

Persistence of pyrethroid insecticides in farm soils

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INTRODUCTION

Pyrethroid insecticides are widely employed in California agriculture to control a variety of crop pests. Recently, pyrethroid residues have been detected in agriculture-affected drains and streams in the Central Valley, indicating that off-site transport of these compounds is occurring (Weston et al., 2004). Due to the strong hydrophobicity of pyrethroids, this transport is mediated by movement of fine particles in irrigation return flows or rainfall events (Gan et al., 2005). While irrigation in fields occurs throughout the growing season for many crops, the timing and volume of water applications can be managed. Loss of suspended sediments and associated pesticide residues due to irrigation return flow can potentially be reduced through proper irrigation management. Storm events, however, typically occur from December through March and are less easily managed due to the large volume of runoff water. Therefore, the timing of pyrethroid application relative to rainfall events, and the rate of pyrethroid degradation in the field soils ultimately determine the amount of pesticide susceptible to off-site transport.

Nearly all studies on the persistence of pyrethroids in farms soils are unpublished proprietary data collected by pesticide manufacturers. These data have been compiled and summarized by Laskowski (2002), with only summary information presented regarding methods and test conditions. Additionally, most degradation studies were conducted with spiked sediments in the laboratory or under controlled greenhouse conditions. In these past studies, degradation rates in soils for nine pyrethroids ranged from half-lives of 3.3-96.3 d under aerobic conditions, and 5-425 d in anaerobic soil. These studies have not addressed potential changes in pesticide bioavailability that may occur during these time periods. Many hydrophobic organic contaminants have been shown to become less bioavailable with increasing contact time between the contaminant and the particles to which they are adsorbed. Thus, the risk of aquatic toxicity may be diminished with time, even if the concentration as measured by conventional chemical means were to remain unchanged.

The current study was intended to provide data regarding pyrethroid persistence in soils under real-world conditions, as well as provide information on changes in bioavailability for residues remaining in the soils. These data are needed to accurately assess the potential risks and environmental impact of increasing pyrethroid use in agriculture, as well as develop farm management practices that reduce these risks.

MATERIALS AND METHODS

General scope of the project

This work was supported by a Pesticide Research, Identification of Source and Mitigation (PRISM) grant to the Sacramento River Watershed Program (SRWP), which provided for the study of pyrethroid persistence in two farm soils with different crops, land-use practices, and pyrethroid use. One farm under study produces tomatoes, an annual crop where fields are disced after harvest, presumably burying and diluting any pyrethroid residues remaining at the end of the season. The second farm produces rice and the fields are flooded for the duration of the growing season, allowing measurement of pyrethroid persistence under aquatic conditions. Funding from the U.S. EPA to the Sacramento Regional County Sanitation District (SRCSD) under a separate contract allowed study at a third farm; a pear orchard with no field cultivation. The results of these complementary studies, detailed in the report below, are analyzed and interpreted together. The complete multi-farm analysis provides a more comprehensive picture of the factors that affect pyrethroid degradation and potential for off-site transport under various field conditions.

At the pear orchard, soil was collected before and at several time points after application of Asana[®], a pesticide product containing the active ingredient esfenvalerate. Sediment from a rice paddy was collected before and at several time points after application of lambda-cyhalothrin (Warrior[®]). Finally, at the tomato farm, soil was collected before and after each application of lambda-cyhalothrin. Like other pyrethroids, esfenvalerate and lambda-cyhalothrin can be found in soil and sediment due to their high K_{oc} values, and have relatively high toxicity to aquatic biota (Cold and Forbes, 2004; Werner et al., 2004; Maund et al., 1998; Amweg et al., 2005). At each site, soil was analyzed for pesticide residues to determine degradation rates, and changes in pyrethroid bioavailability over time were analyzed by conducting sediment toxicity tests with the amphipod, *Hyalella azteca*, a standard toxicity testing organism.

Sample Collection

Soil samples were collected from three producing farms in Northern California: a pear orchard, a tomato farm, and a rice farm. Growers provided notice prior to application of pyrethroids, allowing collection of soil from the farms before and at several time points after

treatment. At the pear orchard, pre-treatment soil samples were collected on February 22, 2005. Esfenvalerate (Asana[®]) was applied to the orchard at a rate of 6 oz/acre on February 25, 2005 using a truck-mounted sprayer. A second treatment at the same rate was applied on March 3, 2005. Soil samples were collected at four subsequent time points: one day, one month, three months, and six months following the second pyrethroid application. Samples were collected from soil between the rows of the orchard. Orchard cover between rows consisted of dense grass, and the orchard received periodic irrigation via a network of impact sprinklers distributed in the rows. Noticeable runoff from the grove was not apparent during or after irrigation.

Pre-treatment samples at the tomato farm were collected on April 28, 2005. Lambda-cyhalothrin was applied aerially three times over the course of the growing season: June 6, July 18, and August 22, 2005. Soil samples were collected two days after each pesticide treatment and again about one month after treatment, just prior to the next aerial treatment. Due to the repeated application of lambda-cyhalothrin, it was not possible to follow the persistence of residues from any one application for more than one month. Fields were disced after the tomato harvest and a post-discing soil sample was collected on Oct 5, 2005. During the growing season, the fields were occasionally irrigated by flooding in between the elevated rows. Soil samples were collected from the tops of the rows to avoid pesticide loss due to particle transport in irrigation flow.

Pre-treatment samples were collected from the rice farm on June 14, 2005 before the field was flooded. The fields were subsequently flooded and treated with lambda-cyhalothrin on June 25, 2005. Lambda-cyhalothrin was applied once aerially along the outer 15 m perimeter of the field. Soil samples were collected within this outer band at three subsequent time points: two days, 1 month, and three months following treatment. Rice was submerged continuously during the growing season by maintaining 5-10 cm water in the field.

All soil samples were obtained by collecting the top 1-2 cm of soil and placing the material into solvent cleaned 4 L glass jars. Individual samples consisted of a composite of five sub-samples taken over an area of 1000 m². In most cases, three replicate composite samples were collected on each sampling date. Samples were transported back to the laboratory and stored at 4°C. Soils were wet-sieved on a 1 mm stainless steel sieve to remove plant material and other debris and to break up compacted soil, and allowed to settle overnight at 4° C. Overlying water was removed, and the sample was homogenized. Sub-samples were frozen at -20° C for

analysis of pesticide residues and organic carbon, and sub-samples for grain size and toxicity testing were stored at 4°C.

Chemical analyses

Pre-treatment soil samples were analyzed for 28 pesticides, including esfenvalerate, lambda-cyhalothrin, five other pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, and permethrin), chlorpyrifos, and 20 organochlorines or their degradation products. Analysis followed the methods described by You et al. (2004). Briefly, analysis was performed on an Agilent 6890 series gas chromatograph with an Agilent 7683 autosampler, an electron capture detector, and two columns, an HP-5MS and a DB-608 (Agilent Technologies, Palo Alto, CA). Qualitative identity was established using a retention window of 1% with confirmation on a second column and calibration was based on area using external standards. Sediment samples were sonicated with a solution of acetone and methylene chloride and the extracts were cleaned by column chromatography with deactivated Florisil prior to analysis. The method reporting limit for all compounds was 1 ng/g. Post-treatment samples were analyzed only for esfenvalerate and lambda-cyhalothrin (the pyrethroids applied), or DDT/DDD/DDE and dieldrin (the only analytes detected in pre-treatment samples). Tenax samples were extracted with hexane and analyzed as described above.

Total organic carbon was determined on a CE-440 Elemental Analyzer from Exeter Analytical (Chelmsford, MA), following acid vapor treatment to remove inorganic carbon. (Hedges and Stern, 1984).

Toxicity Testing

Soils were tested for toxicity to the amphipod, *H. azteca*, following standard U.S. EPA protocols (U.S. Environmental Protection Agency, 2000). An objective of this study was to determine if farm soils transported to surface water bodies contained toxic pesticide residues, therefore, dry soils were wet sieved and treated as aquatic sediment for toxicity testing purposes. In summary, approximately 50-75 ml sediment was placed into 400 ml beakers and 250 ml moderately hard water was added. The beakers were maintained under test conditions for 24 h prior to test initiation. Juvenile amphipods approximately 7-10 d in age were separated by sieving and added to the beakers. Each beaker received five 100 ml pulses of fresh water each

day, resulting in two volumes of water exchange daily. Beakers were provided one ml of a yeast-cerophyll-trout chow mixture daily and water chemistry measurements were made at test initiation and termination. Temperature and dissolved oxygen levels were measured regularly throughout the test. After 10 d, the contents of the beakers were sieved through a 425 μm mesh screen to separate *H. azteca* from the sediment and determine *H. azteca* survival.

Because undiluted farm soils were often expected to cause complete mortality to *H. azteca*, soils were diluted with clean material to determine median lethal concentrations (LC50), i.e. the percent of farm soil in dilution required to achieve 50% survival in toxicity tests. Soil samples were diluted with clean reference sediment in varying concentrations. This reference material consisted of sediment from the South Fork of the American River (pear soil dilutions) or from San Pablo Dam reservoir, Orinda, CA (tomato and rice soil dilutions). Both reference sediments had been analyzed by the methods described above for 28 pesticides, including seven pyrethroids, and all analytes were below the 1 ng/g reporting limit except for 1-2 ng/g DDT in the San Pablo Dam reservoir sediment. These reference sediments also have had consistently high (>90%) *H. azteca* survival when used as control sediment. Dilutions were based on dry weight of the sediment, and tests included at least five concentrations of farm soil (100%, 50%, 25%, 12%, 6%) in addition to a 0% control treatment (reference sediment only). Soil dilutions were tested in triplicate and were prepared 24-48 h prior to test initiation.

Data analysis

Toxicity data were analyzed using ToxCalc Version 5.0 (Tidepool Scientific Software, McKinleyville, CA). The maximum likelihood probit method was used to identify median lethal concentrations. Tenax data was tested using the Kruskal-Wallis method ($p < 0.05$) and differences among groups were determined by Conover's multiple comparison test.

Toxicity Units

Pesticide concentrations in the sediments were used to calculate predicted toxicity units on an organic carbon basis (TU_{OCs}) and these values were compared to the observed toxicity units in the dilution tests. Because pyrethroids are extremely hydrophobic, sediment concentrations were first normalized to total organic carbon (OC) content, and then divided by

the reported *H. azteca* 10-d median lethal concentration (LC50) (Amweg et al., 2005; Weston et al., 2004) for each compound according to the formula:

$$\text{Eq. 1:} \quad \text{Predicted TU}_{\text{OC}} = \frac{\text{actual soil concentration (ng/g OC)}}{H. azteca \text{ 10-d LC50 (ng/g OC)}}$$

Therefore, a concentration yielding 1 TU would be expected to cause 50% mortality in a 10-d *H. azteca* toxicity test, regardless of which compound is present. In this study, the two pyrethroids applied for treatment were detectable in the soil as well as some organochlorines present from historical use. Specifically, DDT was present at concentrations approaching those expected to cause toxicity to *H. azteca* in some samples. In order to consider the cumulative toxic effect of these compounds, in some analyses the predicted TU_{OCs} of both pyrethroids and DDT were summed, assuming additivity, since both compounds share a similar mode of neurotoxic action (Klaassen, 2001).

In the toxicity test dilution series, the farm soil was mixed with reference sediment in varying concentrations to obtain an LC50, expressed as the percent dilution of farm soil (dry weight) in which 50% mortality was observed. The LC50 is related to observed TU_{DWs} on a dry weight basis by the equation:

$$\text{Eq. 2:} \quad \text{Observed TU}_{\text{DW}} = 100 / \text{LC50}_{\text{DW}} (\%)$$

However, dilution sediments contained a different organic carbon content (1.39% for American River, 0.30% for San Pablo Dam) than farm soils (range: 0.95- 3.35%). It is well established that organic carbon content of soils or sediments is a pivotal factor controlling bioavailability and hence toxicity of hydrophobic toxicants. Therefore, addition of the clean sediment can alter toxicity in the sample not only through dilution, but also by changing the total organic carbon content of the mixture, altering pesticide bioavailability and toxicity of the sample. For example, using a diluent with an organic carbon content higher than the original test soil would cause a relatively rapid reduction in toxicity, with a resulting high LC50 value and low TU estimate. Conversely, using a diluent with low organic carbon content would yield a

lower LC50 and higher TU estimate. To account for these differences, the observed LC50_{DW}'s and TU_{DW}'s were normalized to total organic carbon by the following equations:

Eq 3:
$$LC50_{OC} = LC50_{DW} \times (\% \text{ OC in original test soil}) / (\% \text{ OC at LC50}_{DW})$$

Eq 4:
$$\text{Observed TU}_{OC} = 100 / LC50_{OC} (\%)$$

Since it is rarely possible to dilute a test material with reference material containing an identical organic carbon content, calculating the LC50_{OC} and observed TU_{OC} by equations 3 and 4, rather than the traditional method of equation 2, mathematically removes the influence of organic carbon in the diluting sediment. This approach provides an LC50 and TU value as if the diluent and test sediment contained the same organic carbon content.

RESULTS AND DISCUSSION

Soil characteristics and complete pesticide residue data are provided in Appendix 1. The <1 mm soil fraction used for toxicity testing and chemical analysis contained on average 2.3% OC for pear soil, 1.2 % OC for tomato soil, and 1.7% OC for rice sediment.

Pear orchard – esfenvalerate

Initial conditions - Prior to pesticide application in late spring, 2005, orchard soil was not toxic to *H. azteca* in standard 10-d sediment toxicity tests. Average survival was 90.8% (±3.8%).

Esfenvalerate remaining from previous years was detectable at 4.5 ng/g in the orchard soil, or 0.16 µg/g OC, equivalent to 0.10 predicted TU_{OC}s. None of the remaining six pyrethroid analytes (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, lambda-cyhalothrin, and permethrin) were detectable.

Orchard soil contained dieldrin and DDT and its breakdown products (Table 1). Organochlorine residues originated from historical use of these compounds at the orchard, a fact confirmed by the current grower. Concentrations of DDT in the initial pre-spray samples averaged 940 ng/g, equivalent to 0.13 predicted TU_{OC}s. The highest average DDT occurred in the six month samples at an average concentration of 2378 ng/g, a concentration equivalent to

Table 1. DDT concentrations and TU_{oc}s in pear orchard soil over time. TU_{oc}s were calculated using a *H. azteca* LC50 of 260 µg/g OC (Weston et al., 2004).

| Time (d) | DDT ng/g (s.d) | DDT µg/g OC (s.d.) | DDT TU _{oc} s |
|---------------|----------------|--------------------|------------------------|
| pre-treatment | 940 (374) | 33.5 (10.1) | 0.13 |
| 1 d | 1716 (844) | 82.6 (46.2) | 0.32 |
| 1 mo | 11450 (310) | 60.3 (20.3) | 0.23 |
| 3 mo | 1485 (484) | 54.8 (14.5) | 0.21 |
| 6 mo | 2378 (757) | 103.3 (42.0) | 0.40 |

0.4 TU_{OCs}. Thus, DDT may have contributed to toxicity observed in the six month sample and potentially to a lesser degree in other samples as well. DDE, DDD, and dieldrin concentrations averaged 1167, 295, and 407 ng/g, respectively, throughout the study period. These three compounds are much less toxic than DDT; each had average TU_{OCs} less than or equal to 0.03, well below effects thresholds for *H. azteca* (Shuytema et al., 1989; Nebeker et al., 1989; Hoke et al., 1990; U.S. Environmental Protection Agency, 1993).

Chemical degradation - One day after pyrethroid application, the maximum esfenvalerate concentration of 143 ng/g (6.24 μ g/g OC, 4.05 TU_{OC}) was detected in one replicate sample. At this time, the average soil concentration among the three replicates was 111 ng/g, which decreased to 5.2 ng/g six months later (Figure 1). Over this period, the mean temperature was approximately 21 °C (www.ncdc.noaa.gov). The esfenvalerate half-life over this period was calculated at 40 d using a first-order decay model. The value is similar to the esfenvalerate half-life of 38.6 d reported by Laskowski (2002) who reported a weighted mean of 10 laboratory studies using a range of soil types and experimental conditions.

Bioavailability: toxicity testing - In toxicity tests with *H. azteca*, orchard soils were highly toxic for three months following esfenvalerate application (Table 2), causing complete or near complete mortality in the tests. In order to achieve 50% survival in the tests, soils required dilution with clean sediment to 19.2%, 26.4%, and 30.2% on an organic carbon-adjusted basis (equation 3) at the first three time points, respectively (equivalent to 5.2, 3.8, and 3.3 observed TU_{OCs}). By six months after treatment, 43% of the amphipods were able to survive a 10-d exposure, with some of the remaining toxicity possibly attributable to DDT residues in the soil (Table 1).

A comparison of the predicted TU_{OCs} (derived from the chemical concentration and published LC50s) and the observed TU_{OCs} (derived from dilutions) can be used to examine changes in esfenvalerate bioavailability over time. The predicted TU_{OCs} utilize published LC50 values obtained two weeks after spiking the sediment with esfenvalerate. If bioavailability does in fact decrease over time, the observed TU_{OCs} immediately after orchard application of esfenvalerate should be greater than predicted TU_{OCs}, and over time, the observed TU_{OCs} should fall farther and farther below the predicted TU_{OCs}.

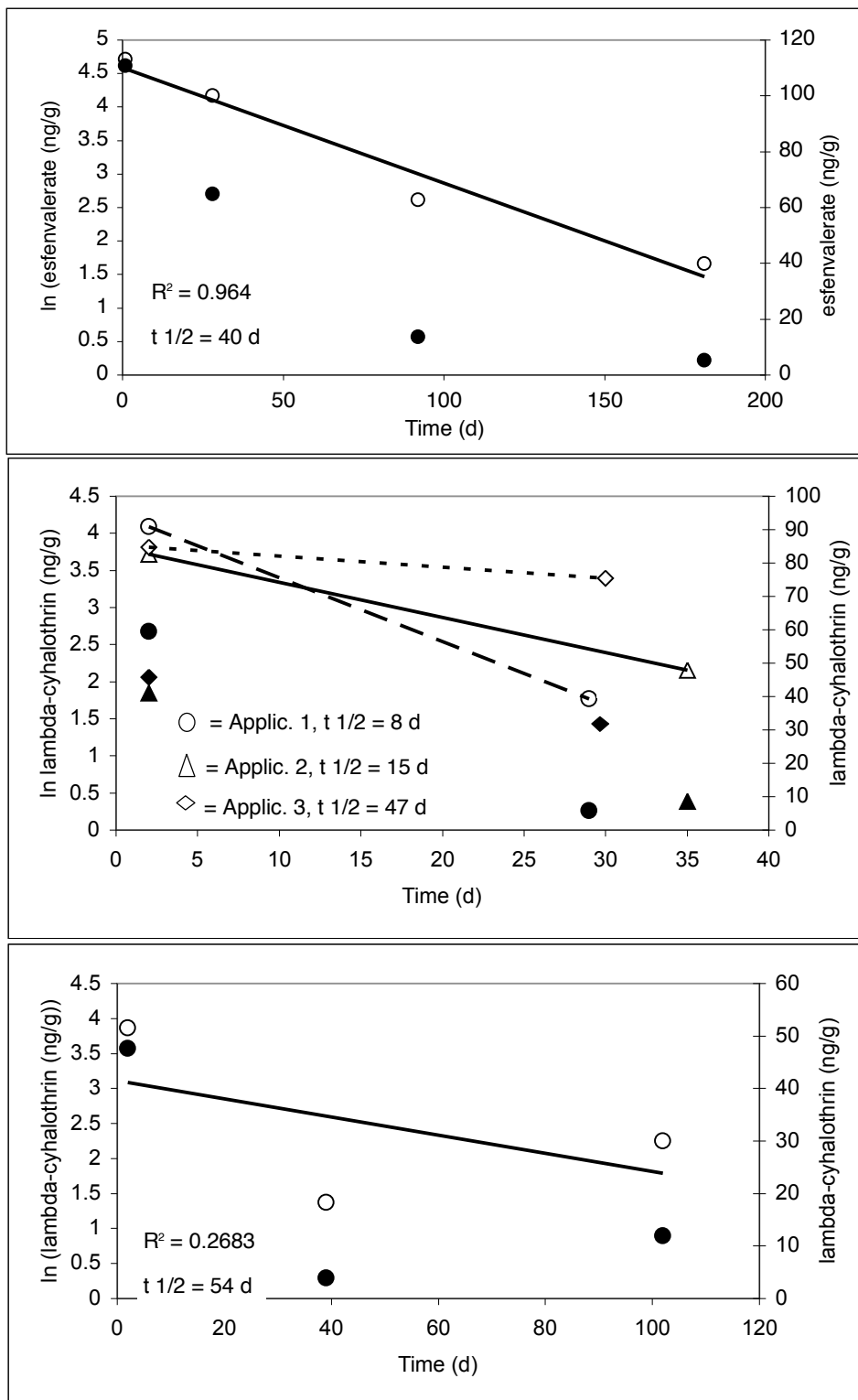


Figure 1. Pyrethroid concentrations over time at the pear (panel A), tomato (panel B), and rice farm (panel C). Time 0 refers to the day of pyrethroid application. Filled symbols refer to concentration on right axis; open symbols refer to natural log concentration on left axis, used to calculate half-life.

Table 2. Toxicity testing results for *H. azteca* exposed to farm soils, pyrethroid concentrations, and pyrethroid TU_{OCs}. Predicted pyrethroid TU_{OCs} calculated using esfenvalerate LC50 = 1.54 µg/g OC, lambda-cyhalothrin LC50 = 0.45 µg/g OC (Amweg et al., 2005).

| Field type | Time | % Survival in Undiluted Soil mean (s.d.) | <i>H. azteca</i> LC50 (%) OC normalized (s.d.) | Observed TU _{OCs} (from dilution test) | Predicted Pyrethroid TU _{OCs} (based on chemical analysis) | Pyrethroid µg/g OC (s.d.) | Pyrethroid ng/g (s.d.) |
|-----------------|---------------|---|---|--|--|------------------------------|---------------------------|
| Pears | | | | | | | |
| | pre-treatment | 90.8 (3.8) | -- | -- | Esfenvalerate | | |
| | 1 d | 0.0 (0) | 19.2 (0.73) | 5.2 | 0.1 | 0.16 (0.01) | 4.5 (1.2) |
| | 1 mo | 0.0 (0) | 26.4 (3.4) | 3.8 | 3.4 | 5.18 (1.20) | 111 (31.0) |
| | 3 mo | 2.0 (3.5) | 30.2 (1.7) | 3.3 | 2.2 | 3.31 (0.78) | 64.8 (22.0) |
| | 6 mo | 43.3 (28.4) | > 87.9 | < 1.1 | 0.4 | 0.55 (0.05) | 13.6 (2.1) |
| | | | | | 0.1 | 0.22 (0.01) | 5.2 (1.0) |
| Tomatoes | | | | | | | |
| | pre-treatment | 77.1 (4.7) | -- | -- | Lambda-cyhalothrin | | |
| | 2 d | 0.0 (0) | < 13.1 | > 7.6 | 0.0 | nd | nd |
| | 1 mo | 22.5 (17.3) | 78.7 (15.1) | 1.3 | 12.0 | 5.38 (1.80) | 59.6 (19.0) |
| | 2 d | 0.0 (0) | 20.6 (5.4) | 4.9 | 1.1 | 0.50 (0.29) | 5.87 (3.64) |
| | 1 mo | 0.0 (0) | 75.6 | 1.3 | 7.1 | 3.19 (0.54) | 41.1 (3.74) |
| | 2 d | 0.0 (0) | 12.0 (0.5) | 8.3 | 1.7 | 0.78 | 8.64 |
| | 1 mo | 0.0 (0) | 14.3 (0.8) | 7.0 | 8.6 | 3.88 (0.88) | 45.8 (11.0) |
| | post-discing | 6.7 (4.7) | 55.6 (5.1) | 1.8 | 6.4 | 2.88 (1.09) | 31.6 (13.3) |
| | | | | | 1.6 | 0.70 (0.07) | 8.49 (0.17) |
| Rice | | | | | | | |
| | pre-treatment | 94.0 (2.7) | -- | -- | Lambda-cyhalothrin | | |
| | 2 d | 0.0 (0) | 39.4 (12.1) | 2.5 | 0.0 | nd | nd |
| | 1 mo | 94.4 (5.1) | -- | -- | 6.7 | 3.03 (1.72) | 47.7 (26.7) |
| | 3 mo | 94.0 (3.5) | -- | -- | 0.5 | 0.24 (0.04) | 3.96 (0.66) |
| | | | | | 1.4 | 0.63 (0.40) | 11.9 (7.93) |

At the one-d time point, the observed TU_{OC} of 5.2 is somewhat higher than the predicted TU_{OC} of 3.4 as expected (though an additional 0.3 predicted TU_{OC} s could come from DDT). Over time, the predicted esfenvalerate TU_{OC} s decrease as a consequence of degradation of the esfenvalerate, but the observed TU_{OC} s fail to show a comparable decline. At the three-month time point there is very high toxicity (3.3 TU_{OC} s) when only slight toxicity is predicted based on soil esfenvalerate concentrations (0.4 TU_{OC} s). This disparity is likely due to toxicity introduced from additional pesticide application between the one and three month sample collections. Avermectin, a fungicide, was applied to the orchard in late April, 2005, about five weeks prior to the three month sample collection. Avermectin is relatively short-lived in aerobic soil ($t^{1/2} = 39$ d; Gruber et al., 1990; Bull et al., 1984), but little is known about its toxicity to aquatic invertebrates. Phosmet, an organophosphorus insecticide, was also applied to the orchard just three weeks prior to collection of the three-month sample. Soil concentrations of these compounds in the orchard and their effects thresholds for *H. azteca* are unavailable, and therefore the contribution of avermectin and/or phosmet to toxicity can not be directly quantified. Avermectin is relatively hydrophobic ($\log K_{oc} = 3.67$) and would reasonably be expected to partition into soils and sediment (Gruber et al., 1990). Phosmet however, is less likely to adsorb to particles ($\log K_{oc} = 2.91$) (Wauchope et al., 1992). Similar to esfenvalerate, both compounds are applied in an oil carrier, which may also alter the bioavailability of pesticides in soil toxicity tests. Over the course of the study, the orchard also received repeated applications of various fungicides (including terramycin, streptomycin, and trifloxystrobin) and pheromone biopesticides. These compounds appear to have had minimal, if any, impact on *H. azteca* toxicity, as they were applied in some cases just days before the one-month sample collection, and yet no toxicity was observed that could not be explained by esfenvalerate residues.

After six months, 43.3% ($\pm 28.4\%$) of the amphipods survived the test in undiluted sediment. Esfenvalerate concentrations after six months had declined approximately to pre-treatment levels. However, much greater toxicity was observed at this time than in pre-treatment toxicity testing where survival was greater than 90%. These results may be explained by several factors. First, pesticide residues become less bioavailable over time, with the effect being most pronounced in the initial weeks and months following application (Bondarenko and Gan, 2004). Theoretically, residues remaining in the soil from the previous year would be much less bioavailable and therefore less toxic, than residues originating from recent pesticide applications.

Post-treatment toxicity testing data from this study could not confirm this bioavailability vs. time relationship because results were obscured by the application of additional pesticides. Another potential explanation is that avermectin and/or phosmet were contributing to toxicity in the six-month sample as well as the three-month sample. With a half-life of 39 d in aerobic soil for avermectin (Bull et al., 1984), it is conceivable that biologically significant residues could still exist in soil over the approximately four months from application to the six month sampling time point. The phosmet half-life in aerobic soil is much shorter, just seven days (<http://www.pesticideinfo.org/Index.html>). While phosmet degrades much more rapidly and appears unlikely to persist at toxic concentrations after three months, without soil concentrations after treatment or effects thresholds for *H. azteca* it is not possible to definitively rule out phosmet effects on toxicity. Finally, DDT may also be contributing to toxicity in some samples. In particular, DDT concentrations were highest in the six-month sample (2378 ng/g), contributing 0.4 TU_{OCS} compared to just 0.14 TU_{OCS} of esfenvalerate. DDT in the orchard appears quite spatially patchy, and residues may still be sufficient to contribute to toxicity in some locations.

Site-specific conclusions - Esfenvalerate concentrations decreased rapidly in the orchard soil, yielding a half-life of 40 d. This value is consistent with previously published data regarding esfenvalerate degradation in soil. Esfenvalerate concentrations at six months were similar to those remaining from applications in prior years, and unlikely to contribute greatly to *H. azteca* toxicity.

The orchard under study applied esfenvalerate in late February and early March. While most of the heavy winter rain events would have passed prior to this time, there would still be the potential for a storm event that would transport the recently applied pesticide. However, by the next rainy season, approximately nine months later, esfenvalerate residues would be unlikely to remain in the soil at toxicologically significant concentrations. The predicted soil esfenvalerate concentration nine months after treatment, based on the degradation rate determined in this study, would be just 1.1 ng/g. Rains occurring in at that time would have the potential to carry just 0.03 predicted TU_{OCS} from the orchard soils.

Interpretations of the changes in esfenvalerate bioavailability over time from data produced in this study are more equivocal. The use of toxicity results to analyze time-dependent

changes in bioavailability was complicated by the presence of additional pesticides in the orchard soil. DDT present from historic use probably contributed significantly to the toxicity on some occasions. Toxicity data from the three and six month samples also suggest that pesticides applied late in the growing season, such as phosmet and/or avermectin, caused mortality to *H. azteca*. Thus, field studies may not be best suited to measure changes in bioavailability of a single compound unless growers can guarantee use of only a single pesticide and the site pesticide use history is well documented. Both conditions are difficult, if not impossible, to achieve on a producing farm.

Tomato and rice farms - lambda-cyhalothrin

Initial conditions - Survival of *H. azteca* in standard 10-d tests was excellent in rice farm soil, averaging 94.0 (± 2.7)% whereas survival in tomato farm soil was lower (77.1 ± 4.7 %). In both rice and tomato farm soils, any lambda-cyhalothrin remaining from application in previous years was undetectable in pre-treatment samples. Lambda-cyhalothrin had been used at the rice farm the prior summer; historical use at the tomato farm is unknown. Organochlorine residues were detectable at low ng/g concentrations at both locations (sum of DDT/DDD/DDE averaging 70 ng/g at rice farm, 13 ng/g at tomato farm). These values are typical of soils throughout the heavily agricultural Central Valley of California where organochlorines remain from historical use. DDT and breakdown products were detected in all tomato and rice samples; however, concentrations were orders of magnitude below effects thresholds for *H. azteca* and did not contribute to toxicity on any occasion. Dieldrin was detected near the reporting limit of 1 ng/g in one tomato farm sample and two rice farm samples.

Chemical degradation (tomatoes) - Lambda-cyhalothrin was applied aerially to the tomato field in three separate treatments at a rate of 3.8 oz/acre each approximately one month apart. Two days following each treatment, similar soil concentrations were measured. On the first, second, and third treatments, soil lambda-cyhalothrin averaged 59.6 (± 19.0) ng/g, 41.0 (± 3.7) ng/g, and 45.8 (± 11.0) ng.g, respectively. These concentrations are equivalent to 5.38, 3.19, and 3.88 $\mu\text{g/g}$ OC, or 12.0, 7.1, and 8.6 TU_{OCs}, respectively. Half-lives were calculated independently for each one month period. For the first two months, half-lives were similar and showed rapid loss from farm soils: 8 d and 15 d respectively, calculated using a first-order decay model (Figure 1B).

During the last one month period, lambda-cyhalothrin residues did not decline as rapidly, and a half-life of 47 d was determined. The reasons for this discrepancy are not immediately apparent, and several contributing factors may exist. First, the approximate mean temperature during the three-month study period was 23°C (www.ncdc.noaa.gov). Although the average daily temperature was slightly lower during the last one-month period (20°C), the difference was not expected to cause a significant increase in lambda-cyhalothrin persistence. Secondly, sulfur was applied to the field with lambda-cyhalothrin during the second treatment, and again two weeks prior the third one-month sample. The fungicides chlorothalonil and azoxystrobin were also applied during the third aerial treatment on Aug 22, 2005. It is possible that the applied fungicides altered microbial composition in the soil, resulting in decreased breakdown of lambda-cyhalothrin following the third application. Finally, the reduced degradation rate may be a result of crop maturation. As the tomato plants matured over the growing season, the dense canopy created by the large plants eventually closed in over the furrows. The plants created shade on the soil surface, possibly decreasing pyrethroid loss due to photodegradation.

The mean of the three one-month degradation rates is 23 d, a value about half that measured by Bharti et al (50.5 d; cited in Laskowski, 2002) in a laboratory study conducted using wet soil held at 20°C).

After harvest and field discing, soil lambda-cyhalothrin concentrations were lower, averaging 8.5 (± 0.2) ng/g (0.70 $\mu\text{g/g}$ OC, 1.6 TU_{OCs}). The post-discing samples were taken only 14 d after a soil concentration of 31.6 (± 13.3) ng/g was measured. Therefore, the reduction was most likely due to dilution with clean soils that are mixed to the surface during discing.

Chemical degradation (rice) - Lambda-cyhalothrin in rice soils, which remained submerged during the growing season, rapidly dissipated. Two days after aerial treatment at a rate of 12 oz/acre, the mean soil concentration was 47.7 (± 26.7) ng/g, equivalent to 3.0 $\mu\text{g/g}$ OC and 6.7 TU_{OCs}. Interestingly, the 2-d sediment concentration was similar to that found in tomato farm soil, although a four-fold higher application rate was used in the rice paddy and the pesticide was applied to the overlying water instead of directly to the soil surface. At the one and three month time points, lambda-cyhalothrin was detectable at just 4.0 (± 0.7) ng/g (0.24 $\mu\text{g/g}$ OC, 0.5 TU_{OCs}) and 11.9 (± 7.9) ng/g (0.63 $\mu\text{g/g}$ OC, 1.4 TU_{OCs}), respectively (Figure 1C). Over this time period, the average temperature was approximately 25°C. The replicate samples at each time point were

quite variable, possibly due to sampling near the edges of the pesticide-treated band which was not marked in any manner after treatment. Additionally, as the growing season progressed, dense rice root masses developed on the sediment surface, preventing collection of only the upper 1-2 cm of sediment. Deeper sediments (up to 5 cm) were sometimes inadvertently sampled. Difficulty sampling within the pyrethroid-treated areas of rice likely led to significant heterogeneity between samples and time points. The increase in lambda-cyhalothrin from one to three months is likely an artifact from this heterogeneity.

Over the entire three months, the lambda-cyhalothrin half-life was 54 d (Figure 2C). A study by Marriot et al. (cited in Laskowski, 2002) measured an average lambda-cyhalothrin half-life of 27.7 d in aerobic sediment-water systems, however the experiments were conducted in the dark at 20° C with constant aeration (in [3]).

Toxicity testing (tomatoes) - In toxicity tests with *H. azteca*, tomato farm soils were highly toxic following treatment with lambda-cyhalothrin (Table 2), causing complete mortality in each of the three 2-d post-treatment samples. In order to achieve 50% survival in the tests, soils required dilution with clean sediment to 13.1%, 20.6%, and 12.0% on an organic carbon-adjusted basis (equation 3) at the three 2-d time points, respectively (equivalent to 7.6, 4.9, and 8.3 observed TU_{OCs}). The herbicide trifluralin was applied two weeks before the first one-month sample, yet 23% of the amphipods were able to survive a 10-d sediment exposure at this time. However, one month following the second and third aerial treatments, farm soil caused total mortality in the tests, with 50% survival achieved only after dilution to 76% and 14%, respectively. Lambda-cyhalothrin was applied with sulfur during the second aerial treatment and chlorothalonil, and azoxystrobin during the third treatment to control black mold. Sulfur was also applied separately two weeks before the third one-month sample. The toxicities of these various pesticides to *H. azteca* and their concentration in farm soils are unknown, and therefore it is not possible at this time to quantify the potential contribution of these non-pyrethroid pesticides to the observed toxicity.

A comparison of the predicted TU_{OCs} (derived from the chemical concentration and published LC50s) and the observed TU_{OCs} (derived from toxicity testing dilutions) show a relatively good match in most cases. In all tomato farm samples, the predicted TU_{OCs} were within 60% of observed TU_{OCs}, and were frequently with 25% of the observed TU_{OCs}. Predicted TU_{OCs}

often slightly overestimated observed toxicity as well. The good correlation between predicted and observed TU_{OCs} s suggests that non-pyrethroid pesticides applied to the tomato field had a relatively small impact on *H.azteca* in toxicity tests. Greater mortality in the second and third one-month samples is consistent with higher lambda-cyhalothrin concentrations remaining in the soil at these time points.

Measurement of changes in bioavailability over time by toxicity testing was limited due to the repeated application of lambda-cyhalothrin. From two days to one month, the ratio of predicted:observed TU_{OCs} was expected to increase, as residues become less bioavailable over time. This trend was observed only in the last month. However, this time point was a mixture of soil containing residues from earlier lambda-cyhalothrin treatments with much longer aging in the field, possibly creating an artificial decrease in bioavailability over this one-month period.

Toxicity testing (rice) - Under aquatic conditions, rice sediments caused total mortality to *H. azteca* two days after aerial lambda-cyhalothrin treatment (Table 2). The median lethal concentration at this time was 39% rice sediment diluted with clean reference material, or 2.5 observed TU_{OCs} . One month following treatment, no toxicity was observed. At both the one and three month time points, survival in the tests had returned to pre-treatment levels of 94%.

Predicted TU_{OCs} in rice sediment overestimated the observed toxicity in every sample. However, because no toxicity was seen in the one and three month time points, the predicted toxicity can not be compared to observed in order to determine changes in bioavailability over time. Hand et al. (2001) showed that aquatic plants and macrophytes have a dramatic effect on the degradation of lambda-cyhalothrin in microcosm studies, reducing the amount of pyrethroid that reaches the sediment phase through adsorption and subsequent metabolism. Hand et al. report that the presence of aquatic vegetation may reduce sediment concentrations up to 90% relative to aquatic non-vegetated systems. The rice paddy in this study contained dense growth of young rice plants at the time of pesticide application, and their presence likely contributed to the rapid dissipation of toxicity compared to tomato farm soil.

Site-specific conclusions (tomatoes) - The half-life of 23 d generated in this study for lambda-cyhalothrin in aerobic soil is about half that reported by Bharti et al (cited in Laskowski, 2002). Although the lambda-cyhalothrin half-life was short compared to the length of the growing

season, the soil remained highly toxic throughout the summer due to repeated pesticide applications. In general, observed mortality in toxicity tests matched predicted toxicity based on chemical concentrations and published toxicity data well, suggesting that the toxicity was in fact due to lambda-cyhalothrin and not other pesticides (herbicides, sulfur, and fungicides) applied during the growing season. After field discing and dilution with relatively clean deeper soils, lambda-cyhalothrin concentrations, measured at 8.49 ng/g (0.70 µg/g OC, 1.6 TU_{OCs}), were still great enough to cause 93% mortality to *H. azteca* in standard 10-d sediment toxicity tests.

Off-site transport of these toxic soil residues to surface waters occurs primarily by movement in irrigation flow or by storm-driven transport. Rainfall in northern California during summer months is negligible, and unlikely to be a major factor in transporting pyrethroid-contaminated sediments until heavy rains begin in early winter. By this time, at least three half-lives will have elapsed, and the predicted soil concentration would be 1.1 ng/g, and unlikely to contribute to toxicity at just 0.09 predicted TU_{OCs}. Transport in irrigation water during the growing season is likely to result in entry of residues in to creeks however. Furrows between the rows of tomatoes are flooded approximately every 10 d during the growing season. This method of irrigation allows ample opportunity for sediment-bound pyrethroids to move into bed sediments in downstream water bodies. These toxic residues would require significant dilution with clean material in order to achieve survival in toxicity tests. Unlike rainfall however, irrigation-driven transport is highly predictable. Many techniques exist to minimize off-site transport of contaminated suspended solids, such as managing the timing and duration of flows, and using simple technologies to reduce loss of suspended solids. These techniques could potentially be utilized to reduce pyrethroid loading to creeks during the growing season.

Site-specific conclusions (rice) - Under aquatic conditions in a submerged rice paddy, lambda-cyhalothrin persistence was at least twice as great as in aerobic soil, with a half-life of 54 d. Toxicity was quickly reduced however, and after one month sediment samples had returned to pre-treatment survival levels of 94%.

Transport of sediment-bound pyrethroids from rice paddies during the growing season appears unlikely. Although irrigation water is maintained at 5-10 cm in the field, flow is extremely low and water appears clear and static. Rainfall is negligible during summer months in areas of rice production, eliminating transport in storm flow. Additionally, roots of the rice plants

quickly form a dense mat trapping most sediment particles in the paddy until harvest. Lambda-cyhalothrin was applied only once at the beginning of the growing season and toxicity had dissipated by one month, so transport of toxic residues would only be possible shortly after pesticide treatment. When the paddy is drained at the end of the season, suspended sediments potentially move into downstream surface waters, however at this time no toxicity was observed even though chemical analyses predicted 1.4 TU_{OCS} in the sediment. The difference may be explained by decreased bioavailability of lambda-cyhalothrin after aging three months in the rice paddy.

General Conclusions

Pyrethroid transport from fields to surface waters would occur primarily via irrigation-driven sediment transport or movement in storm-related flows. In the Central Valley of California, heavy rainfall occurs only in the winter months. Therefore, potential for transport in winter storms is heavily dependent on the crop and the timing of pesticide applications. For example, the largest amount of esfenvalerate applied on a per month basis occurs in January (Figure 2). This use is predominantly dormant spray applications on stone fruit and almonds. It occurs well within the winter rainy season, and soil particles carrying esfenvalerate residues transported off-site immediately after treatment are likely to be toxic at this time. For summer crops however, there would be little potential for storm-related transport of esfenvalerate at toxic levels. Approximately 60% of the total annual agricultural esfenvalerate use in California occurs during the April to September irrigation season, and for these applications several half-lives would typically elapse prior to major rain events. In the case of lambda-cyhalothrin, February and March are the two months with highest average use. Off-site transport potential will depend on the exact timing of late storms relative to individual pyrethroid applications by growers. Use during February and March is primarily on alfalfa, onions, and lettuce and these fields have the potential to release particle-bound pyrethroids to surface waters during occasional high flow events. In the summer months however, lambda-cyhalothrin is applied to rice, tomatoes, corn, and cotton, (with lettuce applications year-round). Summer use represents about half the annual agricultural use of lambda-cyhalothrin in California, and residues from these applications are unlikely to persist until the following winter storm season.

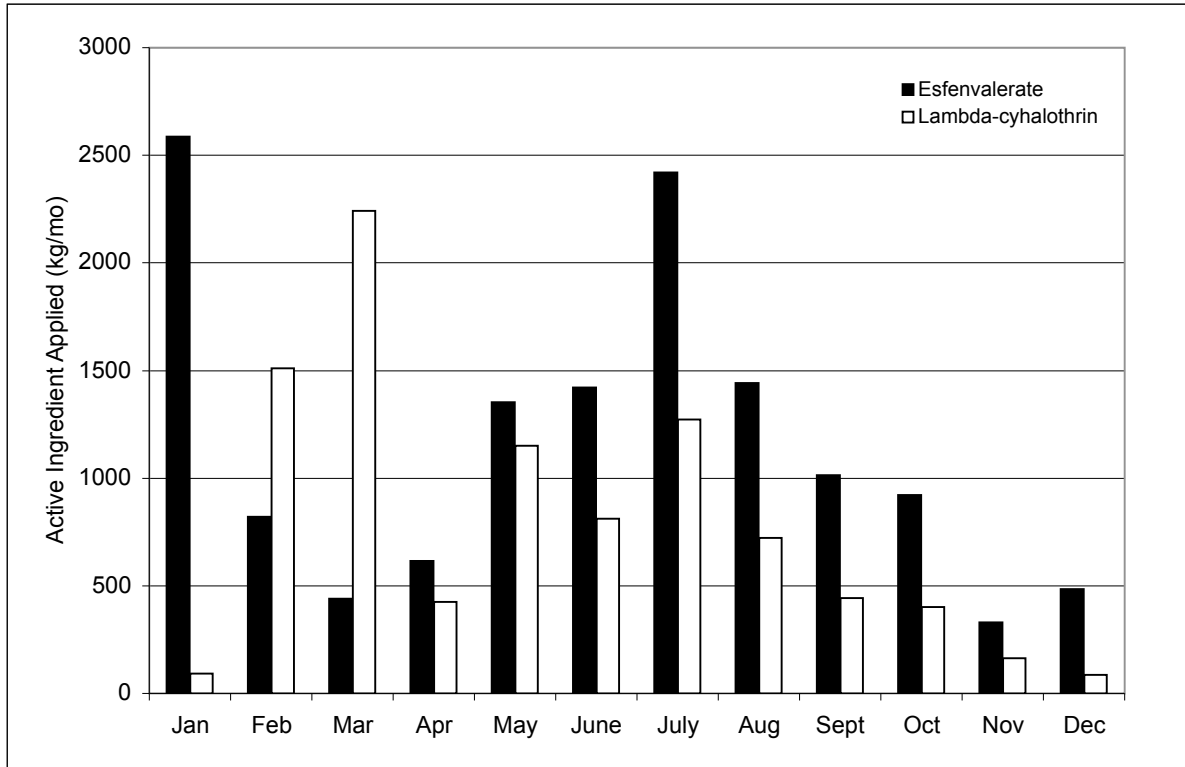


Figure 2. Average monthly use of esfenvalerate and lambda-cyhalothrin in California agriculture (2000-2003).

Irrigation throughout the growing season appears to have the potential to transport sediment containing much higher pyrethroid concentrations. However, by controlling factors such as the method of irrigation, its duration, and its timing, there is potential for management of irrigation flow to minimize sediment export during periods when high pesticide concentrations are present in the soils. Irrigation-related transport of soil-adsorbed pesticides is inherently more manageable than storm-driven transport.

Some data are available to assess transport of esfenvalerate and lambda-cyhalothrin to downstream water bodies. In a study of nearly 200 agricultural sediments from sites throughout California, Weston et al. (in review) found 53 samples were toxic to *H. azteca*. Ten of the toxic samples contained >0.5 TU lambda-cyhalothrin, and only six had > 0.5 TU esfenvalerate. In most toxic samples therefore, lambda-cyhalothrin or esfenvalerate residues were too low to independently cause acute toxicity. However, both compounds were frequently present at concentrations that contributed to observed toxicity in an additive manner when present with other pyrethroids. In order to determine whether irrigation flow or storm events carry these residues, seasonality and magnitude of pyrethroid detection can also be considered. In this database of sediment samples from agriculture-dominated water bodies analyzed for pyrethroids, there were 20 sites that were sampled both in spring, after winter rains, and also at the end of irrigation season in late summer, and contained esfenvalerate on at least one of these occasions. Sixteen of these 20 sites had higher esfenvalerate concentrations in late summer, suggesting that irrigation flow is the main vector for off-site transport of esfenvalerate residues. For lambda-cyhalothrin, 14 sites were sampled in both spring and late summer and contained residues on at least one of these occasions, and nine had higher sediment concentrations in late summer. Lambda-cyhalothrin use is less seasonal than esfenvalerate, with nearly equal amounts used in summer and the rainy season. Use patterns may contribute to the fact that both irrigation and storm-related flows appear to be responsible for transporting lambda-cyhalothrin into surface waters.

Chemical degradation studies conducted on producing farms afford a valuable opportunity to track pesticide persistence under real-world conditions. However, these same sites may not be well suited to measure changes in pesticide bioavailability with standard methods, such as toxicity testing, due to the potential application of other toxic compounds during the growing season or the presence of residues from historical pesticide use. The farms studied used

other pesticides more or less concurrently with pyrethroids, including phosmet and avermectin (pear orchard), chlorothalonil, azoxystrobin and sulfur (tomato farm). Additionally, recurring pyrethroid applications, such as the three lambda-cyhalothrin applications within a single growing season at the tomato farm, prevent accurate measurement of degradation rates. Future studies of pesticide persistence and bioavailability need to properly control for these potential confounding factors, which obscure interpretation of the data

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Appendix 1. Farm soil characteristics and pesticide residues. All samples were sieved to 1 mm prior to chemical analysis and toxicity testing.

| Sample | Location | Collection Date | % silts & clays (<1 mm fraction) | % TOC (< 1mm fraction) | Pyrethroid (ng/g) | DDT (ng/g) | DDE (ng/g) | DDD (ng/g) | Dieldrin (ng/g) |
|--------------|----------|-----------------|----------------------------------|------------------------|-------------------|------------|------------|------------|-----------------|
| Pear Orchard | | | | Esfenvalerate | | | | | |
| 1.1 | | 2/22/05 | 81.7 | 2.65 | 4.18 | 1125 | 1618 | 534 | 473 |
| 1.2 | | 2/22/05 | 75.7 | 2.26 | 3.45 | 510 | 616 | 224 | 328 |
| 1.3 | | 2/22/05 | 78.6 | 3.35 | 5.74 | 1186 | 1802 | 407 | 381 |
| 2.1 | | 3/4/05 | 87.4 | 2.11 | 82.0 | 1238 | 1671 | 500 | 452 |
| 2.2 | | 3/4/05 | 83.9 | 2.29 | 143 | 1220 | 1339 | 503 | 470 |
| 2.3 | | 3/4/05 | 72.8 | 1.98 | 107 | 2690 | 794 | 335 | 404 |
| 3.1 | | 3/31/05 | 77.9 | 2.16 | 90.2 | 1183 | 1452 | 494 | 518 |
| 3.2 | | 3/31/05 | 70.4 | 1.90 | 50.7 | 825 | 973 | 308 | 385 |
| 3.3 | | 3/31/05 | 77.9 | 1.74 | 53.5 | 1441 | 1638 | 759 | 657 |
| 4.1 | | 6/3/05 | 68.4 | 2.30 | 14.0 | 1279 | 623 | 48.4 | 255 |
| 4.2 | | 6/3/05 | 68.9 | 2.28 | 11.4 | 1141 | 865 | 48.5 | 235 |
| 4.3 | | 6/3/05 | 73.8 | 2.87 | 15.5 | 2040 | 1233 | 64.1 | 332 |
| 5.1 | | 9/1/05 | 71.3 | 2.18 | 4.49 | 2299 | 913 | 51.3 | 338 |
| 5.2 | | 9/1/05 | 70.0 | 2.76 | 6.41 | 1663 | 806 | 78.8 | 485 |
| 5.3 | | 9/1/05 | 70.0 | 2.20 | 4.82 | 3171 | 1163 | 71.9 | 394 |

Appendix 1. Continued

| Sample | Location | Collection Date | % silts & clays (<1 mm fraction) | % TOC (< 1mm fraction) | Pyrethroid (ng/g) | DDT (ng/g) | DDE (ng/g) | DDD (ng/g) | Dieldrin (ng/g) |
|-------------|----------|-----------------|----------------------------------|------------------------|-------------------|------------|------------|------------|-----------------|
| Tomato Farm | | | | Lambda-cyhalothin | | | | | |
| 10.1 | | 4/28/05 | 54.1 | 1.45 | ND | 11.5 | 8.92 | ND | 1.32 |
| 10.2 | | 4/28/05 | 57.1 | 1.13 | ND | 2.04 | 1.61 | ND | ND |
| 10.3 | | 4/28/05 | 49.3 | 0.95 | ND | 4.17 | 3.56 | ND | ND |
| 11.1 | | 6/8/05 | 56.9 | 1.12 | 80.1 | 1.81 | 2.18 | ND | ND |
| 11.2 | | 6/8/05 | 47.8 | 1.03 | 55.8 | 3.62 | 8.57 | ND | ND |
| 11.3 | | 6/8/05 | 51.9 | 1.20 | 42.8 | 2.65 | 9.19 | ND | ND |
| 12.1 | | 7/5/05 | 57.4 | 1.19 | 5.16 | 2.73 | 4.02 | ND | ND |
| 12.2 | | 7/5/05 | 52.1 | 1.07 | 2.63 | 2.71 | 4.99 | ND | ND |
| 12.3 | | 7/5/05 | 55.1 | 1.21 | 9.81 | 2.29 | 8.61 | ND | ND |
| 13.1 | | 7/20/05 | 53.5 | 1.32 | 44.9 | 2.15 | 3.04 | ND | ND |
| 13.2 | | 7/20/05 | 53.4 | 1.14 | 40.9 | 1.81 | 3.07 | ND | ND |
| 13.3 | | 7/20/05 | 52.1 | 1.45 | 37.4 | 3.68 | 8.68 | ND | ND |
| 14.1 | | 8/22/05 | 51.6 | 1.11 | 8.64 | 2.92 | 2.61 | ND | ND |
| 15.1 | | 8/24/05 | 49.8 | 1.17 | 38.1 | 2.59 | 5.33 | ND | ND |
| 15.2 | | 8/24/05 | 54.8 | 1.19 | 53.6 | 2.52 | 3.74 | ND | ND |
| 16.1 | | 9/21/05 | 46.7 | 1.13 | 46.3 | 7.60 | 9.51 | 1.00 | ND |
| 16.2 | | 9/21/05 | 40.9 | 1.02 | 20.4 | 5.69 | 10.26 | 1.17 | ND |
| 16.3 | | 9/21/05 | 46.1 | 1.11 | 28.2 | 10.80 | 35.3 | 2.19 | ND |
| 17.1 | | 10/5/05 | 49.0 | 1.15 | 8.61 | 6.05 | 11.19 | 1.00 | ND |
| 17.2 | | 10/5/05 | 54.0 | 1.29 | 8.37 | 8.73 | 25.0 | 2.31 | ND |

Appendix 1. Continued

| Sample | Location | Collection Date | % silts & clays (<1 mm fraction) | % TOC (< 1mm fraction) | Pyrethroid (ng/g) | DDT (ng/g) | DDE (ng/g) | DDD (ng/g) | Dieldrin (ng/g) |
|--------|------------|-----------------|----------------------------------|------------------------|-------------------|------------|------------|------------|-----------------|
| | Rice Paddy | | | Lambda-cyhalothin | | | | | |
| 20.1 | | 6/14/05 | 72.1 | 1.53 | ND | 6.55 | 4.76 | 21.1 | ND |
| 20.2 | | 6/14/05 | 76.5 | 1.60 | ND | 4.29 | 3.34 | 12.8 | ND |
| 20.3 | | 6/14/05 | 74.5 | 1.68 | ND | 8.31 | 7.33 | 8.31 | ND |
| 21.1 | | 6/27/05 | 71.6 | 1.59 | 16.9 | 3.83 | 6.18 | 26.7 | ND |
| 21.2 | | 6/27/05 | 70.8 | 1.54 | 65.0 | 9.35 | 7.56 | 13.5 | ND |
| 21.3 | | 6/27/05 | 73.2 | 1.60 | 61.1 | 5.10 | 4.67 | 26.8 | ND |
| 22.1 | | 8/3/05 | 78.3 | 1.62 | 3.25 | 2.68 | 3.24 | 18.5 | ND |
| 22.2 | | 8/3/05 | 79.0 | 1.67 | 4.57 | 6.19 | 5.66 | 35.6 | ND |
| 22.3 | | 8/3/05 | 77.6 | 1.69 | 4.05 | 3.36 | 3.79 | 19.4 | ND |
| 23.1 | | 10/5/05 | 81.0 | 1.92 | 19.1 | 12.60 | 17.7 | 84.8 | 2.60 |
| 23.2 | | 10/5/05 | 82.2 | 1.68 | 3.44 | 5.30 | 13.2 | 52.9 | 4.32 |
| 23.3 | | 10/5/05 | 79.4 | 1.89 | 13.2 | 262 | 21.3 | 95 | 2.08 |