Best Management Practices in Stone Fruit Project

Final Project Report
by
Nicole David
San Francisco Estuary Institute





SAN FRANCISCO ESTUARY INSTITUTE

7770 Pardee Lane, Second floor, Oakland, CA 94621 p: 510-746-7334 (SFEI), f: 510-746-7300, www.sfei.org

This report should be cited as:
David, N. 2009. Best Management Practices in Stone Fruit Project. Final Project Report. San Francisco Estuary Institute, Oakland, CA. SFEI Contribution Number 590.

TABLE OF CONTENTS

1. Abstract	4
2. Introduction	4
2.1. Recent Patterns and Trends in OP and Pyrethroid Pesticide Application	tions in
California	5
2.2 Best Management Practices Used in this Project	7
3. Methods	
3.1 Study Area and Sampling Locations	8
3.2 Sediment and Bioassessment Sampling	11
3.3 Water Sample Collection	
3.4 Analytical Methods	
3.4.1 Bioassessment Analysis	
3.4.2 Pesticides Analysis	
3.4.3 Nutrients Analysis	
4. Results and Discussion	
4.1 Bioassessment	
4.2 Pesticides	19
4.2.1 Pesticides in Water and Sediment	19
4.2.2 Pesticide Loads	24
4.3 Risk Quotients (RQ)	26
4.4 Nutrients	
4.4.1 Nutrients in Water	29
4.4.1 Nutrient Loads	32
4.5 Ancillary Measurements	34
5. Conclusion	
5.1 Recommendations	
6. Acknowledgments	
7. References	

1. Abstract

Contamination from pesticide application to orchard crops is a major water quality issue in California. This study was initiated to evaluate water and sediment quality in runoff from peach, prune, and walnut orchards before and after the implementation of Best Management Practices (BMPs). The information provided by this study will be useful in developing policy and related management practices to reduce pesticide and nutrient concentrations in water discharging into streams and rivers included on the 303(d) List of impaired water bodies. This project also included outreach, education, and technical support for growers to test alternatives to synthetic pesticides and inorganic fertilizers. BMPs implemented by participating growers included low-risk pesticides, improved pest control timing, cover crops, and monitoring of insects and insect fertility. Average pesticide concentrations in water and estimated loads for chlorpyrifos, diazinon, and phosmet were not statistically significantly different after the implementation of BMPs due to sample size limitations. However, there was a trend toward lower pesticide concentrations and loads in the second year of this study. Nutrient results did not vary appreciably before and after BMP implementation. Interannual variability probably accounts for part of the observed changes, and results from this short-term study may not reflect the effectiveness of BMPs accurately. A longer study with a larger sampling effort would be necessary to fully evaluate the efficacy of these BMPs. The trend toward lower water quality contaminant concentrations after BMP implementation suggests that a longer study is warranted.

2. Introduction

Intensive use of organophosphate (OP) pesticides, pyrethroids, herbicides, and fungicides in orchards and other agricultural fields appears to be a consistent source of pesticide contamination to water bodies in the Central Valley. This Project targeted several pesticides, including the OP pesticide chlorpyrifos, which is particularly harmful to aquatic organisms. According to U.S. EPA (2002), a single application of chlorpyrifos poses risks to small mammals, birds, fish, and aquatic invertebrate species for nearly all registered outdoor uses. According to the California Department of Pesticide Regulation's Annual Pesticide Use Report (2007), the OP pesticides phosmet, diazinon, and chlorpyrifos had the highest statewide use out of all monitored pesticides in the present study, with a total of over 97,000 pounds of active ingredient applied (Table 1a). In addition, monitoring by the US Geological Survey, Department of Pesticide Regulation, and others has confirmed widespread occurrence of diazinon, chlorpyrifos and other OP pesticides in the Sacramento and Feather Rivers and their tributaries (Lydy and Austin 2004). Thus, reducing use and runoff of these pollutants would help to improve the health of watersheds throughout the Central Valley.

The Best Management Practices (BMPs) in Stone Fruit Project is a multi-faceted effort that promotes agricultural practices to reduce the risk of water pollution from orchard crop production. In this Project, the Community Alliance of Family Farmers (CAFF) trained growers to apply BMPs for pollution prevention and to introduce them to various techniques intended to decrease contaminants in drainage water. The overall goal was to reduce pesticide and nutrient concentrations in Sutter and Butte county water bodies

included on the 303(d) List of impaired water bodies. Peaches and prunes comprise the majority of the stone fruit grown in Sutter and Butte counties.

The objectives of this Project were:

- 1) Outreach to and training of growers to introduce various BMPs intended to decrease contaminants in drainage water
- 2) Evaluate water and sediment quality in runoff from peach, prune, and walnut orchards before and after the implementation of BMPs
- 3) Evaluate potential pesticide and nutrient load reductions to water bodies receiving orchard drainage water.

As part of this Project, demonstration sites were set up on 13 different farms in order to reach out to hundreds of local growers (a total of 550 were on the mailing list) who had not adopted any measures to reduce pollutant runoff from their orchards, and to demonstrate how to implement BMPs in their orchards effectively. Surveys were conducted with participating growers to obtain information on crops, acreage planted, and BMPs implemented to document the success of the demonstration sites. An additional goal within this outreach component was to strengthen linkages between growers and their pollution prevention resources, with a special emphasis on the East Indian community. Yuba City is one of the centers of Punjabi-American culture in the United States and a large number of Punjabi-Americans are residing and farming in this region. To reach this community, CAFF conducted outreach targeted to Punjabi-American farmers through local media, including radio, television, newsletter, and fact sheets.

Water quality monitoring for this Project was conducted by the San Francisco Estuary Institute to evaluate differences in pesticide and nutrient concentrations in water and sediment in ditches that drain orchards in the study area and discharge to the Lower Feather River and the Sacramento River. Chemical concentrations and flow were measured to estimate and evaluate pesticide and nutrient load changes over the course of two years.

2.1. Recent Patterns and Trends in OP and Pyrethroid Pesticide Applications in California

While many factors, including weather and crop variation, determine the amount of pesticides used, it appears that the total use in the Central Valley has dropped from 129 million pounds in 1993 to 114 million pounds in 2003. However, the amount of active ingredient applied is an incomplete measure of pesticide use impacts. Different pesticides vary, not only in the amount needed to target pests, but also in the extent to which their application causes environmental and health impacts.

Statewide, peach and prune acres treated with pesticides monitored in this study and pounds of active ingredients applied were low in 2007 (Table 1a). The insecticide use decreased by about 9% in 2007 compared to previous years due to relatively light pest pressure. The major synthetic and natural insecticides used in stone fruit were: esfenvalerate, phosmet, diazinon, chlorpyrifos, horticultural oils, oriental fruit moth

(OFM) mating disruption pheromones (E–8–dodecenyl acetate, Z–8–dodecenyl acetate, and Z–8–dodecenol), and spinosad. Sutter and Butte county applications constituted the majority by mass of statewide applications for diazinon and phosmet (Tables 1a and 1b). However, application rates of chlorpyrifos, diazinon, phosmet, parathion, methidathion, and esfenvalerate were generally lower for Sutter and Butte counties in 2007 than in many prior years (Table 2).

Table 1a. Statewide use of pesticides monitored in this study in peaches and prunes in 2007 (DPR 2007).

	lbs applied	applications	acres treated
Azinphos-methyl	64	2	32
Chlorpyrifos	20,869	682	11,846
Cyfluthrin	2	4	47
Diazinon	30,153	543	16,960
Esfenvalerate	5,238	3,941	95,871
Lambda-Cyhalothrin	462	684	16,227
Malathion	33	3	9
Methidathion	4,730	83	3,521
Permethrin	1,310	230	5,215
Phosmet	46,522	1,383	18,628
Propargite	814	33	216

Table 1b. Pesticide use in Sutter and Butte counties in peaches and prunes in 2007 (DPR 2007).

	lbs applied	applications	acres treated
Diazinon	16,000	198	8,200
Chlorpyrifos	322	3	190
Phosmet	36,647	72	3,067
Esfenvalerate	2,037	1,095	34,144

The overall use of OP pesticides on tree crops in California has been steadily decreasing over the past decade but they are being replaced by the more toxic pyrethroids, especially esfenvalerate and permethrin (Epstein et al. 2000) (Table 2). While pyrethroid pesticides have the potential to be acutely toxic to many aquatic organisms and especially fish, their chemical properties cause them to bind strongly to sediment particles. Therefore, the bioavailability of pyrethroids in water may be reduced. However, data on chronic effects to aquatic organisms are limited and acute and chronic impacts on sediment-dwelling organisms and bottom feeders have been reported (Muir et al. 1985, Amweg et al. 2005).

Table 2. Reported applications (pounds) of organophosphate and pyrethroid pesticides in California (DPR 2007).

AI	1997	1998	1999	2000	2001
Chlorpyrifos	3,212,165	2,451,980	2,259,221	2,094,179	1,673,097
Diazinon	956,267	901,388	983,628	1,058,311	999,578
Phosmet	568,933	645,380	638,704	580,522	482,481
Esfenvalerate					

Table 2, continued

AI	2002	2003	2004	2005	2006	2007
Chlorpyrifos	1,419,665	1,545,670	1,778,342	2,006,062	1,922,547	1,430,034
Diazinon	690,375	523,957	492,148	398,620	385,923	350,640
Phosmet	405,236	341,541	658,087	547,813	628,892	421,109
Esfenvalerate		26,709	32,367	34,763	24,222	14,246

2.2 Best Management Practices Used in this Project.

To minimize the environmental impacts of pesticide use, applicators have to consider weather and wind conditions, adjustment of the spray nozzles and droplet size for spray, and pest monitoring results. Careful management of pesticide applications reduces the amount of chemicals applied per season and lowers costs for the grower. Implementing these management practices with participating growers and CAFF's efforts to optimize spraying helped to reduce chemical concentrations in the drainage water. Spraying optimization methods included adjustment of sprayers and spray nozzles to targeted tree height and distance.

Another BMP that has been successfully employed to reduce pesticide application and discharge are cover crops. The benefits from growing cover crops include

- improving soil quality by adding organic matter and nitrogen
- protecting the soil from undesirable weeds
- attracting beneficial insects
- reducing overall runoff from the orchards.

CAFF demonstration projects for low cost, reseeding cover crops that are easily maintained included winter green manure crops that are mowed or cultivated in spring, annual reseeding legumes or grasses, and perennial sods. The participating growers in this study aimed to reduce the use and runoff of pesticides and nutrients by applying the techniques learned through the BMPs in Stone Fruit Project.

3. Methods

Six sampling sites were selected in an area of Sutter and Butte counties where intensive outreach and demonstration was conducted with the goal to have a significant impact on production practices. At the sites, samples were collected from drainage ditches that received runoff from 5 to 15 orchards each. Some of the growers in each watershed transitioned to BMPs over the course of the study. Sites were monitored over two years with two wet season and one dry season sample collected in each year. The temporal distribution of sampling was chosen to determine pesticide and nutrient concentrations in orchard runoff during the dormant season and the irrigation season before and after BMP implementation. Most growers in this area irrigate utilizing sprinklers to reduce the cost for water and prevent potential root damage on trees but flood irrigation is still used in approximately 30 to 40% of the orchards that drained to monitored ditches. Chemical analysis was conducted for 19 OP, pyrethroid, and organosulfite pesticides and four

nutrient forms to assess potential pesticide and nutrient load reductions resulting from outreach and the introduction of BMPs.

3.1 Study Area and Sampling Locations

The Sacramento Valley is the portion of the California Central Valley that lies to the north of the Sacramento-San Joaquin River Delta. The Sacramento River and its tributaries dominate the geography of the Sacramento Valley, and the Sacramento River flows about 620 km (382 miles) southwest between the Pacific Coast Range Mountains and the Sierra Nevada Mountain Range. The primary economic activity in the Sacramento Valley is agriculture. Peach and prune growing is particularly important in this region. California prune orchards produce 99% of U.S. production and 70% of the world's prune crop. Sutter and Butte counties have the greatest prune acreage, leading the top ten counties in the state in prune production (USDA 2008).

Sutter and Butte counties are located along the Sacramento River in the west and the Feather River in the east in the Central Valley of California north of the state capital Sacramento. Together they span an area of approximately 5,920 km² (2,290 mi²) (US Census Bureau 2000). Approximately, 88% of the area is prime farmland and grazing land. Agriculture in Sutter and Butte counties is diversified with approximately 70 different commodities. However, the majority of land use consists of fruit orchards, rice fields, and cattle grazing. Tree crops are critical to the regional economy, accounting for about \$454 million in farm revenue in 2007.

The orchard drainage ditches monitored in Sutter and Butte counties were selected to cover geographical areas with similar agricultural uses, site characteristics, and similar pest problems. The similarity was essential to provide a good temporal comparison between orchards with predominantly conventional practices before the beginning of this Project and the same group of orchards with increased focus on BMP implementation. The sites were within a 17-mile radius of each other.

Each selected site was visited during field reconnaissance and recorded (Figure 1, Table 3). At each site, Physical Habitat Quality Field Forms for lotic systems (David, N. and D. Yee. 2007. Quality Assurance and Project Plan for the Project (QAPP)) were completed to document site characteristics and land use. Information recorded at each site included station ID, date, time, water depth, weather conditions, water color/clarity, latitude, longitude, and estimated position error. Flow rate, flow diversions, flow volumes, anthropogenic impacts, and wildlife presence were also noted.

Table 3. Latitudes and longitudes for sampling sites.

Site ID	Address	Lat	Long	Accuracy
A	405 West Evans Reimer	39.3385000	-121.7056800	17 feet
В	4332 Pennington Rd.	39.3385000	-121.7056800	13 feet
C	8361 Sheldon Ave.	39.25405	-121.644708	15 feet
D	8055 Sinnard Rd.	39.2524920	-121.6492500	19 feet
E	Paseo Rd.	39.2503580	-121.6543220	17 feet
F	Butte House Rd.	39.161546	-121.696041	16 feet

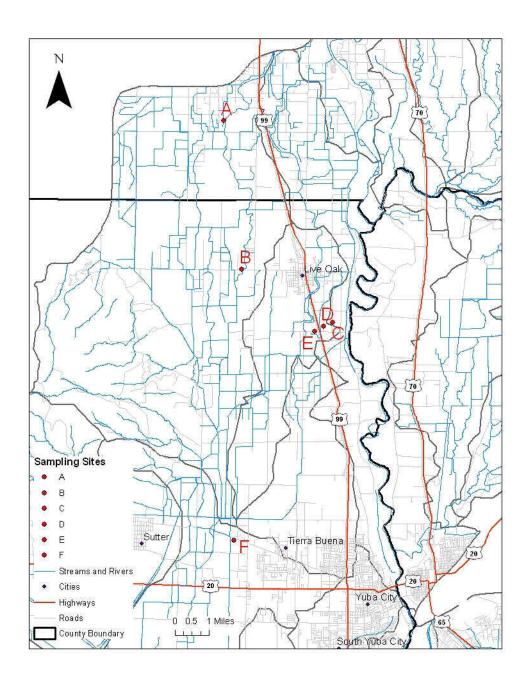


Figure 1. Map of all sampling sites in Sutter and Butte counties, in California, USA. Horizontal accuracy of coordinates was better than 30 feet.

Site Descriptions

Site A

This site is on West Evans Reimer Road in Gridley, CA, on the north side of the street and the east side of the channel. The channel is lined with grasses (Johnson grass and Rice grass), blackberry bushes, and thistles and is completely overgrown with invasive aquatic weeds, predominantly parrot's feather (*Myriophyllum aqualicum*) and coontail (*Cyratophyllum demersum*). Few open patches allow the sampling of sediment at this site, which has a higher clay content and becomes darker and anoxic below 3 cm. Asian clams are abundant, also a few mosquito fish are present.

Site B

Site B is located on Pennington Road, Live Oak, CA, and is in a steep channel with dense blackberry bushes. This sampling site is on the south side of the street and the east side of the channel where the water crosses underneath an overpass. Mosquito fish are present. Sediment characteristics show more consolidated fines with a higher clay content than Sites E, D, and C. The color of the sediment changes to a darker gray and smells anoxic below 3 cm. Bioassessment samples were not collected at this site because of the steep channel bank and the difficult access to the mid-channel sediment.

Site C

Site C is located on Sheldon Avenue in Live Oak, CA, upstream of Sites E and D. Samples were collected on the west side of the road where the channel comes out from underneath the street. The channel bottom is sandy and silty. Invasive grasses (Johnson grass or *Sorghum halipense* and Rice grass or *Glycera*) and blackberry bushes line the channel sides (no trees adjacent to sampling location). Asian clams are present. In 2009, cattail (*Typha spp.*), sedge grass (*Carex spp.*), and corkscrew rush (*Juncus spp.*) seemed to be more abundant along the ditch, very likely due to higher rainfall during the wet season.

Site D

This site is located on Sinnard Road and is part of the same channel as Site E, upstream of the Paseo Road location. The channel is lined by grasses and rocks, and no trees are present. The bottom of the channel is also rocky and sandy. Samples were collected before the channel crosses underneath the street on the east side of the road. Asian clams are abundant. In 2009, cattail (*Typha spp.*), sedge grass (*Carex spp.*), and corkscrew rush (*Juncus spp.*) seemed to be more abundant along the ditch, as observed for Site C.

Site E

This site is on Paseo Road in Live Oak, CA, right across from a lumberyard. The drainage channel is lined by trees (oak [3], tree of heaven [2], oleander [1]) that partly shade the channel. Mosquito fish are present. Dissolved oxygen levels were always above 5.7 mg/L. A pipe likely from the lumberyard across the street discharges into the channel although during the times of sampling no effluent was visible. Samples were collected upstream of the pipe on the north side of the road. A yard with a small cottage, front lawn, and a parking lot is adjacent on the channel side of the street. Higher pH (8.26 – 9.04) compared to the other sampling locations was measured. Sediment from this site is

semi-consolidated with sand and silt. Bioassessment samples showed snails (*Cipangopaludina* or Chinese mystery snail), many bivalves (Asian clam), and worms (*Capitellid*, a polychaete) present at this site.

Site F

Site F is located on Butte House Road in Yuba City, CA. Runoff is collected directly from an approximately 80 acre prune orchard at the end of the orchard before the runoff enters the drainage ditch. The sampling site is located on the south side of the street between the west end of the orchard and the east side of an irrigation canal that runs perpendicular to the street. Site F is the only monitored site where runoff was directly collected from the tailditch of an orchard. Bioassessment samples were not collected at Site F because extended dry periods between irrigations caused an additional stressor to aquatic organisms.

3.2 Sediment and Bioassessment Sampling

Sediment sampling was conducted using a Petite Ponar grab with a surface area of 0.1 m². The grab was made of stainless steel, and the jaws and doors were coated with Dykon[®] to make them chemically inert. All scoops, buckets, and stirrers used to collect and homogenize sediments were also constructed of Teflon[®] or stainless steel coated with Dykon[®]. Sediment sampling equipment was thoroughly cleaned (sequentially with detergent, acid, methanol, and rinsed with ultrapure water) at each sampling location prior to each sampling event. In order to further minimize sample contamination, personnel handling samples wore clean, powder-free nitrile gloves. Sampling equipment was cleaned at each station with a five step rinsing procedure: Alconox TM rinse, water rinse, 1% HCl rinse, methanol rinse, and final de-ionized water rinse. Further QA requirements are described in the Project QAPP (David and Yee 2007).

To ensure the quality of the sediment samples, each grab had to satisfy several criteria in order to be accepted: complete closure of the Ponar doors, no evidence of sediment washout through the Ponar doors, even distribution of sediment in the grab, minimum disturbance of the sediment surface, and minimum overall sediment depth appropriate for the sediment type.

Samples were rejected under the following conditions:

- 1. There was a rock or shell fragment wedged between the jaws of the grab allowing the sample to wash out.
- 2. The sample surface was significantly disturbed.
- 3. The sample was uneven from side to side, indicating that the grab was tilted when it penetrated the sediment.
- 4. The surface of the sample was in contact with the doors of the grab, indicating over-penetration of the grab and possible loss of material around the doors.

Redox potential (Eh) was measured in each sediment grab with a multifunctional water quality meter (e.g., WTW Multi 340). After the measurements were completed, the top 5 cm of sediment were scooped from the remaining area (avoiding portions probed) in each of the grabs and placed in a compositing bucket to provide a single composite sample for each site. Between sample grabs, the compositing bucket was covered with aluminum foil to prevent airborne contamination. After all sediment grabs were placed into the compositing bucket, the bucket was thoroughly mixed to obtain a uniform, homogeneous mixture. Aliquots were subsequently split for sediment chemistry and total organic carbon analyses.

Bioassessment sampling was performed at sites A, C, D, and E. At Site B, bioassessment sampling was not conducted due to safety concerns. Site F was excluded due to extended dry periods, and bioassessment samples from this site would have been biased by this hydrology (see Site Description). For bioassessment, a Petite Ponar grab was used to collect 0.005 m³ sediment samples. Two to three sediment grabs were taken and composited from each site. The composited sediment was washed in a 0.5 mm mesh sieve bucket, with large debris being cleaned manually to retain attached invertebrates in the sample.

The material remaining in the bucket was transferred to the sample jar using a wash bottle, followed by transfer with forceps and by hand. Samples were preserved with 95% v/v ethanol in the field, and then transferred to 70% ethanol two to three days after collection. Samples were processed within five months after collection. Processed samples that needed longer storage for QA and other reanalysis (e.g., remnant examination) were supplemented with 10% glycerol to help reduce sample deterioration.

3.3 Water Sample Collection

Water samples were collected at a depth of 1 m (sites > 2 m deep) or mid-water column (sites <= 2 m deep). A portable peristaltic pump was used to transfer water, with all tubing cleaned prior to each sampling event. To avoid aerosol contamination, the sample tubing inlet and outlet was kept covered with clean foil at all times that truck engines were operating. The inlet of the sampling pump tubing was attached to an extendable sampling pole and deployed upstream (and upwind when possible) of the sampling site. Before filling sample containers, tubing was flushed with site water for at least two minutes. Each sample container was triple rinsed with site water unless the container contained a preservative. The containers were filled completely to eliminate any headspace, and care was taken to minimize exposure of samples to sunlight. Immediately after collection, the containers were closed and placed on ice in a cooler.

Samples were shipped to and received at the laboratories in good condition between January 2008 and June 2009. All of the coolers containing water and sediment samples for pesticide and nutrient analysis were received at the lab at the recommended temperature of approximately 4°C.

Dissolved oxygen, pH, temperature, specific conductance, and salinity were determined with a multifunctional water quality meter (e.g., WTW Multi 340). At a minimum,

surface readings were taken at 1 m depth or mid water column for sites shallower than 2 m. Where possible, data (particularly DO) from the bottom, middle and top portions of the water column were also taken. Turbidity was measured either in the field or in the laboratory. Turbidity samples, if not measured in the field, were stored at 4°C and processed within two weeks of collection. Velocity at each site was measured with a Global Water Instrumentation, Inc. (Sacramento, CA) FP 211 digital water velocity meter (Figure 2).



Figure 2. SFEI staff taking velocity measurements at Site D.

3.4 Analytical Methods

3.4.1 Bioassessment Analysis

Due to the very low number of individuals in each sample, every individual was counted and taxanomically identified to order and family. Because of the low numbers of organisms found at each site, the bioassessment results cannot be used as an indicator of stream ecosystem health or for identifying potential impairment when compared between years. Three biological metrics were quantified in this study.

- Number of total taxa (designating an organism or a group of organisms)
- Number of total individuals
- Percent highly tolerant taxa

Quality assurance in bioassessment samples was ensured through re-counts of total relative abundance, species richness, and species diversity in one out of every 10

bioassessment samples. All re-counts were within 10% of the original numbers. The bioassessment counts therefore met the scoring guidelines outlined in the QAPP (David and Yee 2007). All samples were counted and re-counted by the same practitioner for consistency.

3.4.2 Pesticides Analysis

Sediment and water samples were analyzed for the following chemical groups and pesticides generally applied by growers during the stone fruit season.

- Organophosphate pesticides monitored in water samples: Chlorpyrifos
 (insecticide, nematicide), diazinon (insecticide), azinphos-methyl (insecticide),
 dimethoate (insecticide), disulfoton (insecticide, acaricide), malathion
 (insecticide), methidathion (insecticide, acaricide), parathion (insecticide,
 miticide), phorate (insecticide, acaricide), phosmet (insecticide), and the
 organosulfite pesticide propargite (acaricide) in water
- 2. Pyrethroid pesticides monitored in sediment samples: Bifenthrin (insecticide, acaricide), cyfluthrin (insecticide), cypermethrin (insecticide), deltamethrin (insecticide), esfenvalerate (insecticide), fenpropathrin (insecticide, miticide), lambda-cyhalothrin (insecticide, acaricide), permethrin (insecticide)

The analytical methods for OP pesticides (in water: EPA 8140) and for pyrethroids (in sediment: EPA 8081BM) were chosen to attempt to ensure that measured concentrations were above the detection limit for the method (see Project QAPP; David and Yee 2007). Six out of 11 monitored pesticides in water (azinphos-methyl, dimethoate, disulfoton, malathion, phorate, and propargite) were not detected in this study. However, according to the pest control advisor, the application rates for these pesticides were negligible or they were not used at all in 2008 and 2009.

OP pesticides in surface water were analyzed by modified EPA Methods 8140 and 8141AM. Analysis entailed liquid-liquid extraction and high resolution gas chromatography with Flame Photometric Detector (FPD) in phosphorus mode and Thermionic Bead Specific Detector (TSD). Sample extraction entailed treating a measured sample volume with methylene chloride (DCM) using a separatory funnel. The DCM extract was dried with sodium sulfate, evaporated using Kuderna-Danish (K-D) and solvent exchange into petroleum ether. The extract was concentrated with a microsnyder (micro K-D) apparatus and adjusted with iso-octane, prior to analysis by gas chromatography.

Pyrethroid pesticides in sediment were analyzed using a modified EPA Method 8081BM (see project QAPP; David and Yee 2007). Samples were prepared using an automated extraction system for the determination of trace residue levels of selected pyrethroid pesticides. Dual column high-resolution gas chromatography was used with electron capture detection to determine concentrations of target compounds.

The Relative Percent Differences (RPDs), calculated as the difference in concentration of a pair of analytical duplicates divided by the average of the duplicates, were all within the target range of +/-25% (Table 4a and 4b). The Percent Recoveries (PRs) for Laboratory Control Solution (LCS) and Laboratory Control Solution Duplicates (LCSDs) were predominantly within the target range of 75-125%, with the exception of a few chemicals in different batches for pyrethroid and OP pesticides that were marginally outside the target range (Table 4a and 4b). The quality assurance samples included one to two method blanks for each analytical batch and in all cases no pesticide concentrations were detected in the method blank samples. Also, all field blank samples were below the MDL for all pesticides. No blank correction factor was applied to the results.

Table 4a. Quality Assurance results for pesticides measured in water. All blanks were below detection limits.

Parameter	Detection Limit (MDL) in ug/L	Reporting Limit (RL) in ug/L	Relative Percent Difference (RPD) +/- 25%	Percent Recovery of Lab Control Solution (LCS and LCSD)
Azinphosmethyl	0.03	0.05	0*	75 - 119
Chlorpyrifos	0.005	0.02	11.8 - 12.5	90 - 119
Diazinon	0.005	0.02	1.5 - 3.6	81 - 109
Dimethoate	0.03	0.05	0*	70 - 117
Disulfoton	0.01	0.05	0*	54 - 108
Malathion	0.03	0.05	0*	76 - 110
Methidathion	0.03	0.05	10	70 - 118
Parathion, Ethyl	0.01	0.02	0*	86 - 106
Parathion, Methyl	0.01	0.05	0*	70 - 107
Phorate	0.03	0.05	0*	81 - 108
Phosmet	0.03	0.05	0*	89 - 105
Propargite	0.20	0.50	0*	68 - 118

^{*} Non-detects in all samples with duplicates.

Table 4b. Quality Assurance results for pesticides measured in sediment. All blanks were below detection limits.

Parameter	Detection Limit (MDL) in ng/g	Reporting Limit (RL) in ng/g	Relative Percent Difference (RPD) +/- 25%	Percent Recovery of Lab Control Solution (LCS and LCSD)
Bifenthrin	0.5	1.0	0.0 - 8.0	71.2 - 104
Cyfluthrin	2.0	4.0	0.0 - 19.2	62.4 - 110
Cypermethrin	2.0	4.0	0.0 - 14.9	59.4 - 105
Deltamethrin	2.0	4.0	0.0 - 8.5	38.2 - 122
Esfenvalerate	1.0	2.0	0.0 - 22.7	68.4 - 147
Fenpropathrin	2.0	4.0	0.0 - 3.6	72.4 - 93.4
Lambda-Cyhalothrin	1.0	2.0	0.0 - 4.7	71.6 - 92.0
Permethrin	4.0	8.0	0.0 - 8.7	85.9 - 94.7
Permethrin, Cis	2.0	5.0	0.0 - 19.0	69.2 - 99.2
Permethrin, Trans	2.0	5.0	0.0 - 20.0	74.1 - 98.8

^{*} Non-detects in all samples with duplicates.

3.4.3 Nutrients Analysis

Analytical methods selected for nutrients were California Department of Fish and Game methods QC 10107041B for nitrate and nitrate, QC 10107062E for total Kjeldahl nitrogen, QC 10115011D for total phosphorus, and QC 10115011M for dissolved-ortho phosphate (see Project QAPP; David and Yee 2007). For the analysis of inorganic compounds Lachat QuikChem Flow Injection Analyzer (FIA) methods were used. Orthophosphate was determined using a modified EPA Method 365.1 (see Project QAPP; David and Yee 2007). During FIA analysis, the orthophosphate ion produced reacted with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex was reduced with ascorbic acid to form a blue complex, which absorbed light at 880 nm. The absorbance was proportional to the concentration of orthophosphate in the sample.

Nitrite and Nitrate (NOx) were analyzed using EPA Method 353.2 (see Project QAPP; David and Yee 2007). Nitrate was quantitatively reduced to nitrite by passage of the sample through a copperized column of cadmium granules. The resulting nitrite (in addition to the nitrite initially present in the sample) was determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water-soluble dye had a magenta color, which was read colorimetrically at 520 nm. Nitrite alone could be determined by performing the same analysis without the cadmium reduction column step. Once nitrite had been quantified, this amount could be subtracted out of the NOx results to yield the nitrate concentration alone.

Total Kjeldahl nitrogen (TKN) (sum of organic and ammonia nitrogen) was analyzed by EPA Method 351.2 (David and Yee 2007). The sample was heated for two and a half hours in the presence of sulfuric acid and potassium sulfate, to convert nitrogen compounds to ammonium. During FIA analysis the sample pH was raised wherein the ammonium ion was converted to ammonia. The ammonia was heated with salicylate and hypochlorite to produce a blue color, which is proportional to the ammonia concentration. Total nitrogen was calculated by summing total Kjeldahl nitrogen (TKN) and nitrate plus nitrite nitrogen (NO₃+NO₂).

Total Phosphorus was analyzed using EPA Method 365.4 (David and Yee 2007). This method utilized an off-line digestion to convert all forms of phosphorus into orthophosphate using an acidic persulfate digestion. During FIA analysis, the orthophosphate ion produced reacted with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex was reduced with ascorbic acid to form a blue complex, which absorbed light at 880 nm. The absorbance was proportional to the concentration of orthophosphate in the sample.

The RPDs for nutrients ranged from 0 to 35% and were within the QA target range with the exception of total phosphorus for which the RPD was 10% above the target range (Table 5). The PRs for LCS and LCSDs were within the target range and spanned from 89-116%. The quality assurance samples included one to two method blanks for each analytical batch and were in all cases below the detection limit. Also, all field blank

samples were below the method detection limit and no correction factor was applied to the results.

Table 5. Quality Assurance results for nutrients measured in the BMPs in Stone Fruit Project. All blanks were below detection limits.

	Detection Limit (MDL) in	Reporting Limit (RL)	Relative Percent Difference	Percent Recovery of Lab Control Solution (LCS and
Parameter	mg/L	in mg/L	(RPD) +/- 25%	LCSD)
Nitrate + Nitrate	0.005	0.01	0.0 - 5.49	89 - 111
TKN	0.25	0.40	1.56 - 19.1	92 - 109
Total Phosphorus	0.0250	0.0300	0.0 - 35.0	95.0 - 116
ortho-Phosphate	0.002	0.005	0.0 - 5.29	92.7 - 103

The BMPs in Stone Fruit Project began in September 2006 with the preparation of the Project Assessment and Evaluation Plan, the Monitoring Plan, and the Quality Assurance Project Plan. After the Central Valley Regional Water Quality Control Board approved these documents, water, sediment, and bioassessment sampling began in the wet season of 2007/2008. The Sampling and Analysis Plan was closely tailored to addressing the goals and objectives of the Project. The results provide information on the effectiveness of BMP implementation. All monitoring efforts were compatible with Surface Water Ambient Monitoring Program (SWAMP) data collection criteria, and the monitoring plan was developed with full consideration of current SWAMP requirements.

4. Results and Discussion

4.1 Bioassessment

No clear trend in biodiversity and abundance of organisms at the monitored sites was observed in the study (Figure 3). Biodiversity was measured by number of taxa (order and family) present at the sites and ranged from 0 (Site C) to 5 (Site A). Abundance was measured by the number of organisms per taxa, and only one site (Site E during sampling event 3, in August 2008) had a substantially higher number of aquatic organisms compared to the other sampling locations.

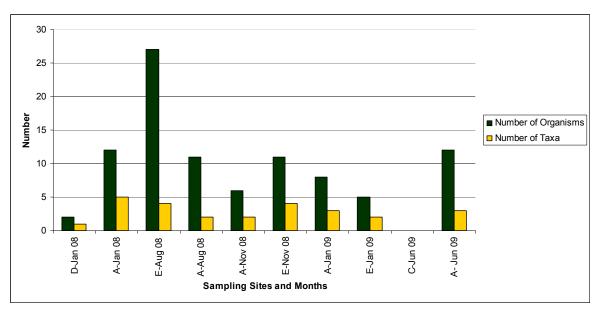


Figure 3. Bioassessment samples collected at Sites A, C, D, and E during five different sampling events in 2008 and 2009. Two sites were sampled for each of the five sampling events.

Site E had the highest number of individual organisms per sample, while Site A showed the most biodiversity with the most taxa. Benthic organisms found in the bioassessment samples predominantly belonged to the taxa polychaeta, oligochaeta, and bivalvia (mostly the clam *Corbicula fluminea*). All of these are tolerant taxa; however, identification to species was not performed. In a few samples, pelagic species were also identified. These included diving beetles (*Coleoptera*) and fly larvae (*Tipulidae*).

Possible improvements in water and sediment quality at the monitored sites over a two-year period would not be expected to be reflected in benthic community composition immediately. Changes in habitat quality would likely take several years to be reflected in organism-sediment relationships which accompany benthic disturbances. Although species may vary regionally or seasonally, their life-history attributes and functional relationships to the associated sediment appear to be relatively stable (Rhoads and Germano 2004). Over time, it would be expected that less-tolerant species will be able to inhabit the ditches that improved in water quality and that biodiversity at the monitored sites will increase slowly.

Because of the low numbers of organisms found at each site, the bioassessment results cannot be used as an indicator of stream ecosystem health, identifying potential impairment, or interannual comparison. The bioassessment part of this study was also different from standard bioassessment studies in several ways. Typically these studies are performed in permanent water bodies and not in intermittent systems like the irrigation water drainage ditches. When evaluating the bioassessment results from this study, interpretations and conclusions have to be drawn carefully, taking into consideration the temporary and altered habitat from which the samples were collected. The drainage ditches receiving orchard runoff are artificially created to carry surface water from irrigation off the field. Water passes through the tail ditches during irrigation and winter

storms only. They are dry throughout extended parts of the growing season, which adds another stressor for the organisms that try to live in these ditches. Comparison of benthic communities from site to site is therefore challenging and the results should not be interpreted as a sensitive indicator of habitat conditions and chemical exposure.

4.2 Pesticides

Trends for pesticides monitored in this study showed a decline from the start of the Project to the end after BMPs had been implemented by many growers. Decreasing pesticide concentrations and loads in this Project are consistent with the concept that the BMPs applied can potentially reduce pesticides in receiving water bodies. However, the complexity of variables that play a role in pesticide runoff and the limits of the spot sampling design do not allow for a statistical comparison of the data. Interannual differences regarding the hydrology of the ditches (e.g., magnitudes of storms, flow regimes, and lengths of wet seasons), as well as differences in pest pressures, pesticide applications, and irrigation timing and intensity all led to varying conditions under which the samples were collected. This caused a large amount of variance in the data (Table 6). Therefore, the comparison between years was only conducted graphically.

Table 6. Average concentrations and standard errors (SE) for pesticides and nutrients.

Date	Jan-08	May-08	Aug-08	Nov-08	Feb-09	Jun-09
Event type	2nd Flush	Irrigation	Irrigation	1st Flush	2nd Flush	Irrigation
Flow (m ³ /sec)	0.70 ± 0.46	0.33 ± 0.01	0.32 ± 0.13	0.39 ± 0.21	0.03 ± 0.12	0.38 ± 0.28
SSC (mg/L)	93 ± 40	6.4 ± 2.1	10 ± 2.8	40 ± 16	50 ± 25	6.3 ± 1.4
Chlorpyrifos (µg/L)	0.014 ± 0.005	0 ± 0	0.713 ± 0.568	0.002 ± 0.001	0 ± 0	0.014 ± 0.008
Diazinon (µg/L)	2.31 ± 1.82	1.97 ± 1.97	0 ± 0	0 ± 0	0.53 ± 0.18	0 ± 0
Methidathion (μg/L)	0 ± 0	0 ± 0	0 ± 0	0 ± 0	0.049 ± 0.003	0 ± 0
Phosmet (µg/L)	2.01*	0 ± 0	0 ± 0	0 ± 0	0.20*	0 ± 0
Parathion (µg/L)	0 ± 0	0 ± 0	0 ± 0	0.02*	0 ± 0	0 ± 0
Esfenvalerate (ng/g)	69.1*	40.9 ± 18.7	18.2 ± 7.9	0 ± 0	51.7 ± 19.8	4.7*
TN (mg/L)	0.71 ± 0.28	0.06 ± 0.05	0.02 ± 0.02	0.46 ± 0.22	1.70 ± 0.70	0.10 ± 0.10
TP (mg/L)	0.41 ± 0.15	0.17 ± 0.13	0.07 ± 0.02	0.20 ± 0.05	0.34 ± 0.11	0.06 ± 0.03

^{*} No SE calculation because n = 1

4.2.1 Pesticides in Water and Sediment

Pesticides were analyzed in 32 water samples over the two-year study period (January 2008 to June 2009). Five out of 11 pesticides analyzed were above the MDL in whole water samples collected during the study period (Figure 4). Forty-one percent of these samples (n = 13) had detectable chlorpyrifos and diazinon concentrations, 9% (n = 3) had detectable methidathion concentrations, 6% (n = 2) had detectable phosmet concentrations, and only one sample had detectable parathion concentrations. In sediment only esfenvalerate was detected out of the suite of pyrethroids that was tested for. Of 32 sediment samples collected, 34% (n = 11) had detectable esfenvalerate concentrations.

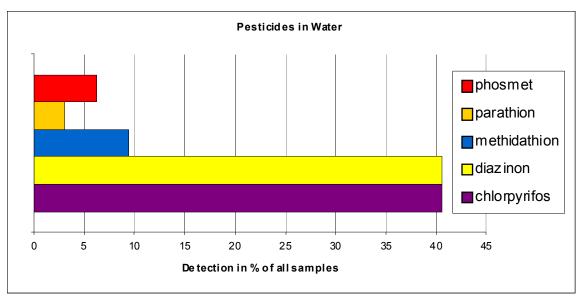


Figure 4. All pesticides detected in whole water samples indicating the % of samples analyzed above the MDL, independent of site location.

Even though the use of chlorpyrifos and diazinon in California was reduced between 1997 and 2007 (Table 2), mostly due to the increase in use of pyrethroid pesticides, they are still commonly used in orchards and were present in environmental samples in this study. OP pesticides, like chlorpyrifos, diazinon, and parathion, have also been found in ambient air samples in high concentrations in the Central Valley (Harnly et al. 2005). Aerial deposition and spray drift may contribute to the consistent chlorpyrifos concentrations found at all sampling sites in this study.

The average chlorpyrifos concentration ranged from below the 0.005 µg/L detection limit in May 2008 and January 2009 (Figure 5, sampling event 2 and 5) to 3.2 μg/L in August 2008 (Figure 5, sampling event 3). LC50 concentrations as low as 0.27 µg/L have been reported for the amphipod Ampelisca abdita (Scott and Redmond 1986) and LC50 concentrations have been reported as low as 0.01 µg/L for the water flea Daphnia magna (Van der Hoeven and Gerritsen 1997), showing that the average concentrations at the monitored sites posed a potential risk to the environment during the August 2008 sampling event. Two individual samples collected in August 2008 were above the LC50s for Daphnia (0.01 µg/L) and Ampelisca. The elevated concentrations were 3.2 µg/L at Site C and 0.3 µg/L at Site D. The high concentrations in August 2008 probably occurred due to chlorpyrifos applications in one or multiple orchards that drain into the monitored ditches prior to the sampling event. Additionally, longer irrigation periods at the end of the summer could have caused the peak in concentrations by flushing the soil more thoroughly. Between the dormant season application and the summer application, chlorpyrifos was likely not being applied to the monitored orchards since all results for the sampling events in May 2008 were below the detection limit.

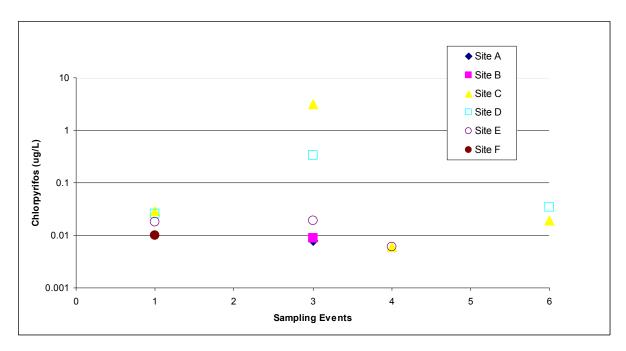


Figure 5. Chlorpyrifos concentrations in water (μ g/L) at all monitored sites. Sample dates were Feb 08 (1), May 08 (2), Aug 08 (3), Nov 08 (4), Jan 09 (5), Jun 09 (6). Note logarithmic scale that does not plot 0 values (May 2008 and January 09).

Diazinon concentrations (Figure 6) ranged from below the $0.005~\mu g/L$ detection limit to $11.8~\mu g/L$. Although the highest concentration was found during the dry season, diazinon was detected more frequently during the wet season. Two out of 32 samples were above the LC50 for *Daphnia magna* (1.0 $\mu g/L$) during the first year (Site E and F, in February and May 2008) and one during the second year (Site E, in November 2008). All results were far below the LC50 for rainbow trout (2,600 $\mu g/L$). Diazinon had an average concentration of 1.5 $\mu g/L$ at all sites during the first year, which exceeds the LC50 for *Daphnia magna*, and an average concentration of 0.2 $\mu g/L$ during the second year.

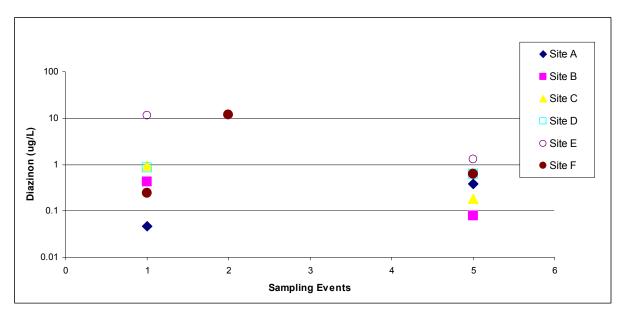


Figure 6. Diazinon concentrations in water (μ g/L) at all monitored sites. Sample dates were Feb 08 (1), May 08 (2), Aug 08 (3), Nov 08 (4), Jan 09 (5), Jun 09 (6). Note logarithmic scale that does not plot 0 values (August 2008, November and June 2009).

Average esfenvalerate concentrations in sediment were similar in the two sampling years (13.4 ng/g in 2008 and 14.1 ng/g in 2009) (Figure 7). Esfenvalerate concentrations ranged from below the 1 ng/g detection limit to 106 ng/g (Site C). All detected samples (11 out of 32) posed a potential risk to mysid shrimps, *Daphnia magna*, and rainbow trout, exceeding the LC50s of 0.04, 0.24, and 0.26 ng/g, respectively. As the detection limit (1 ng/g) was greater than these LC50s, it is also possible that samples below detection limits posed potential risk.

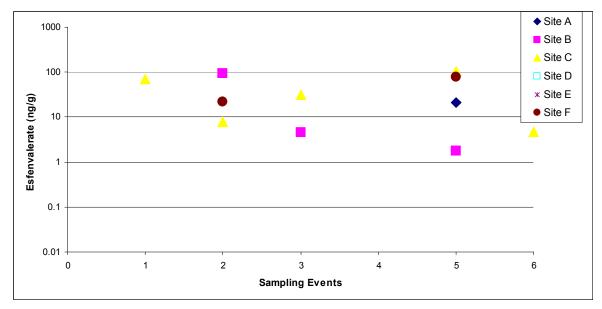


Figure 7. Esfenvalerate concentrations in sediment (ng/g) at all monitored sites. Sample dates were Feb 08 (1), May 08 (2), Aug 08 (3), Nov 08 (4), Jan 09 (5), Jun 09 (6). Note logarithmic scale that does not plot 0 values.

For a better evaluation of ecological concerns, pesticide sediment concentrations were carbon-normalized (Figure 8). The LC50 for *Hyalella* for esfenvalerate is 0.89 ug/g OC (Amweg et al. 2005). Six out of 32 samples had esfenvalerate concentrations above this LC50 for *Hyalella*, indicating a potential risk for sensitive species. Four exceedances occurred during the first year of monitoring and two during the second year.

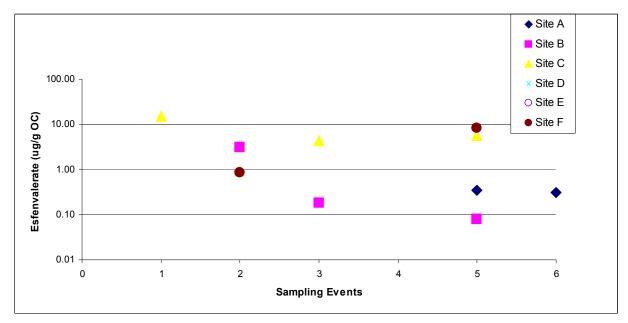


Figure 8. Organic carbon normalized esfenvalerate concentrations in ug/g TOC at all sites. Sample dates were Feb 08 (1), May 08 (2), Aug 08 (3), Nov 08 (4), Jan 09 (5), Jun 09 (6). Note logarithmic scale.



Figure 9. Sample collection at Site C.

4.2.2 Pesticide Loads

The calculation of loads (mass of a substance flowing through each sampling channel cross section) provides an alternative method for evaluation of potential impacts on receiving waters. Loads can also be compared to the amount of chemical applied to provide an estimate of proportional losses.

Pesticides loads in g/day were calculated using the following equation:

Load (g/day) = Pesticide Conc. (ng/L) x flow rate (cfs) x 0.00245 (multiplier for unit conversion into g/day)

Flows in drainages ditches were highly variable throughout the day depending on the site (sometimes greater than 50% variability). As real-time flow data were unavailable, the "average" flow rate was estimated, based on field measurements during site sampling events. Furthermore, the constituent concentration was only representative of the runoff at the sampling time and should not be extrapolated to subsequent irrigation or rainfall events. The load calculations made for agricultural tailwater flows in this study are therefore preliminary estimates.

Estimated average pesticide loads (Table 7) during the first year of this study were generally higher than the second year. The only exceptions were methidathion and

parathion, which had slightly higher loads in the second year and were not detected during the first year. Chlorpyrifos, diazinon, and phosmet loads were reduced drastically in the second year. The second year loads were between 1% (chlorpyrifos in dry season) to 14% (chlorpyrifos in wet season) of the first year loads. Diazinon and phosmet loads from the second year were calculated at only 2% and 4% of the first year loads, respectively. However, differences in loads from the first to the second year were not statistically significantly different due to the high signal to noise ratio experienced in this study.

Table 7. Average pesticide load (g/d) for the wet and dry season of the first and second years of this study. Only one flow measurement and one pesticide analysis were obtained for each sampling event. The daily load calculations therefore represent a limited snapshot in time (a small part of the entire tree crop irrigation and farming season).

	Pesticide loads in g/d						
	1st wet season	2nd wet season	1st dry season	2nd dry season			
Chlorpyrifos	0.07	0.01	2.40	0.02			
Diazinon	14.16	0.31	0.02	0			
Methidathion	0	0.003	0	0			
Phosmet	0.0046	0.0002	0	0			
Parathion	0	0.02	0	0			

OP insecticides, like chlorpyrifos, diazinon, and phosmet, are predominantly applied to tree crops during the dormant season between late December and February. This coincides with seasonal rainfall in the Central Valley, which greatly increases the likelihood of pesticides leaving the orchards with runoff water drastically (Domagalski et al. 1997). In this study, diazinon and phosmet residues in surface waters were approximately three times higher during the wet season compared to the dry season, and consequently load estimates for diazinon and phosmet were also much higher (Table 7).

Suspended sediment loads during the second year were approximately 55% of the loads calculated for the first year. The biggest difference in sediment concentration was observed for the two January sampling events (Figure 10). However, it has to be taken into consideration that the January 2008 storm had a greater intensity with 1.7 in of rainfall on January 4, compared to 0.8 in of rainfall on January 23, 2009. Decreased sediment concentrations during the second year were likely due to storm magnitude as well as implemented BMPs. Planted cover crops increased the soil infiltration rate and reduced the amount of sediment that was washed off of the orchards. Pesticides that bind to sediment particles, like the pyrethroid esfenvalerate, were therefore also likely reduced in the runoff (Kelley 2003).

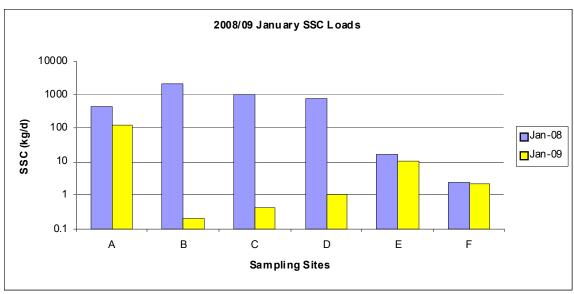


Figure 10. Suspended sediment loads (kg/d) calculated for the first flush event for all monitored sites in January 2008 and November 2008. Note the logarithmic scale.

4.3 Risk Quotients (RQ)

Another way of evaluating the results is to perform an assessment of ecological risk. An ecological risk assessment is conducted by calculating the Risk Quotient (RQ). This risk characterization integrates exposure and effects data (Table 8) and states a potential for risk, expressed by the Level of Concern (LOC). The RQ is calculated as follows.

RQ = Exposure / Toxicity

- Exposure = Field data concentrations
- Toxicity = Published toxicity endpoint (LOEC, NOEC, EC50, LC50, MATC)

Where:

LOEC is the "lowest observed effect level," or the lowest level (concentration) at which adverse effects are observed.

NOEC is the "no observed effect level (concentration)," or the level below which, no adverse effects are observed.

EC50 is the effective concentration of the pesticide in mg/L or μ g/L that produces a specific measurable effect in 50% of the test organisms within the stated study time. The measurable effect is reproduction or lethality for zooplankton and a reduction in photosynthetic activity by 50% for phytoplankton.

LC50 is defined as the amount of pesticide present per liter of aqueous solution that is lethal to 50% of the test organisms within the stated study time.

MATC is the "maximum acceptable toxicant concentration" and is a hypothetical threshold concentration that is the geometric mean between the NOEC and LOEC concentration

Table 8. Toxicity data for detected pesticides. Source: Pesticide Action Network Pesticide Database http://www.pesticideinfo.org/

Pesticide	Rainbow	Bluegill	Fathead	Water Flea	Selenastrum
	Trout	Sunfish	Minnow		
Chlorpyrifos	LC50	LC50	LC50	LC50	
(insecticide)	$9.0~\mu g/L$	10 μg/L	330 μg/L	0.01 μg/L	
Diazinon	LC50		LC50	EC50	EC50
(insecticide)	2.6 mg/L		15 mg/L	$0.22~\mu g/L$	3.7 mg/L
	BCF				
	12 μg/L				
Phosmet	LC50	LC50	LC50	LC50	
	0.23 mg/L	0.07 mg/L	7.3 mg/L	5.6 μg/L	
Methidathion	LC50	LC50		LC50	
	$10~\mu g/L$	$2 \mu g/L$		7.2 μg/L	
Parathion	LC50	LC50	LC50	LC50	
	1.9 mg/L	4.4 mg/L	8.9 mg/L	4.8 μg/L	
Esfenvalerate	LC50	LC50	LC50	LC50	
(insecticide)	0.3 ng/g	0.3 ng/g	0.2 ng/g	0.24 ng/g	
			(killfish)	0.04 ng/g	
				(Mysid	
				shrimp)	

Using the field data from this study, the RQs were calculated for detected chemicals, according to the EPA approach (http://www.epa.gov/oppefed1/ecorisk/#Deterministic), as follows:

```
RQ (chlorpyrifos) = 3.19/9 = 0.35 (rainbow trout) for first year of study
```

RQ (chlorpyrifos) = 3.19/0.01 = 319 (water flea) for first year of study

RQ (chlorpyrifos) = 0.04/9 = 0.004 (rainbow trout) for second year of study RQ (chlorpyrifos) = 0.04/0.01 = 4 (water flea) for second year of study

RQ (diazinon) = 11.8/2,600 = 0.005 (rainbow trout) for first year of study

RQ (diazinon) = 11.8/0.22 = 53.6 (water flea) for first year of study

RQ (diazinon) = 1.3/2,600 = 0.001 (rainbow trout) for second year of study

RQ (diazinon) = 1.3/0.22 = 5.9 (water flea) for second year of study

RQ (phosmet) = 2.0/70 = 0.03 (bluegill sunfish) for first year of study

RQ (phosmet) = 2.0/5.6 = 0.4 (water flea) for first year of study

RQ (phosmet) = 0.2/70 = 0.003 (bluegill sunfish) for second year of study

```
RQ (phosmet) = 0.2/5.6 = 0.04 (water flea) for second year of study
```

```
RQ (methidathion) = 0.06/2 = 0.03 (bluegill sunfish) for second year of study RQ (methidathion) = 0.06/7.2 = 0.008 (water flea) for second year of study
```

RQ (parathion) =
$$0.02/1,900 = 0.000$$
 (rainbow trout) for second year of study RQ (parathion) = $0.02/4.8 = 0.004$ (water flea) for second year of study

RQ (esfenvalerate) =
$$93/0.3 = 310$$
 (rainbow trout) for first year of study RQ (esfenvalerate) = $93/0.24 = 388$ (water flea) for first year of study

RQ (esfenvalerate) =
$$106/0.3 = 353$$
 (rainbow trout) for second year of study RQ (esfenvalerate) = $106/0.24 = 442$ (water flea) for second year of study

The RQ for each chemical was then compared to a unitless value, called the Level of Concern (LOC) (Table 9). Comparison to the LOCs showed exceedances of the acute risk threshold for three pesticides (bold above). The LOC was exceeded for chlorpyrifos for acute risk for water fleas during the first year (approximately 319 times higher) and during the second year (approximately 4 times higher), indicating that there is a high threat to aquatic invertebrates at the chlorpyrifos concentrations observed in this Project. Concentrations for diazinon also exceeded the LOC during the first (approximately 54 times higher) and second year (approximately 6 times higher). Even though the sampled water was still toxic to water fleas, a decrease in the level of exceedance was observed in year 2. The third chemical exceeding the LOCs was esfenvalerate in sediment during the first year (approximately by 310 times for rainbow trout) and during the second year (approximately by 353 times for rainbow trout). It should be noted, however, that the bioavailability of pyrethroids in sediment is strongly dependent on the carbon content of the soil, and not all of the measured esfenvalerate concentration was available for uptake by aquatic life.

Table 9. Risk Quotient (RQ) compared to Level of Concern (LOC) for four different risk presumptions.

Risk Presumption	RQ	LOC
Acute Risk	LC50 or EC50	0.5
Acute Restricted Use	LC50 or EC50	0.1
Acute Endangered Species	LC50 or EC50	0.05
Chronic Risk	MATC or NOEC	1

These comparisons represent a worst-case scenario since the maximum concentration detected in the entire period of the study was used to evaluate the potential ecological risk. This very conservative approach is a good balance to comparing detected pesticide concentrations to LC50s alone. But it must also be kept in mind that it is possible that the spot sampling design used in this study missed the highest concentrations in runoff from the orchards.

For pesticides for which both, the LOC and the toxicity threshold (LC50), were exceeded (e.g., chlorpyrifos, diazinon, and esfenvalerate), a high degree of ecological risk for sensitive aquatic species is evident. Even though the RQs for chlorpyrifos and diazinon showed a decrease in the second year, the peak concentrations still exceeded the LOC threshold by several-fold.

4.4 Nutrients

4.4.1 Nutrients in Water

Nutrient concentrations in this study were relatively high and did not vary greatly for most nutrient forms between 2007/08 and 2008/09 with the exception of NOx. NOx concentrations ranged from below the limit of detection to 5.0 mg/L (Figure 11). The average NOx concentration in year 1 was 0.3 mg/L (n = 17) and the second year's average was higher at 1.1 mg/L (n = 15). The EPA's reference conditions for ecoregion 1, subregion 7 (California Central Valley) recommend 0.1 mg/L for NOx in the ambient water quality criteria for rivers and stream (CRWQCB 2007). In contrast to NOx, other nutrient forms did not exhibit a dramatic difference between years. TKN concentrations, for example, ranged from below the limit of detection to 2.24 mg/L with an average of 0.63 mg/L (n = 17) for the first year and an average of 0.87 mg/L (n = 15) for the second year (Figure 12). EPA reference conditions recommend TKN at 0.2 mg/L (US EPA 2001). EPA reference conditions are used as guidelines only and are not enforceable regulations. However, concentrations within the range observed in this study indicate that nitrogen represents a potential water quality concern.

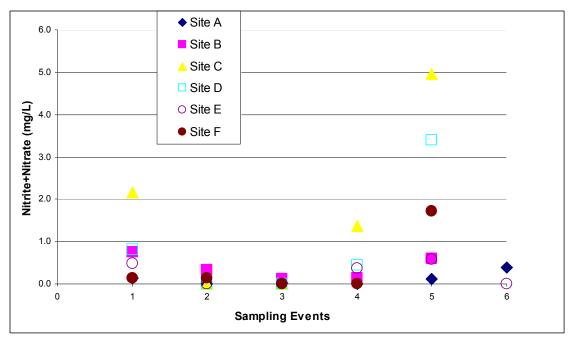


Figure 11. Nitrite and Nitrate concentrations in water (mg/L) at all sites.

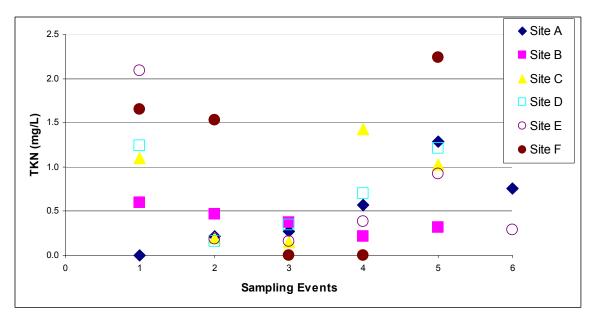


Figure 12. Total Kjeldahl nitrogen concentrations in water (mg/L) at all sites.

NOx concentrations reported in peer-reviewed literature have been measured in soybean tailwater as high as 20 mg/L (Strock et al. 2004). All measured results in this study were far below these maximum reported concentrations. Interestingly the highest TKN concentrations were observed at Site F where runoff water was collected directly from the tailditch of only one prune orchard and dilution was minimal compared to the other sites. At the same time NOx concentrations at Site F were relatively low, consistent with a higher organic fraction of the applied nitrogen fertilizer or urea applications. Urea can be readily nitrified (converted to nitrate [NO₃]). When a urea particle dissolves, the area around it becomes a zone of high pH and ammonia concentrations (Wang et al. 1992) and one of the highest pH value (9.5) in this study was also observed at Site F. Other sites that were sampled farther downstream with higher dilution and runoff from multiple orchards in the area did not show such clear results.

Ortho-phosphate (PO₄) concentrations ranged from below the limit of detection to 0.6 mg/L at all sites during the two-year study (Figure 13). The first year average was 0.12 mg/L (n = 17) and the second year average was very similar at 0.13 mg/L (n = 15). Total phosphorus (TP) concentrations ranged from below the limit of detection to 1.0 mg/L with an average of 0.3 mg/L for both years of monitoring (Figure 14). EPA recommendations for TP are reported at 0.08 mg/L (US EPA 2001), also indicating that phosphorus represents a potential water quality concern during most (22 out of 32) of the sampling events.

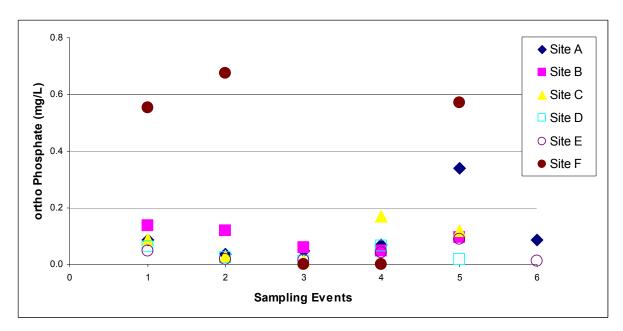


Figure 13. Ortho-phosphate concentrations in water (mg/L) at all sites.

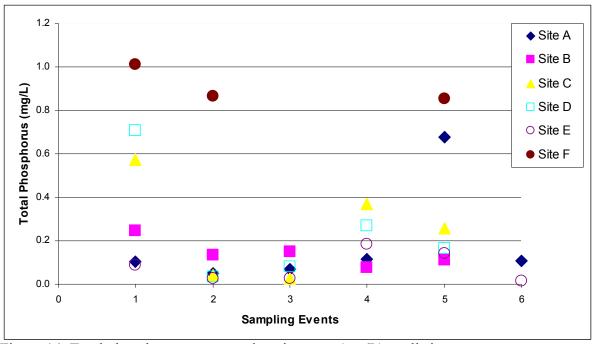


Figure 14. Total phosphorus concentrations in water (mg/L) at all sites.

Since nutrient concentrations occasionally had high peaks, probably caused by sample collection shortly after fertilizer application in adjacent orchards, median and maximum concentrations are also presented in Table 10a. This table was generated to minimize the bias of one extremely high concentration in the entire batch of samples collected. Average nutrient concentrations (Table 10b) also indicated a higher total phosphorus concentration at Site F (runoff collected directly from orchard), probably due to the use

of chicken manure that has a high content of total phosphorus. The same site had by far the lowest average suspended sediment concentration (SSC) measured in this study, which could be the result of cover crops improving overall soil health and infiltration rates.

Table 10a. Median and maximum nutrient concentrations in mg/L for all sites.

Nutrient	A	В	C	D	E	F
Nitrate + Nitrite	0.07 (0.39)	0.32 (0.76)	1.37 (4.95)	0.44 (3.40)	0.18 (0.58)	0.14 (1.72)
TKN	0.42 (1.29)	0.38 (0.60)	1.03 (1.43)	0.70 (1.24)	0.33 (2.09)	1.65 (2.24)
ortho-Phosphate	0.08 (0.09)	0.09 (0.14)	0.09 (0.17)	0.02 (0.07)	0.03 (0.08)	0.57 (0.68
Total Phosphorus	0.11 (0.68)	0.14 (0.25)	0.26 (0.57)	0.16 (0.71)	0.06 (0.18)	0.87 (1.01)
SSC	5.40 (30.2)	7.40 (19.7)	10.3 (105)	28.7 (232)	9.40 (95.1)	159 (187)

Table 10b. Average nutrient concentrations in mg/L for all sites.

Nutrient	Ι	D	C	n	E	E
Nutrient	Α	Б	C	ע	L	Г
Nitrate + Nitrite	0.11	0.38	1.70	0.93	0.24	0.67
TKN	0.52	0.40	0.78	0.73	0.67	1.81
ortho-Phosphate	0.11	0.09	0.08	0.04	0.04	0.60
Total Phosphorus	0.19	0.14	0.25	0.25	0.08	0.91
SSC	31	44	62	130	68	9

4.4.1 Nutrient Loads

Nutrient loads were reduced for all parameters from the first to the second wet season of this study (Table 11). Nutrient loads during the second winter were between 17% (NOx) and 50% (TKN) of the nutrient loads of the first winter. For the dry season, nutrient loads were higher during the second year. NOx loads during the first dry season were 20% of the second year loads while ortho-phosphate loads estimated for the first year were approximately 60% of the second year loads. Overall, changes in loads from the first to the second year were not statistically significantly different.

Table 11. Nutrient loads (kg/d) for the first and second year of this study.

	Nutrient loads in kg/d					
	1st wet seaon	2nd wet season	1st dry season	2nd dry season		
NOx	23.55	4.02	2.07	10.17		
TKN	13.93	7.02	7.82	21.42		
ortho phosphate	6.19	1.16	1.39	2.31		
total phosphorus	10.01	2.20	2.17	6.36		

Nutrient inputs from rainfall, nitrogen fixation (N only), soil and bedrock weathering (P only), and potentially from animal and human waste (N and P) to all orchards from which runoff was monitored were probably very similar given the relatively small size of the study area and the similar site characteristics represented by the sampling locations. The only major difference in nutrient input would be expected to come from differences in fertilizer applications. Sustainable soil management in tree crop orchards includes the application of poultry manure and compost, while synthetic fertilizer is predominantly used on the conventional orchards that did not participate in this study.

The NOx to TN (total nitrogen) ratios would be expected to be lower in the second year of the study compared to the first year due to a higher organic portion of the applied fertilizer (poultry manure) but the average NOx to TN ratios were slightly higher. However, this study did not focus on the application of organic fertilizers, and cover crop planting was the only BMP that could have reduced the use of synthetic fertilizers. The second year did show slightly lower average PO₄ to TP ratios, indicating a higher organic content in the fertilizer at some of the orchards that drained to the monitored ditches.

Average nutrient concentrations measured in this study were slightly higher than those found in other studies investigating nutrients in orchard runoff. For example, runoff from orchard soil in South China showed TN concentrations higher than 0.35 mg/L in over 90% of the samples collected. TP concentrations were higher than 0.1 mg/L in over 50% of the samples (Zeng et al. 2008). Median NOx concentrations in streams of mixed landuse and agricultural regions of the Sacramento River Basin (USGS 2005) were similar to the concentrations observed in this study (Figure 15). According to USGS (2005), concentrations in the Sacramento River watershed tend to be low relative to those measured in other areas of the United States with similar fertilizer applications within their watersheds due to dilution with clean water from the Sierra Nevada Mountain Range.

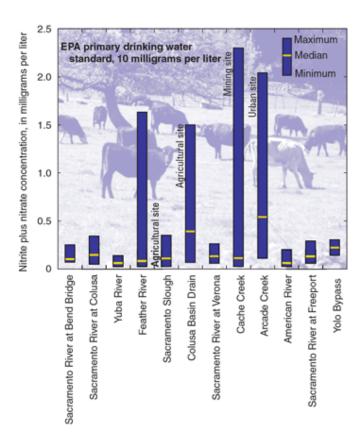


Figure 15. Concentrations of nitrite and nitrate at sites throughout the Sacramento River watershed. The highest concentrations were measured at mining and urban sites (USGS 2005).

Elevated concentrations of nitrogen or phosphorus can stimulate nuisance growth of algae. The lower concentrations in streams of mixed land-use, like the Sacramento River watershed, probably can be attributed to dilution by stream flow. The Sacramento River and its major tributaries are derived from melting snow, which has low nutrient concentrations relative to concentrations measured during this study. These rivers tend to dilute the agricultural drainage, and therefore nutrient concentrations remain low in the major rivers. In addition, some in-stream processes remove nutrients, such as algal growth that can incorporate nutrients in algae biomass.

In general, the majority of samples (89%) collected in this study had low total nitrogen to total phosphorus ratios (1-15:1). High nitrogen to phosphorus ratios (20-50:1) favor the development of *Chlorococcales* while lower ratios frequently lead to communities dominated by *Cyanophyta* (Smith 1983). Since blooms of cyanobacteria, especially of the most toxic and stable form *Microcystis*, have become an increasing threat to fresh and brackish waters, it is important to be aware of this increased risk. This is particularly a concern when the drainage ditch empties into a water body under low-flow conditions. Many uncertainties still remain about the pathways leading to cyanobacterial blooms and how important N:P ratios are under site specific conditions.

4.5 Ancillary Measurements

Dissolved oxygen (DO) is a very important indicator of a water body's ability to support aquatic life. Oxygen concentrations greater than 5 mg/L are generally considered safe for aquatic biota. Dissolved oxygen concentrations varied from 1.9 mg/L at Site C in January 2008 to 11.7 mg/L at Site A in February 2009. The drainage ditch at Site A was completely overgrown with the aquatic weeds *Myriophyllum aquaticum* (parrot's feather) and *Ceratophyllum demersum* (coontail or hornwort) and disintegrating plant material was covering the bottom of the ditch; anaerobic breakdown processes may explain the low oxygen concentrations at this site. Within the observed DO range, concentrations fluctuated without exhibiting any significant patterns at the six sites. A difference in dissolved oxygen concentrations due to BMP implementation was therefore not apparent. A total of four measurements out of 32 were below 5 mg/L, three in August of the first year and one in February of the second year.

Electrical Conductivity (EC) is a measure of how well water can conduct an electrical current. Conductivity increases with increasing abundance of ions. These ions conduct electricity because they are negatively and positively charged when dissolved in water. Therefore, EC is an indirect measure of the presence of dissolved solids such as chloride, nitrate, sulfate, phosphate, sodium, magnesium, calcium, and iron, and can be used as an indicator of water pollution. The EC varied from 0.03 mS/cm at Site E in February 2009 to 0.25 mS/cm at Site B during the same sampling event. Measurements throughout the sampling period were fairly consistent and did not exhibit any patterns associated with BMP implementation. Salinity, a related parameter, ranged from 0.01 ppt at Site D in January 2008 and Site E in February 2009 to 0.3 ppt at Site F in May 2008 with no particular pattern exhibited between the beginning and the end of BMP implementation.

pH is a general indicator for the acidity of a water body as measured by the proton (H+) concentration: pH=-log [H+]. A measurement of pH<7 is acidic, pH=7 is neutral, and pH>7 is basic. pH represents the effective activity of hydrogen ions (H+) in water. Changes in pH can also affect aquatic biota indirectly by altering other aspects of water chemistry. Low pH levels accelerate the release of metals from rocks or sediments in the stream that could potentially cause toxicity. In this study pH values ranged from 7.1 at Site D in June 2009 to 9.6 at Site E in February 2009.

Temperature of water is an important factor for aquatic life. It controls the rate of metabolic and reproductive activities, and determines which species can survive. Temperature also affects the concentration of dissolved oxygen and can influence the activity of bacteria and toxic chemicals in water. Water temperatures ranged from 4.8°C at Site F in January 2008 to 24.7°C at Site B in August 2008. These ditches are sometimes very shallow, often minimally moving, temporary water systems that easily heat up during the summer months.

Turbidity is a measure of the cloudiness of water. It is caused by suspended matter, such as clay, silt, organic matter, plankton, and other microscopic organisms that interfere with the passage of light through water. Turbidity is closely related to total suspended sediment concentration, the most dominant source of turbidity in most natural systems, but also includes plankton, organic debris, and pigments. Turbidity in this study varied widely from 5.3 NTU at Site E in May 2008 to 598 NTU at Site D during a rainstorm in January 2008, while the average turbidity measurements during the second year of sampling were approximately half as high compared to the first year. The recommended turbidity according to EPA's reference conditions for rivers and streams is 5.2 NTU (US EPA 2001), which is still far below the observed average turbidity seen in the second year of the study of 50 NTU.

Hardness is a measurement of the concentration of divalent metal ions. In this study, hardness was measured as a concentration of calcium salt CaCO₃. Water hardness concentrations varied from 12.6 mg CaCO₃/L at Site E in February 2009 to 231 mg CaCO₃/L at Site F during the May 2008 sampling event. Water hardness describes the presence of certain minerals in the water column, and studies have shown that high calcium and magnesium concentrations in water can reduce the effectiveness of pesticides when hardness is above 150-300 mg/L in source water for pesticide mixtures (Boerboom 2001). This suggests that for one out of 32 samples (from the first and the second year together) bioavailablity of pesticides was likely reduced in the ambient water. Insecticides, especially shown for chlorpyrifos and diazinon, are also known to be very susceptible to inactivation depending on the silt and sand fraction of the soil (Harris 1966). Silt and sand were not measured in this study but measured organic carbon concentrations suggested that the bioactivity of pesticides may have been slightly reduced due to the carbon content of the soil.

Dissolved Organic Carbon (DOC) is a broad classification for organic molecules of varied origin and composition within aquatic systems. DOC concentrations ranged from 1.9 mg/L at Site E in May 2008 to 14.0 mg/L at Site F in February 2009 with an

approximately two times higher average DOC concentration during the first year compared to the second year.

5. Conclusion

The data collection period for this short-term study was only two years and a longer study would have been needed to interpret the water quality data in relation to implemented BMPs with more certainty. Interannual variability probably accounts for some of the observed decreases in pesticide concentrations and loads at the monitored sites, but the bigger portion of the described trends are likely attributable to the effects of the mitigation measures that growers applied in the region as a result of the outreach and training.

Even though participating growers used less of the synthetic pesticides that were monitored during the present study, the toxicity thresholds for chlorpyrifos, diazinon, and esfenvalerate were still exceeded in the second year of monitoring. The chemical concentrations found for chlorpyrifos and diazinon in water and for esfenvalerate in sediment samples were also above the LOC for aquatic life.

Nutrient concentrations were slightly higher in the second year of this study. However, nutrient load estimates showed a clear but not statistically significant reduction from the first to the second wet season for all nutrient forms.

5.1 Recommendations

The concentrations and total amounts of pesticides in runoff water are dependent upon the characteristics of the pesticides, methods and rate of chemical application, and timing of post-application irrigation. Previous studies reported the percentage of applied pesticides being carried off the field or orchard in runoff as very low (0.1-1%) (Spencer and Cliath 1991). The percentage for soil-applied herbicides is usually 1-2%. Most OP pesticides and pyrethroids were previously reported at concentrations less than 0.1% of the application rate. Reductions in pesticide loads can be achieved with good timing of the pesticide application and the following irrigation event. Even though it may be difficult for the farmers at times to extend the time period before irrigation, a great benefit for water quality would be achieved after approximately 23 - 31 days post pesticide application. Spencer and Cliath (1991) reported the time between the pesticide application and the irrigation event as inversely related to the log concentration of the pesticide found in runoff water.

Spencer et al. (1985) showed that during the first irrigation, most pesticide concentrations were highest within the first two to three hours of the start of irrigation runoff. Concentrations were much lower after that even though the hydrograph peaked later on during the irrigation. Pesticide runoff and water flow did not seem to be correlated in any of the monitored fields that Spencer et al. studied.

In this study there was also no apparent relationship detected between the pesticide concentrations and flow so that the main focus for additional improvements of water quality should be on elapsed time between application and irrigation. Longer periods

between chemical application and orchard irrigation will reduce pesticide concentrations in runoff. Even if schedules have to be adjusted during the growing season due to unforeseen pest outbreaks, an attempt for pesticide reduction through elapsed time as a BMP will likely show an improvement for water quality.

Additionally, filter strips or vegetated ponds (Hunt et al. 2008) at the end of the tail ditch could reduce pesticide and nutrient loads to receiving water bodies substantially by storing runoff water from approximately the first four hours of runoff, the time period for which the concentrations seemed to be highest. After that critical time period, runoff water could bypass or overflow the pond or filter strip, leaving the more contaminated particles to settle in the retaining structure. Both recommended BMPs would be low-cost, low maintenance practices with a high probability for pesticide mitigation effectiveness.

This Project was a valuable pilot study to evaluate the effectiveness of BMPs in stone fruit and has provided a clearer understanding of how to design a monitoring program to detect improvements in water quality from these practices. For a more definitive conclusion, a longer study would have to be conducted. Several years of monitoring with clear, quantifiable actions taken by the participating growers, and good communication with the growers regarding the BMPs implemented and all pesticide and synthetic fertilizer applied would help in definitively determining the effectiveness of mitigation measures. Additionally, more frequent sample collection (5 instead of 3 times a year) would improve confidence in observed reductions in chemical concentrations in orchard runoff by allowing better characterization of conditions during the dry season.

6. Acknowledgments

The work for this study was an extraordinary effort, and thanks are due to many people for their direct or indirect contributions to this document. SFEI staff that contributed to the sample collection of this study was Alicia Gilbreath, Margarita Quinones, Michelle Lent, and Dan Hermstad. A draft of this document was reviewed and improved by comments received from Ben Greenfield (SFEI), Jay Davis (SFEI), and Lester McKee (SFEI). Dave Crane, Abdou Mekebri, and Patty Brucknell of California Department of Fish and Game, Marine Pollution Control Laboratory managed the main subcontract with SFEI to perform this work. Mark Cady guided this Project as CAFF Project Manager and the author would also like to thank Minghua Zhang (UC Davis), Carolyn Pickel (UC Integrated Pest Management), and Janice Kendall (Sutter County Department of Agriculture) for their knowledge and support with all aspects of the sample collection. The Project was funded by an Environmental Protection Agency Clean Water Act Section 319 grant, while oversight for this project was provided by Diane Beaulaurier, the grant manager at the Central Valley Regional Water Quality Control Board.

7. References

Amweg, E.L., D.P. Weston, and N.M. Ureda. 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California, U.S.A. Environmental. Toxicology and Chemistry, Vol. 24, pp. 966-972.

Boerboom, C. 2001. Ammonium Sulfate Requirements with Glyphosate. Weed Science. University of Wisconsin, Madison, WI.

California Department of Pesticide Regulation. 2008. Summary of Pesticide Use Report Data 2007 Indexed by Commodity. California Environmental Protection Agency, Sacramento, CA, USA.

CRWQCB. 2007. The Water Quality Control Plan (Basin Plan) for the California Regional Water Quality Control Board Central Valley Region. Fourth Edition. Sacramento, CA, USA.

David, N. and D. Yee. 2007. Quality Assurance and Project Plan for the BMPs in Stone Fruit Project. San Francisco Estuary Institute, Oakland, CA, USA.

Domagalski, J. 1997. Results of a prototype surface water network design for pesticides developed for the San Joaquin River Basin, California. Journal of Hydrology, Vol. 192, pp.33-50.

Epstein, L., S. Bassein, and F.G. Zalom. 2000. Almond and stone fruit growers reduce OP, increase pyrethroid use in dormant sprays. California Agriculture, Vol. 54, pp. 14-19.

Harnly, M., R. McLaughlin, A. Bradman, M. Anderson, and R. Gunier. 2005. Correlating Agricultural Use of Organophosphates with Outdoor Air Concentrations: A Particular Concern for Children. Environmental Health Perspectives, Vol.113, No. 9, pp. 1184–1189.

Harris, C.R. 1966. Influence of Soil Type on the Activity of Insecticides in Soil. Journal of Economic Entomology, Vol. 59, No. 5, pp. 1221-1224.

Hunt, J., B. Anderson, B. Phillips, R. Tjeerdema, B. Largay, M. Beretti, and A. Bern. 2008. Use of toxicity identification evaluations to determine the pesticide mitigation effectiveness of on-farm vegetated treatment systems. Environmental Pollution, Vol. 156, No.2, pp. 348 – 358.

Kelley, K. 2003. Environmental Fate of Esfenvalerate. Environmental Monitoring Branch Publications. California Department of Pesicide Regulations, Sacramento, CA, USA.

Lydy, M.J. and K.R. Austin. 2004. Toxicity Assessment of Pesticide Mixtures Typical of the Sacramento–San Joaquin Delta Using *Chironomus tentans*. Archives of Environmental Contamination and Technology, Vol. 48, No.1, pp. 49-55.

Muir, D.C.G., G.P. Rawn, and N.P. Grift. 1985. Fate of the pyrethroid insecticide deltamethrin in small ponds. A mass balance study. Journal of Agriculture Food and Chemisrty, Vol. 33, pp. 603-609.

Rhoads, D.C. and J.D. Germano. 1986. Interpreting long-term changes in benthic community structure: a new protocol. Hydrobiologia, Vol. 142, No.1, pp. 291-308.

Scott, J. and M.S. Redmond. 1986. Acute Toxicity Tests with Chlorpyrifos. U.S. EPA, Naragansett, RI, 3 pp.

Smith, V.H. 1983. Low Nitrogen to Phosphorus Ratios Favor Dominance by Blue-Green Algae in Lake Phytoplankton. Science, Vol. 221, No. 4611, pp. 669-671.

Spencer, W.F. and M.M. Cliath. 1991. Pesticide Losses in Surface Runoff from Irrigated Fields. Chemistry for the Protection of the Environment, Plenum Press, New York.

Spencer, W.F., M.M. Cliath, J.W. Blair, and R.A. LeMert. 1985. Transport of Pesticides from Irrigated Fields in Surface Runoff and Tile Drain Waters. United States Department of Agriculture, Conservation Research Report 31.

Strock, J.S., P.M. Porter, and M.P. Russelle. 2004. Cover Cropping to Reduce Nitrate Loss Through Subsurface Drainage in the Northern US Corn Belt. Journal of Environmental Quality, Vol. 33, pp. 1010-1016.

US Census Bureau 2000. State and County Quick Facts. http://www.census.gov

USDA 2002. Census of Agriculture. Natural Agricultural Statistics Service. http://www.agcensus.usda.gov/Publications/2002/Census by State/California/index.asp

USDA 2008. 2008 California Walnut Objective Measurement Report. United States Department of Agriculture National Agricultural Statistics Service, Sacramento, CA, USA.

US EPA. 2002. Chlorpyrifos Facts. EPA 738-F-01-006. Washington, DC, USA.

USGS. 2005. Water Quality in the Sacramento River Basin, California. U.S. Circular 1215, USGS, Sacramento, CA, USA.

Van der Hoeven, N. and A.A.M. Gerritsen. 1997 Effects of Chlorpyrifos on Individulas and Populations of *Daphnia pulex* in the Laboratory and Field. Environmental Toxicology and Chemistry, Vol. 16, No. 12, pp. 2438-2447.

Wang, Zhengping, R. D. Delaune, C. W. Lindau, and W. H. Patrick Jr. 1992. Methane production from anaerobic soil amended with rice straw and nitrogen fertilizers. Nutrient Cycling In Agrecosystems, Vol. 33, No.2, pp. 115-121.

Zeng, S.-C., Z.-Y. Su, B.-G Chen, Q.-T. Wu, and Y. Ouyang. 2008. Nitrogen and Phosphorus Runoff Losses from Orchard Soil in South China as Affected by Fertilization Depth Rates. Pedoshere, Vol. 18, No. 1, pp.45-53.