



Going Organic Project

Final Report

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1. Summary

Contamination from pesticide and nutrient applications to orchard crops is a major water quality issue in California. This farming practice comparison study – the “Going Organic Project” – was initiated with the goal to evaluate water and sediment quality in runoff from organic versus conventional walnut orchards. 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. Grants from the California State Water Resources Control Board (SWRCB) are providing for outreach, education, technical support, and political advocacy for farmers testing alternatives to pesticides and starting organic farming practices. Best Management Practices (BMPs) implemented by certified organic farmers include organic pesticide and nutrient applications, pheromone disruption, cover crops, filter strips, beneficial insects, and monitoring of insect populations and soil fertility.

Water and sediment samples from the two types of orchards were collected once in each of the dormant seasons (winters) of 2006/7, 2007/8 and 2008/9 and three times during each summer irrigation season in 2007 and 2008. Results from the Project quantified load reductions of several pesticides in the tailditch of various orchards. Specifically, loads for diazinon, dimethoate, lambda-cyhalothrin, and esfenvalerate were lower at the organic sites. In addition, concentrations of TKN were statistically significantly lower ($p < 0.05$) at the organic sites. Concentrations of bifenthrin in sediment were also statistically significantly lower ($p < 0.05$) at the organic sites. Limited bioassessment samples showed a trend toward increased biodiversity and organism abundance at the organic sites compared to conventional orchards. This work, in combination with data collected from the County Agricultural Commissioners and pesticide use reports, is providing an assessment of the effectiveness of BMP implementation and organic farming practices.

2. Introduction

The Going Organic Project (GOP) conducted by the California Certified Organic Farmers Foundation (Foundation) is a multi-faceted effort that evaluates and educates about reducing pesticide and nutrient concentrations in agricultural drainage water. The Foundation promotes and supports organic food and agriculture through research, an extensive training program, and producer and consumer education. The Foundation is training and educating farmers in effectively eliminating the use of synthetic pesticides and fertilizer and reducing the amount of water used for irrigation and produced carbon for a variety of over 150 different crops. Interested conventional farmers are being trained and mentored in organic farming practices by the GOP to increase awareness of water and sediment contamination issues. For example, farmers use: composted manures and cover crops instead of synthetic fertilizer in organic farming; innovative weeding strategies instead of herbicides; beneficial insects and trap crops to control harmful insect populations; and naturally occurring alternatives to synthetic pesticides, such as sulfur, copper, and plant and microbe-based formulations. Organic crops are produced by farmers who emphasize the use of renewable resources and the conservation of soil and water to enhance environmental quality. As a result of this Project, over 50 farmers were

mentored in organic farming practices throughout the Central Valley and the North Coast of California.

Organic farming avoids the release of large amounts of carbon from soil compared to conventional farming by building the level of organic matter in the soil. The reasons for this include the fact that organic farmers typically have grass in their crop rotations, and use manure or compost. In addition to the soil carbon benefit, a study conducted by Cranfield University, UK, has shown that on average organic farming is about 26% more energy efficient than conventional farming for producing the same amount of food (Burgess and Sannier 2006). This is because organic farmers do not use artificial nitrogen fertilizer, which are produced by converting N from the atmosphere into NO_x using fossil-fuels. The manufacture and use of NO_x gives off large amounts of greenhouse gases (producing just one metric tonne of nitrogen fertilizer emits nearly seven tonnes of carbon dioxide equivalent greenhouse gases). Nitrogen fertilizer is the single main use of energy in farming, accounting for 37% of agriculture's total energy use, and the largest global source of the greenhouse gas nitrous oxide, which is over 300 times more damaging than carbon dioxide (Burgess et al. 2006).

The San Francisco Estuary Institute conducted water and sediment quality monitoring for this Project with the goal of evaluating potential differences in contaminant concentrations running off from organic and conventional walnut orchards, evaluating the risk of spray drift and aerial deposition, and calculating pesticide loads to receiving water bodies. The GOP started in June 2005 and a Management Team was formed. The GOP then completed the Project Assessment and Evaluation Plan, the Environmental Monitoring Plan, and the Quality Assurance Project Plan. Water, sediment, and bioassessment sampling began in February of 2007 and continued through November of 2008 with the aim of evaluating the effectiveness of organic farming practices.

3. Background

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 Valley, and the Sacramento River flows about 620 km or 382 miles southwest between the Sierra Nevada Mountain Range and the Pacific Coast Range Mountains. The primary economy of the Sacramento Valley is agriculture. In California, approximately 218,000 acres of farmland are being used to grow walnuts, producing 375,000 tons of walnuts a year (USDA 2008).

Solano County is located between San Francisco and Sacramento and spans an area of approximately 2,348 km² or 907 mi² (US Census Bureau). Agriculture in Solano County is diversified with approximately 70 different commodities including fruits, nuts, vegetables, grains, seed, nursery stock and livestock. Walnuts continue to be the fastest expanding crop in terms of newly planted acres.

There appears to be a consistent source of pesticide contamination to water bodies in the Central Valley from intensive use of organophosphate (OP) pesticides, pyrethroids,

herbicides, and fungicides in walnut orchards and other agricultural fields. This Project targeted several pesticides, including the OP pesticide chlorpyrifos, which is particularly harmful to aquatic organisms. According to U.S. EPA Risk Quotients, a single application of chlorpyrifos poses risks to small mammals, birds, fish and aquatic invertebrate species for nearly all registered outdoor uses (US EPA 2002). According to the CA Department of Pesticide Regulation's Annual Pesticide Use Report (2007), chlorpyrifos was the pesticide with the highest statewide use out of all monitored pesticides in the present study, with over 195,000 pounds of active ingredient applied on walnuts alone (Table 1). 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 River and tributaries (Lydy and Austin 2004). Thus, reducing use and runoff of these pollutants would help improve the health of the targeted watershed.

Table 1. Statewide pesticide use in walnuts of monitored pesticides in 2007.

	lbs applied	Numbers of applications	Acres treated
Azinphos-methyl	822	13	797
Bifenthrin	2,480	823	27,168
Chlorpyrifos	195,102	3,306	108,538
Cyfluthrin	1	1	30
Deltamethrin	4	7	160
Diazinon	4,848	81	2,377
Lambda-Cyhalothrin	400	451	13,827
Malathion	31,086	340	6,555
Methidathion	1,036	24	586
Parathion-methyl	74,377	1,167	43,742
Permethrin	3,151	222	10,844
Phosmet	34,391	356	10,658

4. Methods

4.1 Sampling Locations

The walnut orchards selected for this study were all in Solano County in the Central Valley with the intention of covering geographical areas with similar agricultural uses and site characteristics to provide a good comparison between organic and conventionally grown walnuts. The orchards were within a five-mile radius of each other and also experienced similar pest problems. This sampling design provides a good comparison between organic and conventionally grown walnuts.

Each selected site was visited during field reconnaissance and mapped (Figure 1 and 2). Once sampling started, the general area of stations was located, GPS coordinates were assigned to each station using a hand-held global positioning system (GPS), and then the station location was confirmed on a map (Figure 1, Table 2). At each site, Physical Habitat Quality Field Forms for lotic systems (David, N. and D. Yee. 2007. Quality Assurance and Project Plan for the Going Organic Project (QAPP)) were completed to

document site characteristics and land use. Information recorded included station ID, date, time, station depth, weather conditions, water color/clarity, latitude, longitude, and estimated position error. Flow rate, flow diversions, flow volumes, anthropogenic impacts, and wildlife presence were noted. Profiles of the water body from both aerial and cross-section views were drawn.

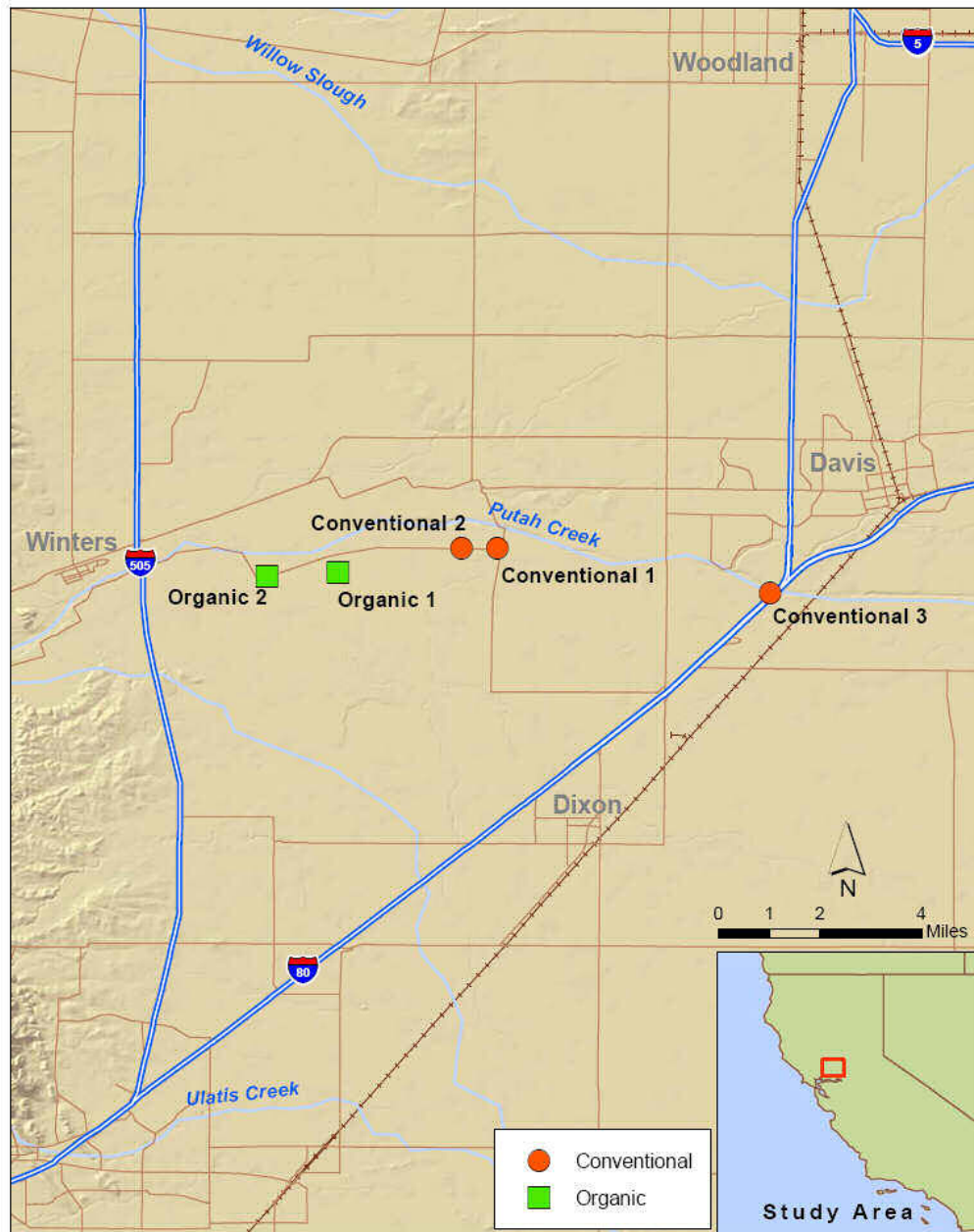


Figure 1. Map of all Going Organic Project sampling sites in Solano County, in California, USA. Horizontal accuracy of coordinates was better than 30 feet.

Table 2. Detailed information on all GOP sampling sites.

Site	Lat	Long	Elevation (feet)
Conventional 1	38.53046°N	121.85055°W	86
Conventional 2	38.53053°N	121.86067°W	86
Conventional 3	38.5174°N	121.7737°W	49
Organic 1	38.52352°N	121.89715°W	60
Organic 2	38.52250°N	121.91638°W	97



Figure 2. Organic orchard next to Putah Creek Road during site reconnaissance.

During the water sampling collection conducted on June 10, 2007 a change in the orchard runoff at the conventional sampling sites (Conventional 1 and 2) was noticed. While runoff from the selected orchards used to drain into a ditch that was accessible from the site of the road on public property (Figure 3), the runoff was re-directed into a newly dug drainage ditch that connected to an old sump on the property so tailwater from irrigation did not reach the roadside ditch anymore. Further sampling was impossible without trespassing onto the farmer's land. We did not have permission to access the orchard and collect samples on the property. Sample collection was discontinued at the two conventional sites, which both drained into the re-directed ditch. An additional conventional sampling site was added shortly afterwards. The new site (Conventional 3) was in close proximity to the existing sites and also drained into Putah Creek. This change in sampling design was approved by the SWRCB after the submission of an addendum to the Project Monitoring Plan.



Figure 3. Tailditch next to Putah Creek Road that was accessible as part of the public road and was then re-directed by the conventional farmer.

4.2 Sediment and Bioassessment Sampling

The first sediment and bioassessment samples were collected during the first flush in February 2007, continued with three irrigation samples during each of the 2007 and 2008 dry seasons, and additional first flush samples in January of 2008 and November of 2008. A total of five walnut orchards (three conventional and two organic) was monitored during this time period.

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 using the following methods:

1. Fill the compositing bucket with a small amount of de-ionized water and add approximately 1/8 cup of Alconox (tm) detergent to the bucket.
2. Place all sampling scoops into the bucket and wash thoroughly with the Alconox (tm) solution. Wash all Dykon (tm)-coated parts of the Petite Ponar grab with Alconox (tm) solution.

3. Completely rinse the grab, bucket, and sample scoops with water.
4. Rinse the grab, bucket, and sample scoops with 1.0 % HCl followed with a rinse of methanol.
5. Completely rinse the grab, bucket, and sample scoops with de-ionized water and let air-dry. Cover all cleaned parts with aluminum foil until use.

To ensure the quality of the sediment samples, each grab had to satisfy several criteria in order to be accepted: complete closure, 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 are rejected under the following conditions:

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

The top 5 cm of sediment was 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 have been placed into the compositing bucket, the bucket was thoroughly mixed to obtain a uniform, homogeneous mixture. Aliquots were subsequently split into appropriate containers for sediment quality and total organic carbon analyses.

At stations where benthic sampling was conducted, a Petite Ponar grab was used to collect benthic samples after sediment collection for pesticide analysis was completed. A composite sample from one grab has a volume of 0.005 m³. Multiple (two to three) sediment grabs were taken at each site. Overlying water was drained off an accepted grab. The content of the grab was 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 had been placed into the compositing bucket, the sediment was transferred into a 0.5 mm mesh sieve bucket. Any large debris in the bucket was removed from the sample and cleaned (invertebrates were removed and added back to the rest of the sample).

The sample was then washed through the sieve in a tub with site water until no more fine sediment washed through the mesh. Washing was accomplished by submerging the bucket half way into the water and gently lowering and raising the bucket with enough

thrust to push water in from the bottom and suspend the sediment, while twisting the bucket to re-suspend the sample and allow fine sediment to fall out. Small portions of the sample were added to the sieve until the entire sample was washed. If the sample contained chunks of clay, the globules were carefully broken up by hand. Care was taken to not allow site water into the bucket from the top as this could allow non-sample organisms to contaminate the sample. The material remaining in the bucket was then washed directly into the sample jar using a wash bottle or transferred by forceps or hand. Water in the sample jar was removed by inverting the jar tightly over a 0.5µm mesh standard sieve and draining the water. Any material left on the sieve was picked off with forceps and placed back into the container. Ethanol (95% v/v) was added to the container as a preservative to achieve a ratio of 30% material and 70% ethanol. A waterproof paper label, written in pencil, was placed in the container indicating the sample identification code, date, water body name, and collector initials. The outside of the container was labeled with sample information (sample identification code, date, water body name, and initials of the sample collector) with the preservative noted. If more than one container was needed for a sample, each container label had all the sample information and was numbered. This information was recorded on the chain of custody form for shipping to the appropriate biological laboratory. The approximate locations of sample collection were denoted by symbol on the aerial view sketch drawn on the back of the Field Data Sheet. Field preserved samples in 95% ethanol were transferred to 70% ethanol between 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.



Figure 4. Tailditch during irrigation.

4.3 Water Sample Collection

The study period for water collection also started with the first flush sampling in February 2007, continued with three irrigation samples during the dry season, another first flush sample in January of 2008, followed by three dry season samples, and ended with a first flush sample in November of 2008. Sampling was conducted at the same five orchards simultaneously with the sediment sample collection (Figure 1).

Water samples were collected at one-meter depth or mid-water column (if water body was less than 2 m deep) at each sampling site. A portable peristaltic pump was used to transfer water from the water body being sampled to the appropriate sample container. For collection of water samples for chemical analyses all tubing was cleaned prior to use at each sampling location. To avoid aerosol contamination, the sample tubing inlet and outlet was kept covered with clean foil until truck engines were turned off, and the engines remained off until sampling was completed and the tubing inlet and outlet were once again covered. The inlet of the sampling pump tubing was attached to an extendable sampling pole and deployed upstream (and upwind if possible) of the sampling site. A sufficient volume of water was collected to fill all necessary sample containers. 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 outlet tubing of the water-sampling pump was positioned at the mouth of the sample container very carefully not to touch the inside of the container or the lid with the tubing. The containers were filled completely to eliminate any headspace. Care was taken to minimize exposure of samples to sunlight. Immediately after collection, the containers were closed and placed on ice in a cooler.

All sampling bottles were labeled prior to transport to the field according to each site-specific sampling plan. Spare bottles and labels were also taken to the field. Water quality measurements were collected at every station during every sampling event using portable field meters. SFEI personnel using the meters were trained on their use and care prior to field use.

- a. A multifunctional water quality meter (e.g., WTW Multi 340 or equivalent) with several probes, was submerged into the water column to collect the following readings:

- i. Dissolved oxygen
- ii. pH and temperature
- iii. Specific conductance and salinity
- iv. Redox potential (Eh) of soil.

Water depth was recorded for each measurement. At a minimum, surface readings were taken at one-meter depth or mid water column for sites shallower than two meters. Where possible, data (particularly DO) from the bottom, middle and top portions of the water column were also taken.

- b. Turbidity was measured either in the field or samples were placed in pre-cleaned containers, stored on ice in a cooler, and in a refrigerator at 4°C on return to the Institute. Samples measured at the Institute were processed within two weeks of collection. For laboratory turbidity measurements,

the containers were removed from the refrigerator and stored in the dark until they reached ambient temperature (approximately one hour). Turbidity measurements were then completed using the same procedures as in the field.

- c. Water depth was recorded for each measurement.

4.4 Analytical Methods

4.4.1 Bioassessment analytical methods and Quality Assurance

The processing of macroinvertebrate samples was conducted like an initial stream screening method. Due to the very low number of individuals in each sample, every individual was counted and keyed. 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 at conventional sites when compared to the organic sites. 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 very 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. Hence, the bioassessment counts 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.

4.4.2 Analytical Methods and Quality Assurance for Samples Analyzed for Pesticides

Sediment and water samples were analyzed for the following chemical groups and pesticides generally applied by farmers during the walnut season.

1. Organophosphorous pesticides: Chlorpyrifos (insecticide, nematocide), diazinon (insecticide), azinphos-methyl (broad-spectrum insecticide), dimethoate (insecticide), disulfoton (insecticide, acaricide), malathion (broad-spectrum insecticide), methidathion (insecticide, acaricide), parathion (broad-spectrum insecticide, miticide), phorate (insecticide, acaricide), phosmet (insecticide)
2. Pyrethroid pesticides: Bifenthrin (insecticide, acaricide), cyfluthrin (insecticide), cypermethrin (insecticide), deltamethrin (insecticide), esfenvalerate (insecticide), fenpropathrin (insecticide, miticide), lambda-cyhalothrin (insecticide, acaricide), permethrin (insecticide)

Samples were shipped to and received at the laboratories in good condition between February 2007 and November 2008. 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.

The analytical methods for OP-pesticides (in water: EPA 8140, in sediment: EPA 8141AM) and for pyrethroids (in water: EPA 8081BM, in sediment: EPA 8081BM) (see QAPP for details (David and Yee 2007)) were chosen to ensure that measured concentrations were above the detection limit for the method. Eight out of 20 monitored pesticides (azinphos-methyl, deltamethrin, disulfoton, malathion, methidathion, parathion, phorate, and phosmet) were not detected in this study. But according to the pest control advisor, the application rates for these pesticides were negligible or pesticides were not used at all in 2007 and 2008.

Organophosphorus pesticides were analyzed with a modified EPA Method 8140, 8141AM for trace level concentrations in surface water using liquid-liquid extraction and high resolution gas chromatography with Flame Photometric Detector (FPD) in phosphorus mode and Thermionic Bead Specific Detector (TSD). In summary, a measured volume of a sample was extracted 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 microsnyder (micro K-D) apparatus and adjusted with iso-octane. The extracts were analyzed by gas chromatography using conditions, which permit the separation and measurement of the target analytes in the extracts by FPD and TSD detection.

Organophosphorus pesticides in sediment were analyzed with EPA Method 8141AM) (see QAPP for details), using an automated extraction system for the determination of trace residue levels of selected organophosphorus pesticides in sediment and high resolution gas chromatographie with Flame Photometric Detector (FPD) on phosphorus mode and/or Thermionic Bead Specific Detector (TSD).

Pyrethroid pesticides in water were analyzed using a modified EPA Method 8081A) (see QAPP for details) for trace level synthetic pyrethroids in surface water using liquid-liquid extraction and high resolution gas chromatographie with electron capture detection (GC/ECD) and gas chromatographie with mass spectrometer an ion trap detector (GC/MS-ITD) for confirmation. In summary, a measured volume of a sample was extracted 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 microsnyder (micro K-D) apparatus and adjusted with iso-octane. The extracts were analyzed by gas chromatography using conditions, which permit the separation and measurement of the target analytes in the extracts by GC/ECD.

Pyrethroid pesticides in sediment were analyzed using a modified EPA Method 8081BM) (see QAPP for details). Samples were prepared using an automated extraction system for the determination of trace residue levels of selected pyrethroid pesticides. Dual column high resolution gas chromatographie 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 within the target range of +/-25% with the only exception of chlorpyrifos in sediment for which one RPD was calculated at 36%. 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 one to two chemicals in different batches for pyrethroid and organophosphorus pesticides that were marginally outside the desirable range. 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 had to be applied to the results. Table 3a and 3b show all QA results for measured pesticides in water and sediment.

Table 3a. Quality Assurance results for pesticides measured in sediment.

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)	Blank Conc. in ng/g
Azinphosmethyl	10.0	20.0	4.8	78 - 122	<MDL
Bifenthrin	0.5	1.0	0.1	76 - 135	<MDL
Chlorpyrifos	2.0	5.0	9.8 - 36.0	71 - 113	<MDL
Cyfluthrin	2.0	4.0	9.0	54 - 109	<MDL
Cypermethrin	2.0	4.0	16.0	55 - 115	<MDL
Deltamethrin	2.0	4.0	20.0	46 - 126	<MDL
Diazinon	2.0	5.0	19.0	81 - 115	<MDL
Dimethoate	10.0	20.0	13.0	74 - 129	<MDL
Disulfoton	10.0	20.0	8.3	40 - 96	<MDL
Fenpropathrin	1.0	2.0	3.0	55 - 112	<MDL
Lambda-Cyhalothrin	2.0	4.0	8.0	60 - 132	<MDL
Malathion	10.0	20.0	10.0	77 - 113	<MDL
Methidathion	10.0	20.0	15.0	79 - 117	<MDL
Parathion, Ethyl	10.0	20.0	3.3	74 - 116	<MDL
Parathion, Methyl	5.0	10.0	19.0	71 - 111	<MDL
Permethrin	4.0	8.0	11.0	66 - 109	<MDL
Permethrin, Cis	4.0	8.0	0*	81 - 119	<MDL
Permethrin, Trans	4.0	8.0	0*	74 - 118	<MDL
Phorate	10.0	20.0	7.1	60 - 102	<MDL
Phosmet	10.0	20.0	1.9	76 - 117	<MDL

* Non-detects in all samples with duplicates.

Table 3b. Quality Assurance results for pesticides measured in water.

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)	Blank Conc. in ug/L
Azinphosmethyl	0.03	0.05	0*	81 - 130	<MDL
Bifenthrin	0.001	0.002	0*	59 - 120	<MDL
Chlorpyrifos	0.005	0.02	21.3	96 - 119	<MDL
Cyfluthrin	0.002	0.004	0*	85 - 125	<MDL
Cypermethrin	0.002	0.004	0*	77 - 148	<MDL
Deltamethrin	0.002	0.004	0*	64 - 100	<MDL
Diazinon	0.005	0.02	0*	84 - 107	<MDL
Dimethoate	0.03	0.05	-10	44 - 109	<MDL
Disulfoton	0.01	0.05	0*	52 - 107	<MDL
Fenpropathrin	0.002	0.004	0*	88 - 116	<MDL
Lambda-Cyhalothrin	0.001	0.002	0*	72 - 109	<MDL
Malathion	0.03	0.05	0*	85 - 110	<MDL
Methidathion	0.03	0.05	0*	80 - 114	<MDL
Parathion, Ethyl	0.01	0.02	0*	83 - 107	<MDL
Parathion, Methyl	0.01	0.05	0*	78 - 115	<MDL
Permethrin	0.003	0.005	0*	71 - 100	<MDL
Permethrin, Cis	0.003	0.005	0*	85 - 105	<MDL
Permethrin, Trans	0.003	0.005	0*	90 - 106	<MDL
Phorate	0.030	0.050	0*	68 - 101	<MDL
Phosmet	0.030	0.050	0*	84 - 122	<MDL

* Non-detects in all samples with duplicates.

4.4.3 Analytical Methods and Quality Assurance for Samples Analyzed for Nutrients

Samples delivered or shipped to the laboratory for nutrient analysis were all in good condition with a temperature of approximately 4°C. 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 QAPP (David and Yee 2007) for details).

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 QAPP (David and Yee 2007) for details). 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 (NO_x) were analyzed using EPA Method 353.2 (see QAPP for details). 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 NO_x results to yield the nitrate concentration alone.

Total Kjeldahl Nitrogen (TKN is the sum of organic and ammonia nitrogen) was analyzed by EPA Method 351.2 (see QAPP for details). 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 (see QAPP for details). 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 22% and were all within the desirable target range for high quality samples (Table 4). The Percent Recoveries (PRs) for Laboratory Control Solution (LCS) and Laboratory Control Solution Duplicates (LCSDs) were within the target range and span from 80-117%. 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. All monitoring efforts were compatible with the Surface Water Ambient Monitoring Program (SWAMP) data collection effort and the SCP database was developed with full consideration of current SWAMP requirements.

Table 4. Quality Assurance results for nutrients measured in the Going Organic Project.

Parameter	Detection Limit (MDL) in mg/L	Reporting Limit (RL) in mg/L	Relative Percent Difference (RPD) +/- 25%	Percent Recovery of Lab Control Solution (LCS and LCSD)	Blank Conc. in mg/L
Nitrate + Nitrite	0.005	0.01	0.0 - 9.38	85 - 104	<MDL
TKN	0.25	0.40	0.0 - 14.8	81 - 117	<MDL
Total Phosphorus	0.0250	0.0300	0.0 - 21.5	80 - 114	<MDL
ortho-Phosphate	0.0050	0.0100	0.0 - 8.74	92 - 103	<MDL

4.4.4 Analytical Methods and Quality Assurance for Samples Analyzed for Pathogens

Pathogen indicators were analyzed by EPA Method SM 9221 (see QAPP for details). Total coliform, fecal coliform, and *E. coli* were measured in water samples from the organic and the conventional sites during all sampling events if possible. Short holding times (6-8 hours) left data qualified whenever rainfall events or irrigation events occurred on Saturdays or late at night and samples could not be transported to the laboratory within holding times.

5. Results and Discussion

The goals set in the Project Assessment and Evaluation Plan for an increase in biological integrity and a reduction in synthetic pesticide and nutrient concentrations at the organic sites were all met. Bioassessment monitoring is a method for measuring biological condition and can be expressed with the Index of Biological Integrity (IBI) score. The IBI measures the stream biota and provides a direct assessment of resource conditions because the characteristics of the biota reflect the influence of human activity in the surrounding watershed. Biological integrity has been specified in the Clean Water Act and is a synthesis of diverse biological information, which numerically depicts associations between human influence and biological attributes. It is composed of several biological attributes or 'metrics' that are sensitive to changes in biological integrity.

The calculation of an IBI score for this study was challenging since the drainage ditches are only filled with water temporarily during irrigation and do not represent stream conditions. Many organisms cannot tolerate this fast changing environment, independent of the pesticide exposure (see bioassessment discussion below). As a result, all monitored drainage ditches scored low, from 10 – 16, indicating very poor stream conditions. However, a trend was observed that showed an improvement in the IBI score at the organic sites, reflected in the total number of taxa (richness) and total number of organisms (abundance). Additionally, an improvement in population attributes or percent dominance from 100% at the conventional sites to 91% at the organic sites was observed. A lower percentage in dominant species is desirable.

Average water concentrations for synthetic pesticides were reduced for lambda-cyhalothrin (31%), diazinon (59%), chlorpyrifos (84%), dimethoate (93%), and esfenvalerate (91%) at the organic sites compared to the conventional sites. Pesticide loads were reduced by up to 96% in the case of lambda-cyhalothrin at the organic sites compared to the conventional sites. Average sediment concentrations were also reduced between 90 and 100% for bifenthrin and lambda-cyhalothrin. The only exception was the average chlorpyrifos concentration in sediment that was 53% higher at the organic sites compared to the conventional sites, possibly due to spray and wind drift (see OP pesticide discussion below).

Nutrient concentrations for almost all nutrient forms were reduced from 50% (ortho-phosphate) to 78% (NO_x) at the organic sites. The only exception was the average total phosphorus concentration that increased by 4% at the organic sites, probably due to the use of chicken manure to increase soil fertility.

5.1 Bioassessment

A clear trend in greater biodiversity and abundance of organisms at the organic sites was observed (Figure 5 and 6), however due to a low sample number ($n = 7$), statistical analysis was not conducted. Biodiversity was measured by number of taxa present at the sites, and the organic sites had approximately twice the diversity of aquatic organisms compared to the conventional sites. Abundance was measured by the number of organisms per taxa, and the organic sites had approximately two to three times higher counts of individuals compared to the conventional sites.

Benthic organisms found in the bioassessment samples predominantly belonged to the taxonomic classes of polychaeta and oligochaeta. It is assumed that 100% of these organisms represent highly tolerant species, however, identification to genus or species was not performed. In a few samples, diving beetles (coleoptera) and fly larvae (tipulidae) were also identified, even though they are not part of the benthic community and were just floating on top of the sample.

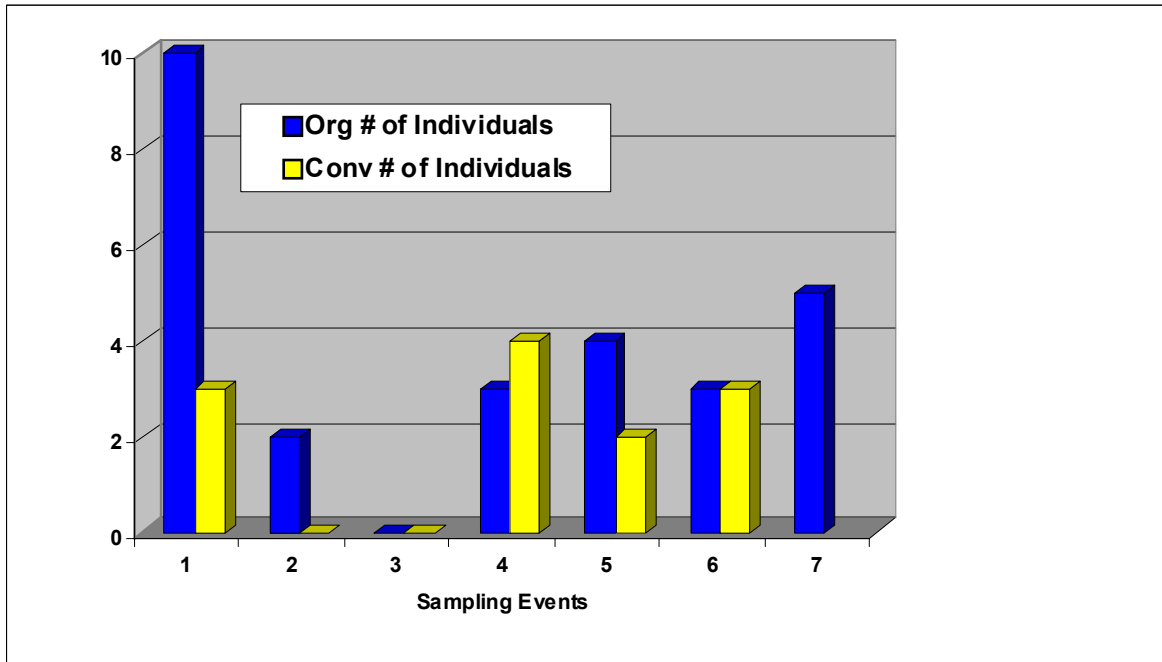


Figure 5. Number of individuals found at organic and conventional sampling sites.

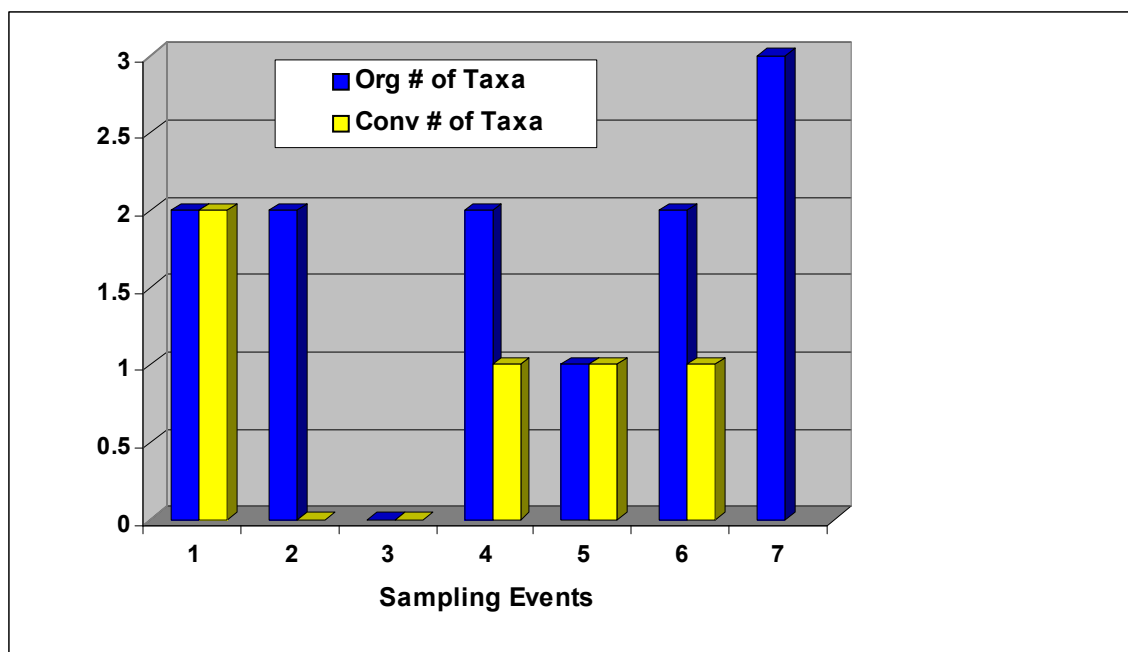


Figure 6. Number of taxa found at organic and conventional sites.

The bioassessment part of this study was different from standard bioassessment studies in very important ways. Typically these studies are performed in permanent water bodies and not in intermittent systems like the irrigation tail ditches. When looking at the bioassessment results from this study, interpretations and conclusions have to be drawn carefully, taken into consideration the temporary and altered habitat from which the samples were collected. The tailwater ditches at the lower end of the walnut orchards are artificially created to carry surface runoff from irrigation off the field. They are dry throughout most of the walnut season, which adds another stressor to the habitat of the organisms that try to live in these ditches. Water is passing through the tail ditches during irrigation for approximately 36 hours every two to three weeks. A comparison of aquatic benthic organisms from site to site is therefore challenging and numbers should be interpreted as trends only instead of an evaluation of habitat conditions due to chemical exposure.

5.2 Pesticides

5.2.1 Pesticides in Water and Sediment

Ten out of 20 pesticides were analyzed above the MDL in whole water samples collected during the period of this study from February 2007 to November 2008 (Figure 7). A total of 30 water samples were collected for each parameter over the course of the two monitored seasons. Forty-three percent of these samples had detectable chlorpyrifos concentrations, 18% had detectable diazinon concentrations, and only 13% had detectable lambda-cyhalothrin concentrations. Six out of the 20 monitored pesticides were detected in sediment samples (Figure 8). The total of sediment samples that were collected is also 30, out of which 34% had detectable chlorpyrifos concentrations, 26% detectable bifenthrin concentrations, and only 8% had detectable lambda-cyhalothrin concentrations. Figure 7 and 8 neglect individual concentrations of samples and only compare the

number of samples in which a pesticide was detected to the number of samples in which the pesticide was below the MDL.

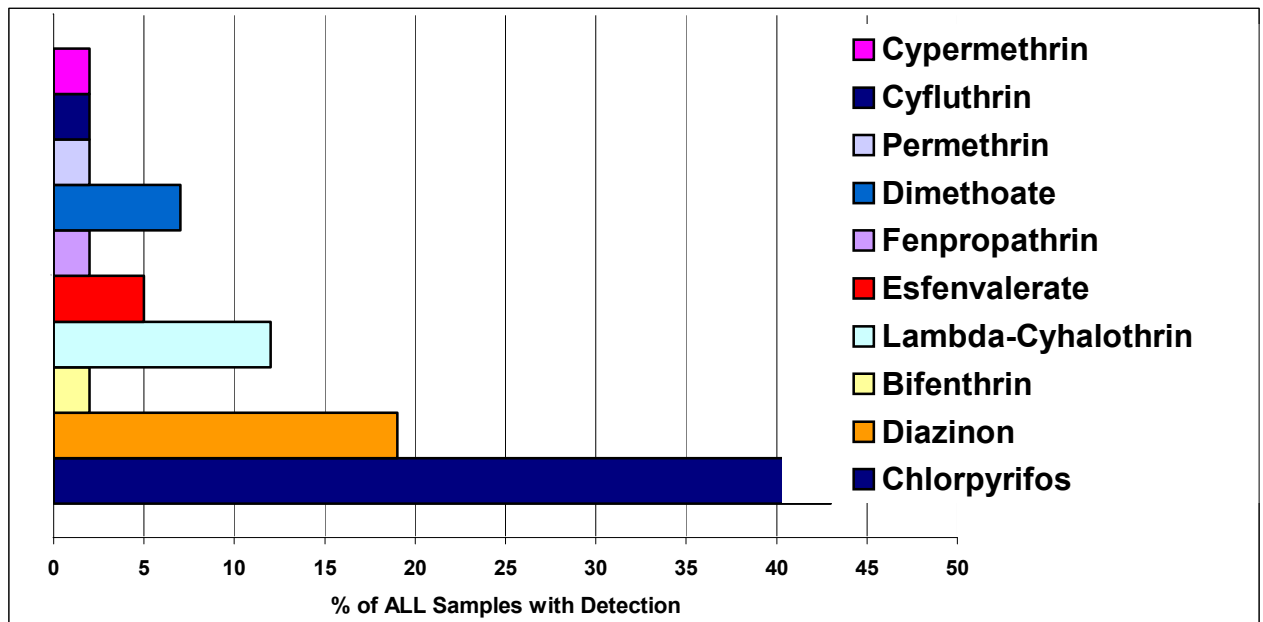


Figure 7. All pesticides detected in whole water samples indicating the % of samples analyzed above the MDL, independent of different farming practices.

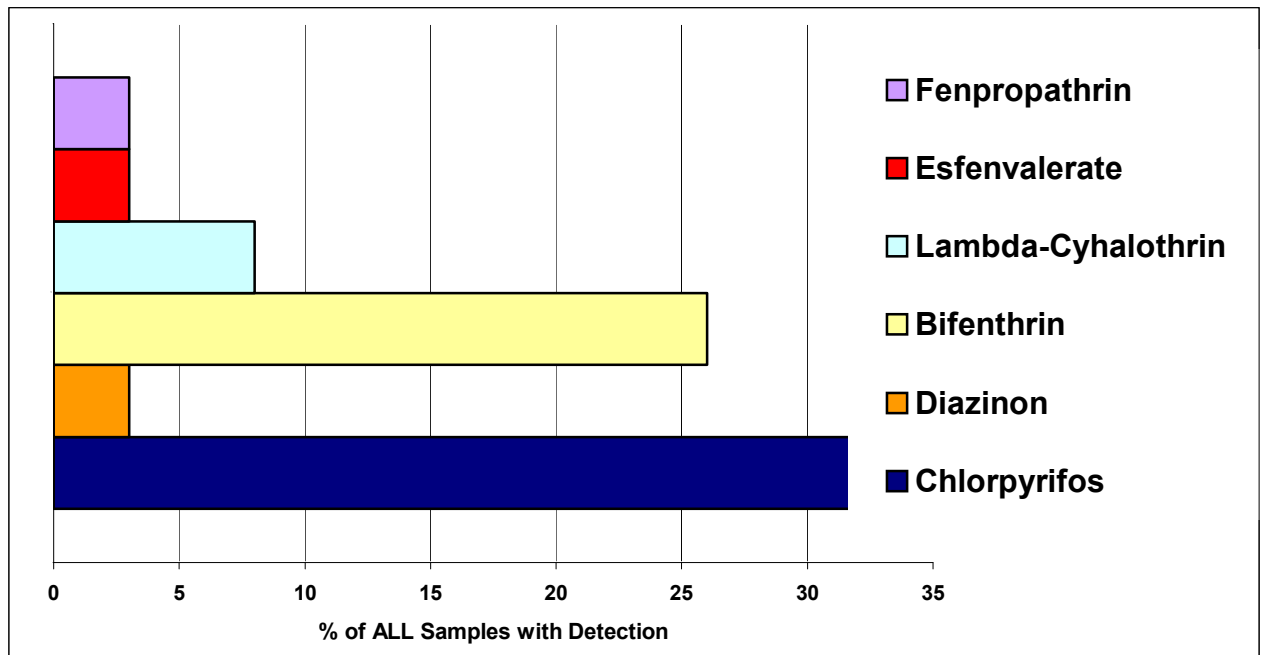


Figure 8. All pesticides detected in sediment samples indicating the % of samples analyzed above the MDL, independent of different farming practices.

Even though the use of chlorpyrifos in California was reduced between 1997 and 2007 (Figure 9 and 10), mostly due to the increase in use of pyrethroid pesticides, chlorpyrifos

is still commonly present in environmental samples. It was the most frequently detected chemical throughout the present study (detected in 43% of all water samples and 34% of all sediment samples. OP-pesticides, like chlorpyrifos, diazinon, and parathion have been found in ambient air samples in high concentrations in the Central Valley (Harly et al. 2005), and aerial deposition and spray drift may account for low but consistent chlorpyrifos concentrations found at both orchard types in the GOP.

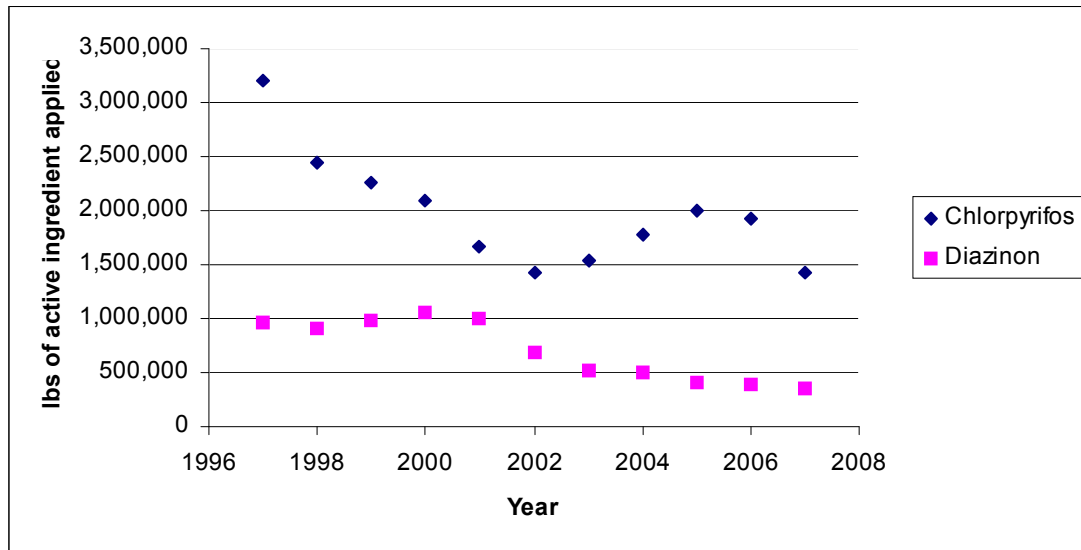


Figure 9. Pounds of active ingredient of chlorpyrifos applied on walnuts in California between 1997 to 2007.

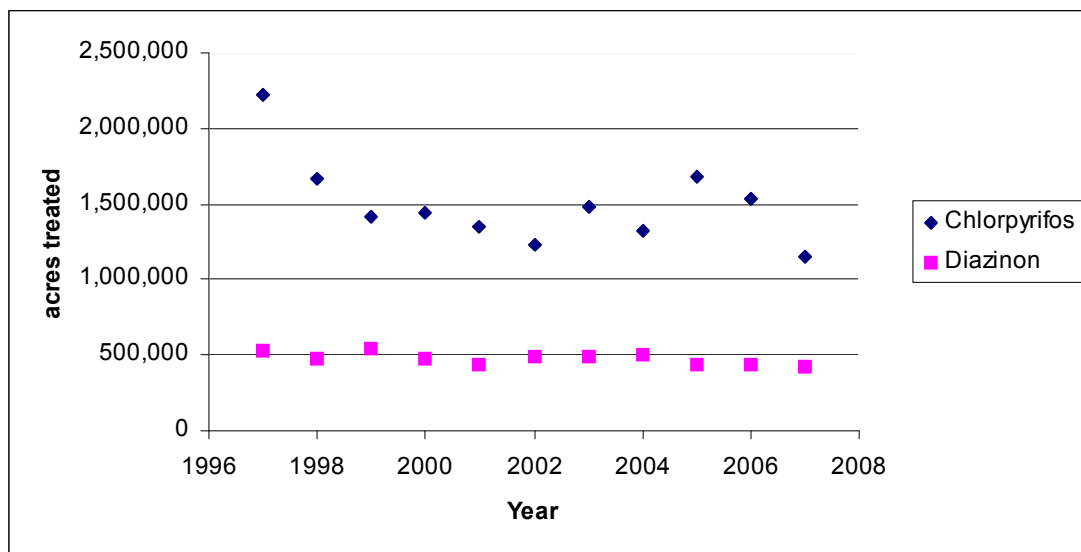


Figure 10. Acres of walnuts treated with chlorpyrifos in California between 1997 and 2007.

In the present study, the average chlorpyrifos concentration at the conventional sites was 0.13 ug/L and at the organic sites 0.02 ug/L with no chlorpyrifos being applied. LC50 concentrations as low as 0.27 ug/L have been reported for the amphipod *Apelisca abdita*

(Scott and Redmond 1986) and LC50 concentrations have been reported as low as 0.09 ug/L for the waterflea *Daphnia magna* (Van der Hoeven and Gerritsen 1997), showing that even the low concentrations at the organic sites can cause a potential risk to the environment.

In isolated sampling events (Figure 11), pesticide concentrations in water showed low levels of diazinon, cypermethrin, lambda-cyhalothrin, and permethrin all below the LC50 for sensitive aquatic species, while concentrations at the organic sites were non-detectable. Similar results were observed in sediment samples for the same sampling event (Figure 12). In sediment bifenthrin, esfenvalerate, fenpropathrin, and lambda-cyhalothrin were detected, again at relatively low concentrations, while only non-detects were observed at the organic site. The hypothesis at the beginning of the study was that this kind of pattern would be more predominant throughout the sampling period.

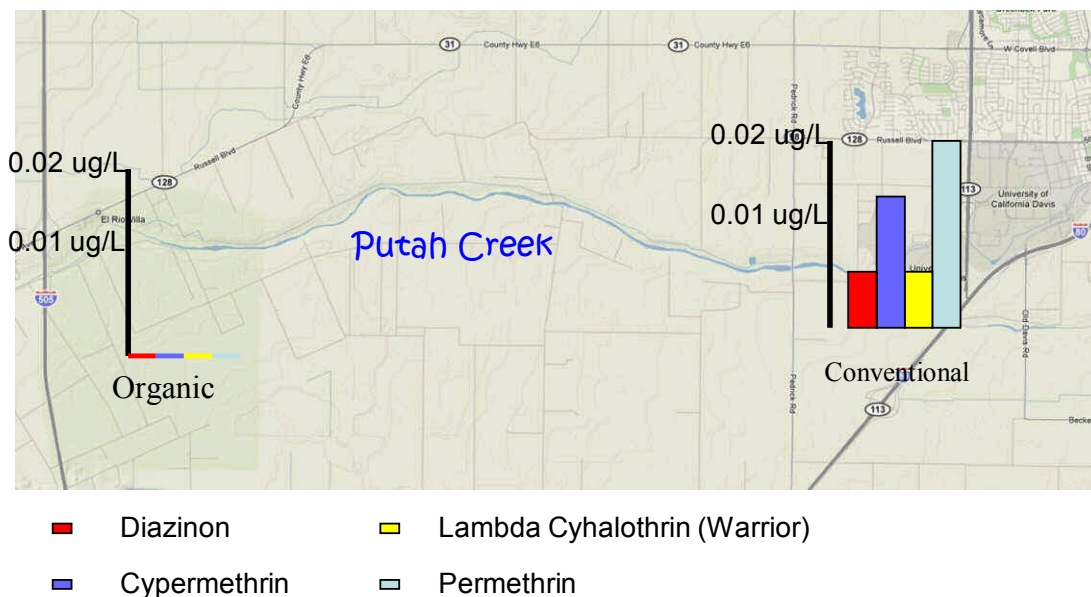


Figure 11. Concentrations in water for the April 2008 sampling event for water samples comparing one organic and one conventional orchard along Putah Creek.

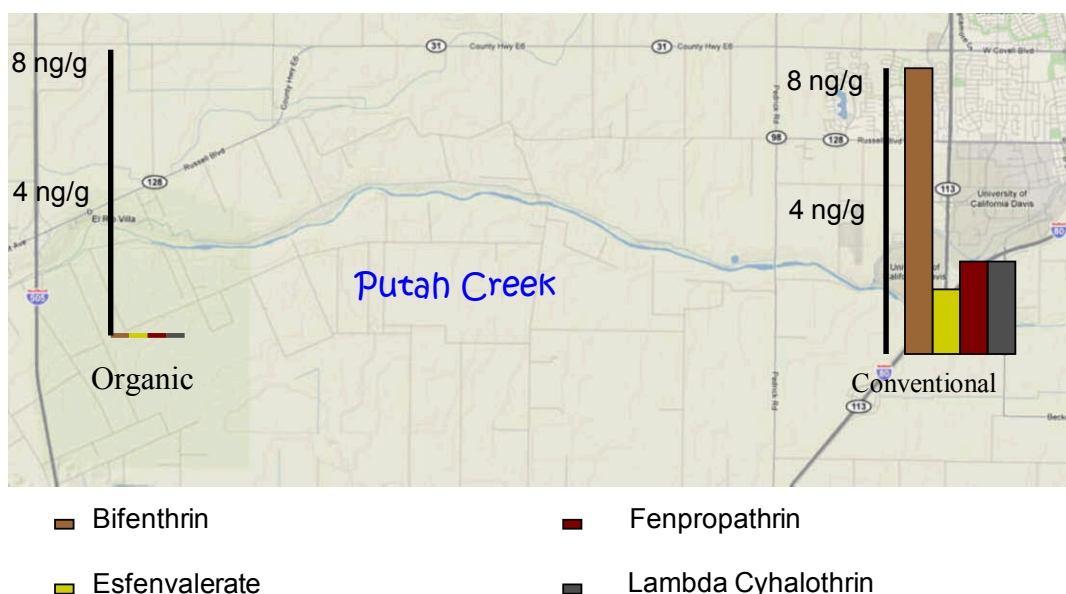


Figure 12. Concentrations in sediment for the April 2008 sampling event for sediment samples comparing one organic and one conventional orchard along Putah Creek.

Even though all organic orchards have been certified organic for approximately 10 years and part of an all-organic operation with no synthetic pesticides being used on the entire property, the results seen in this study for pesticide concentrations suggest these substances are present. There is a range of possible reasons for this observation. Pesticides could be entering the orchard with contaminated irrigation water, spray drift during pesticide applications in neighboring orchards, transport of contaminated dust particles, or biological transfer.

In addition to the transfer of pesticides, the selection of orchards for this study was limited. Flood irrigated orchards are used to collect runoff during the dry season and those systems are mostly replaced by sprinklers and installed drip irrigation to conserve water. The selected organic sites for this study ended up being smaller, flood irrigated orchards at the perimeter of the property that bordered against conventional orchards from different farmers at two sides. More protected organic orchards may have shown different results. Also, the conventional farmers, whose runoff was monitored in this study, were very open to best management practices and pesticide reduction; one of them was raising his own bats to control the codling moth population on his property. Ideally, runoff from farmers that are more dependant on pesticide usage should have been sampled but those farmers did not agree to participate in this study. The location for organic sites and the low pesticide usage at conventional sites resulted predominantly in pesticide concentrations with little observable differences between the different growing practices.

Diazinon concentrations (Figure 13) at both site types were very low and far below the LC50 for waterflea (1.0 ug/L) and rainbow trout (2,600 ug/L). Diazinon showed an

average concentration of 0.002 ug/L at the conventional sites and an average concentration of 0.001 ug/L at the organic sites. Similar to chlorpyrifos, no significant difference between farming practices was observed ($p > 0.05$).

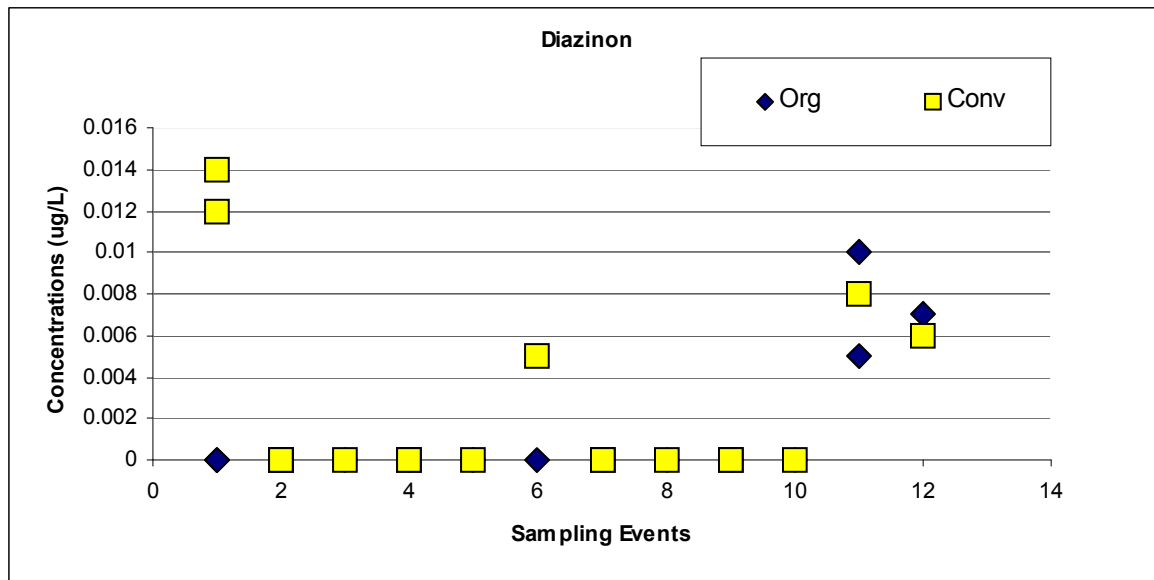


Figure 13. Diazinon concentrations at organic and conventional sites in ug/L.

Also, concentrations of lambda-cyhalothrin in water (Figure 14) showed no significant difference in different farming practices. Surprisingly, the highest concentration found in water during this study was at an organic site (0.02 ug/L). Average concentrations were still slightly higher at the conventional sites (0.002 ug/L) compared to the organic sites (0.001 ug/L). Pyrethroid aerial concentrations die away much faster after applications than those of op-pesticides but they are still transported and re-deposited with dust particles for a long time which may explain the higher lambda-cyhalothrin concentration at the organic site.

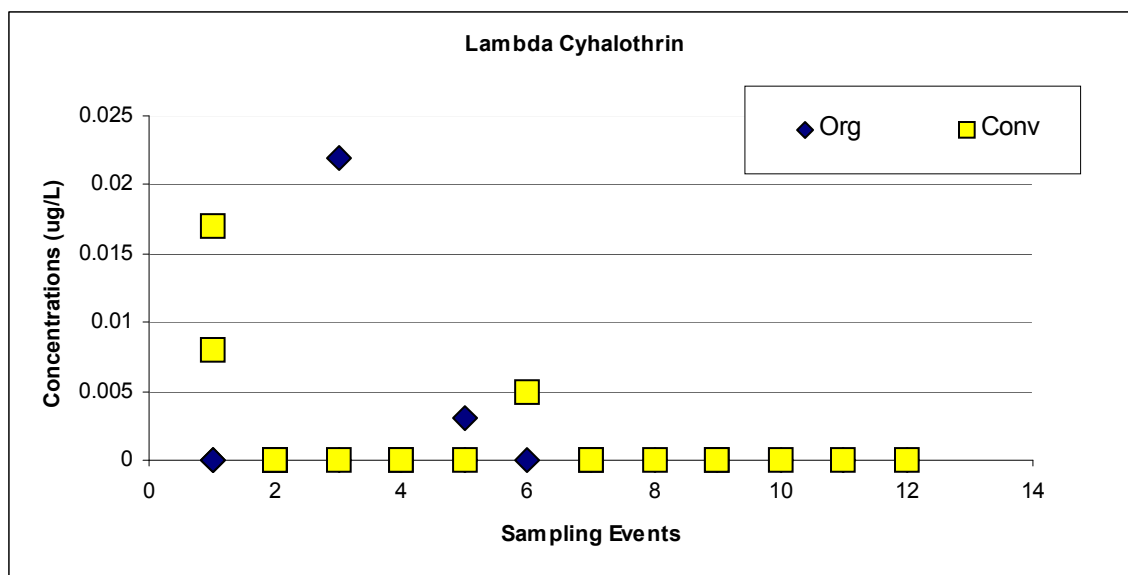


Figure 14. Lambda-cyhalothrin concentrations at organic and conventional sites in ug/L.

Pyrethroid concentrations in sediment exhibited the only significant difference between different farming practices. Bifenthrin concentrations in sediment (Figure 15) were higher at the conventional sites compared to the organic sites. The average concentration for the organic sites was 0.44 ng/g while the average concentration for the conventional sites was 5.61 ng/g, exhibiting a significant difference between the two site types ($p = 0.002$).

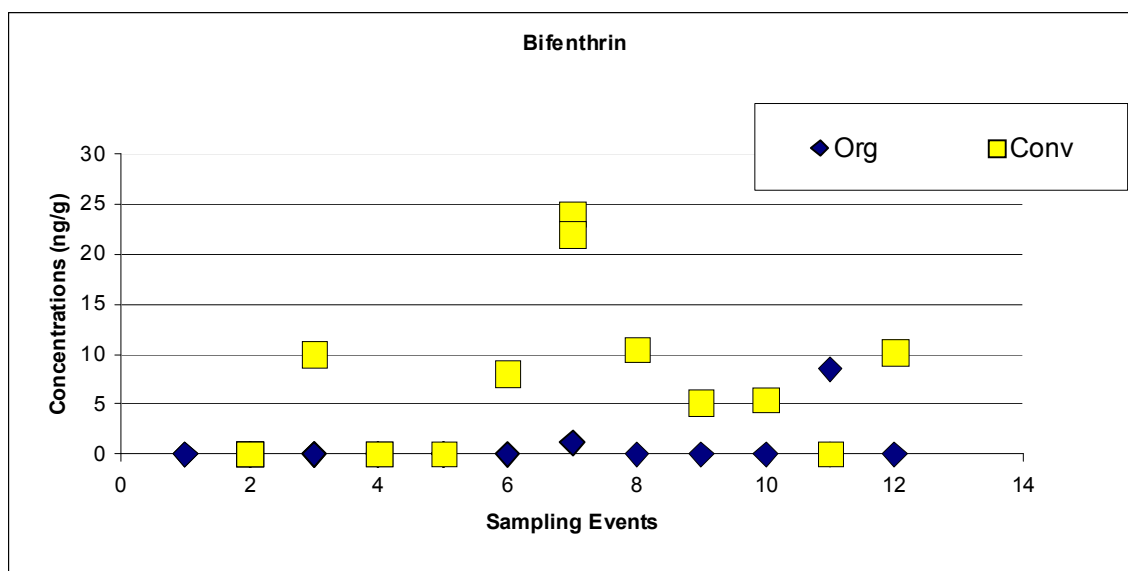


Figure 15. Bifenthrin concentrations at organic and conventional sites in ng/g.

For better ecological relevance, pesticide sediment concentrations were carbon-normalized and displayed in Figure 16. The LC50 for *Hyalella* for bifenthrin is 0.18 ug/g OC (Amweg et al. 2005). According to this guideline, seven out of 16 conventional samples had bifenthrin concentrations above the LC50 for *Hyalella*, indicating a potential

risk for sensitive species at the conventional sites. Only one out of 19 samples at the organic sites was above that threshold. The threshold for lambda-cyhalothrin is 0.45 ug/g OC (Amweg et al. 2005) and all conventional and organic sediment samples in this study were below the LC50 for *Hyalella* toxicity.

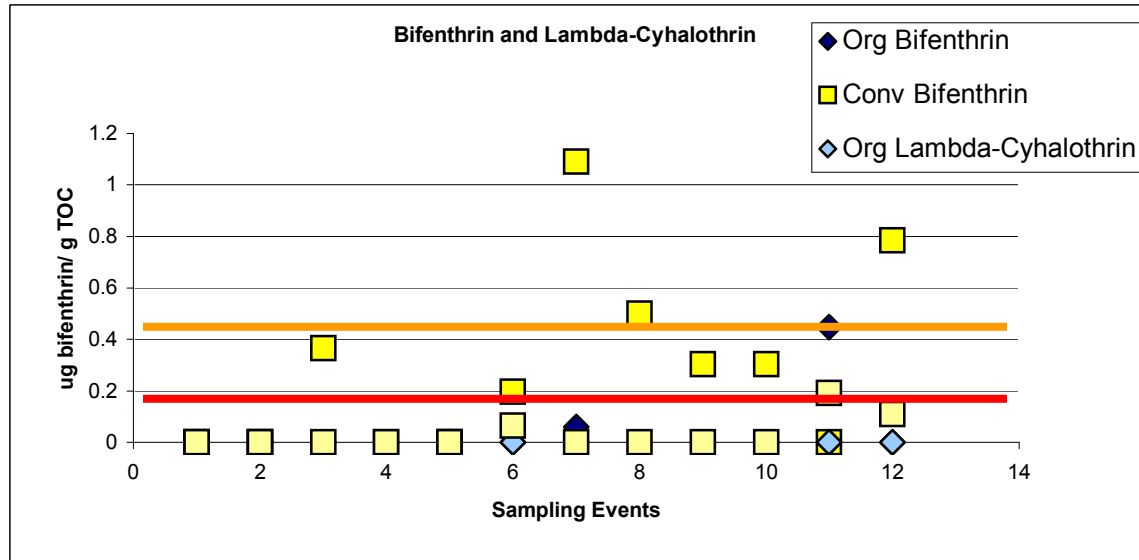


Figure 16. Bifenthrin (darker colors) and lambda-cyhalothrin concentrations (pale colors) in ug/g TOC at organic and conventional sites. The dark red line shows the LC50 for *Hyalella* for bifenthrin of 0.18 ug/g OC published by Amweg et al. in 2005. The pale orange line shows the threshold for lambda-cyhalothrin of 0.45 ug/g OC with all samples being below the LC50 for *Hyalella* toxicity (Amweg et al. 2005).

5.2.2 Pesticide Loads

So far the data have been presented as concentrations and compared to various water quality guidelines. The calculation of loads (mass of a substance flowing through each sampling channel cross section) provides an alternative method for evaluation of potential impacts. Loads are also useful for the farmer as they can be compared to the amount of chemical applied to provide a first order approximation of proportional losses. Pesticides loads in g/day were calculated using the following equation:

$$\text{Load (g/day)} = \text{Pesticide Conc. (ng/L)} \times \text{flow rate (cfs)} \times 0.00245 \text{ (multiplier for unit conversion into g/day)}$$

Tailwater flows were highly variable throughout the day (often greater than 50% variability). Without real-time flow data (not feasible in this project due to budget restraints), the “average” flow rate had to be estimated. Furthermore, the constituent concentration was only valid for the runoff at the sampling time and should not be extrapolated to subsequent irrigation events. The load calculations made for agricultural tailwater flows in this study are therefore 1st order estimates.

The average pesticide loads (Table 5) from the conventional sites were generally higher compared to the organic sites. Diazinon, dimethoate, and esfenvalerate/fenvalerate were

rarely detected in the runoff from the organic sites, and the estimated loads were negligible, while loads ranging from 0.13 to 1.05 milligrams per hour (mg/h) were calculated for the conventional sites. For lambda-cyhalothrin the estimated loads were 28 times higher at the conventional sites. The only exception was chlorpyrifos for which the average load from the organic sites was approximately six times higher than from the conventional sites, but the average calculated flow was also approximately three times higher at organic sites during the time of sample collection resulting in a higher pesticide load number. Flow during the time of sample collection does not reflect the amount of water used during the entire irrigation event but rather the time of sample collection within the irrigation event. The information given by the organic farmers about planned irrigation events was more frequent and reliable and samples were collected within one to three hours after runoff occurred. The conventional sites were mostly sampled with a delay (when water flow may have been lower) because the communication with conventional farmers was not as efficient. Previous studies (Spencer and Cliath 1991, Spencer et al. 1985) showed most pesticides to peak within the first 2-3 hours after the start of the irrigation and the sampling design aimed to target that time window.

Table 5. Pesticide load averages (milligrams per hour) at organic and conventional sites. Only one flow measurement and one pesticide analysis were conducted for each sampling event. The daily load calculations can only represent a snapshot in time (a small part of the entire walnut orchard irrigation and farming season).

Pesticide	Load off Organic Site (mg/h)	Load off Conventional Site (mg/h)
Lambda-Cyhalothrin	11.5	326
Diazinon	0.00	1.05
Chlorpyrifos	23.9	3.79
Dimethoate	0.00	0.13
Esfenvalerate/Fenvalerate	0.00	0.25

Suspended sediment loads shown in Figure 17 are slightly higher ($p = 0.2$) from the organic sites compared to the conventional sites. This is not surprising since the soil is less compacted than it is at the conventional sites. During winter storm events the organic sites soaked up water like a sponge and runoff started much later, approximately two inches of precipitation later, than at the conventional sites. During the first winter, 2007/2008, no measurable runoff occurred at all from the organic sites, which also meant no sediment or pesticide runoff from the organic orchards.

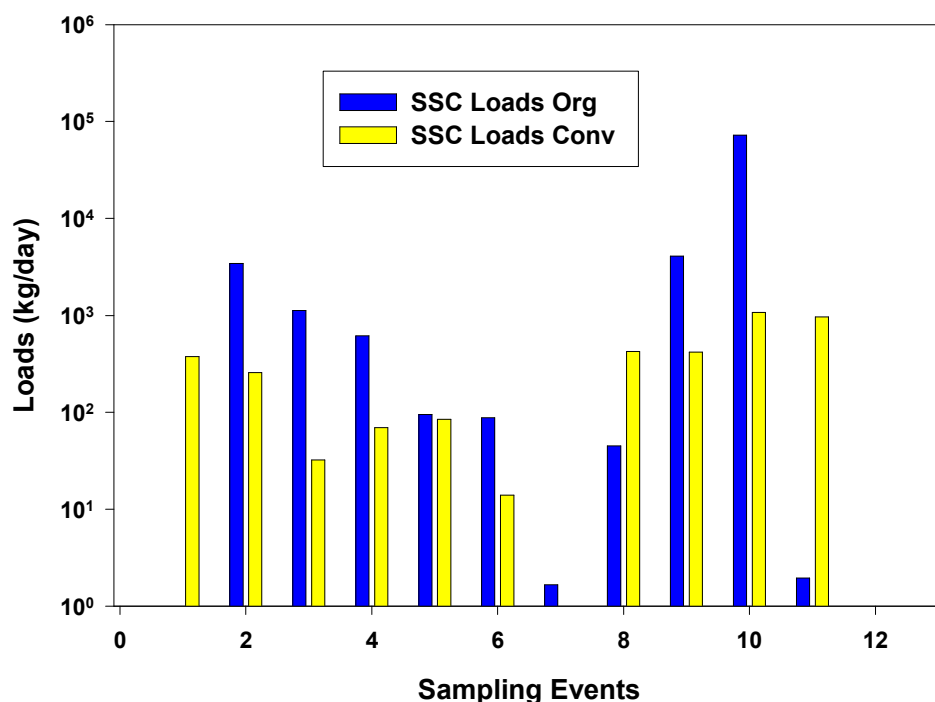


Figure 17. Suspended sediment loads in kilograms per day running of organic and conventional sites during the study period. Note the logarithmic scale.

5.3 Risk Quotients (RQ)

A different way of reporting the data is to compare the results regarding concern for an ecological risk instead of lethal or effect concentrations. An ecological risk assessment is conducted to evaluate the ecological risk of a certain pesticide by calculating the Risk Quotient (RQ). This risk characterization integrates exposure and effects data (Table 6) and states a potential for risk, expressed by the Level of Concern (LOC). The RQ is calculated as follows.

$$RQ = \text{Exposure} / \text{Toxicity}$$

- 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 ug/L that produces a specific measurable effect in 50% of the test organisms within the stated study time.

The measurable effect is 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 6. Toxicity data for detected pesticides. Source: Pesticide Action Network Pesticide Database <http://www.pesticideinfo.org/> Note range of units used (micrograms per liter, milligrams per liter, parts per billion)

Pesticide	Rainbow Trout	Bluegill Sunfish	Fathead Minnow	Water Flea	<i>Selenastrum</i>
Chlorpyrifos (insecticide)	LC50 9.0 ug/L	LC50 10 ug/L	LC50 330 ug/L	LC50 0.01 ug/L	
Diazinon (insecticide)	LC50 2.6 mg/L BCF 12 ug/L		LC50 15 mg/L	EC50 0.22 ug/L	EC50 3.7 mg/L
Dimethoate (insecticide)	LC50 6.2 mg/L	LC50 6.0 mg/L		EC50 80 ug/L	EC50 15 ug/L
Bifenthrin (insecticide, acaricide)	LC50 0.15 ppb	LC50 0.35 ppb	LC50 17.5 ppb (sheepshead minnow)	EC50 1.6 ppb	
Lambda-cyhalothrin (insecticide, acaricide)	LC50 0.24 ug/L	LC50 0.21 ug/L	LC50 0.81 ng/L (sheepshead minnow)	EC50 0.03 ug/L LC50 0.3 ug/L	
Esfenvalerate (insecticide)	LC50 0.3 ug/L	LC50 0.3 ug/L	LC50 0.2 ug/L (killfish)	LC50 1.0 ug/L	

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

RQ (chlorpyrifos) = $0.014/9 = 0.0016$ (rainbow trout) for organic sites

RQ (chlorpyrifos) = $0.014/0.01 = 1.4$ (**water flea**) for organic sites

RQ (chlorpyrifos) = $0.084/9 = 0.093$ (rainbow trout) for conventional sites

RQ (chlorpyrifos) = $0.084/0.01 = 8.4$ (**water flea**) for conventional sites

RQ (diazinon) = $0.01/26,000 = 0.000$ (rainbow trout) for conventional and organic sites

RQ (diazinon) = $0.01/0.22 = 0.05$ (water flea) for conventional and organic sites

RQ (dimethoate) = $0.42/60,000 = 0.000$ (bluegill sunfish) for conventional sites

RQ (dimethoate) = $0.42/80 = 0.01$ (water flea) for conventional sites

NO dimethoate detected at organic sites.

RQ (bifenthrin) = $8.5/0.15 = 7.9$ (**rainbow trout**) for **organic sediment**

RQ (bifenthrin) = $8.5/1.6 = 5.3$ (**water flea**) for **organic sediment**

RQ (bifenthrin) = $24/0.15 = 160$ (**rainbow trout**) for **conventional sediment**

RQ (bifenthrin) = $24/1.6 = 15$ (**water flea**) for **conventional sediment**

RQ (lambda-cyhalothrin) = $0.02/0.21 = 0.1$ (**bluegill sunfish**) for **conventional and organic sites**

RQ (lambda-cyhalothrin) = $0.02/0.3 = 0.1$ (**water flea**) for **conventional sites and organic sites**

RQ (esfenvalerate) = $0.01/0.2 = 0.05$ (killfish) for conventional sites

RQ (esfenvalerate) = $0.01/1 = 0.01$ (water flea) for conventional sites

No esfenvalerate detected at organic sites.

The Risk Quotient for each chemical was then compared to a unitless value, called the Level of Concern (LOC) (Table 7). The LOCs showed exceedances for three pesticides (bold above). The LOC was exceeded for chlorpyrifos for acute risk for water fleas at the organic sites (approximately three times higher) and at the conventional sites (approximately 17 times higher), indicating that there is a high threat to aquatic invertebrates at chlorpyrifos concentrations found at organic and conventional sites. Concentrations for lambda-cyhalothrin also reached but did not exceed the LOC for acute risk for restricted use pesticides, indicating that there is a potential ecological risk for bluegill sunfish and water fleas at the conventional and the organic sites. The third chemical exceeding the LOCs was bifenthrin in sediment at the organic (approximately by eight times for rainbow trout) and conventional sites (approximately by 160 times for rainbow trout). The bioavailability of pyrethroids in sediment is strictly dependent on the carbon content of the soil though and not all of the measured bifenthrin concentration was available for uptake by aquatic life.

Table 7. 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

The LOC calculation is considering a worst-case scenario since the maximum concentration detected in the entire period of the study is 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 technique used during this study missed the highest concentrations in runoff from the walnut orchards.

5.4 Nutrients

Nutrient concentrations in this study were relatively high and did not vary greatly between different farming practices. NO_x concentrations ranged from below the limit of detection to 12 mg/L at organic sites with an average of 5.7 mg/L (n=19), while the conventional sites had a NO_x concentration range of below the limit of detection to 190 mg/L with an average of 26 mg/L (n=15). The EPA's reference conditions for ecoregion 1, subregion 7 (California Central Valley) recommend 0.1 mg/L for NO_x in the ambient water quality criteria for rivers and stream (CRWQCB 2007). In contrast to other nutrient forms, TKN concentrations at the organic sites were significantly lower than at the conventional farming sites (p = 0.04). TKN concentrations at organic sites ranged from below the limit of detection to 15 mg/L with an average of 2.5 mg/L (n=19), while concentrations for TKN at the conventional sites ranged from below the limit of detection to 46 mg/L with an average of 8.1 mg/L (n=15). EPA reference conditions recommend TKN at 0.2 mg/L (US EPA 2001). EPA reference conditions are used as guidelines only and are not enforced regulations. However, concentrations within the range observed in this study indicate that nitrogen represents a potential water quality concern.

The extremely high NO_x concentration at the conventional site (190 mg/L) was confirmed by a duplicate sample (152 mg/L) but is over an order of magnitude higher than any NO_x value reported in the literature for various cropping systems. The highest NO_x concentrations reported were measured in soybean tailwater at approximately 20 mg/L (Strock et al. 2004). There is no apparent analytical reason for the high result to be qualified but it has to be taken into consideration that this NO_x peak could have been caused by one-time malfunctioning of the equipment dosing the nitrate granulate application since the median NO_x concentration for this site is much lower and was calculated at 1.7 mg/L. It is also possible that concentrated parts of granules were collected with the tailwater carrying a disproportionate amount of NO_x and accounting for the high result in the sample.

Additionally, a previous water sample collected at the same site indicated the highest TKN concentration (46 mg/L) out of all samples, which could indicate the application of urea at that time. 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 the highest pH value (9.4) in this study was also observed at this conventional site. Mechanical failure during application is the most likely explanation of the extremely high TKN and NO_x concentrations that do not represent the overall nutrient concentration in the tailwater of this site.

Ortho-phosphate (PO₄) concentrations ranged from below the limit of detection to 1.3 mg/L at organic sites with an average of 0.5 mg/L (n=19), while ortho-phosphate concentrations at conventional sites ranged from below the limit of detection to 1.3 mg/L with an average of 1.1 mg/L (n=15). Total phosphorus (TP) concentrations at organic sites ranged from below the limit of detection to 6.1 mg/L with an average of 1.8 mg/L while total phosphorus concentrations at conventional sites ranged from below the limit of detection to 7.0 mg/L with an average of 1.8 mg/L. EPA recommendations for TP are reported at 0.08 mg/L (US EPA 2001), also indicating that phosphorus represents a potential water quality concern at all of the sampled locations.

Since nutrient concentrations occasionally had high peaks, probably caused by sample collection shortly after fertilizer application to the orchard, the data is also presented as median concentrations and maximum concentration in Table 8a. This table was generated to minimize the bias of one extremely high concentration in the entire batch of samples collected. Average nutrient concentrations (Table 8b) at the conventional sites were two to four times higher compared to the organic sites, except for total phosphorus concentrations. Total phosphorus concentrations were slightly higher at the organic sites, probably due to the use of chicken manure that has a high content of total phosphorus.

Table 8a. Median Nutrient (and Maximum) Concentrations in mg/L for Organic and Conventional Walnut Orchards.

Nutrients	Organic Sites (mg/L)	Conventional Sites (mg/L)
Nitrite + Nitrate	0.13 (13.4)	1.73 (190)
TKN	1.29 (14.7)	2.67 (47)
Ortho-Phosphate	0.49 (1.3)	0.29 (7.6)
Total Phosphorus	1.00 (6.1)	0.57 (7.0)

Table 8b. Average Nutrient Concentrations in mg/L for Organic and Conventional Walnut Orchards.

Nutrients	Organic Sites (mg/L)	Conventional Sites (mg/L)
Nitrite + Nitrate	5.73	26.3
TKN	2.49	8.13
Ortho-Phosphate	0.54	1.08
Total Phosphorus	1.83	1.76

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 the organic and conventional walnut orchards 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 difference in nutrient input would be expected to come from differences in fertilizer applications. Sustainable soil management for organic walnut orchards includes the application of poultry manure and compost, while synthetic fertilizer is predominantly used on the conventional orchards.

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 NO_x concentrations in streams of mixed land-use and agricultural regions of the Sacramento River Basin were similar compared to the concentrations observed at the organic sites and approximately nine times higher relative to the concentrations observed at the conventional sites (Figure 18). According to USGS studies, concentrations in this watershed tend to be lower relative to those measured in other areas of the United States with similar fertilizer applications within their watersheds (USGS 2005).

The NO_x to TN (total nitrogen) ratios would be expected to be lower at the organic sites compared to the conventional sites due to a higher organic portion of the applied fertilizer but only 22% of the organic nutrient samples had lower NO_x to TN ratios. The remaining 78% of the samples had a slightly higher ratio. However, the NO_x concentrations that peaked at 190 mg/L at the conventional sites were on average more than three times lower at the organic sites. The organic sites had slightly lower PO₄ to TP ratios in 55% of all nutrient samples, additionally indicating a higher organic content in the fertilizer. Even though the PO₄ concentrations were on average almost twice as high at the conventional sites compared to the organic sites, the PO₄:TP ratio at the organic sites is only approximately 4% lower.

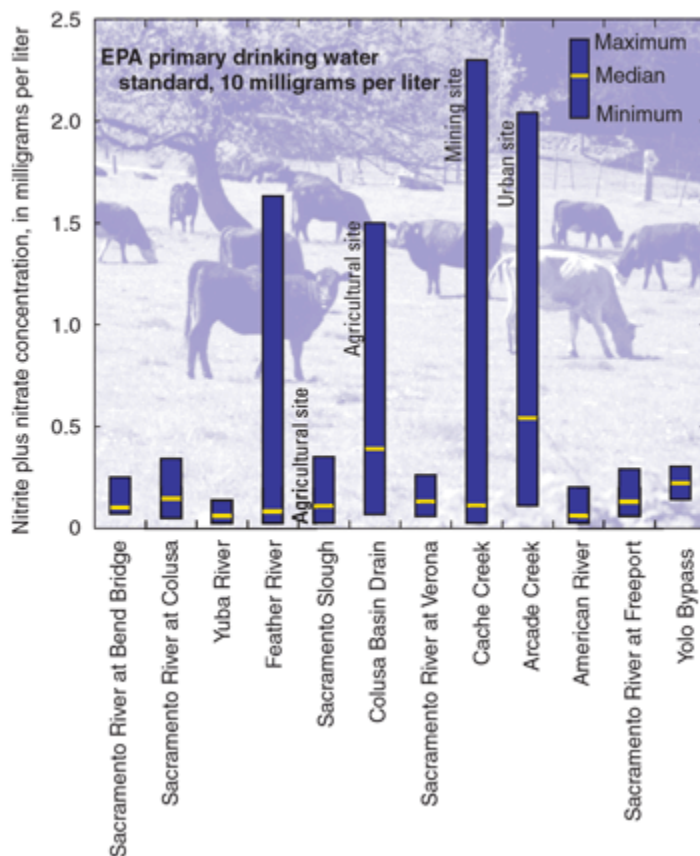


Figure 18. Concentrations of nitrite and nitrate at sites throughout the Sacramento River watershed. The highest concentrations were measured at mining and urban sites (USGS 2005).

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 streamflow. 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 instream processes remove nutrients, such as algal growth that incorporates nutrients in algae biomass.

In general, the majority of samples (63%) collected in this study had low nitrogen to 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 should particularly be of concern when the drainage ditch empties into a water body under low-flow conditions. Integrated research programs are required to generate predictive models capable of quantifying key variables at appropriate spatial and temporal scales to better understand the success of corrective actions for this problem. Many uncertainties still remain about the pathways leading to cyanobacterial blooms and how important N:P ratios are under site specific conditions.

5.5 Pesticides and Water Used in Organic vs. Conventional Farming Practice

Differences in water used for irrigation of the orchards showed that the organic sites used 25 to 100% more irrigation water compared to the conventional sites (Table 9). Since the organic sites have a much higher amount of organic matter in the soil they are more porous than the conventional sites. The high infiltration rate that helps to reduce or eliminate runoff completely off the sites during winter rain storms causes a problem during summer irrigation when up to twice as much water has to be applied to achieve uniformity in the flow pattern across the orchards.

Table 9. Comparison of water, fertilizer, and pesticides used at organic and conventional sites per year, according to personnel communication with farmers.

Parameter	Organic Sites	Conventional Sites
Water used per year	400,000 - 625,000 L/ha	300,000 L/ha
Fertilizer (chicken or turkey manure)	260 - 280 kg/ha	-
Fertilizer (ammonium sulfate, AmSO ₄)	-	6.8 kg/ha
Copper hydroxide	5.8 – 11 kg/ha	-
Spinosad	Applied per tree	-
Surround WP	68 – 135kg/ha	-
Chlorpyrifos	-	5.5 L/ha

Turkey or chicken manure was applied to the organic orchards in March while the synthetic fertilizer ammonium sulfate was applied in form of a granular material that was then watered into the conventional orchard in April and June. Organic manures contain variable proportions of total nitrogen in inorganic forms immediately available to the walnuts. The organic forms must be mineralized before they become available. Both, rate and time, of microbial breakdown will be optimized when manure is applied regularly, because of an increase in soil organic matter. Hence, an increased amount of nitrate can be mineralized (Johnston 1994). A study that tested silty clay loams (similar to the soil in the GOP study area) in the UK found that manure treated soil contained 50 to 100 kg/ha more mineral nitrogen than fertilizer treated soil with a potential for leaching and loss (Powlson et al. 1989).

Spinosad is a Dow Agrosiences product (GF-120) that is applied to the trunks and the main limbs of a walnut tree by handgun. Its formulation is syrup like and contains bait that attracts Husk flies. The active ingredient is derived from a naturally occurring soil dwelling bacterium called *Saccharopolyspora spinosa*. Spinosad was applied once at the organic sites in August.

Surround WP is made from 95% kaolin clay, a naturally occurring mineral. When applied to fruit trees or other crops it forms a white film. Surround WP suppresses a wide range of pests, especially those which damage fruit crops including pears, apples, grapes, berries, and some vegetables through forming a barrier film that acts as a broad spectrum crop protectant.

Copper hydroxide is used in organic farming as an alternative to fungicides and nematocides. It was applied twice in April at the monitored organic sites by helicopter. Two applications of chlorpyrifos were reported by the conventional grower, one in July, one in August.

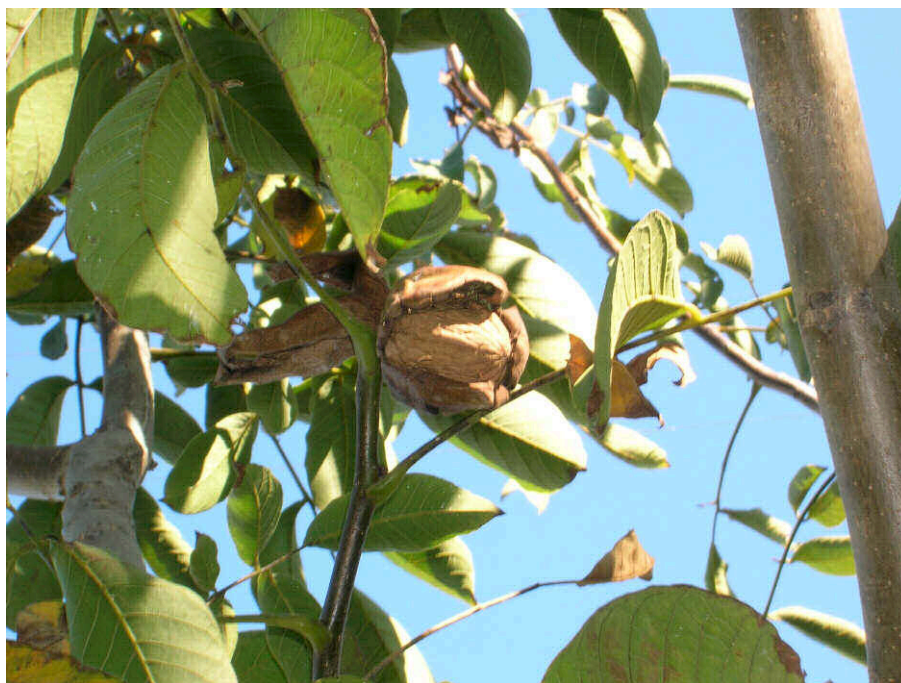


Figure 19. Walnuts on tree prior to harvest.

5.6 Pathogen Indicators

Pathogen indicators measured during this study were total coliform, fecal coliform, and *E. coli*, also referred to as Fecal Indicator Bacteria (FIB). This project was started right after the *E. coli* contamination in packed organic spinach killed three and sickened over 200 people in California. However, the results for concentrations in water in the present study showed no statistically significant differences ($p > 0.05$) in the distribution of any of the FIBs at the organic and conventional sites (Figures 20 to 22). There does not seem to be a higher risk for the presence of pathogens through the use of manure versus synthetic fertilizer. Since personnel communication with the farmer indicated that no manure was used in addition to synthetic fertilizer at the conventional sites, the high FIB concentrations are challenging to interpret. When the first flush sample results were omitted from the analysis to achieve a better seasonal comparison for the time period when fertilizer was actually applied, there still was no statistically significant difference observed between the two farming practices. Other contributions to the orchards could have been human and animal waste.

E. coli

E. coli is an indicator microorganism for other pathogens that may be present in feces. *E. coli* are not always confined to the intestine, and their ability to survive for brief periods outside the body makes them an ideal indicator organism to test environmental samples for fecal contamination (Carson et al. 2001). While there was no runoff at the organic sites during the 2007/08 wet season and pathogen concentrations equaled zero, *E. coli* concentrations were highest at the organic sites during the August 2007 and April 2008 sampling events. For all other sampling events, concentrations of *E. coli* were within a similar range at the organic and the conventional sites (Figure 20a and 20b).

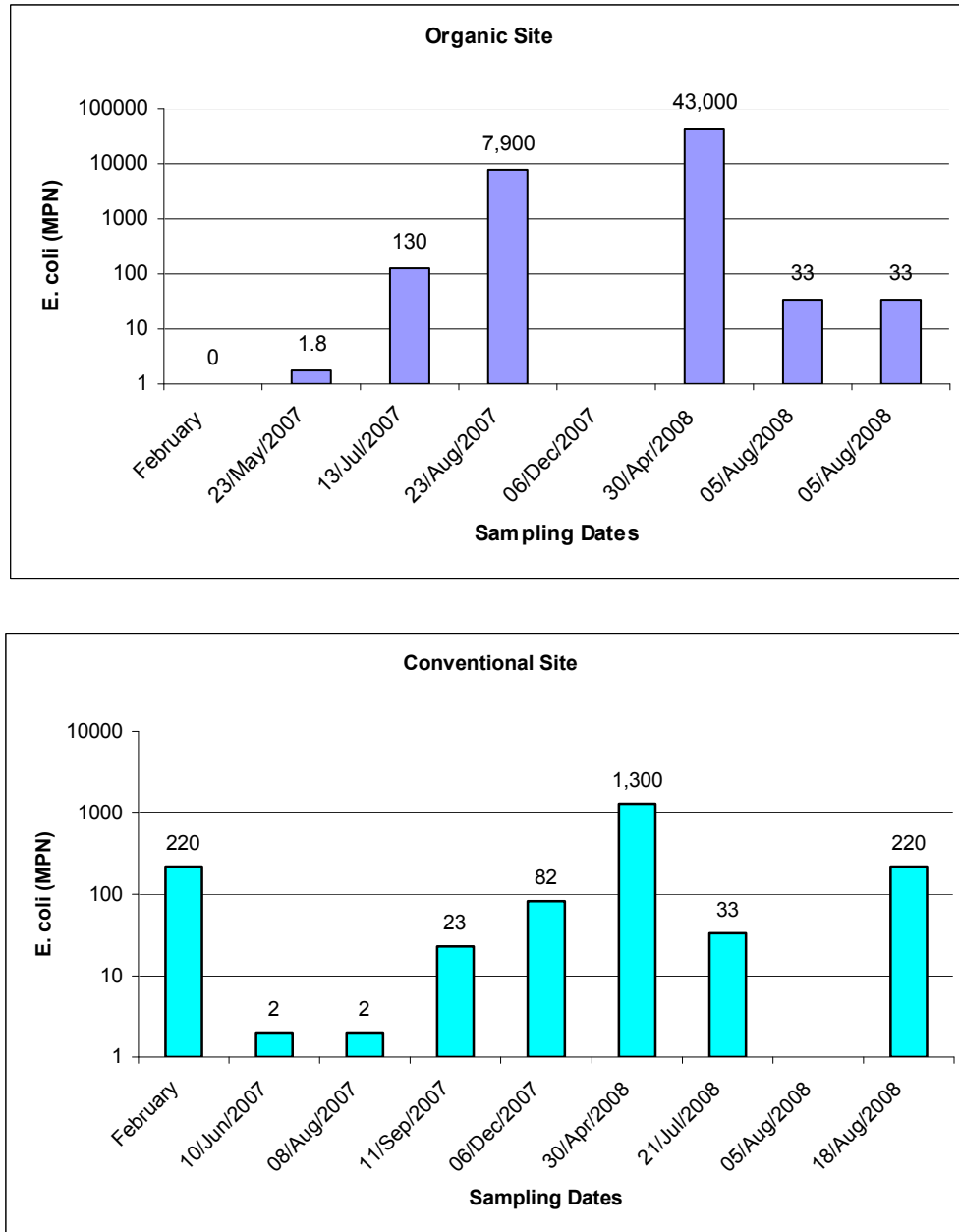


Figure 20a and 20b. *E. coli* concentrations at organic (a) and conventional (b) sites during the course of this study. Note logarithmic scale. MNP = most probable number.

Theoretically, it would take the presence of approximately 140 humans (Table 10) in each orchard to reach an *E. coli* concentration similar to what was observed in this study, assuming complete dilution of *E. coli* and no attenuation for the distance the water travels to the tailditch. Similarly, it would take the “metabolic presence” of 1,980 turkeys on a daily basis to account for the measured *E. coli* concentration without the application of manure. This example is only intended to demonstrate how high the FIB concentrations were in the measured runoff based on human and bird fecal production.

Table 10. Coliform sources and production.

Creature	Fecal Production (g/day)	<i>E. coli</i> cells per g feces	<i>E. coli</i> load (cells/day)
Human	150	1.3×10^7	1.9×10^9
Cow	23,600	2.3×10^5	5.4×10^9
Hog	2,700	3.3×10^6	8.9×10^9
Sheep	1,130	1.6×10^7	1.8×10^{10}
Duck	336	3.3×10^7	1.1×10^{10}
Turkey	448	3.0×10^5	1.3×10^8
Chicken	182	1.3×10^6	2.4×10^8
Gull	15	1.3×10^8	2.0×10^9

Source: Personnel communication with Dr. Wuertz, UC Davis.

Fecal coliform

Fecal coliforms include the genera that originate in feces, *Escherichia*, as well as genera that are not of fecal origin, *Enterobacter*, *Klebsiella*, and *Citrobacter* (Carson et al. 2001). Spreading manure as fertilizer can contribute to fecal coliform contamination. Fecal coliform concentrations were highest at the organic sites during the April 2008 sampling event and second highest at the conventional sites in August 2007 (Figure 21a and 21b). In comparison, fecal coliform concentrations in water used for contact recreation activities must not exceed 400 MPN/100 ml (CRWQCB 2007).

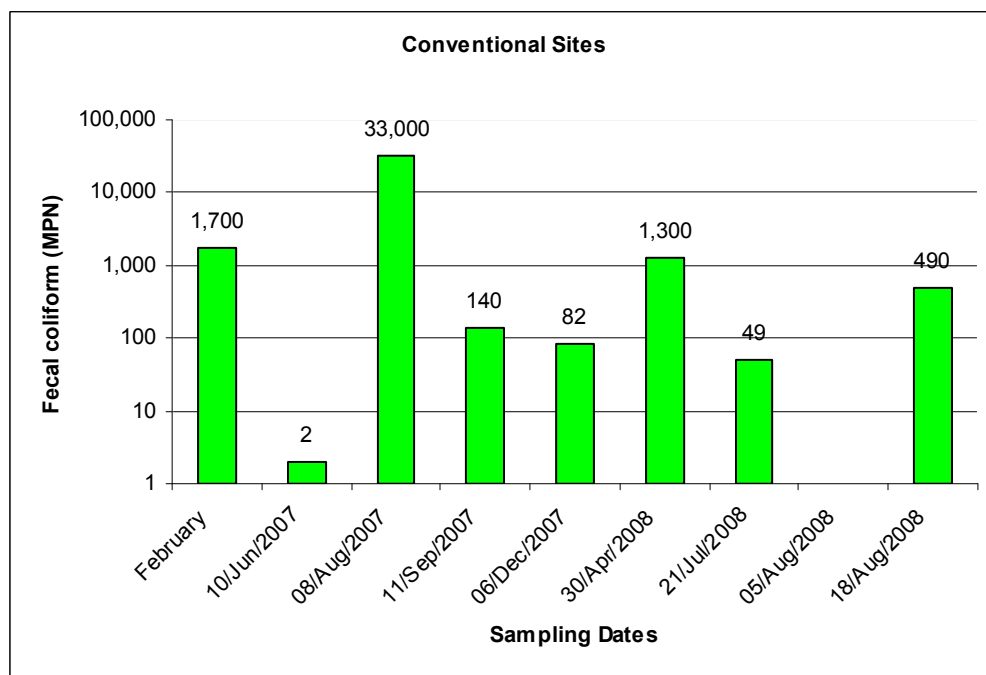
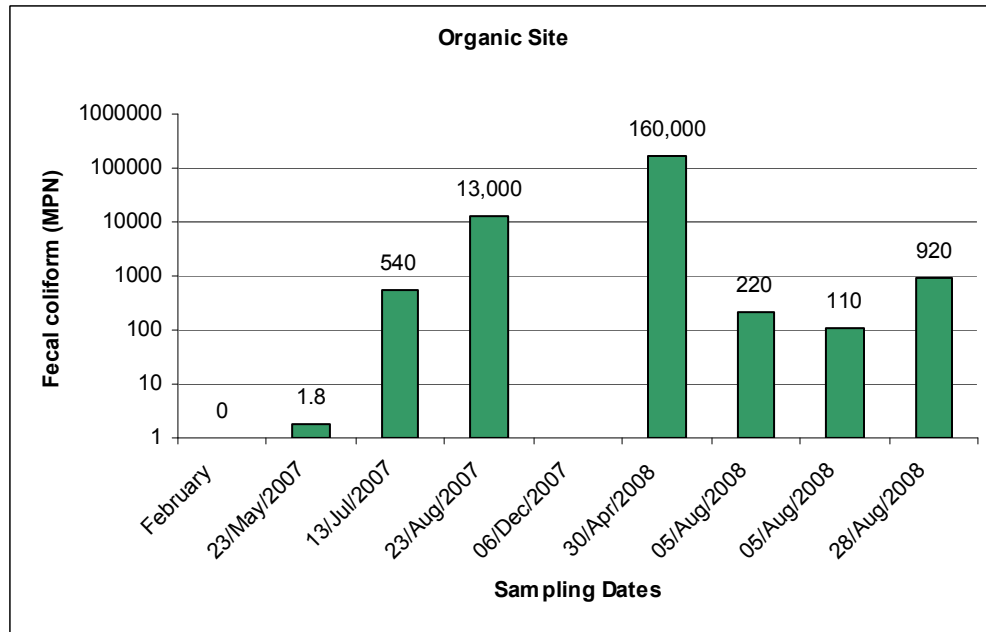


Figure 21a and 21b. Fecal coliform concentrations at organic (a) and conventional (b) sites during the course of this study. Note logarithmic scale. MNP = most probable number.

Total coliform

Total coliform are a group of closely related, mostly harmless bacteria that live in soil and water as well as the gut of animals (Carson et al. 2001). The extent to which total coliforms are present in the source water can indicate the general quality of that water

and the likelihood that the water is fecally contaminated. Total coliform concentrations were highest (>160,000 MPN) at the conventional sites during the first winter storm, when there was no runoff at the organic site, and during the December 2007 and April 2008 sampling events. Total coliform concentrations at the organic sites reached the same magnitude only once, during the April 2008 sampling event (Figure 22a and 22b). For statistical analysis, a value of 160,000 was used when the result for the water sample was >160,000 MPN (the laboratory does not dilute the samples), even though the number was not directly quantifiable. No statistically significant difference between the different farming practices was observed.

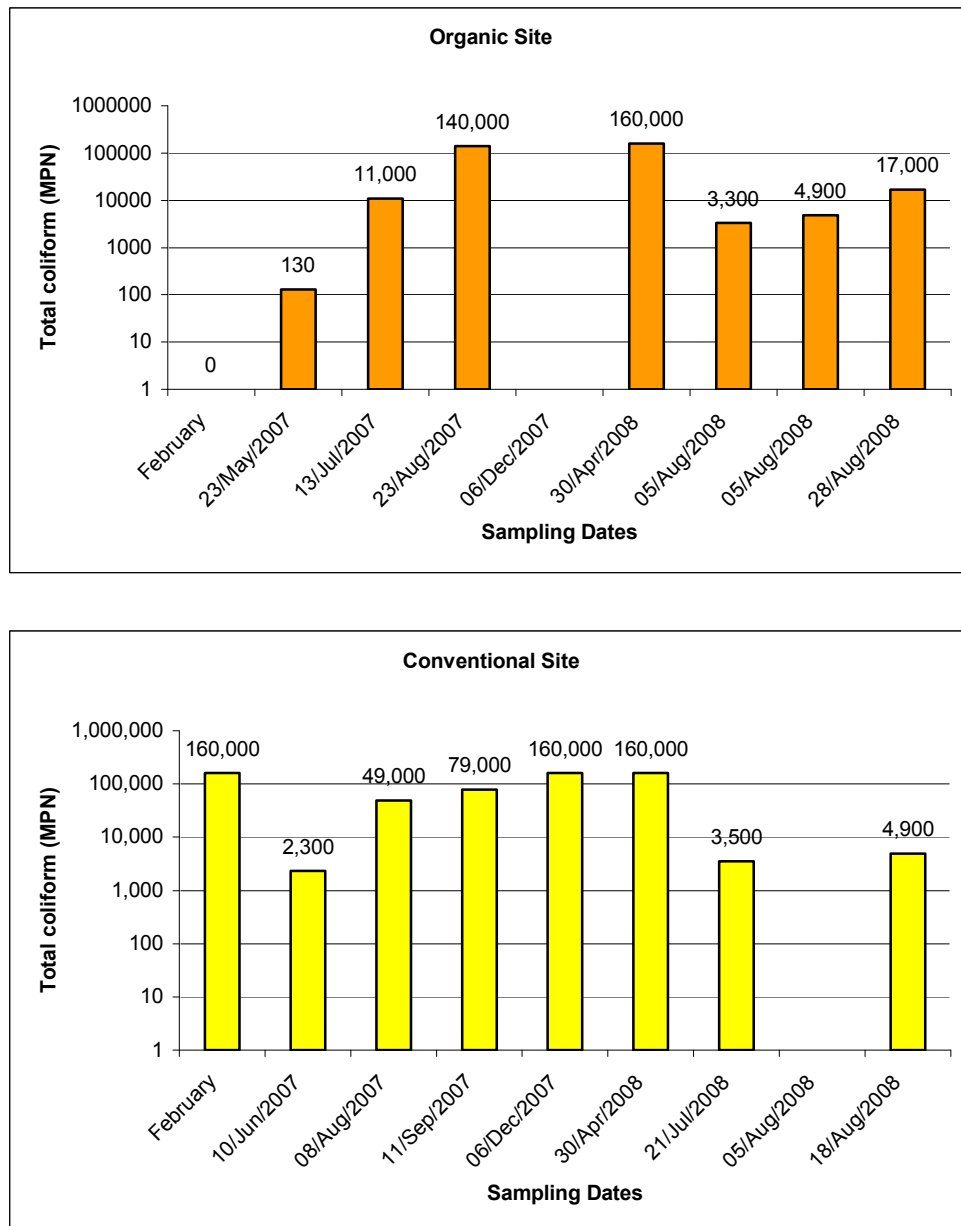


Figure 22a and 22b. Total coliform concentrations at organic (a) and conventional (b) sites during the course of this study. Note logarithmic scale. MNP = most probable number.

Total coliform concentrations in this study were almost consistently very high with very little seasonal changes that could be attributed to manure applications alone. The decay of FIBs would be expected within approximately three to four weeks of application (Anderson et al. 2005), but since there was a more continuous high FIB level, other sources of microbial contamination need to be taken into consideration for the monitored sites. Fecal source tracking of water samples would be an option to narrow down the origin of the contamination. Sources can be tracked down to human, seabird, cattle/horse, and dog waste.

5.7 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 0.01 mg/L at a conventional site in August to 11.5 mg/L at an organic site in April. Within this range, concentrations fluctuated without exhibiting any significant patterns at the five sites. A difference in dissolved oxygen concentrations due to each farming practice is therefore unlikely. A total of five measurements out of 28 were below 5 mg/L during the study period, two at organic sites and three at conventional sites.

Electrical Conductivity (EC) is a measure of how well water can conduct an electrical current. Conductivity increases with increasing mobility of ions. These ions, which come from the breakdown of compounds, 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 0.06 mS/cm at an organic site in November to 1.93 mS/cm at a conventional site in June. Measurements throughout the sampling period were fairly consistent and did not exhibit any significant differences associated with farming practices. Salinity ranged from 0.01 ppt at an organic site in January to 0.96 ppt at a conventional site in June with no particular pattern exhibited for the different farming practices.

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 considered 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 7.4 at a conventional site to 9.4 at an organic site.

Temperature of water is an important factor for aquatic life. It controls the rate of metabolic and reproductive activities, and determines which aquatic biota 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 9.0°C

at an organic site in January to 36.5°C at a conventional site in August. But again, these ditches are sometimes very shallow, often minimally moving, temporary water systems.

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 0.1 NTU at a conventional site in August to 8,900 NTU at a conventional site during a rain storm in February, while the average flow during these turbidity measurements was three times higher at the organic sites. The turbidity fluctuation exhibited no consistent change related to different farming practices over the course of this study. The recommended turbidity according to EPA's reference conditions for rivers and streams is 5.2 NTU (US EPA 2001).

Hardness is a measurement of the concentration of divalent metal ions. In this study, hardness was measured as a concentration of calcium salt CaCO_3 . Water hardness concentrations varied from 37.3 mg CaCO_3/L at a conventional site in February to 750 mg CaCO_3/L at an organic site in July. 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 during 93% of the sampling events (at organic and conventional sites) bioavailability of pesticides was likely reduced in the ambient water. Insecticides, especially shown for pyrethroids 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 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 an organic site in August to 45 mg/L at a conventional site in February with a five times higher average DOC concentration for all conventional sites compared to the organic sites.

6. Conclusion

Even though organic farmers did not use the synthetic pesticides that were monitored during the present study the water and sediment samples collected from the organic orchards were not pesticide free. The chemical concentrations found, especially for chlorpyrifos and lambda-cyhalothrin in water samples and bifenthrin in sediment samples, were above the Level of Concern for aquatic life.

Nutrient concentrations in the present study were extremely high but in general 50-80% lower at the organic sites compared to the conventional sites with the exception of total phosphorus. Total phosphorus was slightly higher at the organic sites, possibly due to the use of chicken manure, which has high phosphorus content.

No increased risk for the presence of pathogens indicators in water samples was detected during the course of the study. Organic as well as conventional orchards exhibited a similar distribution of *E. coli*, fecal coliform, and total coliform in runoff water with a peak of concentrations in April of 2008. Especially at the organic sites, concentrations were lower in August of 2008, indicating a decline of pathogen indicators as walnut harvest approached.

6.1 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 accomplished 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. Prolonged time periods between chemical application and orchard irrigation will contribute to the decrease in 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.

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