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Organophosphate Dormant Spray Pest Control Efficacy, Pesticide Concentration and Toxicity in Storm Runoff

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Dormant spraying is a practice that involves the application of insecticides or fungicides to dormant orchards (trees that are not leafed out) between the months of December and March depending on tree species (Zalom 2002). Diazinon, an organophosphate (OP) insecticide, has been one of the most widely used dormant spray pesticides for controlling a variety of economically important pests in most California orchard crops since the 1970s. Dormant spraying with OPs and horticultural mineral oil was long advocated by University of California scientists as part of an IPM strategy which is effective yet preferable to multiple in-season insecticide applications for controlling the same suite of insect species in terms of reduced worker exposure, food residues and impact on natural enemies of pests (Rice et al. 1979). Other broad spectrum insecticides including carbamates and synthetic pyrethroids are also registered for use on most orchard crops. The pyrethroids esfenvalerate and permethrin were not commonly used as dormant spray insecticides until the mid-1990s (Epstein et al. 2000) due, in part, to the relatively low cost of the OP insecticides and concerns for secondary spider mite outbreak following pyrethroid application (e.g. Zalom et al. 2001). Increased use of pyrethroids has resulted both from increased cost of OP insecticides and water quality concerns.

Diazinon has been found in surface waters of California's Sacramento and San Joaquin River watersheds at concentrations toxic to the cladoceran, *Ceriodaphnia dubia* Richards (Kuivila and Foe 1995, Werner et al. 2000). In 1998, the State of California placed the Sacramento and San Joaquin Rivers and their delta on the Clean Water Act 303(d) list of impaired waterways due, in part, to elevated levels of diazinon and chlorpyrifos. Urban runoff, orchard dormant sprays and other agricultural uses have been implicated as main sources by agencies monitoring water quality (e.g. Domagalski et al. 2000, and Sheipline 1993).

In 1997, our multidisciplinary team of UC research and extension scientists began to study alternative practices intended to mitigate the effects of dormant season OPs used in orchard crops (Zalom et al. 2002, Werner et al. 2002, Angermann et al. 2002). One potential mitigation measure is earlier treatment timing. It is presumed that drier soil conditions and lower probability of storm occurrence

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associated with the early part of the dormant season would facilitate water infiltration and allow time for pesticides to break down before winter rains produce stormwater runoff. However, the timing at which dormant sprays are applied may also impact their efficacy against target pest species. This research examines effects of adjusting dormant spray application timing on pest control efficacy and toxicity of stormwater runoff.

MATERIALS AND METHODS

Studies to determine the effect of dormant season treatment timing on pest control efficacy were conducted in almond orchards near Waterford, California (2001 and 2002) and Cortez, California (2001), and in a French prune orchard near Sutter, California (2002). The Sutter orchard was also the site for the runoff study described in this paper. Insecticides were applied using a Rears® 500 Gallon Powerblast standard orchard sprayer (Rears Manufacturing, Eugene, Oregon). The Waterford. orchard was divided into 12 plots of ~500 trees per plot. Four treatments, each replicated three times, were assigned to the plots in a randomized complete block design. The treatments were 7.0 L/ha Diazinon AG500 (Makhteshim-Agan North America Inc., = 3 pounds diazinon ai/acre) with 56.1 L/ha of Volck Supreme horticultural mineral oil (Valent Agricultural Products, molecular wt = 352, 50% distillation point = 476°F) and 466.7 L/ha of water applied on either December 18, 2000, January 6, 2001, or January 30, 2001, and untreated. Treatments the following year were 4.7 L/ha Lorsban 4E (Dow AgroSciences Inc., = 2 pounds chlorpyriphos ai/acre) with 37.4 L/ha of Volck Supreme horticultural mineral oil (Valent Agricultural Products, molecular wt = 352, 50% distillation point = 476°F) and 466.7 L/ha of water applied on either 13 December, 2001, 7 January, 2002, or 30 January, 2002, and untreated. The Cortez orchard was divided into 9 plots of ~400 trees per plot. Three treatments, each replicated three times, were established in a randomized complete block design. The treatments were 7.0 L/ha Diazinon AG500 (Makhteshim-Agan North America Inc., = 3 pounds diazinon ai/acre) with 56.1 L/ha of Volck Supreme horticultural mineral oil (Valent Agricultural Products, molecular wt = 352, 50% distillation point = 476°F) and 934.7 L/ha of water applied on 18 December, 2000, or 6 January, 2001, and untreated. Experimental design and treatments in the Sutter orchard are described below. Pesticide concentrations and water volume were those normally used by the cooperating grower and are within the normal range applied by California almond growers.

San Jose scale, *Quadraspidiotus perniciosus* (Comstock), adult males and their parasitoids were monitored using San Jose scale traps and pheromone lures (Trece Inc., Salinas, California) (Badanes-Perez et al. 2002). Both the trap and the lure were changed every four weeks. Two of the traps were placed in trees in the center row of each treatment replicate at a height of 2 m by mid-March. The number of San Jose scale males on each trap was determined in the laboratory under magnification, and all scale parasites present were recorded. The number of San Jose scale males per trap were summed for the first generation to provide an estimate of population density per trap (Badanes-Perez et al. 2002). In the Waterford orchard, peach twig borer, *Anarsia lineatella* Zeller, density in each treatment replicate was assessed by randomly collecting 25 watersprouts from trees near the center of each plot during the first week of May, and returning them to the laboratory where the flagged shoot tips were dissected to determine if the flagging was due to peach twig borer, the oriental fruit moth, *Grapholitha molesta* Busck, or the fungal disease brown rot (*Monilinia laxa*). Of these, only peach twig borers are affected by the dormant sprays. Pest densities for treatments were compared by analysis of variance. If significant, treatment means were separated by Fisher's Protected LSD (Sokal and Rohlf 1981).

The runoff experiment was conducted in a mature French prune orchard planted on berms 1.3 m wide and 0.3 m wide at Half Moon Orchards, located near Sutter, California. Treatments were 4.7 L/ha of Drexel Diazinon (Drexel Chemical Co., = 2 pounds diazinon ai/acre) with 28.0 L/ha of Volck Supreme horticultural mineral oil (Valent Agricultural Products, molecular wt = 352, 50% distillation point = 476^{o}F) and 934.7 L/ha of water applied on either 12 January, 2002, 2 February, 2002, or 22 February, 2002. Each application date plot was replicated 3 times in a randomized complete block design. The lower amount applied to this orchard reflects pesticide label differences between prunes and almonds. The size of each treated block was 10 tree rows wide by the entire length of the tree row (110-112 trees). An autosampler unit (Zalom et al. 2002) was deployed in the row middle at the center of each of the 9 experimental plots, and placed 50 m from the upslope end. The row middle was blocked at its uppermost end by a diversion dam made of soil to preclude inadvertent entry of water onto the row middle being sampled from an external source.

The autosampler recorded stormwater runoff volume using a flow meter through which all water leaving each plot was diverted. One percent of the measured runoff was diverted to a covered Nalgene collection tank. Composite samples for chemical analyses and toxicity testing were collected from this tank in washed glass jars, and transported on ice to UC Davis, California, where they were divided for bioassays and a 250 mL sample stored at -4°C for chemical analysis.

Solid phase extraction (SPE) was used for the diazinon analysis. Water samples were thawed at room temperature, and a 100 mL aliquot decanted into a 250-mL separatory funnel. Internal standards (ChemService, West Chester, Pennsylvania) were added, and the mixture shaken vigorously for 1 min then allowed to stand 60 min. The sample was run through a SPE C18 column (Bond Elut, 500 mg, 3 mL, Varian, Harbor City, California) at a slow drip rate under vacuum. The column was eluted twice with a 2 mL volume of ethyl acetate into a test tube, and the eluant transferred to a 5 mL volumetric flask. The tube was washed with 0.5 mL of EtOH, which was added to the flask. Parathion internal standard was added and the volume adjusted to 5 mL Aliquots of 1 µl were injected into the gas chromatograph (Hewlett Packard, model 5890, series II Plus, Palo Ato, California). Diazinon was analyzed using a DB-35MS column (J&W Scientific, Agilent Technologies, Palo Alto, California) and a nitrogen-phosphorus detector (NPD). Diazinon detection limit was 0.070 μg/L and recovery 71.4%.

C. dubia came from an in-house culture maintained at the UC Davis Aquatic Toxicology Laboratory. Mortality was recorded after 48 h according to US EPA protocols (US Environmental Protection Agency 1994). If 100% cladocera mortality occurred within 24 h, dilutions of the respective water sample were tested to determine the lowest observed effect concentrations (LOEC). Toxicity was defined as a statistically significant difference ($P<0.05$) between water sample and laboratory control. Mortality data were compared to controls using Fisher's exact test (Sokal and Rohlf 1981). Treatment groups were compared by analysis of variance or Kruskal-Wallis One Way ANOVA on ranks followed by Fisher LSD or Dunn's method (Sokal and Rohlf 1981), respectively.

RESULTS AND DISCUSSION

A significant difference (F=4.391, P=0.0419, df=3,8) in both San Jose scale males captured in pheromone traps and the proportion of shoot strikes damaged by peach twig borer (F=11.147, P=0.0004, df=3,8) was observed between untreated and diazinon treated plots in the Waterford orchard in 2001 (Table 1). Although there was no significant difference in mean densities between diazinon application dates, there tended to be more peach twig borer shoot strikes on the trees that were treated earlier during orchard dormancy. No significant difference (F=1.139, P=0.3809, df=2,6) in San Jose scale males captured in pheromone traps was observed between treatments in the Cortez orchard. However, the mean (±SD) number of male scales trapped in the early diazinon treatment (81.2±27.1) was only about 60% that of that observed in the late diazinon (132.8±60.9) and untreated (131.8±49.6) plots.

Table 1. Total San Jose scale (SJS) males per trap during the first flight, and proportion of shoots damaged by peach twig borers per plot in the Waterford orchard in experimental plots treated with diazinon.

Treatment	SJS, 2001 mean ± SD	SJS, 2002 mean ± SD	Peach twig borer mean ± SD
Untreated	641.7 ± 176.4 b	225.3 ± 114.7 b	0.217 ± 0.047 b
mid-December	351.7 ± 63.7 a	26.0 ± 10.4 a	0.073 ± 0.042 a
early January	335.0 ± 85.4 a	54.7 ± 36.7 a	0.067 ± 0.021 a
late January	308.3 ± 155.1 a	70.7 ± 26.6 a	0.037 ± 0.006 a

Column means followed by the same letter do not differ significantly (P>0.05) by Fisher's Protected LSD.

A significant difference (F=6.259, P=0.0171, df=3,8) in San Jose scale males captured in pheromone traps was again observed between untreated and diazinon treated plots in the Waterford orchard in 2002 (Table 1), confirming the 2001 results. No significant difference (F=1.193, P=0.3662, df=2,6) in mean (±SD) San Jose scale males captured in pheromone traps was observed between treatment timings in the Sutter orchard (early = 41.0±20.7; middle = 21.0±5.6; late = 30.3±17.2).

San Jose scale parasitoids were not found on pheromone traps in either the Waterford or Sutter orchards, but the parasitic Hymenoptera species *Encarsia perniciosi* and an undescribed *Aphytis* sp. were present on the pheromone traps in the Cortez orchard. No significant difference (F=1.139, P=0.3809, df=2,6) in mean (±SD) parasitoid abundance was found between untreated (81.2±27.1), early treated (132.8±60.9) and late treated (131.8±49.6) plots.

The rainfall pattern in the winter of 2001-02 was somewhat atypical of California's central valley. Heavy rains occurred earlier than normal, primarily from November through early January, unlike more typical winters when most major rainfall events occur during January and February. The first rainfall event following application of the diazinon treatment sufficient to produce runoff in all plots occurred on 11 March, 2002 (37.5 mm). A smaller rainfall event on 6 March (18.8 mm) resulted in runoff from only one of the plots. Cumulative rainfall following each diazinon treatment until 11 March was 103.5 mm, 84.3 mm and 47.5 mm for the early, middle and late application dates, respectively.

Runoff volume from 8 plots (one autosampler malfunctioned) during the 11 March rainfall event averaged 1.03 L/sq m. Average diazinon concentrations (Table 2) in the composite water samples were 3.6 ppb, 11.5 ppb and 31.3 ppb for the early, middle and late treatments, respectively, supporting our hypothesis that OP concentrations are reduced when time between diazinon application and major storm events is increased. It is possible that ground residues of diazinon from the earlier application date infiltrated into the soil following smaller storm events, where they were subjected to environmental degradation over time. Bacterial enzymes can speed the breakdown of diazinon (Howard 1991), and its half life in soil is only 2 to 4 weeks (Wauchope et al. 1992).

Toxicity to *C. dubia* was reduced in plots treated with diazinon earlier rather than later in the season (Table 2), which was temporally closer to the storm event. Although not statistically significant (P<0.05), these data show a clear trend. Diazinon was more concentrated and toxicity higher in the only sample collected on 7 March during a storm that produced little runoff, suggesting that diazinon concentrations in runoff may be higher in the early part of a storm and become diluted with increasing amounts of precipitation.

Economically, acceptable control of San Jose scale and peach twig borer, two of the major target pests of dormant season OP sprays, was achieved at earlier diazinon or chlorpyrifos application dates. Further, diazinon concentrations and toxicity to *C. dubia* were significantly lower in runoff from plots treated earlier versus later in the season.

Table 2. Toxicity to *Ceriodaphnia dubia* of stormwater runoff collected following the 11 March rainfall event.

Treatment	Sample date	n	Diazinon conc. mean ± SD[1] (ppb)	LOEC* mean ± SD (% sample)
Early	3/11	4	3.6±1.3 a	10±7.1 (n=4)
Middle	3/11	2	11.5±2.9 b	5.0±0.0 (n=2)
Late	3/11	3	31.3±4.0 c	1.25±0.0 (n=3)
Late (plot #4)**	3/7	1	91.39	0.5 (n=1)

[1] Column means followed by the same letter do not differ significantly (P>0.05) by Fisher's Protected LSD.

* Percent concentration of runoff sample that was toxic to *C. dubia*. The lower the % the more toxic the sample. LOEC = lowest observed effect concentration.

** Note that only this plot had runoff from rain on 7 March. All plots had runoff on 11 March.

Some growers have expressed concern that phytotoxicity of water stressed trees could be the result of dormant sprays containing horticultural mineral oils. Water stress is more likely to occur early in the dormant season, before the initiation of winter rains. Additional research is warranted to determine whether negative horticultural impacts might occur from earlier treatment timing, and if so to identify possible mitigation measures.

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