Research Article

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Impact of ant control technologies on insecticide runoff and efficacy

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Abstract

BACKGROUND: Insecticides are commonly used for ant control around residential homes, but post-treatment runoff may contribute to contamination of surface water in urban watersheds. This study represents the first instance where runoff of insecticides was directly measured after applications around single family residences. During 2007, houses were treated with bifenthrin or fipronil sprays following standard practices. During 2008, pin stream applicators, spray-free zones and restricting sprays to the house foundation were considered as management options.

RESULTS: During 2007, the resulting runoff from the bifenthrin spray in the irrigation water had a mean concentration of 14.9 μg L^{-1} at 1 week post-treatment and 2.5 μg L^{-1} at 8 weeks, both high enough to be toxic to sensitive aquatic organisms. In comparison, treatments with bifenthrin granules resulted in no detectable concentrations in the runoff water after 8 weeks. The mean concentration for fipronil used as a perimeter spray was 4.2 μg L^{-1} at 1 week post-treatment and 0.01 μg L^{-1} at 8 weeks, with the first value also suggesting a potential for causing acute aquatic toxicity to sensitive organisms. During 2008, insecticide runoff was reduced by using spray-free zones and pin stream perimeter applications.

CONCLUSIONS: It is shown that insecticide runoff from individual home treatments for ants can be measured and used to improve techniques that minimize runoff. The pin stream application and applications limited to the house foundation should be further evaluated for their potential to reduce pesticide runoff from residential homes.

Keywords: fipronil; bifenthrin; urban insecticide runoff; Argentine ant; water quality; urban watershed

1 INTRODUCTION

Ants are one of the major pests around structures in urban environments.[1] Commercial pest management companies throughout California report that 65–80% of their pest control services deal exclusively with ants, and that Argentine ants (*Linepithema humile* Mayr) make up 85% of the ants sampled by pest management professionals (PMPs).[2] A survey of one company showed that 36% of all customer calls concerned ant control, equaling the combined total for the next three pests (cockroaches, spiders and bees). A telephone survey in northern California indicated that ants are the most common pest encountered by homeowners and PMPs.[3] In California, various pest management strategies are used to control Argentine ants in urban settings, which include insecticide baits, sprays and granules.[1,4–7]

As the use of organophosphates has declined over the past decade in the light of regulations, the use of pyrethroids and fipronil has increased concurrently. For instance, the amount of permethrin used for structures and landscape maintenance, as reported by licensed applicators, increased from 70 185 kg (active ingredient) in 1997 to 119 508 kg in 2007.[8] Over the same time period, bifenthrin use increased from 40 to 22 025 kg, and cypermethrin use increased from 41 188 to 88 272 kg.[8] After its registration in 1996 in California, the use of fipronil reached 29 374 kg in 2007.[8] In fact, fipronil (Termidor®) has become one of the primary insecticides applied around structures for insect control, especially for ants. This increase was primarily due to its popularity with PMPs for ant control because of improved efficacy.

The widespread use of insecticides in residential areas apparently contributes to insecticide contamination of urban surface aquatic systems via irrigation- and storm-induced runoff. For instance, bifenthrin has been frequently found at concentrations acutely toxic to sensitive aquatic organisms in California urban creeks during both summer irrigation and winter rain events.[9–13] Likewise, fipronil has recently been found in urban surface streams in ten states, including California.[14–16]

Although there are many reports on the occurrence of insecticide residues in urban surface water, so far no studies have characterized insecticide offsite movement after application at actual home sites. This may be attributed to the great degree of complexity and heterogeneity involved in such studies, including many variables that cannot be controlled by the researcher. For

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instance, the size, shape, type and layout of surfaces subjected to pesticide treatment or runoff can vary drastically among homes, and the type, output and uniformity of irrigation systems may also differ greatly among different homes. However, the general lack of direct measurements hinders the development of mitigation practices for reducing insecticide pollution of sensitive urban aquatic ecosystems. The goals of the present study were: (1) to demonstrate that insecticide runoff of bifenthrin and fipronil, including fipronil's breakdown metabolites, could be measured from single homes; (2) to measure the persistence of these products at these homes over time; (3) to show that mitigation techniques at these homes could reduce insecticide runoff; (4), to correlate the runoff information with efficacy against ants from these treatments, as reported elsewhere as part of this integrated study.

2 MATERIALS AND METHODS

2.1 Site description

All treatments were done during the dry, hot summer in the cities of Riverside and Moreno Valley, CA. All of the residences were single family homes with an irrigated front lawn and a concrete driveway along one side of the lawn. Lawns were not recently planted, and therefore the organic content was probably low, as most people do not add organic fertilizer or mulch to their lawns. These houses had sprinklers (mostly pop-up types with adjustable arcs) in the front lawn. Sprinklers of this type are usually rated from 15 to 30 psi (1–2 bar) pressure and to give precipitation of 1.5–2.0 in h^{-1} (40–60 mm h^{-1}) (Rainbird Tech Specs; Rainbird International, Glendora, CA). Some houses also had potted plants in the front yard. Irrigation runoff usually ran into the driveway and then into the street, although in some cases it ran across the sidewalk and then into the street.

Argentine ants are a major problem in the summer, and, with few exceptions, the only water runoff at this time is from lawn irrigation. The runoff study was part of a larger project investigating the efficacy of different treatments in controlling Argentine ant infestations around urban homes.[6,17] Each house was treated just once with a single or a combination of two insecticides. All households during the hot summer months have daily irrigation in the early morning hours. Daily irrigation continued throughout the trial period, but samples were only collected on the specified dates.

During 2007, the study was conducted between 11 July and 18 September. There was no measurable precipitation in Riverside during this time.[18] Water samples were collected 1, 4 and 8 weeks after insecticide applications. The mean daily high and low temperatures were 35.2 and 17.3 °C for the first week post-treatment, 35.6 and 17.3 °C for weeks 1 to 4, and 36.2 and 17.5 °C for weeks 1 to 8 respectively.

During 2008, the study was conducted between 30 June and 29 July, and water samples were collected 1 day, 1 week and 2 weeks after the application of the insecticides. The mean daily high and low temperatures during these two weeks were 33.3 and 17.2 °C respectively. There were several light rainfalls during this time, totaling 0.3 cm, but they did not result in noticeable surface runoff.

To facilitate the collection of water runoff, the selected houses had visible slopes (>2%) from the front lawn to the street. The percentage slope of the lawn was measured using a Suunto clinometer (Model PM-5/360PC; Suunto USA, Ogden, UT), which is accurate to 1%. In addition, the depth, velocity and width of the runoff stream were also measured. The water velocity was measured by timing how long it took for a 1 cm^2 piece of Styrofoam to move 1 m in the water stream.

2.2 Collection of water

Autosamplers could not be used for this study owing to the involvement of heavily used public areas and private homes. Therefore, to collect the water runoff at the curb, a custom-made 'U'-shaped Styrofoam dam (51 × 28 × 10 cm) was enclosed in a thin plastic can liner (0.7 mL, 33 × 39 in, 33 gals) and placed firmly against the sides of the street curb. Two small sandbags were used to form a tight seal of the Styrofoam dam with the street. Once water began to fill the U-shaped cutout, samples were continuously taken from the center of the pooled water using a 60 mL aquatic glass pipette (Bioquip, Rancho Dominguez, CA). It took only several minutes to fill a 1 L sample bottle (32 oz Boston Round Style Amber Glass Bottle; Fisher Scientific, Pittsburgh, PA), so it is unlikely for sorption onto the plastic film around the Styrofoam to have significantly affected the measured pesticide concentrations. The samples were transported to the laboratory in ice boxes and stored at 4 °C until analysis. All plastic bags and liners were discarded between trials, and the aquatic pipette was thoroughly cleaned with soap, deionized water and acetone.

Knowing the volumes of water applied to and exiting the system as runoff is extremely important in order to understand the extent to which the lawn is acting as a buffer strip. The house water meter was read when the sprinklers turned on, and again when they turned off, to see how much water was applied by the sprinklers. To estimate the volume of water in the runoff, the volumetric flow, Q, was calculated from the relationship $Q = A \times V$, where A is the area (depth × width of the water stream) and V is the uniform average velocity of the water stream. The total volume of runoff was then estimated from Q and the elapsed time. The total insecticide runoff was estimated by multiplying the concentration of the insecticide in the runoff by the estimated runoff water volume.

2.3 Treatments

Four treatments were done in 2007, and six treatments in 2008 (Tables 1 and 2). These treatments are numbered consecutively from 1 to 10. Perimeter treatments refer to sprays applied to the outside house walls and adjacent ground. Spot treatments refer to spray applications only where ants were seen anywhere on the property. Ant trails usually follow guidelines such as lawn/sidewalk/driveway edges. It is therefore very likely that a spot treatment would be near the driveway or sidewalk. Some treatments include both perimeter and spot applications. The substrates for house perimeter treatments can include concrete, soil and stucco. Spot treatments on ant trails can be on any of these substrates, while the driveway is concrete.

2.3.1 *Measuring treatment efficacy*

The methodology used for monitoring Argentine ants is reported in detail elsewhere.[5,6,17] Monitors consisting of 10 mL vials filled with 25% sucrose/water were placed on the ground around the homes. Ten of these vials were placed around the house's foundation, and an additional ten were placed away from the house near the property's perimeter. The vials were covered with flowerpots to protect them from sprinklers and animals. An evaporative control was placed out of reach of the ants. Consumption of the sucrose/water over 24 h was measured. As it

Table 1. Summary of 2007 insecticide treatments, including areas of treatment

Treatment number (*N*)	Treatment name	Nozzle type, volume	AI used[a] (g)	House foundation	Ant trails	Driveway
			Fipronil treatments			
1 (6)	Perimeter + spot	Fan, 11.4 L	6.81	X	X	X
2 (3)	Spot	Fan, 3.8 L	2.27		X	
			Bifenthrin treatments			
3 (3)	Perimeter + spot	Fan, 11.4 L	6.81	X	X	X
4 (3)	Granular	–	1.5–3		Soil only	

[a] AI = active ingredient.

Table 2. Summary of 2008 insecticide treatments, including areas of treatment

Treatment number (*N*)	Treatment name	Nozzle type, volume	AI used (g)	House foundation, doors, windows, openings	Ant trails	Driveway	Spray-free zone
			Fipronil treatments				
5 (3)	Perimeter	Pin, 3.8 L	2.27	X			
6 (3)	Spot	Fan, 3.8 L	2.27		X		
7 (3)	Spot	Fan, 3.8 L	2.27		X		X
			Bifenthrin treatments				
8 (3)	Perimeter + spot	Fan, 11.4 L	6.81	X	X	X	
9 (3)	Perimeter + spot	Pin, 11.4 L	6.81	X	X		X
10 (3)	Spot	Fan, 11.4 L	6.81		X		X

was known that one ant can consume 0.3 mg of sucrose/water, this consumption could be translated into the number of ant visits at the reported time intervals.[19] Using balances precise to 10 mg could detect as few as 33 ant visits, whereas thousands of ant visits are typical during 24 h. Therefore, population changes of 1% or more were usually detectable. The percentage reduction in ant visits over time shows the effectiveness of each treatment. For brevity, this paper will only cite the figures for ant numbers near the house, which are of most concern to homeowners.

2.4 Conventional treatments (2007)

The four treatments evaluated in 2007 are summarized in Table 1. More detailed descriptions of the treatment protocols can be found in Klotz *et al*.[6] Water samples were taken from 3–6 different homes for each of the treatments, with each house treated on only one occasion. Conventional fan-spray nozzles were used in all these treatments. All of these treatments could be typically used by a PMP. Sprays were applied with a 19 L backpack sprayer (Birchmeier, Stetten, Switzerland) that had a 1.5 mm Duro mist nozzle. House perimeter sprays were applied 30 cm up and 30 cm out from the foundation. Some houses were treated with fipronil 91 g L^{-1} SC (Termidor SC®; BASF, Florham Park, NJ) at 0.6 g AI L^{-1}. Other houses were treated with bifenthrin 79 g L^{-1} SC (Talstar One®; FMC, Philadelphia, PA) at 0.6 g AI L^{-1}. Finally, some of the houses receiving the fipronil treatment were also treated with bifenthrin 2 g kg^{-1} granules (Talstar® EZ Granules®; FMC). Water samples were collected pretreatment and 1, 4, and 8 weeks post-treatment.

2.5 Modified treatments (2008)

Table 2 summarizes the treatments completed in 2008. Treatment 8 was included as a standard PMP treatment. More detailed descriptions of the treatment protocols can be found in Klotz *et al*.[17] Three houses were used for each treatment. To collect the first and presumably highest insecticide runoff, this year the first sample was collected 1 day post-treatment, followed by 1 and 2 weeks. The collection at 2 weeks was not from irrigation runoff. Rather, the concrete driveway of the house was flushed with water from a hose for 15 min, and 0.33 L of water was collected from the surface runoff every 5 min into the same 1 L sample bottle. The volume of water used for the flush was estimated by timing how many seconds it took to fill an 18.9 L pail. This treatment was to mimic a rain event and to determine if insecticides had accumulated on the driveway with the potential for runoff.

Some treatments using pin stream applicators in place of the fan applicators were included as a mitigation option. The pin stream nozzle applied a narrow 5.1 cm band of insecticide. When used around the house foundation, it was applied not more than 0.3 m away from the house. Typically, pin stream applicators are used for crack and crevice applications of insecticides and are not used for treating entire house perimeters or ant trails. Another mitigation technique was the use of spray-free zones within 4.6 m of the street and 1.5 m of sidewalks and the driveway.

2.6 Analysis of chemicals

Each collected water sample (1000 mL) was extracted with methylene chloride (40 mL) for three consecutive times using glass separatory funnels. The combined solvent phase was dehydrated by passing through a filter paper filled with anhydrous sodium sulfate (approximately 40 g). The extract was concentrated to near dryness on a vacuum rotary evaporator. For analysis of fipronil and its metabolites, the residue was recovered in petroleum ether + acetone (70 + 30 by volume; 1.0 mL) and subjected to a cleanup using an Alltech silica solid-phase extraction cartridge (500 mg, 3 mL; Deerfield, IL). Prior to sample loading, the cartridge was successively conditioned with petroleum ether + acetone (70 + 30 by volume; 2.0 mL) and petroleum ether (2.0 mL). The extract (1.0 mL) was then passed through the conditioned cartridge and eluted with petroleum ether + acetone (70 + 30 by volume; 10 mL) at a flow rate of 0.5 mL min^{-1}. The volume of the eluate was further reduced to about 0.5 mL under a gentle nitrogen stream and reconstituted to 1.0 mL in petroleum ether + acetone (70 + 30 by volume). For bifenthrin analysis, the residue was recovered in hexane + acetone (90 + 10 by volume; 1.0 mL), and the cleanup was achieved using a PrepSep R Florisil solid-phase extraction cartridge (1000 mg, 14 mL; Fisher Scientific). Prior to sample loading, the cartridge was conditioned with hexane + acetone (90 + 10 by volume; 10 mL). The extract (1.0 mL) was passed through the conditioned cartridge and eluted with hexane + acetone (90 + 10 by volume; 10 mL) at a flow rate of 0.5 mL min^{-1}. The volume of the eluate was further reduced to about 0.5 mL and reconstituted to 1.0 mL with hexane + acetone (90 + 10 by volume). An aliquot of the final sample was taken for gas chromatography (GC) analysis.

The concentrations of target compounds in the final extracts were analyzed using an Agilent 6890 series GC equipped with a Ni^{63} microelectron capture detector (ECD; Agilent Technologies, Wilmington, DE). An HP-5 MS column (30 m × 0.25 mm × 0.25 µm; Agilent Technologies) was employed for separation. The inlet temperature was 260 °C, and the detector temperature was 320 °C. The oven temperature was initiated at 80 °C, then increased to 160 °C at 20 °C min^{-1}, further increased to 240 °C at 5 °C min^{-1} and finally increased to 300 °C at 30 °C min^{-1} and held for 20 min. The flow rates of the carrier gas (helium) and makeup gas (nitrogen) for ECD were 1.0 and 60 mL min^{-1} respectively. The injection of 2 µL sample was conducted by an Agilent 7683 autosampler (Agilent Technologies) in the pulsed splitless mode, and the split mode was turned on after 1.0 min. The typical retention times for desulfinyl fipronil, fipronil sulfide, fipronil, fipronil sulfone and bifenthrin under these conditions were 10.7, 12.9, 13.1, 15.2 and 17.8 min respectively.

A preliminary experiment showed that the method detection limits for the analytes were 0.001 µg L^{-1}. The recoveries of spiked analytes were higher than 85% using the above extraction and analysis steps.

2.7 Statistical analysis

Statistics were done with Systat.[20] Natural log transformed data were used in analysis of variance (ANOVA) to compare different treatment effects, and the same transformed data were also used for determining metabolite half-lives using regression analysis. This transformation improved the normality of the data, which otherwise had a very skewed spread of values. Arithmetic means are reported in the text, while geometric means (means of logged values) are shown in the figures. The geometric means are slightly lower than the arithmetic means.

In some cases where even the log transformed data did not appear normal, nonparametric Kruskal–Wallis tests were done. Nonparametric Spearman rank correlations were done to measure the significance of correlations between water flow velocity and slope.

3 RESULTS AND DISCUSSION

3.1 Conventional treatments (2007)

Over all post-treatment dates and treatments the amount of water applied to the lawn (as measured from the house water meter) for the one bank of sprinklers ranged from 227 to 1416 L (mean ± SE = 691 ± 50.5 L). The estimate of water running off from each site after an irrigation event also varied greatly, ranging from 1.1 to 70.0 L (mean ± SE = 19 ± 3.1 L). The variations were likely due to the different sizes, types and layout of the areas that were irrigated, and the performance of individual irrigation systems. The correlation of slope versus water flow velocity was significant (Spearman rank correlation = 0.794, $P < 0.001$). Table 3, which is broken down by treatments, shows the slopes from the house to the street, the water volume used according to the house water meter, the estimated amount of water runoff, the duration of the runoff into the street and the estimated total amounts of insecticide in the runoff.

3.1.1 Bifenthrin runoff 2007

At 1 week post-treatment, the 11.4 L bifenthrin spray (treatment 3) had a mean runoff concentration of 14.9 µg L^{-1}, while for the granular bifenthrin (treatment 4) it was 0.4 µg L^{-1} (significantly different with ANOVA, $P < 0.05$) (see Fig. 1). The granular runoff

Table 3. Slope from the house to the street, duration of runoff into the street, amount of water applied to the lawn as recorded from the house water meter, estimated water runoff and estimated total insecticide runoff for the first post-treatment sample (1 week for 2007 treatments, 1 day for 2008 treatments). Values shown are mean (± SE)

Treatment[a]	% Slope	Duration of runoff (s)	Water applied (L) [N]	Est. water runoff (L) [N]	Est. total insecticide runoff (µg) [N]
		2007			
1. F perimeter, fan	5.8 (±1.66)	693 (±123.9)	678 (±86.7) [16]	15 (±3.8) [16]	35 (±20.3) [6]
2. F spot, fan	12.3 (±4.67)	539 (±50.1)	642 (±47.7) [6]	8.7 (±1.51) [9]	31 (±29.2) [3]
3. B perimeter/spot, fan	5.0 (±2.64)	589 (±56.6)	754 (±73.1) [8]	36 (±6.8) [9]	301 (±125.7) [3]
4. B granular	3.3 (±1.20)	493 (±41.4)	610 (±79.9) [9]	10 (±4.5) [9]	8 (±7.1) [3]
		2008			
5. F perimeter, pin	5.2 (±2.32)	746 (±59.0)	845 (±134.0) [6]	23 (±3.0) [6]	1.0 (±1.04) [3]
6. F spot, fan	5.5 (±0.76)	802 (±52.7)	552 (±46.9) [4]	98 (±20.8) [5]	603 (±240.4) [3]
7. F spot, fan, SFZ	4.1 (±2.04)	820 (±78.0)	793 (±254.7) [2]	95 (±37.1) [4]	363 (±209.5) [3]
8. B perimeter/spot, fan	5.8 (±1.09)	707 (±38.7)	1380 (±308.5) [4]	33 (±9.8) [6]	566 (±181.9) [3]
9. B perimeter/spot, pin, SFZ	6.8 (±1.61)	1098 (±213.4)	743 (±232.0) [4]	45 (±17.0) [6]	0.4 (±0.36) [3]
10. B spot, fan, SFZ	6.0 (±2.65)	935 (±210.0)	916 (±147.6) [6]	119 (±98.0) [4]	53 (±52.1) [3]

[a] F = fipronil; B = bifenthrin; SFZ = spray-free zone.

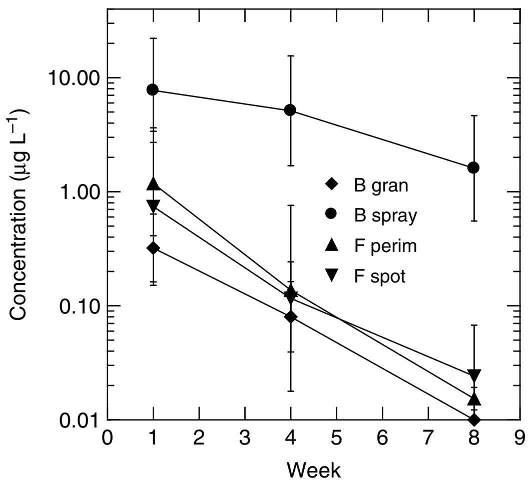

Figure 1. Geometric means (± SE) of log transformed data of bifenthrin and fipronil concentrations in runoff water after 2007 treatments. B = bifenthrin; F = fipronil; gran = granular; perim = perimeter.

Table 4. First-order attenuation rate constant (k, week^{-1}) and average dissipation half-life ($T_{1/2}$, weeks) estimated from decreases in insecticide levels in runoff collected at the curb from individual residences during 2007

Treatment	k	$T_{1/2}$	Adjusted R^2
Fipronil spot (3.8 L)	0.62 (±0.02)	1.12	0.99
Fipronil perimeter (11.4 L)	0.90 (±0.05)	0.77	0.99
Granular bifenthrin	0.87 (±0.19)	0.80	0.91
Bifenthrin spray	0.26 (±0.06)	2.67	0.90

was also significantly lower than that of the bifenthrin spray at weeks 4 and 8. At week 8, the bifenthrin spray treatment also had significantly higher runoff than that of the fipronil treatments ($P < 0.01$, Tukey's HSD test), with a mean concentration of 2.5 µg L^{-1}, while the other treatments were close to 0.

Bifenthrin is acutely toxic to a range of aquatic invertebrates. For instance, the median lethal concentration (LC_{50}) for *Ceriodaphnia dubia* Richard, a frequently used indicator invertebrate, is only 0.078 µg L^{-1}[21] (all LC_{50} and EC_{50} citations in this manuscript refer to water-only systems). When applied as a spray, bifenthrin concentrations in the runoff water greatly exceeded the LC_{50} at all sampling times (Fig. 1). When a granular formulation was applied around bushes and trees, the detected concentration in runoff exceeded the LC_{50} at all three houses at 1 week post-treatment. After 4 weeks, only one of the three houses produced runoff with bifenthrin concentrations above the quoted LC_{50}. After 8 weeks, none of the houses produced measurable bifenthrin runoff.

The concentrations detected at different time points were further fitted to a simple first-order decay model, and the dissipation half-life ($T_{1/2}$) was then estimated (Table 4). The dissipation half-life of bifenthrin after the spray treatment was 2.7 weeks, while after the granule treatment it was only 0.8 weeks. The much lower runoff of bifenthrin following the granule application (Fig. 1) may be due to the fact that the granular product consisted of sand particles that may not be washed away easily, especially when applied to the soil surface and planted areas. In contrast, given its strong adsorption to soil ($K_{OC} = 1.31-3.02 \times 10^5$),[22] after application by spray of a dilute solution, most of the applied bifenthrin may be associated with the top film of soil surface that was susceptible to surface-induced erosion. It is also likely that off-target drift (e.g. to driveway or sidewalks) was minimized during application of granules as compared with spray treatments, where the use of fan-type nozzles could easily lead to deposition of fine droplets on the adjacent concrete surfaces.

3.1.2 *Fipronil runoff 2007*

With respect to fipronil (Fig. 1), at 1 week post-treatment the 11.4 L fipronil treatment 1 resulted in a mean concentration of 4.2 µg L^{-1} in the runoff, while for the 3.8 L spot treatment 2 it

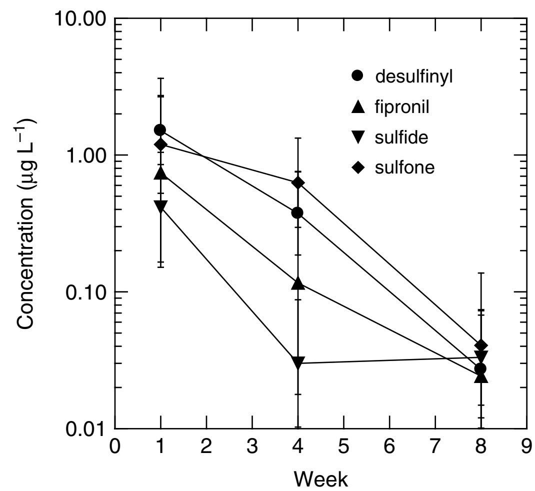

Figure 2. Geometric means (± SE) of log transformed data of concentrations of fipronil and its metabolites in runoff water after the 3.8 L spot treatment during 2007.

was 2.8 µg L^{-1}. After 4 weeks, the respective mean concentrations were 0.2 and 0.5 µg L^{-1}, and after 8 weeks they were 0.007 and 0.04. Therefore, after application, fipronil rapidly dissipated, and the levels detected after 8 weeks were only about 0.2–1% of those found after 1 week. Fitting the data to a first-order decay model showed that $T_{1/2}$ values of the fipronil were similar following the spot (1.12 weeks) and the perimeter treatments (0.77 weeks) (Table 4).

3.1.3 *Fipronil metabolites*

The runoff concentrations of fipronil and its metabolites following the 3.8 L fipronil spot treatment are shown in Fig. 2. In general, the levels of fipronil sulfide appeared to be lower than the other compounds, although the difference was statistically significant only for the week 4 samples (Kruskal–Wallis test, $P = 0.04$). Fipronil sulfide is a reductive transformation product, desulfinyl fipronil is formed from photolytic transformations and fipronil sulfone is produced from oxidation transformations.[22] Therefore, results from this study suggested that the conditions at the test sites were not conducive to the formation of fipronil sulfide, while the levels of desulfinyl fipronil and fipronil sulfone in the runoff were similar to those of the parent compound.

Aquatic invertebrates are known to be particularly sensitive to fipronil. For instance, the LC_{50} of fipronil for Mysid shrimp is only 0.14 µg L^{-1}.[23] Therefore, fipronil levels in runoff shortly after treatment may likely contribute to aquatic toxicity, but levels after an extended interval (e.g. 8 weeks) following application would be below such toxicity thresholds. Fipronil is moderately hydrophobic, with K_{OC} of 825.[22] The more rapid dissipation of fipronil may be caused by its transformations to the metabolites. By conducting a suite of *in vitro* and *in vivo* bioassays, Hainzl *et al.*[24] found that fipronil, desulfinyl fipronil and fipronil sulfone had similar biological activities. Other studies showed that the metabolites may have comparable or higher toxicity to aquatic species than fipronil. For example, the LC_{50} values of fipronil, desulfinyl fipronil, fipronil sulfide and fipronil sulfone to *Procambarus clarkii* (Girard) were 14.3, 68.6, 15.5 and 11.2 µg L^{-1} respectively.[25] The 21 day median effective concentrations (EC_{50}) to *Daphnia magna* Straus for fipronil, desulfinyl fipronil, fipronil sulfide and fipronil sulfone were 190, 230, 27 and 4.5 µg L^{-1} respectively.[24] Furthermore, desulfinyl fipronil and fipronil sulfone were respectively about 8.1 and 6.4 times more potent to rainbow trout than fipronil.[24] Therefore, it is important to consider its metabolites as well as fipronil itself when assessing the off-site runoff risk following fipronil use.

3.2 Modified treatments (2008)

With the exception of treatment 8 (fan perimeter + spot), all of these treatments were modified to reduce runoff. Table 3 shows by treatments the slopes from the house to the street, the volume of water used according to the water meter, the estimated volumes of the water runoff, the duration of the runoff into the street and the estimated total amounts of insecticide runoff. According to the house water meter, water usage 1 or 7 days post-treatment over all treatments varied from 340 to 1982 L (mean ± SE = 879 ± 84.8 L). For the same period, estimates of runoff volume were 1.8–412 L (mean ± SE = 63 ± 14.4 L). Over all treatments and dates (except for the flush at day 14), the correlation of slope versus water flow velocity was significant (Spearman rank correlation = 0.429, $P < 0.005$). The volume of water used for the 15 min driveway flush on day 14 was estimated at 189.3–334.0 L (mean ± SE = 252.1 ± 10.20 L).

3.2.1 Fipronil runoff 2008

At 1 day post-treatment (Fig. 3), the pin stream application (treatment 5) displayed significantly lower runoff concentrations than the fan spot treatment (treatment 6), while the treatment with the spray-free zone (treatment 7) was intermediate ($P < 0.05$, Tukey's HSD test). Only one house that received the pin stream application had any detectable fipronil in the runoff, and, when detected, the level was relatively low (0.25 µg L^{-1} on day 1). At 7 days post-treatment, while there was no detectable fipronil runoff from houses treated with the pin stream application, the other two treatments contained detectable residues.

For the day 14 driveway flush there was no detectable insecticide runoff from the pin stream application (treatment 5) or the spot treatment that included a spray-free zone (treatment 7), while runoff from the spot treatment that did not include a spray-free zone (treatment 6) was significantly higher (Kruskal–Wallis test, $P < 0.05$). Therefore, both the pin stream application restricted to the foundation and the inclusion of a spray-free zone contributed to decreases in fipronil runoff.

3.2.2 Bifenthrin runoff 2008

At day 1 post-treatment (Fig. 4), the fan perimeter + spot treatment (conventional treatment 8) resulted in significantly higher runoff levels than either treatment 9 (pin perimeter + spot + spray-free zone) or 10 (fan spot + spray-free zone) ($P < 0.001$, Tukey's HSD test). Thus, inclusion of a spray-free zone near the street or driveway and the pin stream application with a spray-free zone significantly reduced bifenthrin runoff.

On day 14, in the runoff water derived from driveway flushing, bifenthrin levels were the lowest for the pin perimeter treatment with the spray-free zone (treatment 9). Increased runoff from the fan spot treatment (treatment 10) on days 7 and 14 suggests that the effect of the spray-free zone diminished over time. Compared with the other treatments, the pin stream treatments consistently showed the lowest bifenthrin runoff (Fig. 4).

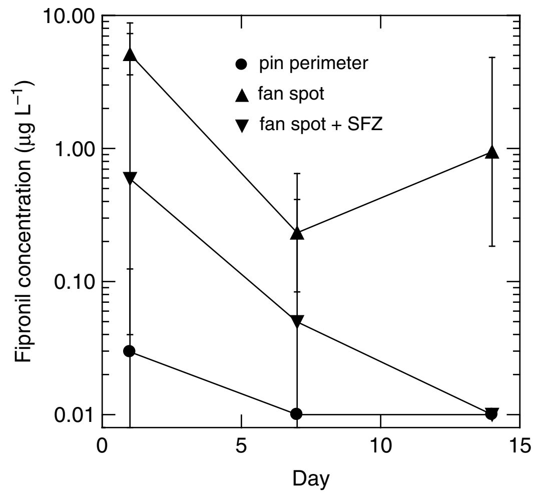

Figure 3. Geometric means (± SE) of log transformed data of fipronil concentrations in runoff water after different treatments during 2008. The day 14 results are from a driveway flush instead of irrigation water runoff. SFZ = spray-free zone.

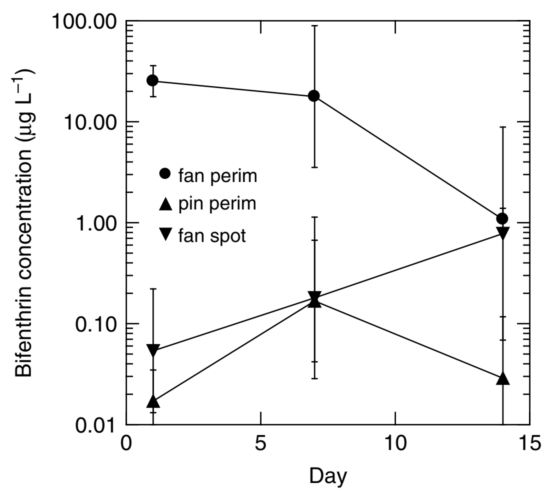

Figure 4. Geometric means (± SE) of log transformed data of bifenthrin concentrations in runoff water after different treatments during 2008. The day 14 results are from a driveway flush instead of irrigation water runoff. perim = perimeter.

3.3 Pest control efficacy and management implications

Here, the insecticide runoff data are correlated with the efficacy of ant treatments (Table 5). From the ant efficacy evaluation in 2007,[6] the combined treatment of fipronil perimeter spray and bifenthrin granules (treatments 1 + 4) gave the highest reduction in ant numbers after 8 weeks (93%), followed by the fipronil perimeter spray (treatment 1, 77%), bifenthrin perimeter spray (treatment 3, 71%) and fipronil spot treatment (treatment 2, 46%). With regard to insecticide runoff, the bifenthrin perimeter spray treatment produced the highest runoff among all treatments at all dates. The fipronil runoff from treatments 1 and 2 contained relatively high levels of fipronil and metabolites after 1 week, although only about 1% of the initial runoff was found 8 weeks after the treatment. It has also been shown that fipronil breakdown metabolites have concentrations similar to the fipronil itself.

Spot treatments were initially expected to have reduced insecticide runoff because they used only 3.8 L of fipronil solution instead of the 11.4 L needed for the perimeter spray treatment. However, runoff of fipronil was not significantly diminished by using the spot treatment method (Fig. 1), and, in addition, during 2007 it was not as efficacious against the ants as the perimeter spray (46 versus 79% reduction). However, spot treatments were more effective in 2006 (90% reduction)[5] and 2008 (82% reduction).[17]

During the 2008 season, several strategies were included to evaluate options for minimizing insecticide runoff. One strategy was to establish spray-free zones near the sidewalks or driveways so that there would be barriers between surface runoff and insecticide-treated areas. In addition, the volume of fipronil applied was limited to 3.8 L. Another strategy was to use a pin stream applicator for some treatments because this applicator laid down a narrow band of insecticide (about 5.1 cm) instead of the broad band produced by a traditional fan nozzle (about 30 cm). It was hypothesized that, if less area were treated, the off-site insecticide movement would be proportionally reduced.

Efficacy data for 2008 (Table 5) were given in Klotz *et al.*[17] (except for the following data involving spray-free zones, which have not previously been published). Although the treatments involving spray-free zones reduced runoff for both bifenthrin and fipronil, they were not very effective at controlling ants. After 8 weeks, the fipronil treatment with spray-free zones (treatment 7) only reduced ant numbers by 8%. The bifenthrin treatments with spray-free zones (treatments 9 and 10) included both a pin stream and a fan nozzle applicator. Ant numbers for these two treatments were reduced by only 26 and 13% respectively. The remaining standard bifenthrin treatment (perimeter plus spot, treatment 8) only reduced ant numbers by 54%.

Fipronil treatments 5 and 6, i.e. the pin stream treatment and the spot treatment, reduced ant numbers by 80 and 82% respectively. Detectable runoff of fipronil from houses treated with the pin stream occurred at only one of the three houses and only on day 1. The spot treatment, in contrast, led to much higher fipronil runoff than the pin stream treatment. The reason that the pin stream application of fipronil was effective in controlling ants may be due to the unusual horizontal transfer of this insecticide by ants. As an ant walks over the fipronil-treated area, the chemical adheres to the cuticle and is then transferred to other ants by contact.[26] Much less transfer occurs with bifenthrin. Therefore, a narrow band of fipronil-treated area, when applied at the edges of buildings where ants frequently have trails, may be sufficient to control ants.

The combination of excellent ant control and minimal insecticide runoff provided by fipronil following a 3.8 L pin stream application just around the house foundation is an important finding of this integrated study. However, the fipronil pin stream application (treatment 5) did not have a comparable treatment using a fan spray (see Table 2). Therefore, additional comparisons of pin stream and fan applications that are confined to the house foundation need to be done to show how much of the runoff reduction is due to the pin stream and how much to restricting

Table 5. Efficacy of treatments and insecticide runoff (F = fipronil; B = bifenthrin; SFZ = spray-free zone)

Treatment	Days post-treatment	Reduction in ant numbers (%)	Insecticide runoff Mean (± SE) (μg L^{-1})
1. F perimeter, fan[a]	7	96.7	4.16 (±2.32)
	14	94.3	–
	28	92.5	0.21 (±0.10)
	56	77.1	0.01 (±0.01)
2. F spot, fan[a]	7	59.4	2.77 (±2.53)
	14	64.6	–
	28	62.0	0.48 (±0.44)
	56	46.2	0.04 (±0.03)
3. B perimeter/spot, fan[a]	7	81.4	14.9 (±11.41)
	14	82.9	–
	28	70.5	10.1 (±7.55)
	56	71.1	2.5 (±1.16)
4. F perimeter + B granular[a,d]	7	90.1	0.4 (±0.17)
	14	97.6	–
	28	87.5	0.09 (±0.05)
	56	93.3	0.0
5. F perimeter, pin[b]	1	–	0.08 (±0.083)
	7	87	0.0
	14	85	0.0
	28	91	–
	56	80	–
6. F spot, fan[b]	1	–	5.45 (±1.24)
	7	80	0.42 (±0.31)
	14	93	2.19 (±1.08)
	28	86	–
	56	82	–
7. F spot, fan, SFZ[c]	1	–	3.04 (±1.53)
	7	35	0.41 (±0.41)
	14	60	0.0
	28	20	–
	56	8	–
8. B perimeter/spot, fan[b]	1	–	26.9 (±6.09)
	7	87	42.2 (±23.19)
	14	70	1.1 (±0.22)
	28	66	–
	56	54	–
9. B perimeter/spot, pin, SFZ[c]	1	–	0.01 (±0.01)
	7	76	0.42 (±0.35)
	14	43	0.08 (±0.0)
	28	37	–
	56	26	–
10. B spot, fan, SFZ[c]	1	–	0.14 (±0.12)
	7	70	0.99 (±0.96)
	14	64	9.98 (±9.85)
	28	48	–
	56	13	–

[a] Efficacy data from Ref. 6.
[b] Efficacy data from Ref. 17.
[c] Efficacy data not previously published.
[d] Runoff shown is for bifenthrin.

the sprays to the foundation. On the other hand, the bifenthrin pin stream application (treatment 9) included more treated locations around the house than the bifenthrin fan spot application (treatment 10), but had lower insecticide runoff (see Table 2 and Fig. 4), suggesting that the pin stream applicator is one factor in reducing the runoff. Homeowners using over-the-counter bifenthrin or other pyrethroid sprays should be advised to keep sprays near the house and away from driveways and sidewalks.

Results from this study show the importance of an integrated consideration of both efficacy and insecticide runoff risks. The same approach should be used for further evaluating other management options, such as the use of ant bait stations or combinations of bait stations and pin stream applications of fipronil near the house foundation, so that the developed pest management practices are not only efficacious but also have reduced environmental risks.

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