

Factors Contributing to the Off-Target Transport of Pyrethroid Insecticides from Urban Surfaces

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ABSTRACT: Pyrethroid insecticides used in urban and suburban contexts have been found in urban creek sediments and associated with toxicity in aquatic bioassays. The objectives of this study were to evaluate the main factors contributing to the off-target transport of pyrethroid insecticides from surfaces typical of residential landscapes. Controlled rainfall simulations over concrete, bare soil, and turf plots treated individually with pyrethroid insecticides in a suspension concentrate, an emulsifiable concentrate, or a granule formulation were conducted at different rainfall intensities and different product set-time intervals. Pyrethroid mass washoff varied by several orders of magnitude between experimental treatments. Suspension concentrate product application to concrete yielded significantly greater washoff than any other treatment; granule product application to turf yielded the least washoff. Fractional losses at 10 L of runoff ranged from 25.9 to 0.011% of pyrethroid mass applied, and 10 L nominal mass losses ranged from 3970 to 0.18 μg . Mass washoff depended principally on formulation and surface type combination and, to a lesser degree, on set-time interval and rainfall intensity. Treatment effects were analyzed by ANOVA on main factors of formulation, surface type, and set time. Factor effects were not purely additive; a significant interaction between formulation and surface type was noted.

KEYWORDS: *pyrethroid, washoff, transport, concrete, turf, emulsifiable concentrate, suspension concentrate, granule, rainfall simulation*

■ INTRODUCTION

Pyrethroid insecticides in urban creek sediment and water have been identified as causes of toxicity in bioassays.^{1–3} Studies finding pyrethroid residues linked with toxicity in residential land use dominated watersheds have pointed to applications on landscape components and structures as likely sources of pyrethroid insecticides in urban streams.⁴ Due to the complexity of these watersheds, including the routing of runoff from the variety of surface types as well the seasonality and type of pyrethroid product formulations in use, scant information is presently available to users and water resource managers as to problematic applications and/or behaviors resulting in off-target pyrethroid transport and associated toxicity. An improved understanding of the particular sources and mechanisms controlling pyrethroid insecticide transport is necessary to minimize pyrethroid insecticide impact on aquatic environments and to more efficiently allocate resources and determine appropriate management actions.

It is a common practice for pesticides to be used in and around the residential home for the control of nuisance and wood-destroying pests. Whether applied by a residential user or a licensed professional pesticide applicator, pesticides are often applied to the various outdoor surfaces of the residential property including building structures, foundations, patios, turf grass, landscape vegetation, and bare soil. Residues of the applied pesticides may be transported from their site of application by means of rainfall or irrigation runoff. Aquatic invertebrates are especially sensitive to pyrethroid insecticides; for example, if a 100 m² lawn was treated with a typical granule commercial product containing bifenthrin and was subject to a 1% loss of the applied bifenthrin in a runoff event,

approximately 2.2 million liters of water would be required to dilute the bifenthrin mass to concentrations below estimated LC₅₀ thresholds for the most sensitive aquatic species.⁵

Rainfall simulations are often utilized in investigations of erosion processes and the washoff of contaminants from chemically treated or polluted surfaces. Use of scaled simulations conveniently allows the precise control of rainfall intensity, duration, timing, and drop size. In an early review of studies investigating pesticide losses from agricultural fields, Wauchope⁶ noted that single simulated rainfall events on small-scale plots tended to yield results comparable to those from natural rainfall events on large-scale fields. Whereas numerous studies have found that the active ingredient's chemical/physical properties, product formulation, rainfall/runoff intensity, and product set-time are important determinants of potential product washoff,^{7–11} only product formulation and set-time readily present themselves as available to management action.

Comparatively few studies have looked at pesticide washoff across a variety of surface types typical of a residential land-use setting. Studies investigating washoff characteristics from impervious hard surfaces, such as concrete, are particularly scarce. In a companion study to this investigation, results of rainfall simulations over concrete test surfaces treated with a variety of residential-use pyrethroid containing commercial products were presented.¹² Formulation was identified as an

Received: March 21, 2012

Revised: July 10, 2012

Accepted: July 11, 2012

Published: July 11, 2012

important controlling factor, with those products containing a large weight percentage of surfactant resulting in the greatest mass washoff. In a similar recent study simulating pyrethroid washoff from concrete surfaces, Jiang et al.¹³ observed that factors of precipitation intensity and physical attributes of the concrete surface (i.e., acid washed, stamped, silicone sealed) did not factor significantly in washoff amounts but that detectable residues of pyrethroid remained in runoff water even 221 days after product application. Pesticide application around the home, however, is not entirely on impervious surfaces, and such applications in fact may represent only a small fraction of the total mass of pesticide applied in a residential land-use setting.

In this study our principal objective was to identify the key factors controlling pyrethroid washoff by quantifying the transport of pyrethroid insecticides from concrete, soil, and turf grass treated with a variety of commercially formulated liquid and granule products available off-the-shelf for residential structural and landscape pest control. Our focus was on those controlling variables amenable to management action, such as provision of label advisories and label restrictions. Our expectation was that the surface of application would dominate as a factor controlling the amount of pyrethroid washoff, but would be moderated to some degree by product formulation. In this study we conducted multiple rainfall simulations over soil and turf surfaces treated with different formulations of pyrethroid end-use products. We combine these data with previously published data obtained from concrete surfaces¹² and use an incomplete block study design and ANOVA to draw conclusions about treatment effects.

MATERIALS AND METHODS

Rainfall Simulations. Drop-forming rainfall simulators described by Battany and Grismer¹⁴ were constructed with 1 m² needle panels loaded with 23-gauge hypodermic syringe needles (B-D Precision Glide). Simulators were elevated 1.6 m above the target surface and provided a homogeneous drop pattern and drop size that hit the target surface with approximately 60% of the kinetic energy of natural rainfall.¹⁵ Simulators used groundwater from the University of California at Davis drinking water system with an average hardness of 120 ppm. Prior to use in the simulators, this water was filtered by spun microfiber and dechlorinated by granulated activated carbon. The temperature of simulated rainfall averaged 19 °C over the course of the study.

Average runoff rate and volume of simulated runoff were obtained by collecting surface runoff at timed volume intervals. The slope of the test plots was held constant at 4° from the horizontal, and rainfall intensity was controlled at either 25 or 50 mm/h. Simulations were performed for a minimum of 60 min, or longer, as needed to generate approximately 10 L of runoff. Product set-times investigated were 1 day and 7 days from the time of product application. On some surfaces, a second successive simulation was conducted following the 1 day simulation without an intervening product application (7 days, second).

Concrete Test Surfaces. Multiple 80 × 80 cm plywood forms were constructed, and 5 cm thick concrete slabs were poured (Quickrete 5000, Atlanta, GA, USA). Prior to full curing, concrete surfaces were lightly brushed perpendicular to the course of surface flow and sealed to the forms with self-leveling crack sealant (Quickrete 8640). Plywood forms extended 5 cm above the concrete surface on three sides with the fourth side cut flush with the concrete surface and wrapped with galvanized sheet metal to form a lip, which allowed runoff to flow into an aluminum collection channel. Runoff was collected from the channel through a short length of flexible siliconized tubing into precleaned amber glass bottles (I-Chem 200 series, Rockwood, TN, USA). A galvanized sheet metal shield, connected to the plywood forms, covered the lip and collection channel to prevent

the simulated rain from directly entering the channel. The concrete surfaces were allowed to cure and weather with repeated washings prior to use in simulations. Prior to each product application, concrete surfaces were washed with high-pressure water to remove settled material and then allowed to dry. Treated slabs were stored outdoors, where they were exposed to natural sunlight.

Soil Test Surfaces. Multiple 80 × 80 cm plywood forms were constructed in a similar fashion to that of the concrete forms but with a depth of 30.5 cm. The interior of the form was wrapped in 5 mm plastic and a polyvinyl chloride (PVC) drain was installed in the bottom with the outlet draining to the exterior of the form. The drain was sealed to the plastic and plywood form with silicone sealant. The plywood forms were filled with 5 cm of washed pea gravel and 25.5 cm of locally collected Yolo soil, comprised of approximately 20% sand, 57% silt, and 23% clay (1.2% total organic carbon; pH 7) based on previous research.¹⁶ Soil was collected from an uncultivated section of land used for the practical teaching of no pesticide organic farming techniques. Plywood forms extended 5 cm above the soil surface on three sides, with the surface runoff collection apparatus identical to that described for the concrete test surfaces. Soil surfaces were lightly tamped to simulate compaction.

Turf Test Surfaces. Multiple 80 × 80 cm plywood forms were constructed in identical fashion to that of the previously described soil forms. The plywood forms were filled with 5 cm of washed pea gravel and 20.3 cm of soil prepared in the following ratio: 2 parts Yolo soil and 1 part commercial compost (Ace Hardware, Davis, CA, USA). A commercial tall fescue/Kentucky blue grass blend sod (Endurance brand, Sierra Sod and Supply, Davis, CA, USA) was laid and sealed to the edge of the plywood forms with Yolo soil to prevent short-circuiting; clayey soil made a suitable and compatible sealant. Turf grass was fully rooted at time of experimentation. Prior to product application, turf was trimmed to a 5 cm height and sprinkle irrigated with University of California, Davis, tap water to a depth of 8.4 mm, but in a manner that did not generate any surface runoff. This preapplication trimming and irrigation procedure was conducted for all experiments regardless of planned set-time (1 or 7 days and 7 days, second). For those turf boxes subject to 7 days and 7 days, second, simulations, turf was subsequently irrigated on an approximate 72 h basis to a depth of 8.4 mm with a final irrigation and a second trimming occurring 24 h prior to the scheduled simulation. This postapplication irrigation was necessary to maintain the turf in good health and was matched to estimated water needs given California's Central Valley late summer growing conditions. Cut grass was gently removed from the surface and, therefore, did not contribute to insecticide residues in runoff.

Determination of Pyrethroids and Total Suspended Solids. Neat standards of pyrethroids were obtained from ChemService, Inc. (West Chester, PA, USA). An Agilent 6890 gas chromatograph equipped with a J&W Scientific DB-5 column (30 m × 0.25 mm × 0.25 μm) and an Agilent microelectron capture detector was used for the quantitative determination of pyrethroids in simulated stormwater runoff samples. Use of a slow thermal gradient (from 100 to 200 °C at 15 °C/min, from 200 to 250 °C at 5 °C/min, from 250 to 290 °C at 7 °C/min, and held for 2.5 min) allowed resolution of bifenthrin, λ-cyhalothrin, β-cyfluthrin, and esfenvalerate. The inlet was set to 290 °C and the detector to 310 °C.

Sample extraction occurred 3–24 h following sample collection. Extraction of pyrethroids was accomplished using an octadecyl (C-18) solid phase extraction cartridge (Supelco ENVI-C18, St. Louis, MO, USA) with a 500 mg sorbent bed. Pyrethroids were eluted with 10 mL of hexane/ethyl acetate (50:50 v/v; Fisher, Optima, Waltham, MA, USA) and concentrated to 1 mL by nitrogen evaporation or diluted, if necessary, to be within the range of calibration standards.

Due to the particularly high solids content of runoff samples from soils and turf, all soil and turf runoff samples were prepared for subsampling by first shaking the container to resuspend settled material followed by a 1 h settling period, after which approximately 200 mL sample aliquots were collected for extraction. This procedure of excluding settleable solids was necessary given the use of solid phase extraction in this study and the propensity for the extraction tubes to

plug and foul in the presence of settleable matter. Pyrethroids adsorbed to settled solids were not quantified. Total suspended solids (TSS) measurements were obtained according to similar procedure, after the 1 h settling period, using a Whatman glass fiber filter (Whatman 934AH) following standard protocols.¹⁷ For the concrete runoff samples, which did not contain settleable solids, pyrethroids were subsampled in the laboratory by shaking the container and drawing sample from mid-depth through a large-bore graduated pipet.

For concrete runoff samples, batch permethrin matrix spike surrogate recoveries averaged 93%, with relative standard deviation (RSD) between matrix spike duplicates of 4.9%. Soil and turf runoff samples proved to be more challenging, with batch permethrin matrix spike surrogate recoveries averaging 82% with a relative standard deviation of 8.7%. Measurements are reported without surrogate correction.

Formulated Products. Six off-the-shelf general-use formulated products were used for experimentation (Table 1). Products were

Table 1. Pyrethroid Products Tested and Their Characteristics^a

ai	product type	product % ai (w/w)	surface of application	ai log K_{ow}	ai solubility ($\mu\text{g/L}$)
β -cyfluthrin	SC/dilutable	2.5	C, S, T	5.97	2.3
λ -cyhalothrin	EC/dilutable	0.5	C	7.00	5.0
esfenvalerate	EC/RTU	0.0033	C	5.62	6.0
bifenthrin	EC/dilutable	0.30	S, T	6.40	0.014
γ -cyhalothrin	G	0.05	S, T	7.00	5.0
cyfluthrin	G	0.1	S, T	5.97	2.3

^aai, active ingredient (nominal); SC, suspension concentrate; EC, emulsifiable concentrate; G, granule; RTU, ready-to-use; C, concrete; S, soil; T, turf; K_{ow} and solubility from Laskowski.²² Product trade names: β -cyfluthrin, Bayer Advanced Power Force Carpenter Ant and Termite Killer Concentrate; λ -cyhalothrin, Spectracide Triazicide Once and Done! Insect Killer Concentrate; esfenvalerate, Ortho Bug-B-Gon Max Garden and Landscape Insect Killer; bifenthrin, Ortho Bug-B-Gon Max Lawn and Garden Insect Killer; γ -cyhalothrin, Spectracide Triazicide Brand Soil and Turf Insect Killer Granules; cyfluthrin, Bayer Lawn and Garden Multi-Insect Killer Granules.

diluted, if necessary, and applied to surfaces per label specification and at label rates. In some cases labels did not indicate a specific rate of application, but provided a qualitative suggestion such as "wet the surface with a coarse spray but without soaking". Product application was to the entire test plot, and the application rate was recorded. Liquid products were applied either utilizing the supplied pump action hand sprayer or an aftermarket pump action hand sprayer (Delta Industries, King of Prussia, PA, USA). Granulated products were sprinkled so that the entire surface was evenly covered. Application rates are provided in Table 3.

Table 2. Rainfall Intensity, Rainfall Applied, Fraction of Applied Rainfall as Runoff, Runoff Rate by Surface Type, and TSS Loadings for All Simulations [Mean (%RSD^a)]

rainfall intensity (cm/h)	rainfall applied (cm)	rainfall as runoff (%)	runoff rate (L/min)	10 L TSS loading (mg)
Concrete				
2.5	2.5 (0)	88.8 (4.0)	0.23 (3.9)	99.6 (59.8) ^b
5.0	5.0 (0)	90.8 (1.2)	0.47 (2.2)	70.4 (57.7)
Soil				
2.5	4.4 (5.3)	33.8 (9.8)	0.11 (8.6)	2210 (9.1)
5.0	5.0 (0)	67.6 (14.0)	0.36 (12.5)	3090 (45.1)
Turf				
2.5	6.7 (19.4)	26.4 (23.2)	0.12 (26.3)	468 (55.7)
5.0	5.0 (0)	42.0 (26.5)	0.23 (19.3)	515 (47.9)

^aRSD, relative standard deviation. ^bRepresents 1 day, 7 days, and 7 days, second, pooled results. Actual loadings on concrete are set-time sensitive due to settled dusts: 2.5 cm/h at 1 day, 40.8 (45.4); 2.5 cm/h at 7 days and 7 days, second, 135 (33.5).

Effects Investigation by Analysis of Variance (ANOVA).

Factor and treatment level effects were evaluated by ANOVA. Main factor effects used in the ANOVA were limited to formulation type, surface type, and product set-time, factors subject to alternative management practices. The resulting unbalanced three-way factorial design of the ANOVA model used a series of dummy variables in a regression context. The unbalanced nature of the study was principally due to inherent limitations resulting from label permitted applications. For example, the granule products did not explicitly permit applications to hard surfaces and, therefore, that treatment combination was omitted from the study. The experimental covariate of application rate was not considered in the experimental design because product labels set application based on the type of surface to which the product was to be applied; varying the application rate as an experimental covariate would have created a hypothetical context counter to label instructions, and it was our intention to focus on those factors freely available to alternative management practices.

The ANOVA model was constructed using R statistical software. Total mass runoff at 10 L was used as the response variable, thereby normalizing total runoff volume differences associated with rainfall intensity. Use of a log transformation on the response variable was necessary to correct for nonconstancy of error variance and nonnormality of error terms. Treatment means were compared utilizing a Tukey's 95% family confidence coefficient.

RESULTS AND DISCUSSION

Hydrologic Conditions. Hydrologic conditions for the rainfall simulations are provided in Table 2. In comparison to similarly executed studies on turf and sparsely vegetated soil, hydrologic conditions achieved in this study were within the range of conditions observed by other investigators.^{7,9,10,18,19} As expected, concrete surfaces yielded the highest rainfall recoveries and runoff rates, and turf surfaces yielded the lowest. Bare soil plots gave intermediate rainfall recoveries and runoff rates. Overall reproducibility was very good, with greatest variation associated with turf surfaces. With the exception of the turf and soil simulations at the 25 mm/h intensity, which required additional time to obtain the desired 10 L of runoff, all simulations were terminated at exactly 60 min, thus yielding equivalent rainfall application volumes.

Erosion and transport of particulate matter from surfaces was quantified as TSS concentration. Results for TSS suffered from greater replicate variability than the other runoff parameters, but fit the expected trend of greatest particulate transport from soil, followed by turf and concrete. Interestingly, runoff volume normalized TSS loading for soil did not show a significant sensitivity to rainfall intensity (t test, $\alpha = 0.05$). Nevertheless, our suspended solids results are comparable to those of Kleinman et al.,²⁰ who measured suspended solids in runoff

Table 3. Applied Mass, Total Mass Loss, 10 L Mass Loss, and EMC for Rainfall Simulations Utilizing Formulated Products^a

product ai and formulation	parameter	formulated product experiment (intensity/set time)					
		25/1 day	25/7 days	25/7 days, second	50/1 day	50/7 days	50/7 days, second
		Concrete^b					
<i>β</i> -cyfluthrin SC	applied mass (μg)	14600 (1.6)	12200 (0.2)	15300 (1.6)	15300 (3.6)	c	c
	total mass loss (μg)	2650 (28.9)	998 (0.9)	151 (43.9)	4150 (3.2)		
	mass loss at 10 L (μg)	2590 (29.3)	977 (0.9)	140 (46.4)	3970 (3.5)		
	EMC ($\mu\text{g/L}$)	180 (28.7)	71.3 (1.5)	10.4 (45.3)	143 (1.1)		
esfenvalerate EC	applied mass (μg)	1860 (4.8)	2010 (2.6)	1750 (3.5)	1920 (0.2)	c	c
	total mass loss (μg)	22.6 (0.5)	15.1 (12.2)	17.9 (45.8)	41.4 (3.9)		
	mass loss at 10 L (μg)	18.0 (2.0)	13.4 (9.9)	14.8 (48.0)	22.6 (6.5)		
	EMC ($\mu\text{g/L}$)	1.57 (2.0)	1.10 (6.3)	1.22 (46.0)	1.44 (4.4)		
λ -cyhalothrin EC	applied mass (μg)	1470 (0.1)	1170 (1.6)	c	1410 (0.9)	c	c
	total mass loss (μg)	35.7 (8.7)	2.83 (3.2)		26.2 (12.3)		
	mass loss at 10 L (μg)	28.5 (8.3)	2.47 (4.8)		16.6 (12.0)		
	EMC ($\mu\text{g/L}$)	2.47 (8.9)	0.214 (6.1)		0.897 (11.6)		
		Soil					
<i>β</i> -cyfluthrin SC	applied mass (μg)	12500 (0)	c	c	12500 (0)	12500 (0)	12500 (0)
	total mass loss (μg)	247 (21.1)			195 (7.4)	107 (20.6)	97.8 (13.0)
	mass loss at 10 L (μg)	247 (21.1)			121 (20.3)	82.4 (21.8)	41.9 (12.9)
	EMC ($\mu\text{g/L}$)	24.2 (23.1)			9.2 (9.5)	6.0 (12.2)	3.9 (8.2)
bifenthrin EC	applied mass (μg)	15000 (0)	c	c	15000 (0)	15000 (0)	15000 (0)
	total mass loss (μg)	109 (19.0)			298 (0.5)	79.4 (19.8)	79.8 (12.1)
	mass loss at 10 L (μg)	109 (19.0)			212 (13.4)	59.4 (18.7)	35.1 (8.3)
	EMC ($\mu\text{g/L}$)	10.7 (20.4)			14.2 (2.5)	4.5 (11.3)	3.2 (17.2)
<i>β</i> -cyfluthrin G	applied mass (μg)	c	c	c	6250 (0)	6250 (0)	6250 (0)
	total mass loss (μg)				5.50 (18.4)	2.36 (3.6)	1.36 (1.8)
	mass loss at 10 L (μg)				3.85 (12.2)	1.86 (1.5)	0.79 (0.4)
	EMC ($\mu\text{g/L}$)				0.24 (20.8)	0.126 (0.4)	0.059 (3.7)
γ -cyhalothrin G	applied mass (μg)	1875 (0)	c	c	1875 (0)	1875 (0)	1875 (0)
	total mass loss (μg)	1.68 (34.5)			3.69 (35.2)	3.50 (8.9)	2.02 (22.8)
	mass loss at 10 L (μg)	1.68 (34.5)			2.98 (42.6)	2.90 (11.4)	1.56 (3.5)
	EMC ($\mu\text{g/L}$)	0.162 (38.3)			0.16 (36.9)	0.18 (6.1)	0.087 (20.7)
		Turf					
<i>β</i> -cyfluthrin SC	applied mass (μg)	c	c	c	12500 (0)	12500 (0)	12500 (0)
	total mass loss (μg)				172 (38.5)	57.4 (22.6)	36.4 (21.7)
	mass loss at 10 L (μg)				137 (37.4)	55.8 (24.6)	30.0 (24.7)
	EMC ($\mu\text{g/L}$)				9.9 (31.3)	5.4 (27.8)	2.6 (26.9)
bifenthrin EC	applied mass (μg)	c	c	c	15000 (0)	15000 (0)	15000 (0)
	total mass loss (μg)				29.2 (9.9)	5.92 (78.5)	8.04 (15.2)
	mass loss at 10 L (μg)				24.3 (4.9)	5.2 (2.7)	7.9 (5.7)
	EMC ($\mu\text{g/L}$)				2.2 (13.2)	0.56 (6.8)	0.80 (9.8)
<i>β</i> -cyfluthrin G	applied mass (μg)	6250 (0)	6250 (0)	6250 (0)	c	c	c
	total mass loss (μg)	1.53 (24.8)	0.75 (41.3)	0.82 (61.0)			
	mass loss at 10 L (μg)	1.53 (24.8)	0.70 (27.1)	0.74 (50.0)			
	EMC ($\mu\text{g/L}$)	0.163 (13.5)	0.067 (17.9)	0.060 (25.0)			
γ -cyhalothrin G	applied mass (μg)	1875 (0)	1875 (0)	1875 (0)	c	c	c
	total mass loss (μg)	0.53 (56.6)	0.24 (70.8)	0.22 (50.0)			
	mass loss at 10 L (μg)	0.53 (56.6)	0.22 (54.5)	0.18 (30.0)			
	EMC ($\mu\text{g/L}$)	0.056 (46.4)	0.021 (52.4)	0.016 (14.4)			

^aMean result of two simultaneous replicates and (%RSD). RSD, relative standard deviation; EMC, event mean concentration (i.e., total mass loss/total runoff volume); SC, suspension concentrate; EC, emulsifiable concentrate; G, granule. Fractional loss as percent of applied can be calculated by dividing total mass loss, or mass loss at 10L, by the applied mass, converted as a percentage. ^bConcrete data from Jorgenson and Young.¹²

^cExperiment not conducted.

from field and packed box plots under similar simulation conditions. Observed turf TSS loadings, on the other hand, were artificially elevated due to the plot design. Clay used to prevent short-circuiting of surface flow eroded slightly over the course of simulations, contributing fractionally to the measured TSS.

Pyrethroid Washoff. Rainfall simulation results for concrete and turf compared well to results obtained by Jiang et al.¹³ and Hanzas et al.²¹ Jiang et al. did not report what formulations they used in their applications to concrete; however, their observed bifenthrin event mean concentrations (EMC, i.e., total mass loss/total runoff volume) were within a factor of 2 at 1 and 7 day set-times of those observed for the β -cyfluthrin suspension concentrate (SC) in this study. In Hanzas et al., simulations with bifenthrin and β -cyfluthrin granule and suspension concentrate formulations over turf were performed. Simulations of comparable set-time utilizing the suspension concentrate formulations yielded EMCs bounding those observed in this study, although EMCs from granule-treated turf plots generally yielded 1-day set-time concentrations that were more than an order of magnitude greater than those observed in this study.

Rainfall simulations resulted in order of magnitude differences in single-incident total mass washoff (Table 3). When plotted against volume interval, resultant dissipation curves for initial application simulations showed a strong formulation relationship, with the SC consistently yielding greater washoff losses (Figure 1). When factors are individually viewed in terms

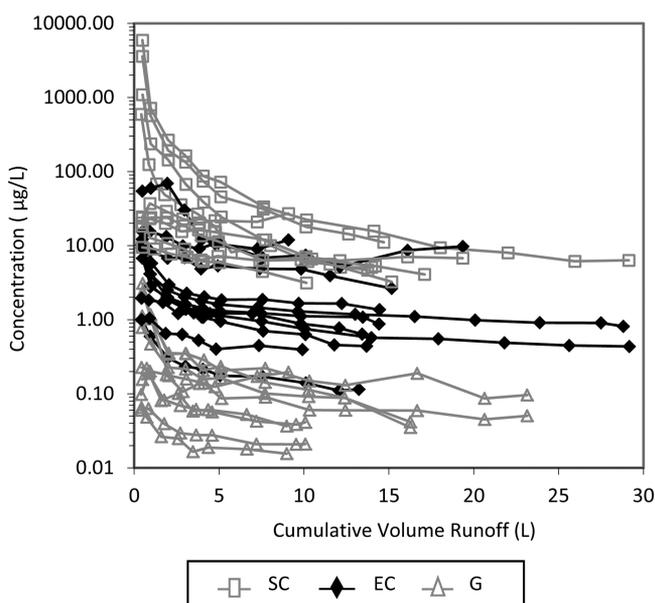


Figure 1. Washoff concentration profiles presented by formulation type for all 1 day and 7 day initial set time simulations. Note the log scale of the y-axis.

of rainfall intensity, normalized 10 L mass washoff amounts (excluding 7 days, second, simulations), the strong influence of the product formulations tested is clearly observed in the descending trend in mass washoff in the form SC > EC > G (Figure 2A). Whereas the descending trend in mass washoff indicates the presence of an effect, the overlap in the range of mass washoff suggests that the factor effect is likely interacting with one or more other main factors. Additional factors of

surface type, product set-time, and rainfall intensity resulted in moderate to weak relationships (Figure 2B–D).

Although the suspension concentrate generally yielded greater total mass washoff, the extent of washoff was clearly influenced by the surface type, as observed in the set-time aggregated interaction plot provided in Figure 3. The emulsifiable concentrates tested in this study, on the other hand, yielded very similar mass washoff fractions between concrete and turf, but yielded elevated washoff comparable to that of the suspension concentrate on bare soil. The fine textured silty Yolo soil resulted in substantial soil erosion, as indicated by the TSS measurements shown in Table 2, and the increased washoff of the emulsifiable concentrate formulated pyrethroid product on soil is suspected to be associated with this erosion.

Set-time shows an expected trend of lower washoff totals with increased time between product application and product washoff, although it appears to be a relatively weak main factor (Figure 2B). Whereas the rainfall intensity main factor plot suggests an overall trend toward lower mass washoff with increasing rainfall intensity (Figure 2D), this is primarily a product of the unbalanced design of the study in which limited rainfall intensity simulation pairing was conducted for the soil and turf surface types. When appropriate pairs are compared in Table 3 (1 day set-times only), doubled rainfall intensity generally yields increased 10 L mass washoff, with some exceptions. Regardless of direction, differences between rainfall intensity 10 L mass washoff are not statistically significant (t test, $\alpha = 0.05$), suggesting that there is little difference in runoff availability of the various pyrethroid products relative to rainfall intensity.

The timing and onset of runoff have been observed to be influential in other washoff studies. In simulated rainfall events over herbicide-treated turf and bare soil plots, Wauchope et al.¹⁰ observed a dependence of the total washoff on the timing of the onset of runoff, indicative of losses due to leaching. In this study, no time-dependent runoff initiation relationship was observed by comparison across equivalent rainfall intensity simulations, suggesting that leaching of pyrethroid was not a significant pathway contributing to early-onset immobilization of pyrethroid residues. This is likely an attribute of the physical–chemical properties of the pyrethroids, by which strong partitioning keeps pyrethroid residues very near the surface, preserving their availability for partitioning and transport during a runoff event.

Successive washoff experiments showed a trend to lower washoff after the second simulation, but the extent of the reduction in washoff appeared to be formulation dependent. As expected, given their formulated properties, the granule formulations tested appear to be less sensitive to set-time or successive simulation, yielding very similar mass washoff across simulations.

Although application rate differences cannot be entirely discounted as a contributing factor, overall application rate appears to be a moderate correlative to 10 L mass washoff when all initial time interval simulations are pooled (Pearson's $r = 0.40$; $p = 0.002$). More importantly, however, an investigation into varied application rate would result in an unrealistic study scenario because application rate, closely related to product efficacy, is prescribed on product labels and, thus, in essence, represents a fixed management variable.

ANOVA Investigation of Treatment Effects. An ANOVA model limited to an investigation on formulation,

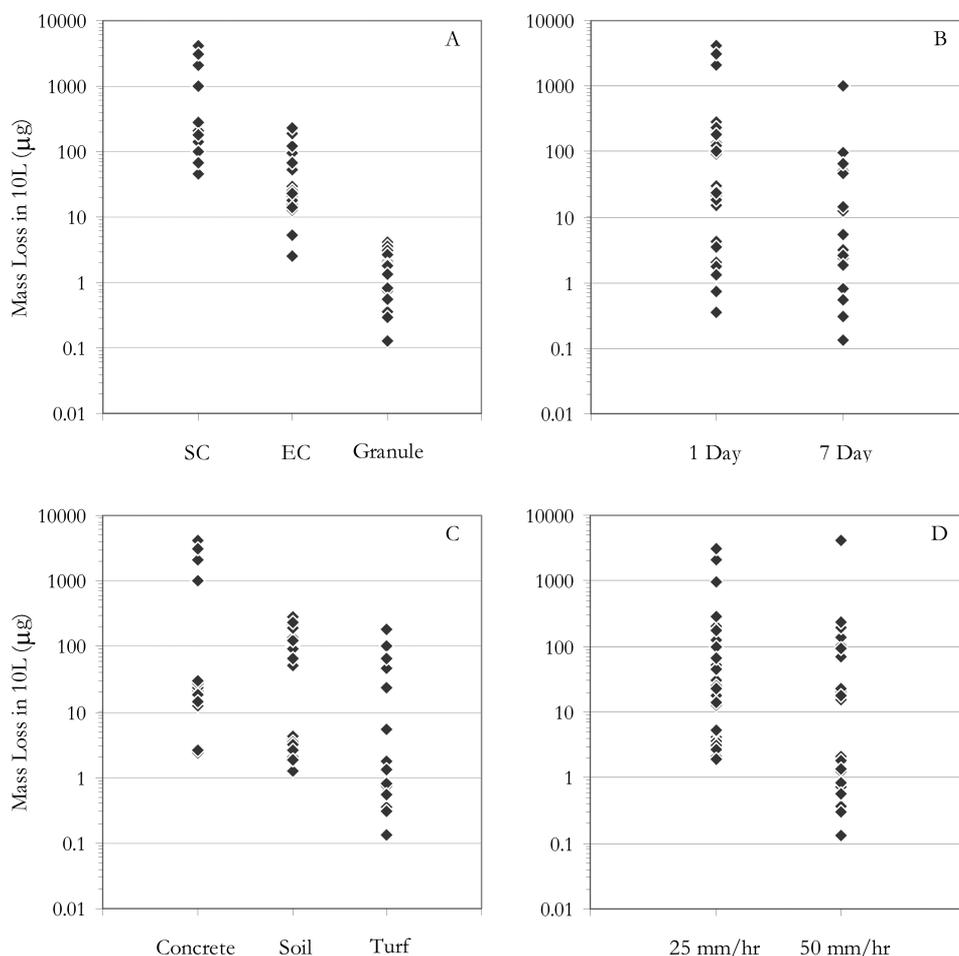


Figure 2. Average 10 L mass washoff aggregated by formulation type, set time, surface type, and rainfall intensity (1 day and 7 day initial set-time simulations only): comparison of washoff by (A) formulation, (B) set-time, (C) surface type, and (D) rainfall intensity. Note the log scale of the y-axis.

surface type, and initial application set time (1 and 7 days only) with 10 L mass washoff as the response variable was constructed to more quantitatively investigate our observations. Statistical inference was limited to these three main factors primarily due to their apparent influence, as graphically presented in Figure 2, and due to their amenability to management action (i.e., physical mitigation). Statistical inference by ANOVA was further limited by structurally absent granule applications to concrete, as no granule product tested was explicitly labeled for such use. As suggested in Figure 3, interactions between formulation and surface type were found to be significant ($p < 0.001$), with surface type moderating formulation effects; thus, treatment effects in lieu of main factor effects were investigated. Results of the ANOVA are presented in matrix form in Figure 3. The unfortunate consequence of such a statistical limitation is the restriction of inference to a series of pairwise comparisons and contrasts. Whereas the central tendency of the average mass washoff depicted in Figure 2 suggests a main factor effect for formulation and surface type, due to the significant interaction, the analysis is confined to the treatment means versus the more desirable factor effect means.

What the statistical analysis of the treatment means highlighted, however, was the importance of product formulation in combination with surface type. We anticipated that surface type would be the greatest determinant of washoff, with formulation playing a lesser moderating role, but the orders of magnitude difference in washoff losses largely associated with formulation were unexpected. Looking primarily

to formulation, application of the SC on concrete resulted in significantly greater mass washoff than any other treatment combination, whereas application of the granule products on turf resulted in significantly less mass washoff than any other treatment. Overall, treatments with the granule products resulted in significantly less mass washoff in comparison to the tested liquid EC and SC products.

With rainfall intensity results pooled in the ANOVA model, extended product set-time did not result in significantly less 10 L mass washoff when equivalent comparisons of like-formulation on like-surface are made. As such, it could be inferred that product set-time is a weak controlling factor. However, in drawing such a conclusion, the unbalanced study design, the pooling of both 25 and 50 mm/h simulation results, and the nature of multiple-comparison analysis must be considered. Extended set-time indeed does result in lower mean point estimates, but longer set-times of possibly weeks in time span are likely necessary before statistically significant differences would be observed. We did not focus our attention on such extended set-times primarily because longer set-time intervals could not be reliably implemented as a mitigation strategy, because the accuracy of weather predictions or rainfall forecasts diminishes quickly with the length of the projection.

The significant interaction between formulation and surface type introduces a challenging complexity that limits our abilities to confidently extrapolate beyond the specific treatments included in this study. What we can conclude from this

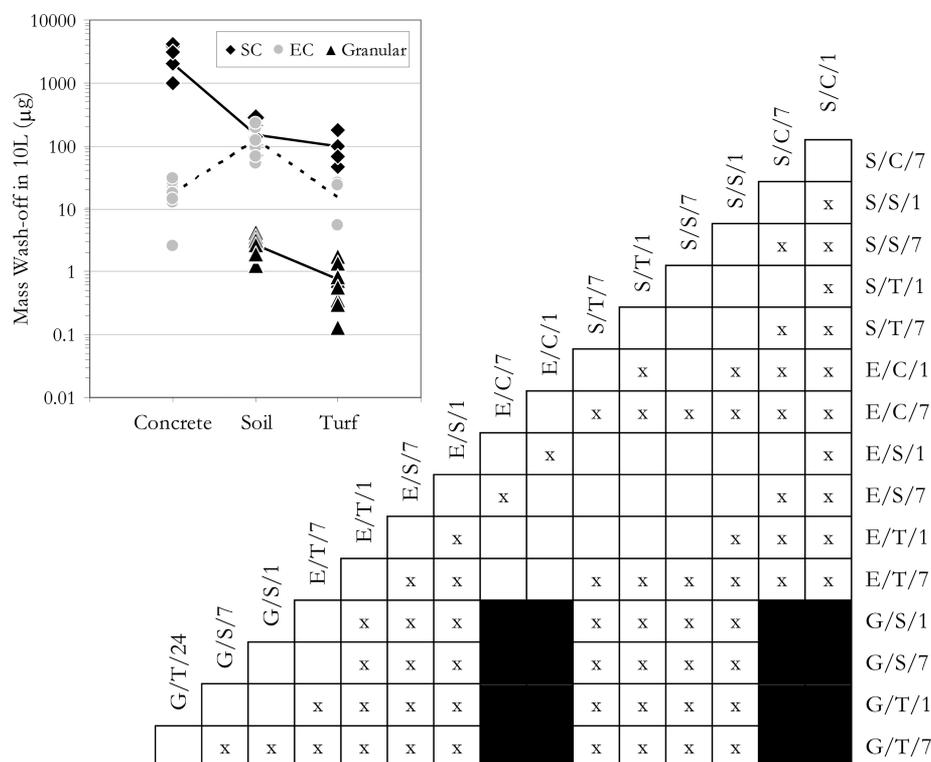


Figure 3. Comparison of treatment means matrix and interaction plot for 10 L mass washoff expressing surface type against formulation (1 day and 7 days simulations only). An “x” in the matrix indicates a significant difference at a 95% family confidence, and blacked out cells indicate that no comparison was made. Lines in the interaction plot connect mean washoff values between a particular surface and formulation type combination. Matrix coding is as follows (formulation/surface type/set-time interval): formulation as suspension concentrate (S), emulsifiable concentrate (E), or granule (G); surface type as concrete (C), soil (S), or turf (T); and set-time interval as 1 day (1) or 7 days (7). For example, the treatment S/S/7 would be interpreted as suspension concentration on soil with a set-time of 7 days.

study, however, is that factors of formulation and surface type will likely yield themselves most amenable to management and mitigation with greatest effect.

There can be no disputing that pyrethroid residues may be transported from their surface of application and, in some cases, transported in substantial quantity. Evidence points to the importance of applications to impervious surfaces and the associated contributing factor of formulation. Suspension concentrates and other flowable formulations represent a significant proportion of the pyrethroid product market, particularly among professional pest control operators, and their use on impervious surfaces should be evaluated critically in light of the evidence presented here. In addition, the means by which these data were collected, where mass applied to a surface and product set-time were measured, and where washoff masses were measured at multiple intervals over the course of a 1 h simulation, make these data suitable for use in deriving washoff functions and coefficients necessary for watershed modeling.

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Funding

This research was supported by grants from the California Department of Pesticide Regulation under Contract 06-0086C and by the National Institute of Environmental Health Sciences

under Award P42E5004699. The content is solely the responsibility of the authors and does not necessarily represent the official views of the California Department of Pesticide Regulation, the National Institute of Environmental Health Sciences, or the National Institutes of Health.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Russell Jones, Bayer Crop Sciences; Drs. Frank Spurlock and Kean Goh, California Department of Pesticide Regulation; and Dr. Herbert Scher, UC Davis Biological and Agricultural Engineering, for their assistance in executing this study.

REFERENCES

- (1) Amweg, E. L.; Weston, D. P.; You, J.; Lydy, M. J. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. *Environ. Sci. Technol.* **2006**, *40*, 1700–1706.
- (2) Hintzen, E. P.; Lydy, M. J.; Belden, J. B. Occurrence of potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. *Environ. Pollut.* **2009**, *157*, 110–116.
- (3) Weston, D. P.; Lydy, M. J. Urban and agricultural sources of pyrethroid insecticides to the Sacramento–San Joaquin Delta of California. *Environ. Sci. Technol.* **2010**, *44*, 1833–1840.
- (4) Weston, D. P.; Holmes, R. W.; Lydy, M. J. Residential runoff as a source of pyrethroid pesticides to urban creeks. *Environ. Pollut.* **2009**, *157*, 287–294.
- (5) Weston, D. P.; Holmes, R. W.; You, J.; Lydy, M. J. Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ. Sci. Technol.* **2005**, *39*, 9778–9784.

- (6) Wauchope, R. D. The pesticide content of surface water draining from agricultural fields – a review. *J. Environ. Qual.* **1978**, *7*, 459–472.
- (7) Armbrust, K.; Peeler, H. Effects of formulation on the run-off of imidacloprid from turf. *Pest Manag. Sci.* **2002**, *58*, 702–706.
- (8) Cole, J. T.; Baird, J. H.; Basta, N. T.; Huhnke, R. L.; Storm, D. E.; Johnson, G. V.; Payton, M. E.; Smolen, M. D.; Martin, D. L.; Cole, J. C. Influence of buffers on pesticide and nutrient runoff from bermudagrass turf. *J. Environ. Qual.* **1997**, *26*, 1589–1598.
- (9) Evans, J. R.; Edwards, D. R.; Workman, S. R.; Williams, R. M. Response of runoff diazinon concentration to formulation and post-application irrigation. *Trans. ASAE* **1998**, *41*, 1323–1329.
- (10) Wauchope, R. D.; Williams, R. G.; Marti, L. R. Runoff of sulfometuron-methyl and cyanazine from small plots: effects of formulation and grass cover. *J. Environ. Qual.* **1990**, *19*, 119–125.
- (11) Gouy, V.; Dur, J.; Calvet, R.; Belamie, R.; Chaplain, V. Influence of adsorption–desorption phenomena on pesticide run-off from soil using simulated rainfall. *Pestic. Sci.* **1999**, *55*, 175–182.
- (12) Jorgenson, B. C.; Young, T. M. Formulation effects and the off-target transport of pyrethroid insecticides from urban hard surfaces. *Environ. Sci. Technol.* **2010**, *44*, 4951–4957.
- (13) Jiang, W.; Haver, D.; Rust, M.; Gan, J. Runoff of pyrethroid insecticides from concrete surfaces following simulated and natural rainfalls. *Water Res.* **2012**, *46*, 645–652.
- (14) Battany, M. C.; Grismer, M. E. Development of a portable field rainfall simulator for use in hillside vineyard runoff and erosion studies. *Hydrol. Process.* **2000**, *14*, 1119–1129.
- (15) Laws, J. O. Measurements of the fall-velocity of water-drops and raindrops. *Trans. Am. Geophys. Union* **1941**, *22*, 709–721.
- (16) Watanabe, N.; Schwartz, E.; Scow, K. M.; Young, T. M. Relating desorption and biodegradation of phenanthrene to SOM structure characterized by quantitative pyrolysis GC-MS. *Environ. Sci. Technol.* **2005**, *39*, 6170–6181.
- (17) Eaton, A. D., Clesceri, L. S., Rice, E. W., Greenberg, A. E., Eds. *Standard Methods for the Examination of Water and Wastewater*, 21st ed.; American Public Health Association: Washington, DC, 2005.
- (18) Kramer, K. E.; Rice, P. J.; Horgan, B. P.; Rittenhouse, J. L.; King, K. W. Pesticide transport with runoff from turf: observations compared with TurfPQ model simulations. *J. Environ. Qual.* **2009**, *38*, 2402–2411.
- (19) Smith, A. E.; Bridges, D. C. Movement of certain herbicides following application to simulated golf course greens and fairways. *Crop Sci.* **1996**, *36*, 1439–1445.
- (20) Kleinman, P. J. A.; Sharpley, A. N.; Veith, T. L.; Maguire, R. O.; Vadas, P. A. Evaluation of phosphorus transport in surface runoff from packed soil boxes. *J. Environ. Qual.* **2004**, *33*, 1413–1423.
- (21) Hanzas, J. P.; Jones, R. L.; White, J. W. Runoff transport of pyrethroids from a residential lawn in central California. *J. Environ. Qual.* **2011**, *40*, 587–597.
- (22) Laskowski, D. A. Physical and chemical properties of pyrethroids. *Rev. Environ. Contam. Toxicol.* **2002**, *174*, 49–170.