REDUCING DORMANT SPRAY RUNOFF FROM ORCHARDS

By

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STATE OF CALIFORNIA
Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch
Environmental Hazards Assessment Program
Sacramento, California 95814-5624

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EXECUTIVE SUMMARY

"Reducing Dormant Spray Runoff from Orchards"

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Department of Pesticide Regulation

PURPOSE

Since 1988, scientists from the Central Valley Regional Water Quality Control Board have tested water quality in the San Joaquin River watershed using toxicity tests. They found that water samples from certain areas of the watershed caused mortality in a species of water flea (*Ceriodaphnia dubia*). *Ceriodaphnia dubia* is used in these toxicity tests because it is sensitive to insecticides and represents aquatic arthropods (one of the components of the U.S. Environmental Protection Agency's three-species toxicity tests). Based on these results, the Central Valley Regional Water Quality Control Board suggested the insecticides chlorpyrifos and diazinon as a possible cause of the toxicity identified in the water samples.

The Department of Pesticide Regulation, which is responsible for preventing pesticide contamination of surface water and ground water, conducted a study to identify mitigation measures to prevent the runoff of chlorpyrifos, diazinon, and methidathion. These are the three most commonly used insecticides applied to orchards during the winter dormant spray season to control overwintering pests. The predominant source of pesticides in streams and rivers is generally believed to originate from surface runoff, as opposed to aerial deposition or subsurface flow. This study was conducted to determine if vegetation between the tree rows of an orchard significantly reduces runoff of these insecticides during rainy periods in the Central Valley.

STUDY METHODS

DPR scientists sampled rain runoff from a peach orchard. Treatments on the site consisted of clover in the row middles, oats in the row middles, and no cover crop in the orchard row middles. Runoff from each treatment was analyzed for the three insecticides and the total amount lost was calculated and statistically analyzed. Half-lives were also determined for each insecticide in soil and vegetation.

RESULTS

The first rain event occurred 12 days after application of the insecticides. For all three insecticides, runoff concentrations were lowest for the clover, followed by oats, then the no-cover-crop treatment. The second rain event occurred 14 days after application. Again runoff from clover-treated rows had the lowest average concentration for all three insecticides, followed by oats and the no-cover-crop treatment. Statistical analyses indicated vegetated rows had a significantly lower amount of pesticide contained in runoff water than non-vegetated rows for each insecticide.

CONCLUSIONS

For all three insecticides, cover crops were effective for reducing insecticide runoff compared to planting no cover crop between rows. The specific mechanisms responsible for the reduction in insecticide runoff have not been definitely determined but appear to be related to the physico-chemical properties of each insecticide. Care should be taken when extrapolating these results to other fields with different soil types and vegetation covers.

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Date 7/15/97

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ABSTRACT

In winter months, many growers in California apply dormant spray insecticides to stone fruit and nut crops to control over-wintering pests. Chlorpyrifos (phosphorothioic acid O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester), diazinon (phosphorothioic acid O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester), and methidathion (phosphorodithioic acid S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl ester) are the predominant insecticides used. All three have been detected in surface water of the Central Valley of California with some concentrations high enough to cause mortality to a water flea used to monitor water quality. Since surface runoff during winter rains is believed the predominant source of these insecticides, this study was conducted to determine if dormant spray runoff could be controlled using cover crops. Runoff from three treatments: no seed, clover and oats, was compared in a peach orchard. Soil half-lives were 15, 6.4 and 9.6 d for chlorpyrifos, diazinon, and methidathion, respectively. Vegetation half-lives were 8.5, 5.7, and 4.4 d for chlorpyrifos, diazinon, and methidathion, respectively. Runoff concentrations and mass were highest in no seed, followed by oats, then clover treated rows. Mass runoff of insecticides in vegetated rows was reduced by as much as 74% over non-vegetated rows. Analysis of variance indicated mass runoff of each insecticide from vegetated rows was significantly lower than non-vegetated rows. Analysis of filtered vs. unfiltered runoff water indicated that 10%, 44%, and 59% of the chlorpyrifos, diazinon, and methidathion lost from the field was in the dissolved phase, respectively. Potential mechanisms involved in cover crop reduction of insecticide runoff include reduction in runoff volume, shorter persistence on vegetation than soil, decrease in insecticide mass with soil borne runoff, and insecticide sorption to plant surfaces.

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INTRODUCTION

During winter months, many growers in California apply dormant spray insecticides to stone fruit and nut crops to control over-wintering peach twig borer (*Anarsia lineatella*), San Jose scale (*Quadraspidiotus perniciousus*), and mites. Chlorpyrifos (phosphorothioic acid O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester), diazinon (phosphorothioic acid O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester), and methidathion (phosphorodithioic acid S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl ester), along with a dormant spray oil, are the predominant insecticides used to control these pests. Ethyl parathion (phosphorothioic acid O,O-diethyl O-(4-nitrophenyl) ester) was also commonly used prior to the U.S. EPA ban on its use at the end of 1991. The dormant spray season usually occurs from December to February, with the highest applications typically occurring in January (DPR, 1991; 1992; and 1993). In the 1991-92 winter season, about 47,000 kg, 181,000 kg, and 80,000 kg of chlorpyrifos, diazinon, and methidathion, respectively, were applied to stone fruit and nut crops in the entire state. In the 1992-93 winter season, about 29,000 kg, 235,000 kg, and 86,000 kg of chlorpyrifos, diazinon, and methidathion were applied, respectively. The use of diazinon increased 30% after the ban on ethyl parathion use in orchards in 1991. In addition, choice of dormant spray varies, depending on grower preference, insect pressure and resistance at a given location, and cost.

In 1988, scientists from the Central Valley Regional Water Quality Control Board of California began testing water quality in the San Joaquin River (SJR) watershed using bioassays. The purpose of these tests was to characterize water quality in the SJR, its tributaries and drains, and to identify sources of toxicity seen. Results indicated waters from certain regions of the watershed caused significant mortality to the water flea, *Ceriodaphnia dubia* (Foe and Connor, 1991). The specific cause of toxicity was not determined but was attributed to pesticides in general.

During the winter of 1991-92, water samples collected in the SJR watershed were again found toxic to *C. dubia* and chlorpyrifos and diazinon were implicated as a potential cause of toxicity (Foe and Sheipline, 1993). During the winters of 1991-92 and 1992-93, the California Department of Pesticide Regulation (DPR) also conducted monitoring in the watershed and determined that 10, 72, and 18% of the 108 samples collected contained chlorpyrifos, diazinon, and methidathion, respectively (Ross et al., 1996). In addition, 2, 13, and 1% of these samples exceeded the *C. dubia* 96-hour LC_{50} for chlorpyrifos, diazinon, and methidathion, respectively. In addition to potential acute toxicity, concentrations measured in between rain events were near the chronic criterion for diazinon, 0.04 µg/L, established by the California Department of Fish and Game to protect freshwater aquatic life (Menconi and Cox, 1994).

The predominant source of pesticides in streams and rivers is generally believed to originate from surface runoff, as opposed to aerial deposition or subsurface flow (Leonard, 1990; Spencer, et al. 1985; Majewski and Capel, 1995; Squillace and Thurman, 1992). In order to control surface runoff of pesticides, various agricultural management practices have been suggested, however, many were originally developed to control soil erosion (Baker and

Johnson, 1983; Fawcett et al. 1994; Leonard, 1990). Management practices to control pesticide runoff gained interest in the 1970s and have included such practices as: conservation tillage (Baker et al., 1978; Hall et al., 1984; Triplett, et al., 1978); vegetative filter strips (Asmussen et al., 1977; Dillaha et al., 1989; Rhode et al., 1980); formulation changes (Kenimer et al., 1989; Mills and Thurman, 1994; Wauchope et al., 1990); addition of polymers (Singh et al., 1996) and soil incorporation (Leonard et al., 1979; Rhode et al., 1979; Wauchope and Leonard, 1980). Each practice has varying degrees of success depending on pesticide properties, climatic factors, and field conditions (Rawls et al., 1980; SETAC 1994). In addition, few management practices have been investigated in an orchard setting to quantify their effectiveness in reducing dormant spray runoff. Glenn and Welker (1989) examined the effectiveness of four soil management systems for improving rain infiltration in a young peach orchard in West Virginia. They found that a mowed sod treatment was superior at improving rain infiltration to killed sod, cultivated strips, and no vegetation. However, pesticide runoff was not measured.

As a substitute for organophosphorous sprays during winter months, *Bacillus thuringiensis* (a biological control agent) and a dormant spray oil have been effective for control of peach twig borer, scale, and mites (Barnett et al., 1993; Hendricks, 1995). However, many growers still prefer dormant insecticide sprays because they afford better coverage, interfere less with post-bloom orchard management, and reduce the impact on beneficial arthropods (Rice and Jones, 1988; Oltman, 1995). Therefore, as long as dormant spray use continues, it will be important to develop control strategies to reduce and/or prevent the movement of these insecticides into surface water if water quality is to be improved.

In-field cover crops may be an effective tool for controlling pesticide runoff (Reddy et al., 1994). Cover crops have been employed to decrease soil erosion, improve water infiltration, prevent surface sealing of the soil, and consequently reduce water and sediment runoff. With a decrease in water and sediment runoff, a decrease in the mass of pesticide lost in surface runoff would also be expected. However, the reduction in pesticide runoff associated with a cover crop can be variable and depends on such factors as: pesticide properties and formulation, time interval between rainfall and application, rainfall intensity and duration, and initial soil moisture content (Leonard, 1990). In addition, foliar sorption may be another important factor, the effectiveness of which is related to pesticide and plant type. In general, only a fraction of the pesticide mass residing on foliage at the time of a rainfall event has the potential for wash-off (Willis et al., 1980). Lipophilic pesticides penetrate waxes of the leaf surface and are difficult to wash off with rain water; e.g. 5-10% of toxaphene residues available for washoff (Willis et al., 1980). However, washoff estimates for more polar compounds, including some organophosphates, range from 46 to 88% (Willis et al., 1980; Reddy et al., 1994; Willis et al., 1986; Willis et al., 1992; McDowell et al., 1984). Dislodgeable chlorpyrifos and diazinon residues from Kentucky bluegrass (*Poa pratensis* L.) on the day of application, measured by rubbing the grass blades, were less than 2.5 and 1.5% of the total applied mass, respectively (Sears et al., 1987). In another study, thatched turf prevented the movement of diazinon to the soil surface and promoted degradation of the parent compound to CO_2 with repeated irrigations (Branham and Wehner, 1985). After three weeks, a maximum of 47% of the parent compound remained in the vegetation, indicating the potential for diazinon to adhere to or absorb into vegetation. In addition, diazinon was not seen to leach during that period, with 96% remaining in the top 10 mm of the soil profile with or without thatched turf present.

Given the potential for plants to retain pesticides on field, the use of cover crops for reducing dormant spray runoff in orchards was investigated. Cover crops are already in use in California, such as grains to promote water infiltration and clover to promote nitrogen fixation. Therefore, differences in the mass runoff of chlorpyrifos, diazinon, and methidathion were investigated in a peach orchard using three treatments: 1. no seed (bare soil), 2. a clover seed mix and 3. oats (*Avena sativa* L).

MATERIALS AND METHODS

Study Site

This study was conducted in a peach orchard, planted in February of 1990, located at the University of California's Wolfskill Ranch in Winters. The test plot was 0.89 ha consisting of 27 rows, each 69.9 m in length and 4.73 m in width (Fig. 1). The soil is classified as a Yolo silty loam (fine silty, mixed, thermic Typic Xerochrepts): 37% sand, 38% silt, 25% clay, with an organic carbon content of 1.2%, and a bulk density of 1.42 g/cm^3. Individual rows were between 1 and 2% slope, sufficient to create runoff during natural rain events.

Prior to planting, the field was disced and land planed. In the no-seed treatment rows, Roundup®, Surflan®, and Goal® were applied at 2.3, 9.4, and 9.4 L ha^{-1}, respectively, to keep the soil free of vegetation. The clover mix (Table 1) was applied at a rate of 84 kg ha^{-1} and oats at a rate of 106 kg ha^{-1}. Both were planted on 16 November 1995, using a Vicon® seed spreader. A springtooth harrow was used to lightly incorporate seed into the soil. The three insecticides were applied together using a mini air-blast sprayer on 4 January 1996, at a nominal rate of 1120 g a.i. ha^{-1}, sprayed with 1,870 L ha^{-1} of water and 3.78 L ha^{-1} of Volk Supreme oil®. Applied formulations were diazinon 50 WP, chlorpyrifos EC, and methidathion 25 WP.

Experimental Design

Treatments were assigned to the peach plot in a randomized complete block (RCB) design with three treatments: no seed, clover, and oats (Fig. 1). The field was blocked from south to north, along a tree height gradient which resulted from a prior study. Treatment rows used for sampling were surrounded on either side by "buffer" rows treated in a similar manner. "Buffer" rows were not sampled, they simply served as protection against cross contamination between treatment rows.

The concentration of each insecticide deposited in the tree canopy was measured (Appendix I) and converted to mass. Mass was analyzed with a RCB analysis of variance, to assure that any row to row differences in runoff were not due to differences in application rates. Results from soil and vegetation analyses were also used in this manner.

Soil and vegetation were collected from each treatment row one week prior to application, on the day of application (day 0), and days 3, 7, 13, 20, 28, and 35 after application. Concentrations (Appendices II and III) were converted to mass, log transformed (to provide homogenous variances over time), and analyzed using a repeated measures RCB design (Little and Hills, 1978) conducted for each insecticide in each medium. Results were examined for significance of block, treatment, and day by treatment terms. Since significant interactions, block, and treatment effects were not found, a model of the change in mass over time for the entire plot was examined for the significance of linear, quadratic, and higher order terms using a lack-of-fit regression analysis (Littell et al., 1991). The significant equations were then identified and used to generate soil and vegetation half-lives for each insecticide.

Rain-runoff water was collected from each treatment row in each block. Water was collected at 30-min intervals between 0 and 3 hours of runoff during the first two storm events that occurred January 16 and 18, 1996. Runoff concentrations of all three insecticides and volume leaving each treatment row were measured (Appendix IV). The total mass of insecticide leaving each treatment row was calculated and analyzed with a RCB analysis of variance.

Sample Collection

Deposition onto peach trees was estimated using absorbent cotton sheets placed at three heights (1.2 m, 2.1 m, and 3.0 m) on a single mast. Deposition sheets were spaced to cover the total height of most tree limbs in the orchard (a total of about 2.4 m). One mast was randomly positioned in each treatment row. In addition, a tank sample was collected from the mini air-blast sprayer just prior to application, to confirm nominal rates. Samples collected on absorbent cotton sheets were placed in glass jars and kept frozen ($\leq 0\,^{\circ}C$) until analyzed. Tank samples were placed in glass jars and kept refrigerated at $4\,^{\circ}C$ until analyzed.

Two composite soil samples were collected from each treatment row (Fig. 1). In rows with vegetation, the vegetation was first cut away and discarded, then the soil below collected. A composite sample consisted of three soil plugs, randomly collected from a single treatment row. Soil plugs were collected with stainless steel cylinders (4.13 cm in diameter), pushed 2.54 cm into the ground. Soil plugs were then composited into glass jars and kept frozen until analyzed for insecticides and moisture content. Samples collected prior to application were all below the reporting limits for each insecticide, although trace amounts of diazinon were detected (see below). The two composite samples collected in each row were averaged prior to statistical analyses.

Two composite vegetation samples were randomly collected from each treatment row in each block. Each composite consisted of 3 - 12 sub-samples from a uniform area (0.023 m^2), enough to collect 50 - 80 g for chemical analysis and moisture determination. The total area sampled was recorded for later use in mass balance calculations. Samples collected prior to application were below the reporting limits for chlorpyrifos and methidathion. However, due to an application of diazinon to an adjacent plot, some diazinon residues were detected on background samples. Background residues ranged from 40 to 225 $\mu g\ kg^{-1}$, dry weight, 3 orders of magnitude below post-application concentrations. Therefore, adjustment for background residues was not performed. As for soil, composite vegetation samples were placed in glass containers and kept frozen until analyzed. The two composite samples from each row were also averaged prior to statistical analyses.

Runoff water leaving each treatment row after the first and second rainfall events was collected automatically using ISCO® water samplers (Models 2700R and 6700, ISCO Inc., Lincoln, NE). Water sampling was triggered by an ISCO® liquid level actuator that sensed the presence of water near the sampling port inlet. Samples were collected into glass jars inside the auto-sampler, and placed on wet ice within one hour after sampling ceased. Runoff-water volume was measured using 75-mm flumes (Plasti-Fab, Inc., Tualatin, OR) equipped with a still well housing a pressure transducer (PDCR 830, Druck Inc., Danbury, CT). Pressure transducers were connected to a Campbell 21X datalogger (Campbell Scientific Inc., Logan, UT) to continuously monitor water height in the flume. Water height was converted to volume using calculations experimentally derived for this flume by Clemmens et al. (1984). The mass of insecticide leaving each treatment row was calculated by multiplying the concentration measured at a given interval, by the corresponding volume of water leaving the row during that interval.

In addition to whole water analysis, paired water samples were filtered with a 0.45-μm cellulose-fiber filter to remove suspended sediment. Analysis was performed on the filtered water to determine the concentration of each insecticide in the "dissolved" phase. The difference in insecticide mass between filtered and unfiltered water concentrations is presumed to be the mass attached to fine particles and suspended sediment ≥0.45 μm.

Rainfall was collected at the field edge during both storm events using a wet/dry deposition sampler (model 301, Aerochem Metrics, Inc., Bushnell, FL). Rainfall was analyzed as above for whole water samples.

Mass Calculations

Deposition concentrations (μg m^{-2}) were converted to mass (g ha^{-1}) by first averaging concentrations deposited at three heights in each row. Mass deposited on tree limbs was then calculated by multiplying the average concentration by the row by height area, converting to grams, then dividing by the row area (0.033 ha).

Soil concentrations (μg g^{-1}, dry weight) were converted to mass (g ha^{-1}) by first averaging the two sub-block replicates in each row. Mass was then calculated by multiplying average concentrations by soil bulk density (measured as g cm^{-3}, dry weight) then by volume of soil per row (measured as cm^3, i.e. row length x row width x depth of soil sample collected), converting micrograms to grams, then dividing by the row area.

Vegetation concentrations (μg g^{-1}, dry weight) were converted to mass (g ha^{-1}) by first averaging the two sub-block replicates in each row. Mass was then calculated by multiplying average concentrations by vegetation density in each row (measured as g m^{-2}, dry weight), then by area of each row (measured in m^2), converting micrograms to grams, then dividing by the row area.

Rain runoff concentrations (µg L^{-1}) were converted to mass (g ha^{-1}) by first multiplying concentrations in each sampling interval by the volume measured in that interval (measured in L), converting micrograms to grams, multiplying by 27 rows (to estimate entire field loss), then dividing by the row area.

Chemical Analysis

Deposition sheets (0.18 m^2) were extracted by shaking for 30 min in 500 ml ethyl acetate. Two mL of extract were placed in an autosampler vial, and if preliminary analysis by gas chromatography (GC) indicated concentrations were less than 800 μg m^{-2}, a 100 mL aliquot of the extract was concentrated before completing the analysis. Extracts were concentrated to 2-3 ml in a 250 mL boiling flask on a rotary evaporator at 62 - 65°C. The extract was quantitatively transferred to a 15 mL graduated test tube, the flask rinsed 3 more times with 2 mL ethyl acetate and transferred to the test tube. The extract was placed on a nitrogen evaporator in a water bath at 40°C, and reduced to a final volume of 2 mL. The extract was analyzed with an HP 5890 GC equipped with dual flame photometric detectors (Hewlett Packard, Palo Alto, CA), and HP-1, 10 m x 0.53 mm x 2.65 μm column and HP-17, 10 m x 0.53 mm x 2.0 μm column, using an injection volume of 3 µL. Initial oven temperature was

140 °C, held for one min, then increased 10 °C min^{-1} and held at 180 °C for 5 min, then increased 40 °C min^{-1} to a final temperature of 260 °C and held for 4 min. Injector and detector temperatures were 220 °C and 250 °C, respectively. The reporting limit for all three insecticides was 3.3 $\mu g\ m^{-2}$.

Soil (50 g) was placed in a jar and 50 - 100 g anhydrous sodium sulfate mixed into the sample. The sample was extracted by shaking vigorously for 10 sec with 100 mL of ethyl acetate, then placed on a gyratory shaker for 60 min at 180-200 rpm. The sample was allowed to settle for 2 min after shaking, then the solvent was decanted into a 500 mL evaporating flask through a 15 cm, #4 Whatman filter paper with 20 g anhydrous sodium sulfate. Extraction was repeated once with 100 mL ethyl acetate, shaken for 30 min, then a second time with 50 mL ethyl acetate, shaken for 15 min. The extract was concentrated to 2 mL on a rotary evaporator, under vacuum, at 62-65 °C. The extract was quantitatively transferred to a 15 mL graduated test tube, with three rinses of 2 mL ethyl acetate aliquots. The extract was placed on a nitrogen evaporator in a water bath at 40 °C, and reduced to a final volume of 5 mL, and 3 µL injected for analysis by GC as above. The reporting limit for all three insecticides is 4 $\mu g\ kg^{-1}$, wet weight.

Vegetation (25 g) was extracted with 100 mL acetonitrile in a blender set at high speed for 2 min. The sample was filtered through #1 Whatman filter paper into a 100-mL mixing cylinder containing 10 g sodium chloride and shaken vigorously for 60 sec. The upper acetonitrile layer (20 ml) was pipetted into a 125 mL boiling flask, and rotoevaporated under vacuum at 60 °C just till dryness. The extract was redissolved in 5 mL ethyl acetate and transferred through a 0.2 μm Nylon Acrodisc filter into a 15-mL test tube. The flask was rinsed two more times with 2 mL ethyl acetate aliquots and filtered into the test tube. The extract was concentrated to just under 1 mL on a nitrogen evaporator in a water bath at 40°C, then brought to a final volume of 1 mL with ethyl acetate and mixed. The injection volume was 3 μL, submitted for GC analysis as described above, except the oven temperature was initially 150°C, held for 1 min, then increased by 10°C min^{-1} until a temperature of 200°C was reached and held for 2 min, then increased 20°C min^{-1} until a final temperature of 260°C was reached and held for 6 min. The reporting limit for both vegetation types and all three insecticides was 16 $\mu g\ kg^{-1}$, wet weight.

Water (500 mL) was placed in a separatory funnel and extracted by shaking for 2 min with 100 mL of methylene chloride. (Water for filtered analysis was filtered through a 0.45 μm cellulose nitrate filter to remove suspended soil and sediment prior to extraction. The celluose nitrate filter was tested in spike-recovery analyses to ensure that the filter did not retain any of the insecticides analyzed.) After the phases separated, the lower layer of methylene chloride was drained through a funnel, containing 20 g sodium sulfate, into a boiling flask. The sample was extracted two more times with 80 mL methylene chloride. The extract was evaporated just to dryness on a rotary evaporator at 35°C. Five mL of acetone was added to the flask and swirled to dissolve remaining residue. The extract was transferred to a graduated test tube, the flask rinsed two more times with 2 mL of acetone and transferred to the test tube. The extract was evaporated to a final volume of 1 mL using a nitrogen evaporator in a 35°C water bath. The injection volume was 3 μL, submitted for GC analysis as for vegetation samples. Reporting limits for water were 0.03, 0.02, and 0.02 μg/L for chlorpyrifos, diazinon, and methidathion, respectively. The reporting limit for filtered water was 0.05 μg/L for all three insecticides.

Prior to the study, each medium sampled was spiked at five concentration levels (three replicates at each level), to assess overall method precision. It was assumed that spike level did not influence variation in recoveries. Average recoveries (standard deviation) for spiked deposition sheets were 97(7.9), 94(7.0), and 101(8.8)% for chlorpyrifos, diazinon, and methidathion, respectively. Spiked deposition sheets used to monitor quality of data generated during field sample analyses were within 10% of average recoveries measured for precision. Average recoveries for spiked soil were 91(3.9), 92(4.0), and 99(6.3)% for chlorpyrifos, diazinon, and methidathion, respectively. Spiked soil samples analyzed with field samples were within 21% of average recoveries measured for precision. Average recoveries for clover were 106(8.3), 107(13), and 109(12)% for chlorpyrifos, diazinon, and methidathion, respectively. Average recoveries for oats were 96(4.9), 91(4.8), and 101(6.8)% for chlorpyrifos, diazinon, and methidathion, respectively. Spiked vegetation samples analyzed with field samples were within 21% of average recoveries measured for precision. Average recoveries for water were 92(4.9), 94(4.8), and 96(5.5)% for chlorpyrifos, diazinon, and methidathion, respectively. Spiked water samples analyzed with field samples were within 24% of average recoveries measured for precision. Average recoveries for filtered water were 85(4.8), 96(3.8), and 110(7.4)% for chlorpyrifos, diazinon, and methidathion, respectively. Filtered-water spikes.analyzed with field samples were within 15% of average recoveries measured for precision. In addition, field blanks and equipment rinse samples were periodically analyzed; all were below the laboratory's reporting limits.

RESULTS AND DISCUSSION

Application Rates and Deposition

Tank samples were collected to ensure that nominal application rates were achieved. The nominal application rate was 1120 g ha^{-1} for each insecticide. Tank sample results were 990, 1110, and 1030 g ha^{-1}, for chlorpyrifos, diazinon, and methidathion, respectively. Tank sample rates were within 12% of nominal rates. Nominal and tank rates do not match exactly due to a couple of sources of error: weighing the product prior to mixing in the spray tank, inadequate mixing in the spray tank prior to tank sample collection, and errors in chemical analysis. However, in spite of these potential sources of error, tank sample results are well within the measured variation seen in the laboratory for other sampling media.

Estimates of mass deposited in the tree canopy averaged 261, 243, and 259 g ha^{-1} for chlorpyrifos, diazinon, and methidathion, respectively: 23, 22, and 23% of nominal application rates, respectively (Table 2). The mass deposition estimate for diazinon was higher than the 3.1% reported by Glotfelty, et al. (1990) in another peach orchard in California. In that study, a twig dip method plus twig surface area estimate was used to measure deposition in the tree canopy. Deposition-sheet measurements used in this study are likely to be less variable than the twig method because of the large error associated with twig surface area mesurements. In addition, replicate tree measurements were not made in that study, whereas multiple measurements at various heights in the tree canopy were used in this study. In contrast, the deposition sheet may over-estimate deposition if sheets are more absorbent than tree twigs, allowing the insecticide spray to adhere to the surface more readily. The most accurate method for estimating tree deposition can not be determined from these data and the differences between methods are provided for informational purposes only. Analysis of variance of mass deposition to trees indicated neither blocks nor treatment terms were significant for each insecticide, indicating a fairly uniform application to the tree canopy (Table 2).

Insecticide Concentrations

Soil and Vegetation

Soil concentrations of chlorpyrifos on the day of application averaged 651, 698, and 591 $\mu g\ kg^{-1}$, dry weight, for no seed, clover, and oat treated rows, respectively (Table 3). For diazinon, initial concentrations were 877, 973, and 721 $\mu g\ kg^{-1}$, dry weight, for no seed, clover, and oat treated rows, respectively. For methidathion, initial concentrations were 1010, 1140, and 792 $\mu g\ kg^{-1}$, dry weight, for no seed, clover, and oat treated rows, respectively.

Vegetation concentrations of chlorpyrifos on the day of application averaged 137 and 158 $mg\ kg^{-1}$ dry weight, for clover and oat treated rows, respectively (Table 4). For diazinon, initial concentrations were 126 and 129 $mg\ kg^{-1}$ dry weight, for clover and oats, respectively. For methidathion, initial concentrations were 154 and 157 $mg\ kg^{-1}$ dry weight, for clover and oats, respectively.

Runoff Water

The first rain event occurred on 16 January 1996, 12 d after application. Total rainfall was 38 mm in 15 h. Due to flooding that occurred from an adjacent road, only the first sampling interval is reported in Figure 2. Average concentrations (n=2) for chlorpyrifos were 23, 11, and 22 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively. Average concentrations (n=2) for diazinon were 68, 25, and 37 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively. Average concentrations (n=2) for methidathion were 170, 58, and 110 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively. For all three insecticides, runoff concentrations were lowest for clover, followed by oats and then the no seed treatment.

The second rain event occurred on 18 January 1996, 14 d after application; total rainfall was 15 mm in 10 h. Concentrations varied with treatment but again runoff from clover treated rows generally had the lowest average concentrations for all three insecticides, followed by oats and the no seed treatments (Fig. 3). Average runoff concentrations[1] of chlorpyrifos in unfiltered water ranged from 6.3 - 8.9 $\mu g\ L^{-1}$, 5.3 - 6.4 $\mu g\ L^{-1}$, and 6.4 - 11 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively (Fig. 3). Average runoff concentrations of diazinon in unfiltered water ranged from 15 - 28 $\mu g\ L^{-1}$, 13 - 20 $\mu g\ L^{-1}$, and 22 - 30 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively. Average runoff concentrations of methidathion in unfiltered water ranged from 37 - 68 $\mu g\ L^{-1}$, 32 - 42 $\mu g\ L^{-1}$, and 33 - 51 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively.

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[1]Average concentrations are a mean of two to three block samples collected during each 30 min sampling interval. See Appendix IV for raw data.

Runoff water collected during the second storm was also filtered and analyzed to estimate insecticide concentrations in the dissolved form. To generate average concentrations where data were below the detection limit, one half the detection limit was used. In the case of chlorpyrifos where trace values were quantified below the reporting limit, those trace values were used (Appendix IV). Average runoff concentrations of chlorpyrifos in filtered water ranged from 0.18 - 2.2 $\mu g\ L^{-1}$, 0.08 - 0.22 $\mu g\ L^{-1}$, and 0.60 - 0.91 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively. Average runoff concentrations of diazinon in filtered water ranged from 2.8 - 13 $\mu g\ L^{-1}$, 3.1 - 11 $\mu g\ L^{-1}$, and 6.8 - 16 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively. Average runoff concentrations of methidathion in filtered water ranged from 16 - 42 $\mu g\ L^{-1}$, 13 - 19 $\mu g\ L^{-1}$, and 18 - 32 $\mu g\ L^{-1}$ for the no seed, clover, and oat treated rows, respectively.

Rainfall

Rain samples were analyzed for all three insecticides during both storm events. Mean concentrations (n=3) for the first storm were 0.30, 0.76, and 0.55 $\mu g\ L^{-1}$ for chlorpyrifos, diazinon, and methidathion, respectively. Mean concentrations (n=2) for the second storm were 0.14, 0.17, and 0.12 $\mu g\ L^{-1}$ for chlorpyrifos, diazinon, and methidathion, respectively. These concentrations were within the range of concentrations reported for chlorpyrifos and diazinon in the San Joaquin Valley of California during the winter of 1992-93 (Ross et al., 1996). Methidathion was not detected in rainfall in that study.

Insecticide Mass

Soil and Vegetation

Insecticide mass of chlorpyrifos in soil ranged from an average high of 270 g ha^{-1} to a low of 41 g ha^{-1} (Appendix V). For diazinon the range was 380 to 7.0 g ha^{-1} and for methidathion 450 to 28 g ha^{-1}. Mass recovered in soil amounts to a maximum of 24, 34, and 40% of nominal application rates for chlorpyrifos, diazinon, and methidathion, respectively. Analysis of variance indicated block, treatment, and interaction terms were not significant (Table 5), therefore a single regression equation across treatments for each insecticide was conducted to estimate the soil half-life. Lack-of-fit tests (Littell et al., 1991) indicated a log-linear equation significantly described dissipation except for diazinon where a day^2 component was also significant (Table 6). However, improvement in the R^2 was small (R^2 was 0.91 with day^2 and 0.90 without), indicating little improvement in the fit of the data. Therefore, diazinon dissipation rates were determined using only the day component. Soil dissipation half-lives were 15, 6.4, and 9.6 days for chlorpyrifos, diazinon, and methidathion, respectively (Fig. 4). The half life for chlorpyrifos was shorter than the field dissipation half-lives reported in DPR's chemistry database (Table 7). The half life for diazinon was similar to those reported previously while the half life for methidathion was longer than the single value reported to DPR (Table 7). Additional dissipation half-lives found in the literature for chlorpyrifos range from 1.3 to over 200 d (Racke, 1993) for diazinon from 7 to 56 d (Branham and Wehner, 1985; Bartsch, 1974), and for methidathion 4.5 to 11 d (Smith et al., 1978). Dissipation half-lives depend on a number of factors such as: temperature, microbial activity, and soil moisture and therefore account for a wide range of half-lives reported in the literature.

Insecticide mass of chlorpyrifos on vegetation ranged from an average high of 260 g ha^{-1} to a low of 11 g ha^{-1} (Appendix V). For diazinon the range was 210 to 2.3 g ha^{-1} and for methidathion 260 to 0.8 g ha^{-1}. Mass recovered on vegetation amounts to a maximum of 23, 19, and 23% of nominal rates for chlorpyrifos, diazinon, and methidathion, respectively. Analysis of variance indicated block, treatment, and interaction terms were not significant (Table 5). Therefore, to estimate vegetation half-lives, a single regression equation for each insecticide, combining blocks and vegetation types, was conducted. Log-linear equations were significant for each insecticide (Table 6). Vegetation half-lives calculated using mass, were 8.5, 5.7, and 4.4 days for chlorpyrifos, diazinon, and methidathion, respectively (Fig. 5). Vegetation half-lives reported in this study were similar to those found in the literature; <1 to 14 d for chlorpyrifos, 2 to 5 d for diazinon and 1 to 5 d for methidathion (Racke, 1993; Bartsch, 1974; Celik et al., 1995).

Runoff Water

Total mass of insecticide lost in runoff water during the second storm showed clover with the lowest loss, followed by the oat and no seed treatments for all three chemicals (Fig. 6). Mass runoff in vegetated rows was reduced by as much as 74% over no-seed treatment rows (Table 8). In addition, mass runoff during the second storm was less than 0.1% of the nominal application rate of each insecticide, for all three treatments (Table 8). Had the rains occurred in less than 12 to 14 d, the total mass lost in runoff would be expected to be higher, but exactly how much higher is unknown. Similar results were seen for mass runoff from irrigated fields in southern California, which ranged from 0.02 to 0.24% of applied chlorpyrifos, 0.04 to 0.07% of applied diazinon, and 0.16 to 2.0% of applied methidathion (Spencer and Cliath, 1991).

In the analysis of variance of unfiltered runoff water, blocks were not significantly different, while treatment results were for each insecticide (Table 8). Orthogonal contrasts were significant for vegetated rows vs. unvegetated rows, while clover was not significantly different from oats. The mass lost from clover treated rows is about half that of oats, which in turn is about half that of the no seed treatment (Table 8). This trend indicates clover may be better than oats at reducing movement of these insecticides in runoff water, but the variation in this field trial may have been too great and/or the sample size too small to statistically distinguish between them.

In addition to whole water samples, runoff water was filtered and analyzed to determine the proportion of insecticide lost in the dissolved phase. The maximum proportion in the dissolved vs. whole water phase was 10, 44, and 59% for chlorpyrifos, diazinon, and methidathion, respectively (Fig. 6). These proportions reflect the solubility and adsorptivity of these insecticides: chlorpyrifos is least soluble with the highest soil adsorption, methidathion is the most soluble with the lowest soil adsorption, while diazinon is in between (Table 7).

Analysis of variance results for filtered runoff water during the second storm indicates treatments are significantly different for chlorpyrifos and methidathion, but not diazinon (Table 9). Orthogonal contrasts indicate vegetated treatment rows are significantly different from rows without vegetation for chlorpyrifos and methidathion, with no seed > oat > clover. The mass of diazinon dissolved in runoff water leaving the three treatment rows was not significantly different. Results from this analysis indicate that chlorpyrifos and methidathion partitioning from water to these plant surfaces may be important in controlling runoff, while for diazinon it is not.

Rainfall

The mass input of chlorpyrifos, diazinon, and methidathion from rainfall to this plot during the second storm amounted to 0.021, 0.026, and 0.018 g ha^{-1}, respectively. Rain contributed less than 0.2% to the mass of material already on field at the time the second storm began. Also, the mass input from rainfall contributed less than 15, 7, and 2% of the maximum mass in runoff water of chlorpyrifos, diazinon, and methidathion, respectively. Even if 100% of the mass input from rain runs off, the contribution of insecticide mass from rain water to the total load in runoff water from this field is small. In addition, it is unlikely that 100% of the insecticide load from rain water will runoff since soil and plant sorption of all three insecticides is considered to occur rapidly (Racke, 1993; Bartsch, 1974; Van Dyk, 1975; Eberle and Hormann, 1971). In addition, in a dormant-spray trial conducted in an almond orchard planted with a cover crop of barley, dislodgeable diazinon residues (those removed with a water/surfactant solution) were only 41% of total vegetation residues 4 h after application, indicating rapid sorption under winter conditions (Ross, unpublished data). Therefore, during the course of a rain event lasting 10 to 15 h, rapid sorption and translocation of these chemicals would be expected. Although sorption of these insecticides was found to be rapid in other studies, it still may be instructive to examine the contribution of rain residues to an entire watershed using a watershed model.

Influence of Cover Crops on Insecticide Mass in Runoff

There are a number of factors influencing the mass of insecticide in rain runoff water from vegetated and unvegetated rows. Mass runoff is calculated as a function of both concentration and volume, and as such, one or both factors may be important in reductions seen in this and other studies (Leonard 1990). Other potential factors include persistence on vegetation, decrease in soil erosion and therefore particles carrying adsorbed insecticides, and insecticide sorption to plant surfaces (Leonard 1990, Fawcett et al., 1994).

In this study, concentrations were not markedly different between treatments, however the trend indicated runoff water from clover generally had the lowest concentrations, followed by oats and then the no seed treated rows. In addition, volume measurements showed the same trend, with clover having the lowest runoff volumes, followed by oats and then no seed treated rows (Fig. 7). Volume differences were significant, with vegetated rows having significantly lower runoff volumes than non-vegetated rows, indicating reduction in volume was a factor in reducing mass runoff (Table 10).

Vegetation half-lives were shorter than soil half-lives for all three insecticides and may be a factor responsible for reducing runoff in vegetated rows. Persistence has been shown to be positively correlated with runoff concentrations and mass in other studies, chemicals with longer persistence tend to have higher runoff concentrations (Leonard 1990). Factors influencing persistence in/on vegetation include degradation and volatilization. Degradation half-lives of chlorpyrifos and diazinon were less than 10 d in turf grass (Lemmon and Pylypiw, 1992). In addition, complete mineralization of diazinon to CO_2 was seen to occur within three weeks of application (Branham and Werner, 1985), indicating the ability of some plants to degrade these insecticides.

In addition to degradation, persistence on vegetation is also a function of volatilization from the plant surface. All three insecticides have been reported in air, fog, and rain of the San Joaquin Valley in California during winter months and post-application volatilization is considered a major source of these residues (Seiber et al., 1993; Glotfelty et al., 1990; Ross et al., 1996). It is generally believed that volatilization is the primary mechanism responsible for the disappearance of pesticide residues from plant surfaces (Racke, 1993; Harper et al., 1983; Seiber et al., 1979; Celik et al., 1995). Volatilization of pesticides from vegetation has been related to cumulative weather variables, such as temperature, solar radiation, humidity, and wind (Willis et al., 1992). For example, the best predictors of methyl parathion disappearance from cotton plants were temperature and wind. With increased temperature, pesticide vapor pressure increases and therefore volatilization from plant surfaces increases (Harper et al., 1983). With increased wind speed there is greater turbulence and decreased thickness of the still boundary layer that leads to greater volatilization from soil and plant surfaces (Spencer et al., 1973; Willis et al., 1992; Willis et al., 1983).

However, during winter volatilization rates should be slower than during other seasons, given cooler temperatures. For example, the vapor pressure of chlorpyrifos decreased two orders of magnitude with a change in temperature from 36.6°C to 15.8°C (Racke, 1993). Average daytime and nighttime temperatures in this study were 16.7°C and 12.9°C, respectively. In addition, slower wind speeds have been measured within an orchard vs. outside an orchard (Johnson, 1995). Also, the addition of oil has been shown to retard the volatilization of chlorpyrifos from plant surfaces and increases absorption into the leaf (Racke, 1993). Therefore, under winter dormant spray conditions with oil as a typical spray component with these insecticides, volatilization from cover crop surfaces in an orchard should be at a minimum.

Also, information from Glotfelty, et al. (1990) indicates greater than 50% of the diazinon applied to trees was lost from tree surfaces in the winter during the first 24 hours after application. The half-life for diazinon on cover crops in this study was 5.7 days, almost six times the half-life estimated for tree surfaces. Therefore, given roughly equal mass applied to tree and cover crop surfaces reported in this study, cover crops may more effectively retain insecticide residues than tree surfaces and contribute less to atmospheric loads. The mechanism of dissipation from cover crops under winter conditions, and relative loss compared with trees may require further investigation if current atmospheric concentrations are a health concern and if these practices are implemented on a broad scale in commercial orchards.

Reduction in soil erosion and adsorbed insecticide mass may also be influenced by the presence of a cover corp. If a majority of the insecticide mass is lost in the dissolved phase, (as for methidathion), sorptive surfaces in and around the field might be a feasible control strategy.

However, if a large proportion of the mass is attached to soil particles, (as for chlorpyrifos), then erosion control practices should help reduce runoff (Singh et al., 1996). Diazinon, an insecticide with properties in between, would best be controlled with a strategy that both reduces erosion and increases sorption in or around the field. Certain insecticide cover crops may be considered such a strategy, reducing soil erosion as well as providing additional surface area for sorption.

To clarify if soil adsorption is involved in runoff patterns seen, a RCB analysis of variance was conducted on the difference in mass between filtered and unfiltered water samples. The difference between mass of insecticide in filtered and unfiltered runoff water is presumed to be the mass attached to soil particles $\geq 0.45\ \mu m$ in diameter. The analysis of variance results indicate treatments are significant for chlorpyrifos and diazinon, with significant differences occurring between non-vegetated and vegetated treatment rows but not between clover and oats (Table 11). In contrast, treatment differences for methidathion are not significant. Results from this analysis indicate chlorpyrifos and diazinon have sufficient soil sorption for erosion control to be a potentially important mechanism for control of total runoff, while the same is not true for methidathion.

In addition to persistence and soil erosion control, adsorption to and/or absorption into plant surfaces is another potential mechanism resulting in lowered concentrations and mass in runoff from vegetated vs. non-vegetated rows. A rapid reduction in dislodgeable chlorpyrifos residues (80-90%) from clover was seen within 2 to 4 h after application (Goh et al., 1986). A similar reduction in dislodgeable chlorpyrifos residues (96%) was seen 24 h after application to cotton leaves (Buck, et al., 1980). In addition, in a dormant-spray trial conducted in an almond orchard planted with a cover crop of barley, dislodgeable diazinon residues were reduced 59% 4 h after application, indicating rapid sorption under winter conditions (Ross, unpublished data). Rapid sorption of methidathion residues was seen in citrus leaves, with an 82% reduction one day after application (Thompson et al., 1979). These data indicate different plant surface and insecticide combinations may have different sorption properties and proper selection of a cover crop to reduce runoff of a given insecticide will be important.

CONCLUSIONS

The effectiveness of cover crops for reducing insecticide runoff from orchards during the dormant spray season was investigated. In addition, dissipation in soil and vegetation was also examined to facilitate our understanding of the behavior of these insecticides in the field. Soil half-lives were 15, 6.4, and 9.6 d for chlorpyrifos, diazinon, and methidathion, respectively. Soil half-lives for chlorpyrifos, diazinon, and methidathion were similar to those reported by other researchers. Vegetation half lives were 8.5 d, 5.7 d, and 4.4 d for chlorpyrifos, diazinon, and methidathion, respectively. These half-lives fell within the range of half-lives reported in the literature for these insecticides. Vegetation half-lives were shorter than soil half-lives and may be a factor responsible for reducing runoff in vegetated rows since persistence has been shown to be positively correlated with runoff concentrations and mass in other studies.

Cover crops were effective for reducing insecticide runoff in unfiltered water relative to non-vegetated treatment rows for all three chemicals. Gradients in runoff concentrations and mass occurred, with highest concentrations and mass lost from non-vegetated rows, followed by oats, then clover. Mass runoff of insecticides in vegetated rows was reduced by as much as 74% over non-vegetated rows. In addition, analysis of variance of unfiltered runoff water showed the mass of each insecticide leaving vegetated rows was significantly lower than from non-vegetated rows.

Filtered vs. unfiltered analyses of runoff water indicate 10, 44, and 59% of the runoff mass was in the dissolved phase for chlorpyrifos, diazinon, and methidathion, respectively, while the remainder was calculated to be attached to eroded soil and fine particles in runoff water. Runoff analyses indicate for chlorpyrifos either plant sorption or soil erosion control should lead to reductions in runoff; for diazinon, erosion control may be useful (unless other more sorptive surfaces can be found); and for methidathion, sorption to oats and clover appears useful for controlling runoff. Care should be taken when extrapolating these mechanisms to other fields since partitioning between water and soil and water and plant surfaces may depend on specific soil and plant characteristics. Additional research should focus on the relative importance of each potential mechanism and the partitioning between water and plant surfaces to better define the ideal cover crop-insecticide combination that will be most effective in reducing runoff.

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Table 1. Species in the clover mix used to seed clover treated rows in the runoff study conducted in a peach orchard in Winters, California.

Scientific Name	Common Name	Percent
Bromus hordeaceus (H. & A.)	Blando bromegrass	2.45
Medicago lupulina (L.) cv. 'Santiago'	Santiago burr medic	34.97
Trifolium hybridum (L.)	Rose clover	2.46
Trifolium incarnatum (L.)	Crimson clover	9.99
Trifolium subterraneum (L.) cv. 'Dalkeith'	Dalkeith subclover	4.97
Trifolium subterraneum (L.) cv. 'Koala'	Koala subclover	7.46
Trifolium subterraneum (L.) cv. 'Nungarin'	Nungarin subclover	2.50
Trifolium subterraneum (L.) cv. 'Trikkala'	Trikkala subclover	7.43
Trifolium subterraneum (L.) cv. 'Woogenellup'	Woogenellup subclover	2.49
Vicia sativa (L.)	Common vetch	24.95

Table 2. Mass deposition† in the tree canopy (g ha^{-1}) and analysis of variance mean squares for chlorpyrifos, diazinon, and methidathion.

		Mass Deposition		
Treatment		Chlorpyrifos	Diazinon	Methidathion
No Seed		266 (16.5)	252 (21.8)	269 (16.9)
Clover		238 (21.3)	223 (31.1)	234 (29.2)
Oats		279 (49.2)	257 (40.1)	276 (48.5)
		Analysis of Variance Mean Squares		
Source of Variation	df	Chlorpyrifos	Diazinon	Methidathion
Block	2	1040	1240	680
Treatment	2	1380	986	1520
Error	4	1050	910	1410

None of the mean squares were significant at either P = 0.05 or 0.01.
† Mean (standard deviation in parentheses) of three blocks.

Table 3. Mean† insecticide concentrations ($\mu g\ kg^{-1}$, dry weight) on soil of the peach orchard.

Treatment	Day After Application	Chlorpyrifos	Diazinon	Methidathion
No Seed	0	651 (120)	877 (110)	1010 (120)
	3	758 (174)	929 (42)	1070 (90)
	7	576 (166)	777 (304)	823 (251)
	13	388 (108)	397 (145)	469 (170)
	20	280 (78)	150 (28)	287 (67)
	28	237 (73)	56 (18)	109 (35)
	35	143 (51)	18 (1.2)	94 (6.0)
Clover	0	698 (72)	973 (78)	1140 (35)
	3	698 (361)	948 (510)	1080 (613)
	7	565 (56)	897 (179)	993 (200)
	13	344 (48)	270 (43)	355 (74)
	20	296 (52)	170 (38)	274 (85)
	28	209 (103)	63 (13)	157 (42)
	35	112 (16)	18 (3.3)	134 (36)
Oats	0	591 (37)	721 (131)	792 (120)
	3	419 (263)	664 (453)	714 (477)
	7	532 (279)	622 (384)	574 (370)
	13	375 (283)	283 (194)	352 (255)
	20	235 (160)	124 (54)	129 (79)
	28	323 (164)	86 (47)	138 (63)
	35	133 (37)	25 (7.5)	77 (39)

† Mean (standard deviation in parentheses) of three blocks.

Table 4. Mean† insecticide concentrations (mg kg^{-1}, dry weight) on vegetation of the peach orchard floor.				
Treatment	Day After Application	Chlorpyrifos	Diazinon	Methidathion
Clover	0	137(61.0)	126(73.3)	154(88.6)
	3	98.6(16.1)	77.7(7.81)	141(19.6)
	7	83.0(11.2)	73.1(11.7)	83.1(11.8)
	13	50.5(4.39)	36.3(4.81)	35.6(7.80)
	20	46.4(21.9)	23.1(11.3)	19.8(8.71)
	28	18.8(3.26)	7.26(1.86)	4.45(1.18)
	35	8.32(0.398)	1.63(0.053)	1.46(0.127)
Oats	0	158(95.7)	129(88.6)	157(97.7)
	3	154(90.4)	79.4(33.8)	142(63.3)
	7	81.6(18.3)	44.8(8.66)	60.7(8.99)
	13	46.7(20.0)	26.3(13.4)	20.6(12.3)
	20	30.9(12.5)	15.2(7.86)	6.10(3.80)
	28	14.4(8.38)	5.19(4.37)	1.70(1.18)
	35	6.13(2.30)	1.25(0.846)	0.404(0.288)

† Mean (standard deviation in parentheses) of three blocks.

Table 5. Analysis of variance mean squares for chlorpyrifos, diazinon, and methidathion mass (ln g ha^{-1}) on soil and vegetation.				
		Soil		
Source of Variation	Degrees of Freedom	Chlorpyrifos	Diazinon	Methidathion
Block	2	0.426	0.608	1.71
Treatment	2	0.226	0.234	1.52
Main Plot Error	4	0.173	0.132	0.429
Day	6	3.21 **	18.7**	8.21**
Day * Treatment	12	0.0951	0.125	0.109
Subplot Error	36	0.187	0.163	0.123
		Vegetation		
Block	2	0.247	1.06	0.733
Treatment	1	0.001	0.772	3.66
Main Plot Error	2	0.188	1.10	0.562
Day	6	7.12**	15.6**	25.4**
Day * Treatment	6	0.321	0.420	0.912
Subplot Error	24	0.146	0.289	0.225
*,** indicates significant at $P \leq 0.05$ and 0.01, respectively.				

Table 6. Lack-of-fit test conducted on chlorpyrifos, diazinon, and methidation mass (ln g ha^{-1}) in soil and vegetation. Lack-of-fit tests the significance of first, second, and higher order regressions to determine which significantly defines the dissipation curve.				
		Soil		
Source of Variation	Degrees of Freedom	Chlorpyrifos	Diazinon	Methidathion
Model	6	3.21**	18.7**	8.21**
Day	1	18.5**	110**	48.2**
Day*Day	1	0.0001	1.23**	0.450
Remainder	4	0.194	0.230	0.140
Error	56	0.177	0.171	0.248
		Vegetation		
Model	6	7.12**	15.6**	25.4**
Day	1	41.7**	91.9**	150**
Day*Day	1	0.0341	1.03	0.120
Remainder	4	0.241	0.194	0.418
Error	35	0.180	0.415	0.489
*,** indicates significant at $P \leq 0.05$ and 0.01, respectively.				

Table 7. Physical and chemical properties of chlorpyrifos, diazinon, and methidathion.†

Property	Chlorpyrifos	Diazinon	Methidathion
Molecular Weight	350.6	304.4	302.3
Vapor Pressure (Pa)	0.002 (at 23°C) 0.0004 (at 16°C)	0.009 (at 20°C) 0.02 (at 25°C)	0.0005 (at 25°C)
Solubility (mg/L)	1.4	60	220
Henry's Law (Pa m^3 mol^{-1})	0.67 (at 25°C)	0.088 (at 25°C)	0.0002 (at 22°C)
Hydrolysis Half-life at pH 7 (days)	72 (at 25°C)	140 (at 24°C)	41 (at 20°C)
Aerobic Soil Metabolism Half-life (days)	57 - 180	40	3.1
Soil Adsorption (K_{oc})	3700	1100-1900	31-900
Field Dissipation Half-life (days)	33 - 56	7.0 - 30	5 (Approximate)

† Data from Kollman and Segawa, 1995.

Table 8. Analysis of variance mean squares for chlorpyrifos, diazinon, and methidathion mass (g ha^{-1}) in unfiltered runoff water from the second storm.

Source of Variation	Degrees of Freedom	Chlorpyrifos	Diazinon	Methidathion
Block	2	1.26×10^{-3}	7.73×10^{-4}	1.21×10^{-2}
Treatment	2	7.66×10^{-3}*	6.06×10^{-2}*	3.53×10^{-1}*
No Seed vs. Vegetation	1	1.34×10^{-3}*	1.02×10^{-1}**	6.76×10^{-1}*
Clover vs. Oats	1	1.97×10^{-3}	1.88×10^{-2}	3.04×10^{-2}
Error	4	8.83×10^{-4}	4.62×10^{-3}	3.81×10^{-2}

*,** indicates significant at $P \leq 0.05$ and 0.01, respectively.

Mean mass (g ha^{-1}) and standard deviation of three blocks.

		Chlorpyrifos	Diazinon	Methidathion
	No Seed	1.37×10^{-1} (4.95×10^{-2})	3.81×10^{-1} (5.13×10^{-2})	8.89×10^{-1} (2.62×10^{-1})
	Clover	3.75×10^{-2} (1.13×10^{-2})	9.91×10^{-2} (6.51×10^{-2})	2.36×10^{-1} (4.10×10^{-2})
	Oats	7.38×10^{-2} (1.72×10^{-2})	2.11×10^{-1} (5.59×10^{-2})	3.79×10^{-1} (1.33×10^{-1})

Table 9. Analysis of variance mean squares for chlorpyrifos, diazinon, and methidathion mass (g ha^{-1}) in filtered runoff water from the second storm.

Source of Variation	Degrees of Freedom	Chlorpyrifos	Diazinon	Methidathion
Block	2	6.53×10^{-6}	1.05×10^{-4}	1.97×10^{-3}
Treatment	2	1.22×10^{-4}*	5.04×10^{-3}	9.18×10^{-2}*
No Seed vs. Vegetation	1	1.88×10^{-4}*	4.97×10^{-3}	1.61×10^{-1}**
Clover vs. Oats	1	5.64×10^{-5}	5.10×10^{-3}	2.29×10^{-2}
Error	4	1.46×10^{-5}	1.15×10^{-3}	7.96×10^{-3}

*,** indicates significant at $P \leq 0.05$ and 0.01, respectively.

Mean mass (g ha^{-1}) and standard deviation in parentheses, of three blocks.

		Chlorpyrifos	Diazinon	Methidathion
	No Seed	1.35×10^{-2} (4.45×10^{-3})	1.15×10^{-1} (2.70×10^{-2})	4.45×10^{-1} (9.41×10^{-2})
	Clover	7.75×10^{-4} (7.64×10^{-4})	3.57×10^{-2} (3.08×10^{-2})	9.94×10^{-2} (4.37×10^{-2})
	Oats	6.91×10^{-3} (3.93×10^{-3})	9.41×10^{-2} (2.69×10^{-2})	2.23×10^{-1} (8.45×10^{-2})

Table 10. Analysis of variance mean squares for the total runoff volume (L) generated during the second storm.

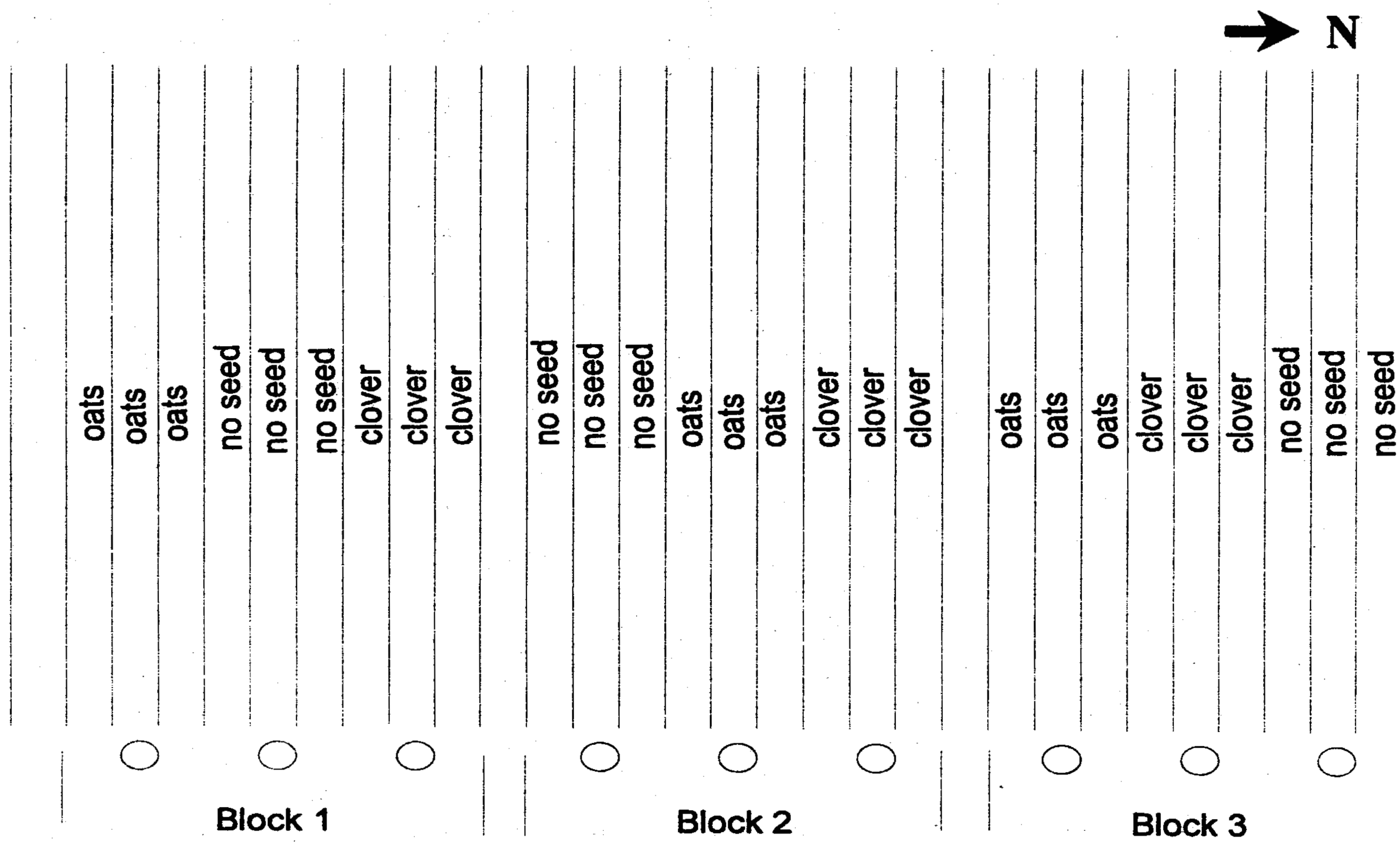
Source of Variation	Degrees of Freedom	Volume
Block	2	7,700
Treatment	2	102,000*
No Seed vs. Vegetation	1	194,000**
Clover vs. Oats	1	8,820
Error	4	8,360

*,** indicates significant at $P \leq 0.05$ and 0.01, respectively.

Mean and standard deviation in parentheses (n=3 blocks).

		Volume
	No Seed	569 (143)
	Clover	219 (21)
	Oats	296 (59)

Table 11. Analysis of variance mean squares for chlorpyrifos, diazinon, and methidathion mass (g ha^{-1}) attached to particles in runoff† occurring during the second storm.				
Source of Variation	Degrees of Freedom	Chlorpyrifos	Diazinon	Methidathion
Block	2	1.10×10^{-5}	9.30×10^{-7}	4.35×10^{-5}
Treatment	2	5.87×10^{-5}*	3.90×10^{-4}**	8.89×10^{-4}
No Seed vs. Vegetation	1	1.04×10^{-4}*	6.97×10^{-4}**	
Clover vs. Oats	1	1.36×10^{-5}	8.28×10^{-5}	
Error	4	6.15×10^{-6}	1.03×10^{-5}	1.53×10^{-4}
*,** indicates significant at $P \leq 0.05$ and 0.01, respectively.				
Mean mass (g ha^{-1}) and standard deviation in parentheses, of three blocks.				
		Chlorpyrifos	Diazinon	Methidathion
	No Seed	1.24×10^{-2} (4.51×10^{-3})	2.67×10^{-2} (3.02×10^{-3})	4.44×10^{-2} (1.77×10^{-2})
	Clover	3.68×10^{-3} (1.05×10^{-3})	4.26×10^{-3} (1.91×10^{-3})	1.37×10^{-2} (1.01×10^{-3})
	Oats	6.69×10^{-3} (1.36×10^{-3})	1.17×10^{-2} (2.96×10^{-3})	1.56×10^{-2} (5.91×10^{-3})



○ Indicates flume location and row used to measure runoff

Figure 1. Randomized complete block layout in the peach orchard located in Winters, California.

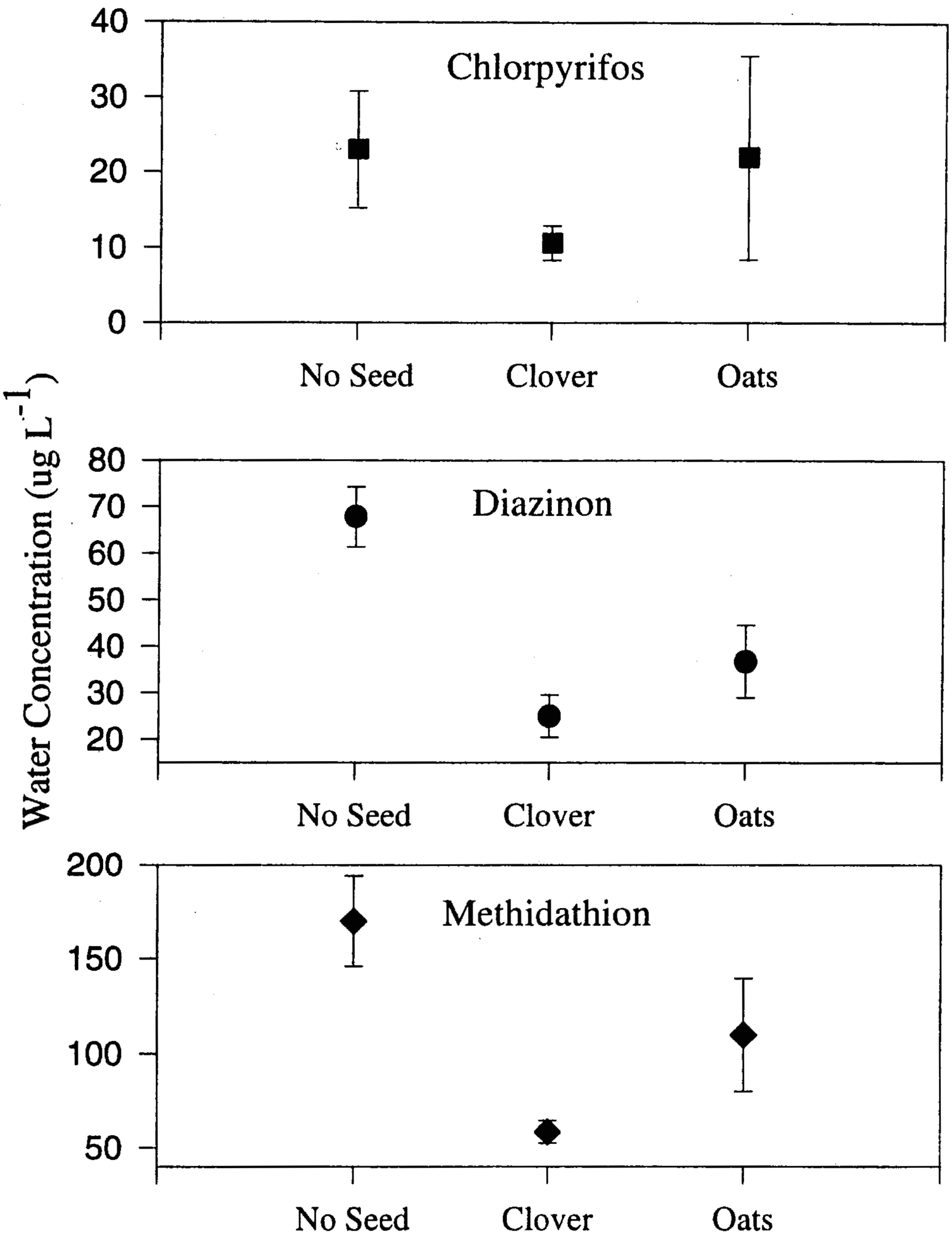


Figure 2. Runoff concentrations from the first storm. Due to flooding, only data from the first interval are are shown. Each data point is a mean and standard deviation of two blocks.

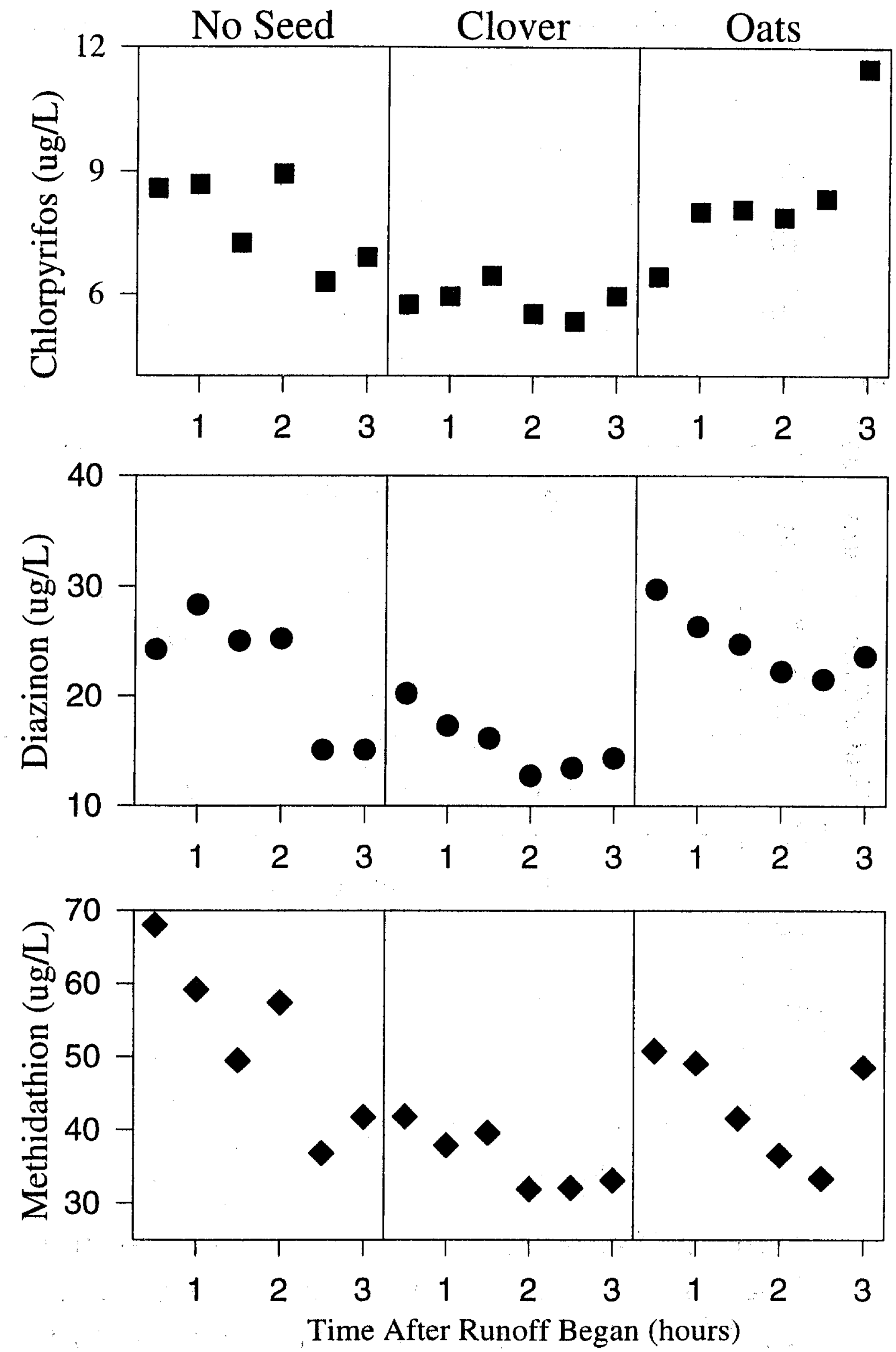


Figure 3. Mean concentration (n=3) of chlorpyrifos, diazinon, and and methidathion in runoff generated during the second storm.

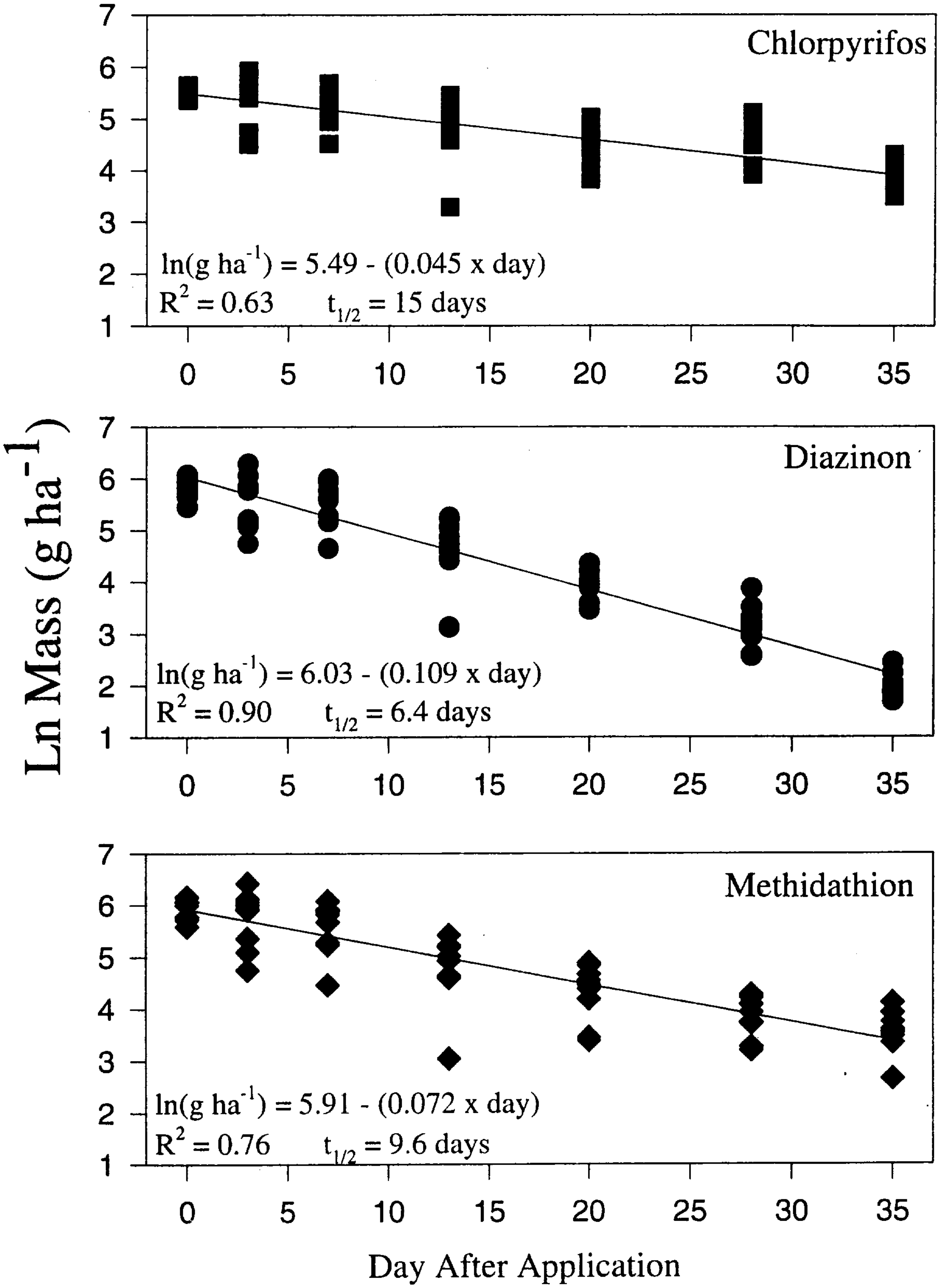


Figure 4. Dissipation of chlorpyrifos, diazinon, and methidathion from soil of the peach orchard.

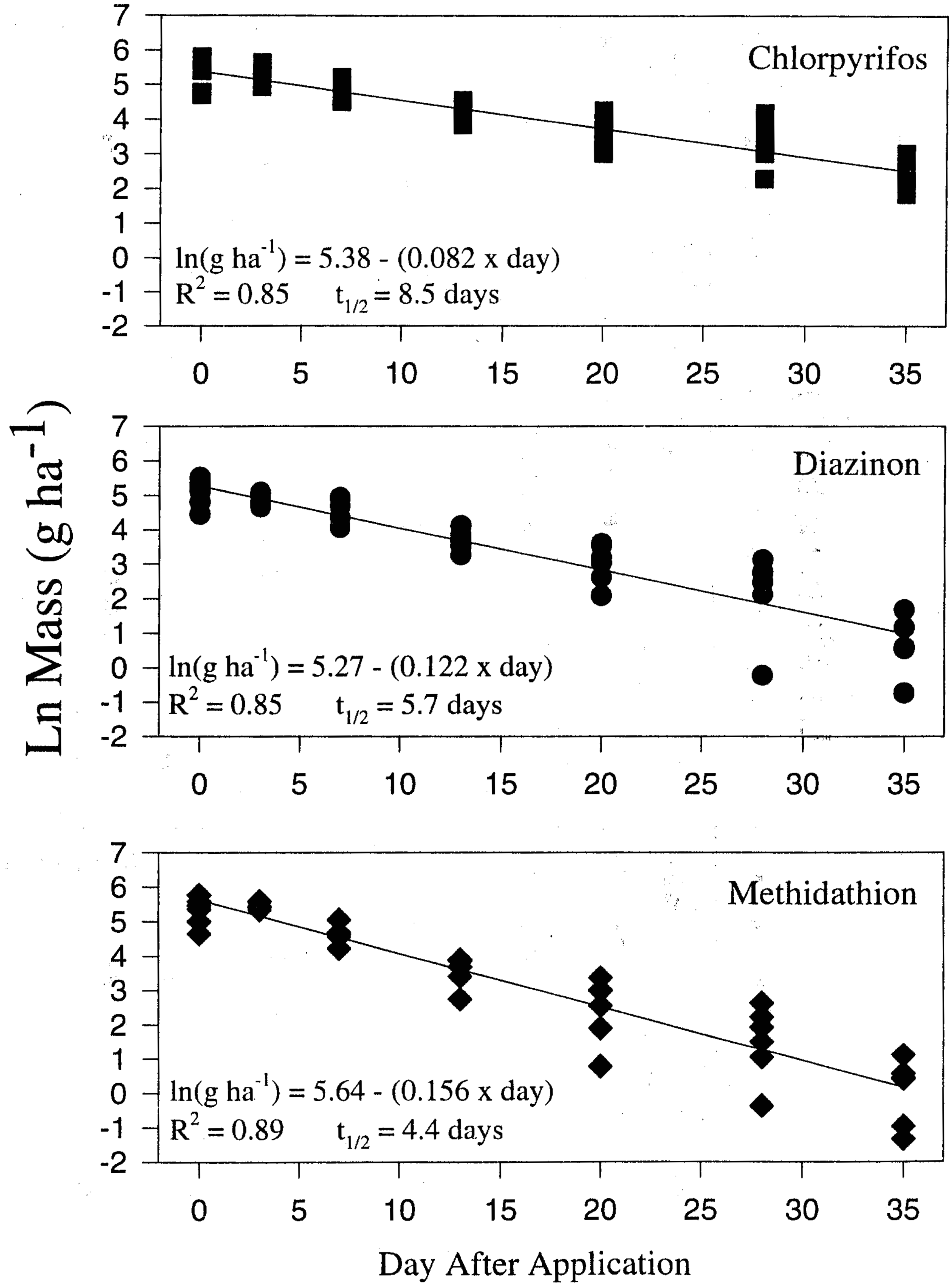


Figure 5. Dissipation of chlorpyrifos, diazinon, and methidathion from vegetation planted on the orchard floor.

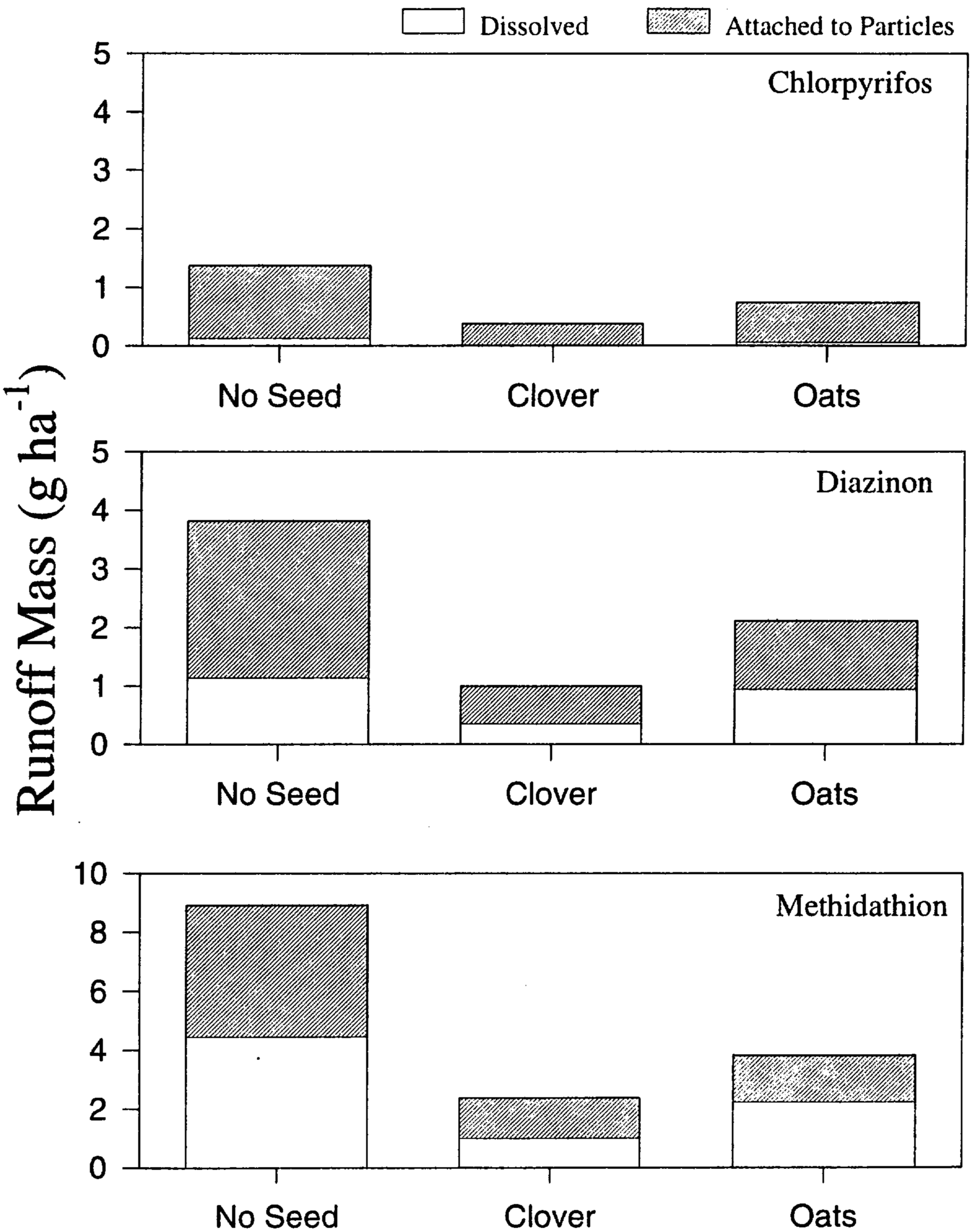


Figure 6. Mass of chlorpyrifos, diazinon, and methidathion dissolved and attached to particles in runoff water generated during the second storm.

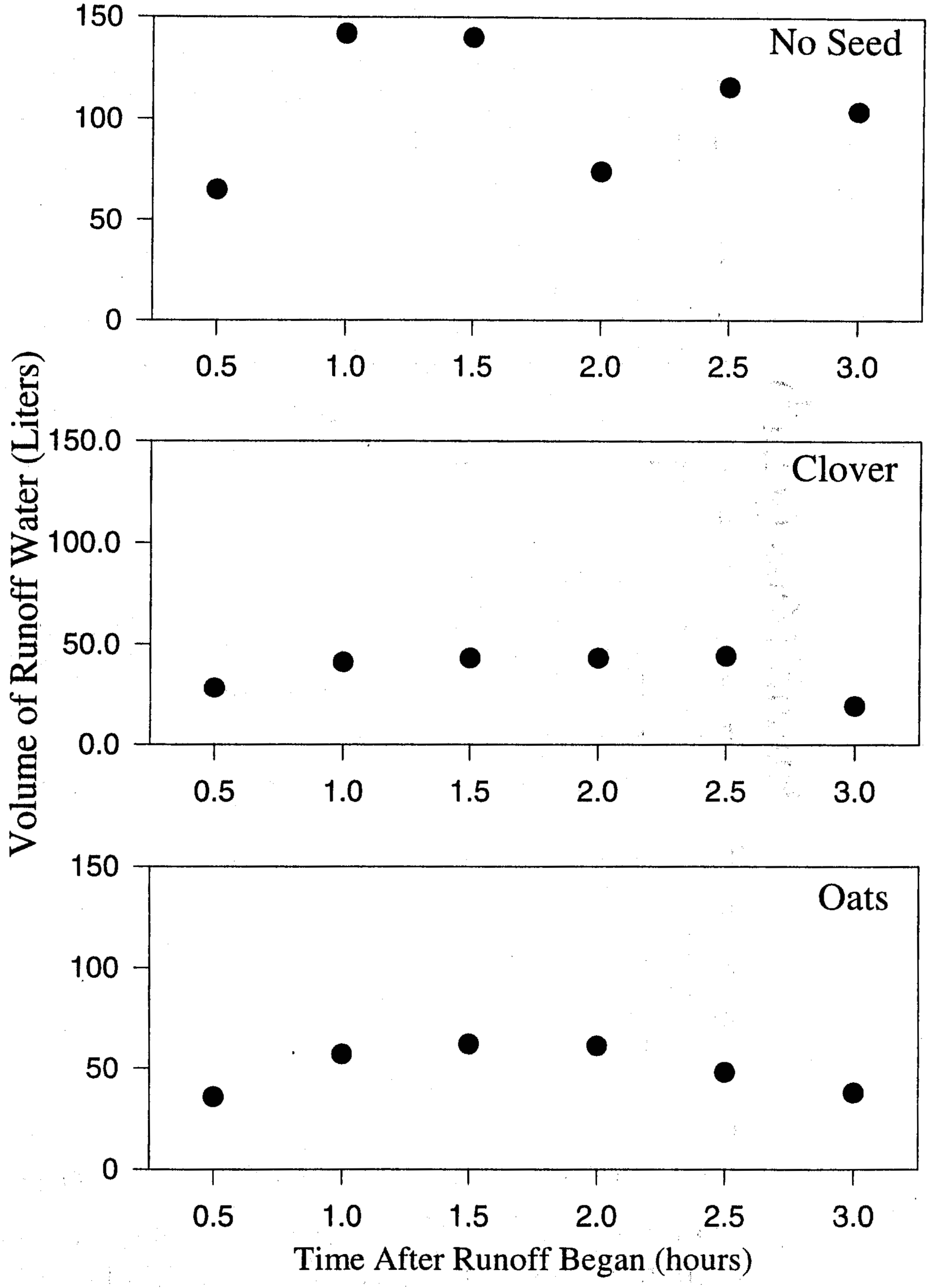


Figure 7. Volume of runoff water measured during the second storm.

Appendix I. Deposition sheet results from the peach orchard in Winters, California.

Sample Number	Date	Time	Treatment Number	Block Number	Sampling Height (ft)	Diazinon (ug/m2)	Chlorpyrifos (ug/m2)	Methidathion (ug/m2)
20	10496	1215	1	1	4	43541	49946	46179
17	10496	1200	1	2	4	41119	46179	42842
31	10496	1210	1	3	4	53283	48116	54898
22	10496	1215	1	1	7	48762	56512	52691
18	10496	1200	1	2	7	54360	61356	59742
32	10496	1210	1	3	7	65662	58127	69429
23	10496	1215	1	1	10	43811	50807	47740
34	10496	1200	1	2	10	46932	55436	52960
33	10496	1210	1	3	10	41604	37998	41927
25	10496	1215	2	1	4	42142	50161	46233
38	10496	1200	2	2	4	39882	45910	42680
16	10496	1200	2	3	4	60280	53122	59742
26	10496	1215	2	1	7	42196	49516	45371
39	10496	1200	2	2	7	32616	38482	33315
29	10496	1200	2	3	7	45371	40312	46986
27	10496	1215	2	1	10	44995	52637	48870
40	10496	1200	2	2	10	39290	45802	41066
30	10496	1210	2	3	10	42304	38213	43326
24	10496	1215	3	1	4	41066	48224	44564
35	10496	1200	3	2	4	62433	70506	71044
14	10496	1200	3	3	4	41712	40635	42304
19	10496	1215	3	1	7	49031	55436	53014
36	10496	1200	3	2	7	61895	69429	68891
13	10496	1200	3	3	7	62971	60280	64586
21	10496	1215	3	1	10	34392	40420	37729
37	10496	1200	3	2	10	46448	55436	50969
15	10496	1200	3	3	10	47632	46932	48009

Appendix II. Soil data collected from the peach orchard in Winters, California.

Sample Number	Date	Time	Day After Application	Treatment	Block Number	Replicate Number	Moisture content	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Sample Weight Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)
43	1/4/96	1300	0	No Seed	1	1	0.2251	28.32	24.89	32.45	50	694	610	795
46	1/4/96	1300	0	No Seed	1	2	0.1666	50.95	36.77	67.04	50	1189	858	1564
59	1/4/96	1330	0	No Seed	2	1	NA	NA	NA	NA	NA	NA	NA	NA
48	1/4/96	1330	0	No Seed	2	2	0.1845	33.12	30.6	36.93	50	785	725	875
53	1/4/96	1300	0	No Seed	3	1	0.2060	36.86	23.15	37.38	50	889	558	902
54	1/4/96	1300	0	No Seed	3	2	0.2206	50.45	26.81	58.91	50	1232	655	1438
41	1/4/96	1300	0	Clover	1	1	0.1929	55.38	39.93	68.44	50	1321	953	1633
44	1/4/96	1300	0	Clover	1	2	0.1234	32.97	22.83	41.8	50	741	513	939
49	1/4/96	1330	0	Clover	2	1	0.2253	28.03	25.49	34.88	50	687	625	855
50	1/4/96	1330	0	Clover	2	2	0.1976	48.76	39.12	56.28	50	1168	937	1348
55	1/4/96	1300	0	Clover	3	1	0.1910	56.11	31.75	61.45	50	1336	756	1464
56	1/4/96	1300	0	Clover	3	2	0.2001	42.71	29.84	46.81	50	1025	716	1124
42	1/4/96	1300	0	Oats	1	1	0.2400	18.56	19.28	22.92	50	460	478	568
45	1/4/96	1300	0	Oats	1	2	0.1978	33.72	32.43	37.14	50	808	777	890
51	1/4/96	1330	0	Oats	2	1	0.2003	55.55	44.54	62.51	50	1334	1069	1501
52	1/4/96	1330	0	Oats	2	2	0.2403	8.89	7.81	10.9	50	221	194	270
57	1/4/96	1300	0	Oats	3	1	0.2160	45.43	34.96	48.27	50	1105	850	1174
58	1/4/96	1300	0	Oats	3	2	0.2149	29	18.56	27.84	50	705	451	676
101	1/7/96	1030	3	No Seed	1	1	0.2488	34.43	39.46	46.59	50	860	986	1164
102	1/7/96	1030	3	No Seed	1	2	0.2011	43.65	38.01	48.9	50	1049	913	1175
125	1/7/96	1100	3	No Seed	2	1	0.1793	37.34	21.64	45.85	50	881	510	1081
126	1/7/96	1100	3	No Seed	2	2	0.2299	35.77	28.71	40.08	50	880	706	986
113	1/7/96	1030	3	No Seed	3	1	0.2343	39.68	30.87	43.19	50	980	762	1066
116	1/7/96	1030	3	No Seed	3	2	0.2009	38.48	27.91	38.8	50	924	670	932
103	1/7/96	1030	3	Clover	1	1	0.2382	11.28	10.56	11.98	50	279	262	297
104	1/7/96	1030	3	Clover	1	2	0.1688	25.69	15.69	25.77	50	601	367	602
127	1/7/96	1100	3	Clover	2	1	0.1844	48.7	32.51	55.68	50	1154	770	1319
128	1/7/96	1100	3	Clover	2	2	0.1915	30.89	30.58	37.57	50	736	729	895

Appendix II. Soil data collected from the peach orchard in Winters, California.

Sample Number	Date	Time	Day After Application	Treatment	Block Number	Replicate Number	Moisture content	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Sample Weight Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)
114	1/7/96	1030	3	Clover	3	1	0.1932	69.01	57.44	80.23	50	1647	1371	1915
117	1/7/96	1030	3	Clover	3	2	0.1855	53.7	29.21	60.49	50	1273	693	1434
105	1/7/96	1030	3	Oats	1	1	0.2119	24.62	19.25	25.37	50	597	467	615
106	1/7/96	1030	3	Oats	1	2	0.2202	1.29	1.22	0.77	50	31	30	19
129	1/7/96	1100	3	Oats	2	1	0.1908	24.02	14.08	28.82	50	572	335	686
130	1/7/96	1100	3	Oats	2	2	0.2021	18.02	9.97	19.9	50	433	240	478
115	1/7/96	1030	3	Oats	3	1	0.2101	33.59	26.08	35.62	50	813	631	862
118	1/7/96	1030	3	Oats	3	2	0.1638	66.04	34.94	69.83	50	1537	813	1625
107	1/11/96	1000	7	No Seed	1	1	0.1731	9.06	6.65	11.47	50	213	156	269
108	1/11/96	940	7	No Seed	1	2	0.1396	32.65	26.93	35.41	50	744	614	807
122	1/11/96	1000	7	No Seed	2	1	0.1787	21.56	18.5	24.97	50	508	436	589
119	1/11/96	1000	7	No Seed	2	2	0.1891	43.04	37.12	52.63	50	1024	883	1252
63	1/11/96	926	7	No Seed	3	1	0.1647	36.35	20.05	32.09	50	847	467	747
131	1/11/96	926	7	No Seed	3	2	0.1753	56.44	38.29	54.23	50	1327	900	1275
109	1/11/96	1000	7	Clover	1	1	0.2004	26.55	21.26	29.6	50	637	510	711
110	1/11/96	950	7	Clover	1	2	0.1764	35.07	23.23	37.37	50	825	547	879
123	1/11/96	1000	7	Clover	2	1	0.1686	35.07	23.53	40.36	50	820	550	943
120	1/11/96	1000	7	Clover	2	2	0.1797	39.19	30.07	44.02	50	925	709	1039
60	1/11/96	926	7	Clover	3	1	0.1598	31.43	15.39	41.37	50	729	357	960
64	1/11/96	926	7	Clover	3	2	0.1713	61.7	30.66	60.97	50	1445	718	1428
111	1/11/96	1000	7	Oats	1	1	0.2181	10.11	11.12	10.02	50	246	271	244
112	1/11/96	1000	7	Oats	1	2	0.1272	14.51	10.23	10.26	50	327	231	231
124	1/11/96	1000	7	Oats	2	1	0.2062	25.58	23.21	25.35	50	617	560	612
121	1/11/96	1000	7	Oats	2	2	0.2229	18.75	21.02	16.99	50	459	514	416
61	1/11/96	926	7	Oats	3	1	0.2034	31	23.84	33.57	50	746	574	808
62	1/11/96	926	7	Oats	3	2	0.2046	55.46	43.31	46.98	50	1336	1043	1132
177	1/17/96	1000	13	No Seed	1	1	0.2497	12.82	15.89	12.59	50	320	397	315
174	1/17/96	1000	13	No Seed	1	2	0.2633	6.14	5.37	9.94	50	155	136	251

Appendix II. Soil data collected from the peach orchard in Winters, California.

Sample Number	Date	Time	Day After Application	Treatment	Block Number	Replicate Number	Moisture content	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Sample Weight Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)
184	1/17/96	1000	13	No Seed	2	1	0.2298	15.94	13.78	21.62	50	392	339	532
182	1/17/96	1000	13	No Seed	2	2	0.2721	18.48	23.85	18.87	50	470	607	480
173	1/17/96	1000	13	No Seed	3	1	0.2541	23.2	13.52	25.29	50	582	339	634
132	1/17/96	1000	13	No Seed	3	2	0.2428	18.52	20.52	24.14	50	460	510	600
178	1/17/96	1000	13	Clover	1	1	0.2569	6.97	7.74	11.69	50	175	195	294
176	1/17/96	1000	13	Clover	1	2	0.2748	14.49	22.11	18.3	50	369	564	467
180	1/17/96	1000	13	Clover	2	1	0.2811	10.77	14.77	10.39	50	276	378	266
89	1/17/96	1000	13	Clover	2	2	0.2767	6.94	7.81	10.84	50	177	199	277
133	1/17/96	1000	13	Clover	3	1	0.2715	11.24	14.69	18.83	50	286	374	479
134	1/17/96	1000	13	Clover	3	2	0.2418	13.64	14.24	14.06	50	339	354	349
179	1/17/96	1000	13	Oats	1	1	0.2686	2.9	3.49	3.02	50	74	89	77
175	1/17/96	1000	13	Oats	1	2	0.2845	2.02	2.24	1.48	50	52	58	38
183	1/17/96	1000	13	Oats	2	1	0.2357	19.65	27.22	22.82	50	486	673	564
181	1/17/96	1000	13	Oats	2	2	0.2799	14.64	23.19	16.18	50	375	594	414
135	1/17/96	1000	13	Oats	3	1	0.2960	14.57	16.6	19.34	50	378	430	501
136	1/17/96	1000	13	Oats	3	2	0.2596	13.26	16.16	20.51	50	334	407	517
90	1/24/96	1000	20	No Seed	1	1	0.2786	2.18	4.72	6.31	50	56	121	161
91	1/24/96	930	20	No Seed	1	2	0.2542	8.6	10.37	14.25	50	216	260	357
161	1/24/96	1000	20	No Seed	2	1	0.2681	5.58	10.45	12.33	50	142	265	313
162	1/24/96	1000	20	No Seed	2	2	0.2643	8.82	16.15	16.35	50	223	408	413
167	1/24/96	930	20	No Seed	3	1	0.2796	3.3	11.84	13.49	50	84	303	345
168	1/24/96	930	20	No Seed	3	2	0.2841	7.11	12.5	5.14	50	183	321	132
92	1/24/96	1000	20	Clover	1	1	0.2916	4.76	8.2	6.67	50	123	212	172
93	1/24/96	930	20	Clover	1	2	0.2902	7.19	10.04	7.35	50	186	259	190
163	1/24/96	1000	20	Clover	2	1	0.2674	4.32	12.26	10.74	50	110	311	272
164	1/24/96	1000	20	Clover	2	2	0.2690	6.9	13.44	12.41	50	175	341	315
169	1/24/96	930	20	Clover	3	1	0.2767	3.36	7.07	15.12	50	86	181	386
170	1/24/96	930	20	Clover	3	2	0.2815	13.29	18.43	12.04	50	341	472	309

Appendix II. Soil data collected from the peach orchard in Winters, California.

Sample Number	Date	Time	Day After Application	Treatment	Block Number	Replicate Number	Moisture content	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Sample Weight Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)
94	1/24/96	1000	20	Oats	1	1	0.3262	1.51	4.13	1.5	50	40	110	40
95	1/24/96	930	20	Oats	1	2	0.3349	5.01	5.29	4.97	50	134	141	133
165	1/24/96	1000	20	Oats	2	1	0.2882	2.7	8.13	8.43	50	70	209	217
166	1/24/96	1000	20	Oats	2	2	0.2964	11.64	24.16	8.67	50	302	626	225
171	1/24/96	930	20	Oats	3	1	0.3105	4.4	7.02	3.52	50	115	184	92
172	1/24/96	930	20	Oats	3	2	0.3136	3.17	5.28	2.67	50	83	139	70
71	2/1/96	945	28	No Seed	1	1	0.2566	1.22	8.52	3.12	50	31	214	78
72	2/1/96	945	28	No Seed	1	2	0.2627	3.95	15.86	5.98	50	100	401	151
150	2/1/96	915	28	No Seed	2	1	0.2641	3.41	12.42	4.94	50	86	314	125
151	2/1/96	915	28	No Seed	2	2	0.2618	1.91	6.75	6.15	50	48	170	155
96	2/1/96	930	28	No Seed	3	1	0.2421	1.37	5.47	2.88	50	34	136	72
97	2/1/96	930	28	No Seed	3	2	0.2426	1.5	7.59	2.88	50	37	189	72
73	2/1/96	945	28	Clover	1	1	0.2516	1.54	8.8	3.86	50	39	220	97
74	2/1/96	945	28	Clover	1	2	0.2803	2.54	16.99	5.02	50	65	435	129
152	2/1/96	915	28	Clover	2	1	0.2559	4.98	7.19	12.64	50	125	181	317
153	2/1/96	915	28	Clover	2	2	0.2700	1.1	4.46	2.98	50	28	113	76
98	2/1/96	930	28	Clover	3	1	0.2371	1.06	6.64	8.67	50	26	164	215
99	2/1/96	930	28	Clover	3	2	0.2473	3.81	5.71	4.32	50	95	142	108
75	2/1/96	945	28	Oats	1	1	0.3202	2.99	12.31	3.12	50	79	325	82
76	2/1/96	945	28	Oats	1	2	0.2953	4	16.48	1.98	50	104	427	51
154	2/1/96	915	28	Oats	2	1	0.2860	8.07	24.26	6.17	50	208	624	159
155	2/1/96	915	28	Oats	2	2	0.2576	2.17	11.32	8.38	50	55	285	211
100	2/1/96	930	28	Oats	3	1	0.2496	0.64	1.82	7.06	50	16	45	176
149	2/1/96	930	28	Oats	3	2	0.2340	2.31	9.39	6.06	50	57	232	150
187	2/8/96	1000	35	No Seed	1	1	0.2041	0.89	4.58	3.09	50	21	110	74
188	2/8/96	1000	35	No Seed	1	2	0.2025	0.62	4.68	4.67	50	15	113	112
145	2/8/96	1000	35	No Seed	2	1	0.2142	0.81	5.82	4.05	50	20	141	98
146	2/8/96	1000	35	No Seed	2	2	0.2080	0.61	3.73	3.23	50	15	90	78

Appendix II. Soil data collected from the peach orchard in Winters, California.

Sample Number	Date	Time	Day After Application	Treatment	Block Number	Replicate Number	Moisture content	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Sample Weight Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)
139	2/8/96	1000	35	No Seed	3	1	0.2205	0.9	6.61	4.84	50	22	161	118
140	2/8/96	1000	35	No Seed	3	2	0.2316	0.7	9.89	3.34	50	17	244	82
189	2/8/96	1000	35	Clover	1	1	0.2004	0.79	3.12	4.56	50	19	75	109
190	2/8/96	1000	35	Clover	1	2	0.2653	0.93	5.67	3.28	50	24	143	83
147	2/8/96	1000	35	Clover	2	1	0.2315	0.71	2.38	7.82	50	17	59	193
148	2/8/96	1000	35	Clover	2	2	0.2423	0.79	5.56	5.76	50	20	138	143
141	2/8/96	1000	35	Clover	3	1	0.2232	0.71	4.84	6.42	50	17	118	157
142	2/8/96	1000	35	Clover	3	2	0.2268	0.49	5.7	4.88	50	12	140	120
138	2/8/96	1000	35	Oats	1	1	0.2658	2.26	10.86	2.19	50	57	275	55
137	2/8/96	1000	35	Oats	1	2	0.2567	0.24	1.9	0.88	50	6	48	22
213	2/8/96	1000	35	Oats	2	1	0.2015	1.84	10.06	5.88	50	44	242	141
160	2/8/96	1000	35	Oats	2	2	0.2268	0.29	2.14	3.68	50	7	53	90
143	2/8/96	1000	35	Oats	3	1	0.2522	0.76	4.68	3.15	50	19	117	79
144	2/8/96	1000	35	Oats	3	2	0.2365	0.58	2.63	3.11	50	14	65	77

Appendix III. Vegetation data from the peach orchard in Winters, California.

Sample Number	Date	Time	Sampling Interval	Treatment	Block Number	Within-Block Replicate Number	Moisture	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Weight Sample Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)	Vegetation Density (kg dry wt./row)
287	1/4/96	1430	0	Clover	1	1	0.4150	1161	1393	1476	25.00	79385	95249	100924	89.5
290	1/4/96	1430	0	Clover	1	2	0.2477	924	1107	1115	25.00	49126	58856	59281	145.7
295	1/4/96	1430	0	Clover	2	1	0.4861	931	1206	1161	25.00	72465	93870	90367	41.5
296	1/4/96	1430	0	Clover	2	2	0.4941	1327	1690	1620	18.80	139529	177697	170336	18.9
291	1/4/96	1430	0	Clover	3	1	0.5109	2707	2503	3249	22.88	241916	223685	290353	17.5
292	1/4/96	1430	0	Clover	3	2	0.3571	2377	2413	2967	21.53	171740	174341	214368	22.3
288	1/4/96	1430	0	Oats	1	1	0.3481	1760	2304	2191	25.00	107995	141376	134442	93.5
289	1/4/96	1430	0	Oats	1	2	0.3824	1182	1637	1642	25.00	76559	106030	106354	81.9
297	1/4/96	1430	0	Oats	2	1	0.4552	1069	1421	1397	25.00	78483	104325	102563	63.8
298	1/4/96	1430	0	Oats	2	2	0.2538	932	1215	1169	25.00	49962	65133	62667	119.9
293	1/4/96	1430	0	Oats	3	1	0.7560	1394	1653	1570	25.00	228485	270937	257333	17.5
294	1/4/96	1430	0	Oats	3	2	0.5172	2787	3161	3350	25.00	230923	261911	277571	40.7
311	1/7/96	1100	3	Clover	1	1	0.3614	1297	1557	2263	23.58	86136	103403	150289	55.0
312	1/7/96	1100	3	Clover	1	2	0.2046	1040	1235	1916	25.00	52299	62105	96350	57.0
275	1/7/96	1215	3	Clover	2	1	0.3875	899	1015	1561	25.00	58710	66286	101943	94.4
276	1/7/96	1210	3	Clover	2	2	0.5693	1190	1402	1883	25.00	110523	130213	174887	44.8
316	1/7/96	1130	3	Clover	3	1	0.4471	1920	1776	2667	25.00	138894	128477	192932	44.6
315	1/7/96	1145	3	Clover	3	2	0.4960	246	1276	1656	25.00	19524	101273	131433	39.8
313	1/7/96	1100	3	Oats	1	1	0.5584	763	1321	1246	25.00	69115	119660	112866	54.5
314	1/7/96	1100	3	Oats	1	2	0.2648	980	1381	1655	25.00	53316	75132	90039	129.2
277	1/7/96	1145	3	Oats	2	1	0.5077	728	1450	1307	22.85	64716	128898	116186	54.7
278	1/7/96	1240	3	Oats	2	2	0.3303	880	1431	1710	25.00	52564	85476	102142	81.6
317	1/7/96	1145	3	Oats	3	1	0.7279	861	1738	1553	25.00	126573	255499	228302	38.4
318	1/7/96	1145	3	Oats	3	2	0.7385	720	1712	1316	25.00	110147	261906	201325	32.5
263	1/11/96	1030	7	Clover	1	1	0.6769	593	755	819	25.00	73407	93461	101384	32.4
264	1/11/96	1100	7	Clover	1	2	0.4620	630	759	795	25.00	46838	56429	59105	59.2
267	1/11/96	1130	7	Clover	2	1	0.5773	1013	1233	1222	25.00	95853	116670	115629	58.2
269	1/11/96	1130	7	Clover	2	2	0.5178	846	902	924	25.00	70178	74823	76648	47.3
319	1/11/96	950	7	Clover	3	1	0.5560	488	633	591	25.00	43959	57021	53237	65.3
320	1/11/96	950	7	Clover	3	2	0.5846	1125	1033	963	25.00	108326	99467	92727	40.2
265	1/11/96	1100	7	Oats	1	1	0.7332	303	515	418	25.00	45422	77202	62661	38.3

Appendix III. Vegetation data from the peach orchard in Winters, California.

Sample Number	Date	Time	Sampling Interval	Treatment	Block Number	Within-Block Replicate Number	Moisture	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Weight Sample Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)	Vegetation Density (kg dry wt./row)
266	1/11/96	1130	7	Oats	1	2	0.6352	350	506	347	25.00	38377	55483	38048	54.9
270	1/11/96	1100	7	Oats	2	1	0.6723	406	673	545	25.00	49560	82152	66528	51.7
268	1/11/96	1100	7	Oats	2	2	0.3970	898	1070	949	25.00	59573	70984	62957	110.3
321	1/11/96	950	7	Oats	3	1	0.8526	68	400	185	25.00	18447	108513	50187	25.0
322	1/11/96	950	7	Oats	3	2	0.7220	400	663	581	25.00	57557	95401	83602	60.8
281	1/17/96	1100	13	Clover	1	1	0.5924	493	631	469	25.00	48377	61918	46022	40.9
279	1/17/96	1100	13	Clover	1	2	0.5395	405	559	494	25.00	35179	48556	42910	32.2
271	1/17/96	1130	13	Clover	2	1	0.4697	505	759	463	24.75	38476	57829	35276	47.2
272	1/17/96	1130	13	Clover	2	2	0.5860	252	392	275	22.70	26813	41709	29260	33.6
283	1/17/96	1130	13	Clover	3	1	0.5964	266	389	242	25.00	26365	38557	23986	44.7
284	1/17/96	1130	13	Clover	3	2	0.7170	303	386	254	25.00	42833	54566	35906	25.4
282	1/17/96	1100	13	Oats	1	1	0.8084	151	272	124	25.00	31530	56796	25892	25.4
280	1/17/96	1100	13	Oats	1	2	0.7114	281	513	245	25.00	38951	71110	33961	38.3
273	1/17/96	1130	13	Oats	2	1	0.4286	715	1044	556	25.00	50050	73080	38920	67.6
274	1/17/96	1130	13	Oats	2	2	0.5917	139	263	103	21.72	15673	29654	11613	43.9
285	1/17/96	1130	13	Oats	3	1	0.6801	109	229	61.7	25.00	13630	28635	7715	98.6
286	1/17/96	1145	13	Oats	3	2	0.7206	57.2	145	40.5	25.00	8188	20756	5797	45.1
251	1/24/96	1045	20	Clover	1	1	0.5232	114	193	94.1	25.00	9564	16192	7895	99.8
252	1/24/96	1030	20	Clover	1	2	0.6866	123	283	105	25.00	15698	36118	13401	40.5
219	1/24/96	1045	20	Clover	2	1	0.7404	132	240	95.8	25.00	20338	36978	14760	34.3
220	1/24/96	1045	20	Clover	2	2	0.7957	116	255	135	25.00	22708	49919	26428	29.8
215	1/24/96	1030	20	Clover	3	1	0.7335	149	264	116	25.00	22361	39619	17408	54.3
216	1/24/96	1110	20	Clover	3	2	0.8581	170	353	137	25.00	47924	99512	38621	24.9
253	1/24/96	1115	20	Oats	1	1	0.7184	140	242	49.1	25.00	19888	34378	6975	50.5
254	1/24/96	1125	20	Oats	1	2	0.7333	147	268	56.7	25.00	22050	40200	8505	57.4
221	1/24/96	1115	20	Oats	2	1	0.8122	101	181	47.8	25.00	21513	38553	10181	24.2
222	1/24/96	1130	20	Oats	2	2	0.8318	63.6	165	31.2	25.00	15129	39251	7422	25.9
217	1/24/96	1030	20	Oats	3	1	0.8283	28.3	52.4	4.9	25.00	6594	12209	1142	46.8
218	1/24/96	1130	20	Oats	3	2	0.8317	24.6	87.3	10	25.00	5847	20749	2377	38.0
203	2/1/96	1020	28	Clover	1	1	0.7140	93.2	194	46.3	25.00	13035	27133	6476	53.3
204	2/1/96	1050	28	Clover	1	2	0.7785	21.1	85	25.6	24.60	3873	15601	4699	22.2

Appendix III. Vegetation data from the peach orchard in Winters, California.

Sample Number	Date	Time	Sampling Interval	Treatment	Block Number	Within-Block Replicate Number	Moisture	Diazinon (ug)	Chlorpyrifos (ug)	Methidathion (ug)	Weight Sample Analyzed (g)	Diazinon (ug/kg, dry wt.)	Chlorpyrifos (ug/kg, dry wt.)	Methidathion (ug/kg, dry wt.)	Vegetation Density (kg dry wt./row)
209	2/1/96	915	28	Clover	2	1	0.6790	48	135	31.4	25.00	5981	16822	3913	81.7
210	2/1/96	915	28	Clover	2	2	0.7019	77.9	172	38.4	25.00	10453	23081	5153	54.5
156	2/1/96	1030	28	Clover	3	1	0.4063	62.8	174	36.3	25.00	4231	11723	2446	272.5
157	2/1/96	1030	28	Clover	3	2	0.7353	39.8	123	26.5	25.00	6015	18589	4005	58.8
205	2/1/96	1045	28	Oats	1	1	0.8399	40.9	93.7	13.4	25.00	10217	23406	3347	47.5
206	2/1/96	1020	28	Oats	1	2	0.8299	9.85	39.4	4.5	24.70	2345	9379	1071	26.8
211	2/1/96	915	28	Oats	2	1	0.5976	35.7	135	13.8	23.27	3813	14417	1474	67.3
212	2/1/96	915	28	Oats	2	2	0.6889	109	225	28	25.00	14014	28929	3600	55.0
158	2/1/96	1030	28	Oats	3	1	0.7038	3.37	32.9	2.54	25.00	455	4443	343	85.0
159	2/1/96	1030	28	Oats	3	2	0.7898	1.61	31.9	1.93	25.00	306	6070	367	45.2
255	2/8/96	1030	35	Clover	1	1	0.7350	8.56	40.9	6.8	25.00	1292	6174	1026	53.2
256	2/8/96	1100	35	Clover	1	2	0.8375	7.53	38.9	7.16	25.00	1853	9573	1762	28.0
223	2/8/96	1100	35	Clover	2	1	0.6952	12	57.1	9.69	25.00	1575	7493	1272	74.3
224	2/8/96	1100	35	Clover	2	2	0.7917	9.16	50.8	10.1	25.00	1759	9757	1940	53.8
259	2/8/96	1100	35	Clover	3	1	0.8028	12.3	54.8	9.41	25.00	2495	11115	1909	33.9
260	2/8/96	1100	35	Clover	3	2	0.7590	4.5	31.8	4.62	22.59	826	5840	848	41.5
257	2/8/96	1050	35	Oats	1	1	0.8547	8.35	28.1	1.29	25.00	2299	7737	355	40.3
258	2/8/96	1030	35	Oats	1	2	0.8081	2.82	14.5	0.382	25.00	588	3022	80	35.8
225	2/8/96	1130	35	Oats	2	1	0.5724	34.4	116	10.2	25.00	3218	10852	954	100.2
226	2/8/96	1100	35	Oats	2	2	0.8317	3.19	27.6	2.17	25.00	758	6559	516	39.4
262	2/8/96	1100	35	Oats	3	1	0.8605	1.98	20.6	1.42	25.00	568	5906	407	47.0
261	2/8/96	1100	35	Oats	3	2	0.8692	0.286	8.79	0.361	25.00	87	2689	110	56.3

Appendix IV. Concentrations in runoff water from the peach orchard in Winters, California, second storm.												
					Unfiltered			Filtered				Runoff
Sample Number	Date	Treatment	Block Number	Interval (min)	Diazinon (ug/L)	Chlorpyrifo (ug/L)	Methidathi (ug/L)	Diazinon (ug/L)	Chlorpyrifo (ug/L)	Methidathi (ug/L)	Sediment dry wt.(g/L)	Volume (L)
563	1/18/96	No Seed	1	0	6.86	8.11	43.3	ND	t 0.216	5.02	2.645	77.4
565	1/18/96	No Seed	1	30	24.9	9.52	49.4	10.2	1.95	37.2	0.7336	252
567	1/18/96	No Seed	1	60	33.9	7.26	54.2	10.2	t 0.453	25.5	0.452	220
569	1/18/96	No Seed	1	90	34.3	10.1	62.3	9.67	0.714	28	0.5554	1.23
587	1/18/96	No Seed	2	0	35.1	6.94	78.6	12.8	1.71	37.3	0.7153	47.0
589	1/18/96	No Seed	2	30	33.3	7.54	63.4	14.8	1.62	41.4	0.5584	76.1
591	1/18/96	No Seed	2	60	25.7	6.9	47.7	4.5	t 0.143	19.04	0.5299	81.6
593	1/18/96	No Seed	2	90	21.6	6.33	41.8	5.67	t 0.220	20.5	0.4372	91.1
595	1/18/96	No Seed	2	120	20.1	6	38.1	4.33	t 0.425	21.8	0.4984	84.8
597	1/18/96	No Seed	2	150	17.4	5.74	39.4	4.81	t 0.221	20.5	0.8174	54.9
599	1/18/96	No Seed	3	0	30.5	10.7	82.2	19	4.61	83.1	0.3975	70.3
601	1/18/96	No Seed	3	30	26.8	8.99	64.8	12.6	0.745	38.9	0.4714	100
603	1/18/96	No Seed	3	60	15.4	7.59	46.6	1.29	t 0.334	11.9	0.5212	118
605	1/18/96	No Seed	3	90	19.7	10.4	68.1	1.71	t 0.140	18.4	0.4609	131
607	1/18/96	No Seed	3	120	9.8	6.59	35.6	1.2	0.606	10.3	0.4306	148
609	1/18/96	No Seed	3	150	12.5	8.07	44	1.03	t 0.140	15	0.3591	154
623	1/18/96	Clover	1	0	22.6	5.21	47.3	9.69	t 0.111	20.1	1.21	36.8
625	1/18/96	Clover	1	30	14.1	5.06	38.3	6.71	t 0.072	16	1.172	42.5
627	1/18/96	Clover	1	60	15.2	5.07	39.4	4.58	t 0.041	19.7	0.496	42.3
629	1/18/96	Clover	1	90	12.3	5.51	36.7	3.44	t 0.084	13.8	1.8973	44.6
631	1/18/96	Clover	1	120	13.7	5.54	38.6	4.77	t 0.154	22	0.4319	42.2
633	1/18/96	Clover	1	150	11.7	5.16	34.9	3.53	t 0.072	15.3	0.3964	14.2
611	1/18/96	Clover	2	0	3.25	4.07	27.4	0.76	t 0.012	6.158	2.235	22.2
613	1/18/96	Clover	2	30	4.31	3.75	26.2	1.48	t 0.012	8.47	1.615	44.2
615	1/18/96	Clover	2	60	5.76	4.09	30.4	0.572	t 0.021	7.65	0.7826	53.6
617	1/18/96	Clover	2	90	4.8	3.76	26.6	0.587	t 0.014	6.71	0.6972	48.1
619	1/18/96	Clover	2	120	3.79	3.58	23	ND	t 0.018	4.75	1.015	53.0
621	1/18/96	Clover	2	150	4.4	3.54	22.3	ND	ND	7.56	0.5149	16.6
413	1/18/96	Clover	3	0	34.9	7.94	50.7	22.4	0.543	32.2	0.6971	25.2
415	1/18/96	Clover	3	30	33.3	9.02	49.3	15.8	t 0.262	23.2	0.4956	38.2
417	1/18/96	Clover	3	60	27.3	10.2	49.1	11	t 0.378	26.6	0.9393	32.2
419	1/18/96	Clover	3	90	21.1	7.25	32:3	6.41	t 0.220	19.6	0.2258	37.1

Appendix IV. Concentrations in runoff water from the peach orchard in Winters, California, second storm.												
					Unfiltered			Filtered				
Sample Number	Date	Treatment	Block Number	Interval (min)	Diazinon (ug/L)	Chlorpyrifo (ug/L)	Methidathi (ug/L)	Diazinon (ug/L)	Chlorpyrifo (ug/L)	Methidathi (ug/L)	Sediment dry wt. (g)	Runoff Volume (L)
421	1/18/96	Clover	3	120	22.6	6.84	34.7	4.62	t 0.068	12.3	0.2371	36.6
423	1/18/96	Clover	3	150	26.9	9.13	42.2	8.65	t 0.241	17.8	0.0571	27.5
635	1/18/96	Oats	1	0	28.4	5.92	52.4	16.6	t 0.179	20.5	1.111	24.1
637	1/18/96	Oats	1	30	26.1	7.39	47.2	13.5	t 0.261	18.6	0.4505	52.7
639	1/18/96	Oats	1	60	24	7	38.2	12.3	0.538	24.9	0.1444	57.2
641	1/18/96	Oats	1	90	21.4	6.69	33.6	8.35	t 0.361	22.6	0.1552	47.8
643	1/18/96	Oats	1	120	22.9	7.5	31.8	8	t 0.402	19.8	0.1541	23.8
645	1/18/96	Oats	1	150	27.6	14.3	74.3	8.84	0.57	23.9	0.13	24.7
575	1/18/96	Oats	2	0	41.5	9.61	84.3	11.9	2.47	29.4	1.422	46.2
577	1/18/96	Oats	2	30	29.7	8.94	65.1	22.2	1.27	59.3	0.9815	61.0
579	1/18/96	Oats	2	60	28.4	9.5	53.9	15.1	1.02	37.4	0.4819	58.6
581	1/18/96	Oats	2	90	25.5	7.85	46.5	10.9	0.73	25.2	0.488	66.4
583	1/18/96	Oats	2	120	23.5	8.05	40.5	9.36	0.724	24.4	0.4188	56.6
585	1/18/96	Oats	2	150	25.2	10.7	44.6	3.49	t 0.225	9	0.846	26.7
551	1/18/96	Oats	3	0	19.3	3.74	15.8	ND	t 0.080	3.77	2.025	43.5
553	1/18/96	Oats	3	30	23.2	7.7	35	12	t 0.302	18.7	0.8087	57.4
555	1/18/96	Oats	3	60	21.8	7.68	32.6	10.9	0.931	30.1	0.8793	69.7
557	1/18/96	Oats	3	90	19.8	9.08	29.8	6.9	0.99	18.9	0.4445	69.9
559	1/18/96	Oats	3	120	18.2	9.43	27.8	5.17	0.881	16.5	0.519	62.7
561	1/18/96	Oats	3	150	18	9.38	26.9	8.18	0.998	23.6	0.3671	38.6

ND = none detected.

t = trace. Values were below stated detection limit and are therefore considered estimates.

Appendix V. Mass† dissipation (g ha^{-1}) of chlorpyrifos, diazinon, and methidathion on soil and vegetation.						
Treatment/ Day	Chlorpyrifos		Diazinon		Methidathion	
No Seed	Soil		Soil		Soil	
0	250(16)		340(51)		390(63)	
3	280(64)		340(15)		390(33)	
7	210(61)		280(110)		300(92)	
13	140(40)		140(53)		170(63)	
20	100(29)		55(10)		100(24)	
28	87(27)		20(6.5)		40(13)	
35	52(19)		7.0(0.44)		34(2.2)	
Clover	Soil	Clover	Soil	Clover	Soil	Clover
0	270(9.8)	160(84)	380(47)	140(67)	450(40)	170(84)
3	260(132	160(23)	350(190)	130(28)	390(220)	230(32)
7	210(20)	120(30)	330(66)	110(28)	360(73)	120(30)
13	130(18)	57(8.8)	99(16)	41(6.4)	130(27)	40(9.7)
20	110(19)	53(15)	62(14)	27(8.3)	100(31)	23(5.2)
28	77(38)	44(19)	23(4.6)	17(55)	57(15)	9.9(3.5)
35	41(5.7)	12(4.1)	7.0(1.2)	2.3(0.80	49(13)	2.0(0.85
Oats	Soil	Oats	Soil	Oats	Soil	Oats
0	220(10)	260(61)	270(35)	210(41)	300(29)	260(57)
3	150(96)	240(32)	240(170)	140(22)	260(170)	240(25)
7	190(100	130(46)	230(140)	86(46)	210(130)	110(46)
13	140(100	72(20)	100(71)	41(19)	130(93)	31(16)
20	86(58)	37(21)	45(20)	19(14)	47(29)	7.2(5.3)
28	120(60)	23(15)	32(17)	8.2(7.4)	51(23)	2.7(1.9)
35	49(14)	11(8.1)	9.0(2.8)	2.5(2.5)	28(14)	0.8(0.83

† Mean (standard deviation in parentheses) of three blocks, extrapolated over the entire field.
Nominal mass applied to the field was 1,120 g ha^{-1} for each insecticide.