using GC/MSMS were achieved by the California Department of Fish and Game, Water Pollution Control Laboratory (water range 0.2-0.5 ng/L; sediment range 0.2-0.5 ng/g). These methods show promise for future field studies conducted in the Delta where pyrethroid concentrations are likely to be very low.

9.1.3. Toxicity Testing

Question posed:

- *Are concentrations high enough to cause toxicity to species of concern?*

The bulk of toxicity testing for pyrethroids has been conducted on whole water samples and results have shown that water toxicity directly due to pyrethroids is rarely found mainly because agriculturally-dominated water body samples usually contain a variety of other high pesticides such as the OP insecticides (diazinon and chlorpyrifos) that could have a greater toxic effect. In addition, when toxicity had occurred over half of the time the responsible toxic agent was not identified. Additive and synergistic effects were also suggested when individual pesticide concentrations were lower than LC50s.

Toxicity testing methods need to be developed and/or improved if they are to be used routinely for monitoring pyrethroids. When toxicity measurements are focused on sediment exposure rather than water exposure, toxicity due to pyrethroids is much more likely to be observed. The concentrations of permethrin, esfenvalerate, bifenthrin and lambda-cyhalothrin in several sediment samples collected from Central Valley agriculturally-dominated water bodies have been shown to be high enough (present at low ng/g range) to cause toxicity to *H. azteca and C. tentans* (Weston et al., 2004). Because the bulk mass of pyrethroids in aquatic systems are adsorbed to sediments, toxicity testing for these insecticides should continue to focus primarily on sediment sample exposures and secondarily on whole water sample exposures. Appropriate benthic species and vulnerable larval and juvenile stages of pelagic species should continue to be used for toxicity testing.

9.2. What We Don't Know: Information and Data Gaps

9.2.1. Field Measurements

Data is lacking from field studies that coordinate pyrethroid use patterns (agricultural and urban practices) with field chemical measurements at important fish spawning and rearing areas. The few field studies that have been conducted focused primarily on measuring pyrethroids in the upper watershed and in agriculturally-dominated water bodies. It is still not known which pyrethroids, if any, are present in key fish spawning and rearing areas of the Delta.

It is still not known which pyrethroid use activities (agricultural and urban) are most important for transporting pyrethroids to key fish spawning and rearing areas. Storm water discharge studies in urban areas have been largely overlooked, which is problematic since urban area pyrethroid use amounts make up nearly half, if not more, due to the unreported amounts used for homes and gardens by consumers, of the total amounts used in the region.

9.2.2. Toxicology

Toxicity is strongly coupled with chemical field measurements, which are few for pyrethroids in the Delta's watershed. It is not known if pyrethroids are present in the Delta's critical spawning and rearing habitats at concentrations that are high enough to cause toxicity to fish species and sensitive life stages.

Toxicity studies have focused largely on EPA approved species and not resident species of the Delta and its watershed. Resident species can at times be more sensitive to some chemicals than non-resident species. There is very little pyrethroid toxicity information on critical fish and food supply species. It is not known if chronic, low doses of pyrethroids cause direct (to fish) and indirect (to food supply species) toxicity. Dose-response studies for critical resident species still need to be conducted.

Toxicity studies have been conducted primarily on water samples and there are limited toxicity measurements reported for sediment samples but both must be evaluated in order to get better representation of potential toxic effects on critical species of concern.

All species are exposed to a variety of individual chemicals and complex chemical mixtures in the Delta at any given moment. It is not clear if pyrethroids can interact with each other or with other chemicals and complex mixtures of chemicals to induce toxicity in critical fish species and sensitive life stages. Research is still needed to better understand the potential for pyrethroids to interact with each other, other chemicals (e.g., pesticides, PBO), and complex chemical mixtures (e.g., PCBs, PBDEs, and dioxins) that are found in the Delta's watershed.

9.2.3. Analytical Methods

Analytical method detection limits (MDLs) usually adopted for field studies that measure pyrethroids in water samples are often higher than the concentrations that are expected in surface waters, which explains why the bulk of reported concentrations in surface water samples are below the MDL. Thus, new chemical methods need to be developed and/or existing ones need to be improved to reach the low ppt or less concentrations that are expected in surface waters, concentrations that are still high enough to potentially cause acute toxicity to critical aquatic species.

9.2.4. Risk Assessments

There is not enough field monitoring data on the spatial and temporal occurrences of pyrethroids for making risk assessments. In this case, risk assessment measures for pyrethroids such as risk quotients (e.g., ambient concentrations divided by the lowest LC50 or NOEC values) cannot be made due to the data gaps in both water and sediment concentrations. LC50 toxicity information on critical resident species is limited.

9.3. Future Challenges

Over the last 30 years or so the emphasis of monitoring in the Delta and its watershed the Central Valley has focused largely on monitoring water and sediments for legacy chemical pollutants such as the polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, DDT and its metabolites, and toxic metals such as mercury and copper. Only recently have we begun to measure the aquatic environment for other chemical contaminants and we are finding that there are a lot more new and previously unmonitored chemicals in the aquatic environment then we would have ever believed existed and some of which can be just as threatening as the legacy organic pollutants once were. In addition, there are limited toxicological data for new chemicals on aquatic biota and a very limited understanding of their sources, transport pathways, behavior, lifetimes, and fate in aquatic systems. These factors pose a huge challenge for protecting the environmental quality of the Delta and its many species.

Pyrethroids are now one the most important and fastest growing insecticides that are applied in the Central Valley primarily for agricultural and urban use purposes. Unfortunately, there are only a limited number of studies and monitoring efforts that have focused on pyrethroid occurrence and toxicity in the region. Given these limitations one of the biggest challenges to managing pyrethroid would be to answer the last question posed at the beginning of this white paper: Is there a link between pyrethroid use and the declining pelagic organism populations in the Delta?

A brief review of pyrethroids has been provided herein and it is obvious that field data, which could have also been collected concurrently with these use activities, is sparse. To gather such data would be costly initially but there is no doubt that the future environmental and economic benefits achieved because of preventative action taken now will far outweigh the costs of future clean-up and species losses.

10. Recommendations

The following recommendations are made to the IEP. Recommendations are prioritized as either high or low priority based on the following criteria: High priority – there is an urgent need and it can be implemented within 0-1 year with available resources; and Low priority – there is no urgency and this can be implemented within 2 or more years. The recommendations are not ranked within each priority set.

10.1. High Priority

1. Existing surface water monitoring programs should include pyrethroids in their chemical and toxicity measurements. Water and sediment samples should both be analyzed for pyrethroid concentrations and toxicity using methods that have biologically relevant MDLs.
2. Dose-response information (LC50) should be developed for ecologically relevant species and standard U.S. EPA sediment toxicity testing species.
3. Toxicity identification evaluation (TIE) procedures should be developed and validated for sediment toxicity tests targeting toxicity caused by pyrethroids (IEP current project).
4. Best management practices (BMPs) and sustainable farming practices, should be developed and implemented for agricultural areas to prevent pyrethroids from entering the aquatic environment and to mitigate unreasonable risks of exposure (IEP current project).
5. Best management practices (BMPs) should be developed and implemented for urban areas to prevent pyrethroids from entering into storm drains and urban water bodies and to mitigate unreasonable risks of exposure.
6. Simple fate and transport models and watershed models should be used to show how much pesticide can run off from both agricultural and urban use areas to assess the potential for water quality impacts (IEP current project).

10.2. Low Priority

1. Chemical analytical methods for pyrethroids should be developed to attain method detection limits (MDLs) in the low ppt range for water samples and in the low ppb range for sediment samples. These are the environmentally relevant concentration ranges for which pyrethroids are expected to be found in aquatic samples.
2. Biological effects indicators of critical species should be developed. This includes relating biological effects at subcellular levels to effects at individual and population levels and extrapolating effects from one animal species to another and then possibly to humans.

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Appendix 1

Chemical: Fipronil

Reason for Concern: The use of fipronil in the Sacramento and San Joaquin Valleys has been steadily increasing over the past 3 years. Fipronil and its major degradates are highly toxic to aquatic organisms especially invertebrates and some fish species at low ppb levels. Studies have linked fipronil exposure to decreased reproductive success particularly linked to sex-specific male reproductive dysfunction in a southeastern estuarine copepod (Chandler et al., 2003; Cary et al., 2004).

Use: Fipronil is a highly effective broad spectrum insecticide used in rice production as an alternative to carbofuran to control rice water weevils, and on pets to control fleas and ticks. Fipronil is also effective on locusts, termites, fire ants, roaches and mites, against insects in both larval and adult stages, as well as insects resistant to pyrethroid, organophosphate and carbamate insecticides. In California, fipronil is used primarily for structural pest controls and can be applied year round for non-agricultural applications. For rice, fipronil is applied primarily during the growing season from June to October. In the Sacramento and San Joaquin Valley watersheds combined, fipronil use has increased from less than 100 pounds annually in 1999 to over 5000 pounds in 2003.

Chemical and Physical Properties: Fipronil is moderately soluble in water (22 mg/L) and has a high affinity for organic carbon rich soils and sediments, as well as biota (log K_{ow} = 4.01). It is also relatively persistent in soils with an aerobic half-life of 630-693 days and an anaerobic soil half-life of 123 days. Fipronil has the tendency to form four degradates in water and soil, including a sulfide, which is the product of reduction in soil; an amide, the product of hydrolysis in water or soil; a sulfone from oxidation in soil; and a photolysis product (desulfinyl). The average log K_{oc} for fipronil is 2.9, while the log K_{oc} for the degradates are 3.4 for the sulfide, 2.2 for the amide, 3.6 for the sulfone, and 3.1 for the desulfinyl. Due to its moderate hydrophobicity and its potential to bind to soils and sediments; fipronil residues tend to stay in the upper 15 cm of the soil and exhibit low potential to leach into groundwater. Also in aquatic environments; fipronil residues move rapidly from the water to the sediment with over 95% found on the sediments within one week of application. The aqueous photo-degradation half-life of fipronil was determined to be about 4 h at pH 5.5 indicating that photolysis is more important than hydrolysis for degradation of aqueous fipronil in the environment (Connelly, 2001). Furthermore, the photolysis product has the potential to bioaccumulate in fatty tissues increasing the impact on aquatic organisms.

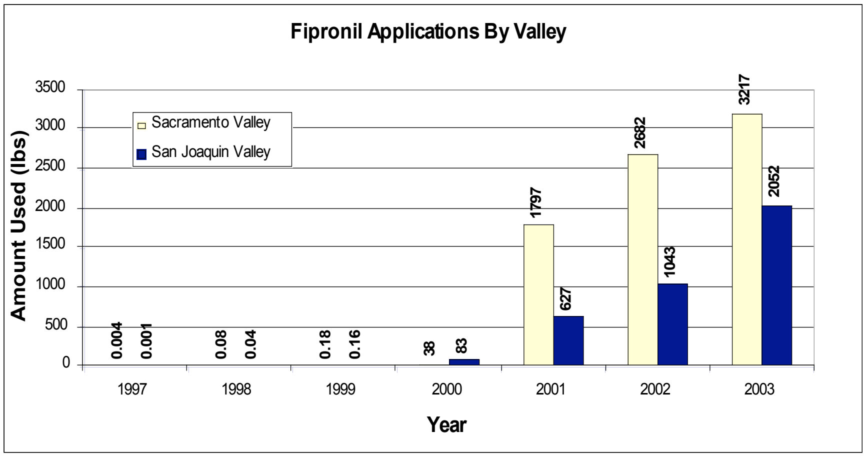
Aquatic Toxicity: Fipronil is an extremely reactive molecule and is a potent disruptor of the central nervous center via the GABA regulated chloride channel in insects. The toxicity of fipronil to fish varies by species. It is considered to be highly toxic to rainbow trout and very highly toxic to bluegill sunfish with an LC50 of 246 ug/L and 86 ug/L, respectively. In early life-stage studies on rainbow trout, fipronil affected larval growth with a NOEC of 6.6 ug/L and a LOEC of 15 ug/L. The sulfone metabolite is 6.3 times more toxic to rainbow trout and 3.3 times more toxic than the parent compound to bluegill sunfish. Fipronil demonstrates high toxicity to freshwater aquatic invertebrates with an LC50 of 100 ug/L for *Daphnia magna*. In acute daphnia life cycle studies, fipronil affected growth; daphnid length decreased significantly at concentrations less than 9.8 ug/L. Fipronil is considered to be highly toxic to adult grass shrimp (LC50 = 0.32 ug/L) and the estuarine copepod (*Amphiascus tenuiremis*) (LC50 = 6.8 ug/L). Laboratory studies with the estuarine copepod reported that fipronil decreased reproduction by 94% at concentrations as low as 0.42 ug/L (Chandler et al., 2003). The degradates exhibit similar lethality to that of the parent within a single species, however, lethality may vary widely between species. The sulfone metabolite is 6.6 times more toxic and the desulfinyl photo-degradate is 1.9 times more toxic than the parent compound on an acute basis to freshwater invertebrates.

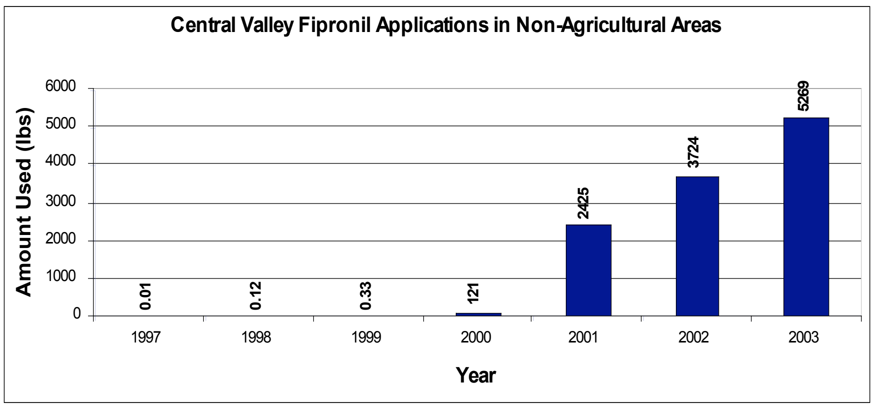
Water Quality Criteria: No water quality criteria exist for this compound

Water Quality Data: Since 2002 fipronil along with the sulfone and sulfide degradates, have been detected at low ppb levels in urban creeks in both the Sacramento and San Joaquin River watersheds (USGS, 2005).

Conclusion: The urban use of fipronil is increasing. Fipronil and its degradates are persistent and may have the potential to bioaccumulate. Larval and adult toxicity of both fipronil and degradates are high, especially to invertebrates. Fipronil may decrease reproductive success in some organisms. Therefore, aquatic organisms could be at risk.

Relevant Citations: Cary et al. (2004); Chandler et al. (2003); Connelly (2001); CA Department of Pesticide Regulation (http://www.cdpr.ca.gov); Madsen et al. (2003); U.S. Geological Survey Water Quality Data 2005 (http://waterdata.usgs.gov/nwis); PAN Pesticide Database (http://preview.pesticideinfo.org/Index.html)


Fipronil Applications By Valley
Sacramento Valley
San Joaquin Valley
Amount Used (lbs)
3500
3000
2500
2000
1500
1000
500
0
0.004
0.001
0.08
0.04
0.18
0.16
38
83
1797
627
2682
1043
3217
2052
1997
1998
1999
2000
2001
2002
2003
Year


Central Valley Fipronil Applications in Non-Agricultural Areas
Amount Used (lbs)
6000
5000
4000
3000
2000
1000
0
0.01
0.12
0.33
121
2425
3724
5269
1997
1998
1999
2000
2001
2002
2003
Year

Chemical: 4-Nonylphenol (NP)

Reason for Concern: Several studies have shown that NP is bioaccumulated, estrogenic, and highly toxic to fish and other aquatic species.

Use: NP is an environmental degradation product of alkylphenol ethoxylates (APEs), which are surfactants that are widely used in terrestrial and aquatic herbicide applications. In 2002, the mass of APES used in the Central Valley exceeded 200,000 pounds.

Chemical and Physical Properties: NP is a technical grade mixture of monoalkyl phenols that are predominantly *para* substituted; Log K_{ow}=5.8; NP is practically insoluble in water.

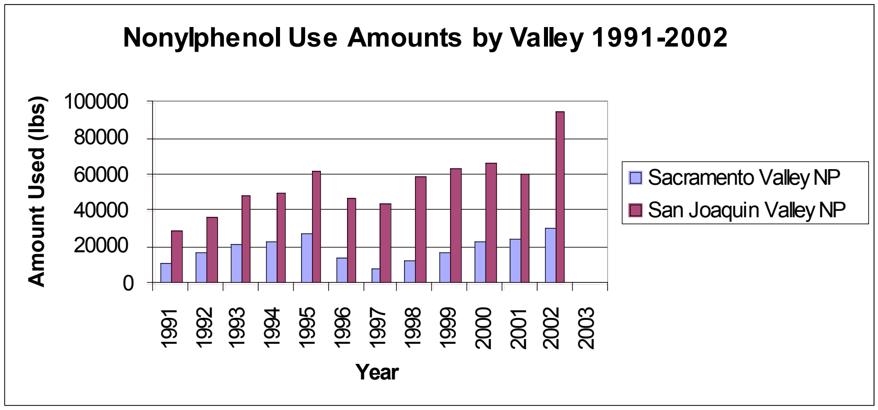
Aquatic Toxicity: Lussier *et al*. (2000) measured the acute toxicity of NP to early life stages of several saltwater invertebrates and fish and reported 96 h LC50 thresholds as the following- Invertebrates: mysid shrimp *Americamysis bahia* (60.6 µg/L), stone crab *Dyspanopeus sayi* (>195 µg/L), American lobster *Homarus americanus* (71 µg/L), amphipod *Leptocheirus plumulosus* (61.6 µg/L), coot clam *Mulinia lateralis* (37.9 µg/L, 48 h LC50), grass shrimp *Paleomonetes vulgaris* (5904 µg/L); Fish: winter flounder *Pleuronectes americanus* (17 µg/L), sheepshead minnow *Cyprinodon variegatus* (142 µg/L), and inland silverside *Menidia beryllina* (70 µg/L). Abnormal gonad development was detected when medaka were exposed to 100 µg/L of NP, while abnormal anal fin (female-like) development was observed in males exposed to the same concentration (Tabata *et al*., 2001). Leblanc *et al*. (1999) conducted developmental toxicity tests on daphnids and showed that NP interfered with the metabolic elimination of testosterone.

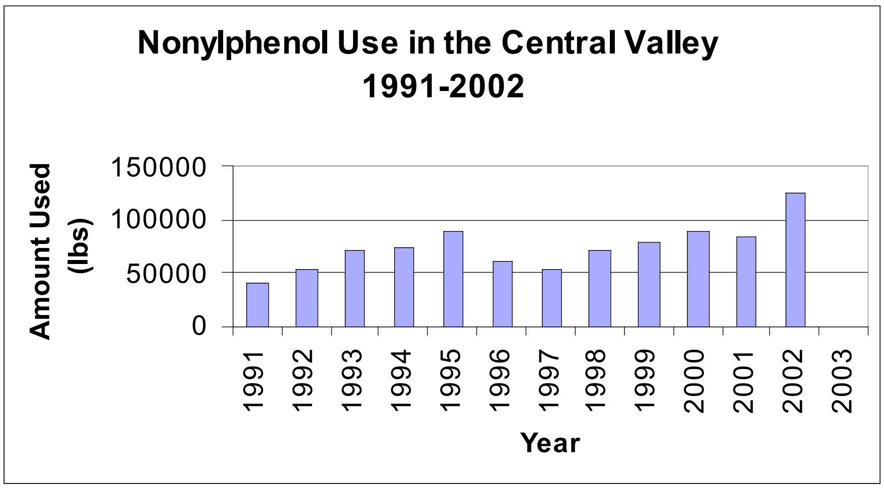
Water Quality Criteria: The U.S. EPA adopted 12.4 µg/L as the national water quality guideline for NP in saltwater (U.S. EPA, 1996).

Water Quality Data: In 2003, the San Francisco Estuary RMP reported NP in water samples from the upper estuary that ranged from 13-37 ng/L (Suisun Bay at 14-37 ng/L; mouths of Sacramento and San Joaquin River each with concentrations at 13 ng/L), while NP in bivalves ranged from 1-22 ng/g dry wt. NP concentrations were well below the USEPA water quality criteria and well below the LC50 for aquatic species listed above. However, NP concentrations are expected to be higher in areas of the Delta and Sacramento and San Joaquin Rivers that receive treatment plant effluents and agricultural runoff.

Conclusion: NP is an endocrine system disruptor and early life stages of aquatic species could be at risk. NPs bioaccumulate potential further increases concern over its occurrence in the aquatic environment.

Relevant Citations: Leblanc *et al*. (1999); Lussier *et al*. (2000); Tabata *et al*. (2001); U.S. EPA (1993)


Nonylphenol Use Amounts by Valley 1991-2002
Amount Used (lbs)
100000
80000
60000
40000
20000
0
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year
Sacramento Valley NP
San Joaquin Valley NP


Nonylphenol Use in the Central Valley 1991-2002
Amount Used (lbs)
150000
100000
50000
0
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

Chemical: Polybrominated Diphenyl Ethers (PBDEs)

Reason for Concern: High volume use has resulted in contamination in water, sediments and aquatic biota. There is high potential for bioaccumulation, biomagnification, and endocrine system disruption. In San Francisco Bay harbor seals PBDE concentrations have doubled every 1.8 years (She et al., 2002). PBDEs can act as agonists of estrogen receptors and exhibit dioxin-like Ah-receptor-mediated induction of cytochrome P450 drug metabolizing and carcinogen activating enzymes (Meerts et al., 2001).

Use: Primarily used as flame retardants in plastics, electronic devices, polyurethane foams, and building materials. Commercial formulations include Penta-BDE, Octa-BDE, and Deca-BDE mixtures. PBDE use has increased over the years and global annual sales are now ~70,000 tons (Hites, 2004).

Chemical and Physical Properties: Similar properties as PCBs with 209 individual compounds (congeners); Penta-BDE water solubility is 0.9 ng/L; Penta-BDE Log K_{ow}=6.5-7.0; Deca-BDE Log K_{ow}=10; PBDEs tend to adsorb to particulate matter and are not readily biodegradable.

Aquatic Toxicity: There are very few studies on PBDEs in lower trophic level aquatic species: total PBDE concentration in mysid shrimp (*Neomysis integer*) ranged from 2095-3562 ng/g lipid (Verslycke et al., 2005). Two studies reported that tetra- and penta-PBDE congeners accumulated rapidly in oligochaetes (*Lumbriculus variegates*) that were exposed to spiked sediments (Leppänen and Kukkonen, 2004; Ciparis and Hale, 2005). Copepods (*Nitocra spinipes*) that were exposed to PBDEs over their full-life cycle (≤26 days) showed reduced larval development and growth rates, which were due to ingestion of particle absorbed PBDEs (Breitholtz and Wollenberger, 2003). The lowest-effect concentration (LOEC) for inhibition of larval development (0.013 mg/L) in copepods exposed to BDE-47 was 338 times below the corresponding 96 h LC50 value of 4.4 mg/L.

Water Quality Criteria: There are no water quality criteria.

Water Quality Data: Separate studies conducted in the San Francisco Bay have identified PBDEs in harbor seals (She et al., 2002), fish (Holden et al., 2003), water, sediments, and bivalves (Oros et al., 2005), and in wastewater treatment plant effluents (North, 2004).

Conclusion: PBDEs are endocrine system disruptors, highly bioaccumulative, and persistent. They biomagnify through the food web. Aquatic species could be at risk.

Relevant Citations: Breitholtz and Wollenberger (2003); Ciparis and Hale (2005); Hites (2004); Holden et al. (2003); Leppänen and Kukkonen (2004); Meerts et al. (2001); North (2004); Oros et al. (2005); She et al. (2002).

Appendix 2

Table 1. Pesticide and related watershed efforts in the Central Valley.

Project Title	Liaison Contact	PI Contact	Project Description
Pyrethroid Insecticides: Analysis, Occurrence, and Fate in the Sacramento and San Joaquin Rivers and Delta ERP-02-P42	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684	Michelle Hladik, USGS mhladik@usgs.gov (916) 278-3183	The purpose of this project is to develop routine, multi-residue methods for analysis of pyrethroid insecticides in water, colloids, sediments and biota. Goals are to develop, test and validate methods for analysis of six or more pyrethroid insecticides in these mediums. This is a joint venture between three labs: USGS Organic Chemistry Lab in Sacramento, CA, CDFG Water Pollution Control Lab in Rancho Cordova, CA, and the CDFA lab in Sacramento, CA.
Assessment of Pesticide Effects on Fish and their Food Resources in the Sacramento-San Joaquin Delta ERP-99-N08	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684	Don Weston, UC Berkeley dweston@uclink4.berkeley.edu Inge Werner, UC Davis iwerner@ucdavis.edu	Integrated laboratory and field study: initial data review to identify pesticides of concern and field sites; develop toxicity tests with resident species focusing on chinook salmon and their prey, and chronic endpoints and target enzyme inhibition; evaluate the influence of local conditions on pesticide, assess toxicity under realistic conditions in which multiple pesticide pulses vary in magnitude, frequency, and duration
Contaminant Effects on Smelt ERP-97-C06	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684	Bill Bennett, UC Davis wabennett@ucdavis.edu 707-875-1979	This project will evaluate the effects of contaminant exposure on delta smelt populations. Tasks include conducting analyses to evaluate relationships between tissue and genetic condition and growth rate, and coordinating field sampling for additional specimens. Geographic areas of study correspond to range of smelt: lower Sacramento & San Joaquin Rivers, Delta, Suisun Bay & Marsh, San Pablo Bay, and Napa River.
Delta Toxicity Monitoring Project, Effects on Anadromous and Estuarine Species ERP-97-N09	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684		Phase I monitoring study primarily on river and back slough sites in the Delta which tested toxic in early Bay Protection and Toxic Cleanup Program projects
Chronic Toxicity of Environmental Contaminants in Sacramento Splittail - A Biomarker Approach ERP-99-N07	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684	Silas Hung, UC Davis SSHung@UCDavis.Edu 530-752-3580	This project will demonstrate the use of biomarkers, in conjunction with ongoing biomonitoring efforts of fish population by DFG and water, sediment, and tissue contaminant monitoring by SFEI and USGS, to evaluate the chronic effects of contaminants on the health of splittail under laboratory and field conditions
Rainbow Trout Toxicity Monitoring: An Evaluation of the Role of Contaminants on Anadromous Salmonids ERP-01-N22	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684		The aim of this project is to determine the toxicity of Sacramento River Basin water bodies to rainbow trout embryos, as an indicator of contaminant effects on Central Valley salmonids.
Transport, Transformation & Effects of Se and C in the Delta: Implications for Ecosystem Restoration ERP-01-C07	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684		The aim of this project is to use newly developed approaches to determine, under a variety of conditions, how the Delta system transports and distributes conservative materials

Table 1. (Continued) Pesticide and related watershed efforts in the Central Valley.

Project Title	Liaison Contact	PI Contact	Project Description
Water Quality Criteria and Toxicity Identification Profiles for Current-Use Pesticides in the Bay-Delta Watershed ERP-01D-C20	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684		This project will provide two key components for evaluating ecological effects from pesticides and their eventual reduction in impacts through identification of the problem and regulatory actions. This project will develop water quality objectives for up to five new priority pesticides.
Assessment and Implementation of Urban Use Reduction of Diazion and Chlorpyrifos (Sacramento County) ERP-97-N01	Mary Menconi, CABDA, marym@calwater.ca.gov 916-445-5684		Identify, evaluate and control the toxicity runoff caused by elevated levels of diazinon and chlorpyrifos within Sacramento County. Tasks include water quality monitoring to determine baseline conditions, developing outreach/education program for residential and other urban users and performing analyses of the fate, transport and risk assessment for the chemicals.
Develop a Sacramento River Watershed Hydrologic Model	Debra Denton, USEPA, Denton.debra@epa.gov 916-341-5520	Steve Carter, Tetra Tech steve.carter@tetratech-ffx.com 619-525-7015	Model is under development to provide a tool for prediction of river flows under a range of hydrologic conditions. This report includes documentation of the model development process, data used, key assumptions, and results of model calibration. Draft report is January 2005. Final is under development.
List of Pesticides of Concern	Joe Karkorski, RB5, jkarkoski@waterboards.ca.gov 916-464-4668	Regional Board Staff	The regional water board is developing a list of priority pesticides based on relative risks of pesticides used in the Sacramento River Watershed. Work in progress.
Sacramento River Toxic Pollutant Control Program (SRTPCP)	Debra Denton, USEPA, Denton.debra@epa.gov 916-341-5520	Marty Williams, Waterborne Inc williamsm@waterborne-env.com 703-777-0005, ext 21	Exposure Assessment Model for Diazinon Sources in the Sacramento River Basin's Main Drainage Canal Final Report available http://www.sacriver.org/
SRTPCP	Debra Denton, USEPA, Denton.debra@epa.gov 916-341-5520	Marty Williams, Waterborne Inc williamsm@waterborne-env.com 703-777-0005, ext 21	The aim of this project is to identify and quantify major sources of pesticide loadings that contribute to runoff or drift mechanisms in the watershed. Quantify loadings in terms of spatial and temporal probability of occurrence. This work builds upon the diazinon source work. Work in progress and to be completed by December 2006.
SRTPCP	Debra Denton, USEPA, Denton.debra@epa.gov 916-341-5520	Don Weston, UC Berkeley dweston@uclink4.berkeley.edu 510-231-5626	The aim of study is to provide data on the persistence of pyrethroid pesticides in farm soils after application in SRWP. This project is a part of another PRISM project. The work is to be completed by October 2005.
SRTPCP	Karen Larsen, RB5, klarsen@waterboards.ca.gov 916-464-4646	TBD	This is a Request for Proposals for a project to investigate sediment toxicity in the Sacramento River watershed. The work is to be completed by December, 2006.
CALFED	Karen Larsen, RB5, klarsen@waterboards.ca.gov 916-464-4646	TBD	The Regional Board is funded through a CALFED grant to develop toxicity identification evaluation (TIE) profiles for high priority pesticides (identified by the pesticide TMDL unit – see Karkoski project). The work is to be completed by Spring, 2006.

Table 1. (Continued) Pesticide and related watershed efforts in the Central Valley.

CALFED Proposal, under review	Debra Denton, USEPA, Denton.debra@epa.gov 916-341-5520	Multidisciplinary Team	Development and application of a numerical simulation model to evaluate and mitigate the transport of pesticides from the Sacramento River watershed into the Bay Delta area.
PRISM BMPs: Vegetated agricultural drainage ditches	Debra Denton, USEPA, Denton.debra@epa.gov 916-341-5520	Paul Robbins, robins@yolorcd.org 530-662-2037 ext 116	Benefits of vegetated agricultural drainage ditches (VADD) as a best management practice in Yolo County to minimize runoff of OP and pyrethroid pesticides. Work in progress.
PRISM BMP work	Amanda Smith, asmith@waterboards.ca.gov 916-464-4716	Parry Klassen, CURES parryk@attbi.com 559-325-9855	Sacramento Valley Regional Pesticide BMP Implementation Program. Work in progress.
PRISM BMP work	Phil Crader, pcrader@waterboards.ca.gov 916-464-4604	?	Western San Joaquin Valley Pesticide BMP Implementation Program. Work in progress.
PRISM	Diane Beaulaurier, Dbeaulaurier@waterboards.ca.gov 916-464-4637	Parry Klassen, CURES parryk@attbi.com 559-325-9855	Methods to measure and optimize spray deposition in orchards. Work in progress.
PRISM	Robert Holmes, Rholmes@waterboards.ca.gov 916-464-4649	Kathy Russick, SWRP krussick@comcast.net 916-201-2703	Distribution and toxicity of sediment associated pesticides in the Sacramento River Watershed. Work in progress.
PRISM UP3 Project	Bill Johnson, RB2, wjohnson@waterboards.ca.gov 510-622-2354	Kelly Moran, TDC Environmental 650-627-8690 kmoran@tdcenvironmental.com	To provide review and analysis of urban pesticide use in the SF Bay Area. Work in progress. http://www.up3project.org/norcal_ipm_documents.shtml
PRISM	Bill Johnson, RB2, wjohnson@waterboards.ca.gov 510-622-2354	Daniel Oros, SFEI, daniel@sfei.org 510-746-7383	The aim of this project is to develop new chemical analytical methods for pyrethroids and carbamates using GC/HRMS and LC/MSMS instrumentation.
PRISM	Bill Johnson, RB2 wjohnson@waterboards.ca.gov 510-622-2354	Sarah Lowe, SFEI, sarah@sfei.org 510-746-7384	Investigation of sources and effects of pyrethroid pesticides in watersheds of the San Francisco Estuary.
DPR Pyrethroids Monitoring	Keith Starner, kstarner@cdpr.ca.gov	Same	Pyrethroid Contamination of Surface Waters and Bed Sediments in High Pyrethroid-Use Regions of California http://www.cdpr.ca.gov/docs/empm/pubs/protocol/study229protocol.pdf
DPR Cover Crop and Infiltration Rate	Sheryl Gill, sgill@cdpr.ca.gov	Same	Determine the Effect of Cover Crop and Filter Strip Vegetation on Reducing Pesticide Runoff to Surface Water. Phase I: Pilot Study and Method Development http://www.cdpr.ca.gov/docs/empm/pubs/protocol/prot223.pdf
DPR Bioassessment and Pesticides Runoff	Nina Bacey, nbacey@cdpr.ca.gov	Same	Bioassessment to Identify Impacts on the benthic macroinvertebrate community due to surface runoff of pesticides; http://www.cdpr.ca.gov/docs/empm/pubs/protocol/225protocol1.pdf

Table 1. (Continued) Pesticide and related watershed efforts in the Central Valley.

Project Title	Liaison Contact	PI Contact	Project Description
Endocrine Disruption in Sacramento Splittail	Tom Maurer, USFWS, 916-414-6594 thomas_maurer@fws.gov	Cathy Johnson, USFWS, cathy_s_johnson@fws.gov 916-414-6596	Assessing endocrine disruption biomarkers (vitellogenin, sex steroids) in conjunction with passive organic chemical sampling devices (SPMDs and POCIS). Concentrating on Sacramento splittail but have also sampled striped bass and carp. Sites in Suisun Marsh and west Delta. Project ongoing as of August, 2005.
Impacts of Mosquito Adulticides on Wetlands	Tom Maurer, USFWS, 916-414-6594 thomas_maurer@fws.gov	Cathy Johnson, USFWS, cathy_s_johnson@fws.gov 916-414-6596	Monitoring water, sediment, and invertebrates in wetlands before, during, and after repeated ground fog applications of mosquito adulticides adjacent to managed wetlands in Sacramento Valley. Pyrethrins with PBO have been used. Project ongoing as of August, 2005.
Fate of Pesticides in Vernal Pools of the Central Valley, CA.	Tom Maurer, USFWS, 916-414-6594 thomas_maurer@fws.gov	Cathy Johnson, USFWS, cathy_s_johnson@fws.gov 916-414-6596	Monitored pesticide concentrations in vernal pools through the wet season. Additional dry deposition sampling. Two years of field sampling completed. Data analysis and internal report being prepared as of August 2005.

Table 2. Agency contacts for pesticide and related watershed efforts in the Central Valley

Contact Person	Topic
Anthony Choi achoi@placerdata.com 510-540-9809	Pesticide Action Network – PUR web page and toxicity
David Crane, CDFG dcrane@ospr.dfg.ca.gov 916-358-2859	Pyrethroid analysis in water, sediment and vegetation; CalFed Grant working with USGS and DPR to achieve lower detection limits
Bill Croyle bcroyle@waterboards.ca.gov 916-464-4611	Regional board agriculture waiver program includes chemical and toxicity testing in the Sacramento and San Joaquin watersheds
Debra Denton, USEPA denton.debra@epa.gov 916-341-5520	Involved with TIE development efforts, pesticide BMP projects, and coordination of USEPA CPP
Kean S. Goh, CDPR kgoh@cdpr.ca.gov 916-324-4072	Monitoring of pesticides in the environment, assessment of effectiveness of runoff mitigation measures, assessment of adverse impacts of pesticide to aquatic systems, regulation of pesticide uses, bioassessment, fate and transport modeling, and analytical methods development
Les Grober lgrober@waterboards.ca.gov 916-341-4851	San Joaquin Valley TMLDs
Michelle Hladik, USGS mhladik@usgs.gov 916-278-3183	Analytical pyrethroid analysis in water, colloids and sediment (suspended and bed); CalFed Grant to work with DPR to achieve lower detection levels; USGS funded to develop methods for pyrethroids used for West Nile virus nationwide
Robert Holmes, Rholmes@waterboards.ca.gov 916-464-4649	CVRWQCB
Cathy Johnson, USFWS cathy_s_johnson@fws.gov 916-414-6596	Pesticide impacts to federally listed species, effects of mosquito adulticides on aquatic habitats, transport of pesticides to vernal pools, endocrine disruption in Sacramento splittail, pesticide analytical techniques.
Joe Karkorski, RB5 jkarkoski@waterboards.ca.gov 916-464-4668	Sacramento Valley TMDLs
Karen Larsen, RB5 klarsen@waterboards.ca.gov 916-464-4646	Sacramento Valley watershed unit involved in TIE development, ambient toxicity testing, and bioassessment evaluations, among other topics.
Jacob McQuirk, DWR jacobmc@water.ca.gov 916-653-9883	
Mary Menconi, CABDA marym@calwater.ca.gov 916-445-5684	Agricultural water quality, pesticides