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Residues and Toxicity of Esfenvalerate and Permethrin in Water and Sediment, in Tributaries of the Sacramento and San Joaquin Rivers, California, USA

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In the Sacramento and San Joaquin valleys organophosphate (OP) insecticides are applied on tree crops such as stone fruits and nut trees between late-December and February when trees are dormant. This coincides with seasonal rainfall, thus increasing the likelihood of insecticides to move offsite to surface water, either dissolved in water or sorbed to sediment. Various monitoring studies conducted by the Department of Pesticide Regulation (DPR) and the U.S. Geological Survey (USGS) have shown that dormant spray OPs such as diazinon and chlorpyrifos are frequently detected during dormant-spray seasons (Domagalski et al. 1997; Kratzer 1998). Use of OPs during the dormant-spray season has been steadily decreasing, but they are being replaced by pyrethroids, specifically esfenvalerate and permethrin (Epstein et al. 2000). While pyrethroids have the potential to be acutely toxic to aquatic species, their physio-chemical properties indicate that they are primarily associated with sediment in aquatic systems. Though sorption to sediment mitigates their acute toxicity by reducing short-term bioavailability, the effect is poorly understood, and data on long-term effects on chronic toxicity is very limited. It has been suggested that there is a potential for acute toxicity to sediment-dwelling aquatic organisms, or those that live just above the sediment (Muir et al. 1985).

The primary objectives of this study were to determine if pyrethroid insecticides, particularly esfenvalerate and permethrin, are moving offsite into surface waters during winter storm events, and to evaluate offsite concentrations and acute toxicity. An additional objective was to obtain more data on OP insecticides and selected herbicide residues in surface water.

MATERIALS AND METHODS

Monitoring sites were chosen that reflect areas with the heaviest historical and current applications of esfenvalerate and permethrin through the dormant-spray season. The sites consisted of Wadsworth canal, which flows into the Sacramento River (Sutter County, CA) and Del Puerto Creek, which flows into the San Joaquin River (Stanislaus County, CA).

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Background samples were collected in December 2002, prior to the beginning of dormant-spray applications. Samples were collected in January, February, and March 2003. Water samples were collected in 1-L amber bottles and were analyzed for the following pesticides: pyrethroids (esfenvalerate and permethrin), organophosphates (Azinphos methyl, Chlorpyrifos, Diazinon, DDVP [dichlorvos], Dimethoate, Disulfoton, Eethoprop, Fenamiphos, Fonofos, Malathion, methidathion, Methyl Parathion, Thimet [Phorate], Profenofos, and Tribufos), and herbicides (Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, DEA [deethylatrazine], ACET [deisopropylatrazine or deethylsimazine], and DACT [didealkylated triazine]). Water samples were also analyzed for total suspended sediment, and bioassays were conducted for acute toxicity to the sensitive aquatic species *Ceriodaphnia dubia*.

In addition to background and storm event sampling, sediment samples were collected seven and fourteen days after each storm event. Sediment samples were analyzed for pyrethroids (esfenvalerate, permethrin, bifenthrin, lambda cyhalothrin, cyfluthrin, and cypermethrin). Samples were collected using either a hand scoop or a 60-cm long by 5-cm diameter, polycarbonate cylindrical tube. The top 2.5 cm of submerged sediment was collected near the water's edge and placed into a 0.55-L, clear glass jar.

Dissolved oxygen (DO), pH, specific conductivity (EC), and water temperature were measured *in situ* at each site at the time of each grab sample. Rainfall and discharge data (where available) were also gathered for the study areas.

Pyrethroid whole water samples, including any suspended sediment, were extracted with hexane: acetone (80:20, v/v). Sample bottles were rinsed with extraction solvent and added to the sample extracts for analysis. Extracts were concentrated using a Brinkmann R110 rotary evaporator (Brinkmann, Westbury, NY), and analyzed using a Hewlett-Packard model 5890 gas chromatograph equipped with a HP-1 column (Hewlett Packard, Avondale, PA) and an electron capture detector (ECD). Pyrethroid analysis results are reported on a whole sample basis (water plus suspended sediment). Reporting limits are 0.05 μg/L. Organophosphate samples were extracted with methylene chloride and the extract was passed through sodium sulfate to remove residual water. The anhydrous extract was evaporated to near dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract was then analyzed by a Hewlett-Packard model 5890 gas chromatograph (Hewlett Packard, Avondale, PA) equipped with an Rtx OP Pesticides column (Restek, State College, PA) and a flame photometric detector (FPD). Reporting limits are 0.03 to 0.05 μg/L.

For herbicide analysis, the water samples were passed through two Oasis MCX cartridges (Waters, Millford, MA) connected in tandem. The cartridges were then eluted under vacuum with 5% ammonium hydroxide in methanol. The eluant was filtered through a nylon Acrodisc 0.2 micron filter (Gelman Sciences, Ann Arbor,

MI), concentrated, reconstituted in 75/25 water/methanol and analyzed by a ThermoQuest/ThermoSeparation HPLC with a Finnigan LCQ Deca mass spectrometer (Finnigan/ThermoQuest, San Jose, CA). Reporting limits are 0.05 μg/L.

Quality control (QC) consisted of 10% of total samples as field blanks and blind spikes. In addition, there were 278 matrix spikes analyzed and compared to established warning and control limits for each analytical method.

Acute toxicity tests were performed in undiluted, unfiltered sample water using 96-hour, static-renewal bioassays with the cladoceran *C. dubia* (U.S. EPA 2002a). Significant toxicity is defined as a difference of 30% or greater between survival of test organisms and control organisms. An additional requirement is that control organism survival must be equal or greater than 90%.

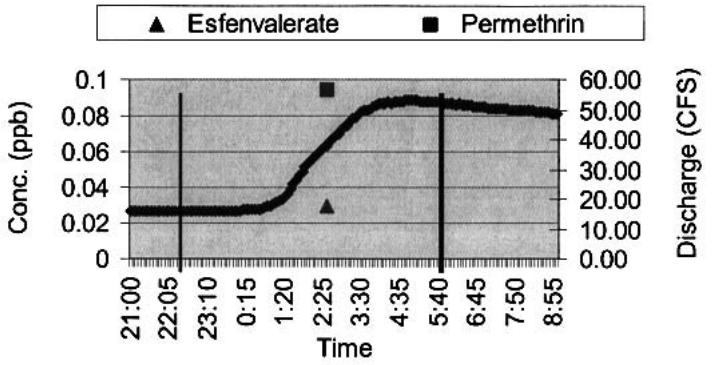
Freely dissolved phase pyrethroid concentrations were estimated in each water sample and compared to available water-aquatic toxicity data. The estimation procedure yielded a probabilistic estimate of freely dissolved pyrethroid concentration. The probabilistic estimate is calculated using Monte Carlo techniques by assuming organic carbon-based sorption equilibrium between the pyrethroid sorbed to suspended sediment and that freely dissolved in the water sample (Spurlock et al., 2003).

RESULTS AND DISCUSSION

The first sampling event occurred in January 2003 at Wadsworth canal. During this period total rainfall for this area was 1.0 cm (UCD IPM 2003). Water quality measurements were relatively constant throughout the sampling period. Suspended sediment samples ranged from 28.0 to 173.2 mg/L. There were no pyrethroid detections. Approximately 153 kg of the active ingredient esfenvalerate and 33 kg of permethrin had been applied in Sutter County during the months of December 2002 through January 2003. None of the other four pyrethroids analyzed had been applied during that period.

The second storm event at Wadsworth Canal occurred in February 2003. Rainfall during this period was approximately 2.4 cm (UCD IPM 2003), and discharge ranged from 15.78 cfs (feet^3/second) to 52.97 cfs (*CVRWQCB* 2003). Suspended sediment ranged from 7.6 to 3114.4 mg/L, peaking at the sixth hour. There was one esfenvalerate detection (trace) and one permethrin detection (0.094 μg/L), both occurring at the sixth hour of the 9-hour sampling period. It is evident that peak runoff concentrations were obtained at the time of peak discharge (55 cfs) and peak total suspended sediment (TSS) levels (800 mg/L; Figure 1).

Approximately 241 kg of the active ingredient esfenvalerate and 33 kg of permethrin had been applied in Sutter County during the months of December 2002 through February 2003. None of the other four pyrethroids analyzed had been applied in that county during that period.



The sampling period is represented by the time between the two black lines.

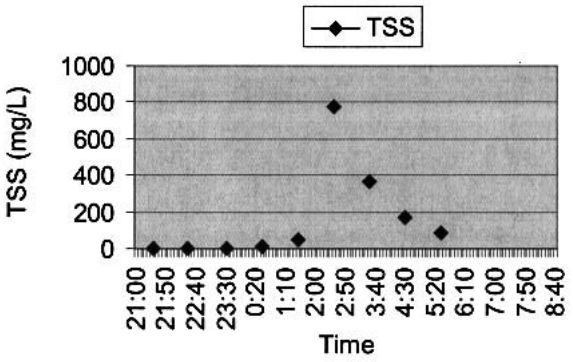
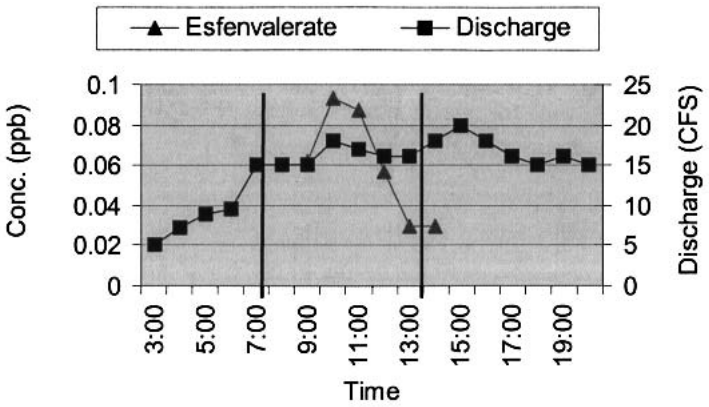


Figure 1. Pyrethroid detections, discharge and TSS at Wadsworth Canal, February 16, 2003.

Using the permethrin detection of 0.094 µg/L the estimated dissolved phase concentration at that time was 0.00699 µg/L to 0.03229 µg/L. This is the 10 to 90th percentile range, with the 50th percentile range being 0.01503 µg/L. At the sixth hour sampling, the estimated dissolved phase concentration was 0.015 µg/L, which was well below the *C. dubia* LC50 of 0.55 µg/L (Mokry and Hoagland 1990). However, the *C. dubia* bioassay results demonstrated that the sample was acutely toxic (0% survival). Diazinon was also detected at this time, though the concentration was also less than the *C. dubia* LC50 (0.436 µg/L; CDFG, 1998). Therefore, permethrin or diazinon alone was apparently not responsible for the observed toxicity. The following hour's sample showed 60% survival of C. dubia. At this time there were no pyrethroid detections, but diazinon was detected at 0.176 µg/L. The presence of pyrethroids or OPs below the reporting limit is possible. The observed toxicity may have been due to the presence of unmeasured constituents or the possible additive or synergistic interactions between measured constituents.

Denton et al. (2003) reported that the combined effect of diazinon and



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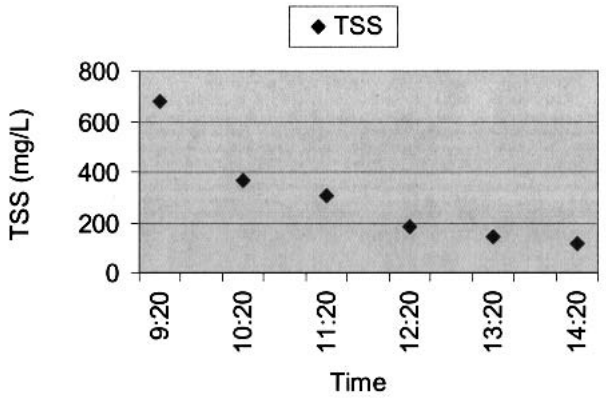

Figure 2. Pyrethroid detections, discharge and TSS at Del Puerto Creek, March 15, 2003.

esfenvalerate on larval fathead minnows were greater than additive, and suggested that synergism was occurring. The cause of toxicity here cannot be determined.

Del Puerto Creek was sampled only one time in March 2003 due to the lack of rainfall in this area. Dissolved oxygen and pH were relatively constant throughout the sampling period. Temperature and EC fluctuated, ranging from 13.7° C to 19.8 ° C, and 223.5 μS and 389 μS, respectively. Suspended sediment ranged from 452.0 to 2708.8 mg/L, peaking at the first hour. Total rainfall for this area during this period was 2.2 cm (UCD IPM 2003). Discharge ranged from less than 5 cfs to approximately 20 cfs over the sampling period (USGS 2003; Figure 2). Peak runoff concentrations were obtained at the time of peak discharge and peak TSS levels (Figure 2).

Esfenvalerate was detected in all six samples collected during this event, with detections ranging from trace amounts to 0.093 μg/L. The estimated dissolved phase concentrations of esfenvalerate ranged from 0.00346 μg/L to 0.03728 μg/L. Bioassays for *C. dubia* demonstrated acute toxicity in all six samples (0% survival). *C. dubia* LC50, for esfenvalerate is unknown. Major water chemical conditions (dissolved oxygen and pH) were within tolerable ranges for *C. dubia* (U.S. EPA 2001, 2002b). Chlorpyrifos concentrations exceeded the *C. dubia* LC50 of 0.038 μg/L (CDFG 1999) in all but the initial sample in which chlorpyrifos was not detected. This alone can account for much of the observed toxicity. The presence of chlorpyrifos in the initial sample at a level below the method detection limit is possible. In addition, diazinon was detected in all samples, although always at concentrations below the *C. dubia* LC50 (0.436 μg/L). Other OPs detected included dimethoate, ethoprop, and methyl parathion.

The presence of these OPs along with the pyrethroid esfenvalerate, in every sample, suggests that additive or synergistic interactions may have contributed to the observed toxicity as well. The following herbicides were also detected, simazine, diuron, bromacil, hexazinone, metribuzin, norflurazon, and ACET. Bifenthrin was detected in one sediment sample at a concentration of 0.0242 μg/g. A recent California study reported that acute toxicity to *Hyalella azteca* from most sediment pyrethroids is expected to occur in a range of 0.002 - 0.02 ug/g (Amweg et al. 2004). Although sediment bioassays were not performed as part of this study, sediment toxicity would be expected. There were no additional pyrethroid detections in any sediment samples collected at this site.

In Stanislaus County a total of 1110 kg of pyrethroids (active ingredient) had been applied during the months of December 2002 through March 2003. Total kilograms per pyrethroid are as follows: cyfluthrin-61 kg, cypermethrin-2 kg, esfenvalerate-344 kg, lambda-cyhalothrin-283 kg, permethrin-420 kg, and bifenthrin-0 kg.

It is evident that pyrethroids are able to move offsite during a rain induced runoff event. In this study typical concentrations of esfenvalerate and permethrin ranged from trace to 0.094ug/L. Discharge in the tributaries sampled reached a maximum of approximately 55 cfs and TSS was as high as 3114.4 mg/L. Due to the physical characteristics of pyrethroids, their tendency to sorb to suspended sediment (organic carbon), and the low concentrations detected, it is probable that measurable concentrations may not be detected in a larger river system such as the Sacramento or San Joaquin River.

Concentrations detected were below acute toxicity LC50 levels, yet, mortality of the test species *C. dubia* was often times 100%. A significant number of OPs were detected as well which may have contributed to the observed toxicity. Detections of diazinon and chlorpyrifos often exceeded DFG water quality standards, and chlorpyrifos levels often exceeded LC50 acute toxicity levels for the test species *C. dubia*. Toxicity may have also been due to possible additive or

synergistic interactions occurring, or possible toxic unmeasured constituents being present.

Bioavailability of pyrethroid pesticides in water and sediment is still not clearly understood. Some studies indicate acute toxicity to water column organisms is sharply reduced by sorption to suspended sediment; hence bioavailability is limited to that which is in the dissolved phase (Maund et al. 1998). Others indicate that sediment-bound pesticides, such as pyrethroids, may be bioavailable to benthic organisms, and toxicity is possible (Conrad et al. 1999; Pereira et al. 1995). Consequently it would be prudent to conduct sediment toxicity testing in addition to sediment chemical analysis in future hydrophobic pesticide studies.

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