Runoff Transport of Pyrethroids from a Residential Lawn in Central California

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An irrigation runoff study on a residential lawn was conducted in California, northeast of Sacramento, during the summer and fall of 2008 to investigate the contribution of turf uses of pyrethroids to residues in Californian urban creek sediments. This study examined how over irrigation (i.e., irrigation that produces runoff) in the summer season may transport recently applied pyrethroids. The study included liquid and granular applications of both bifenthrin [(2-methyl-3-phenyl-phenyl) methyl 3-(2-chloro-3,3,3-trifluoro-prop-1-enyl)-2,2-dimethyl-cyclopropane-1-carboxylate] and β-cyfluthrin [Cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropanecarboxylate]. Generally, runoff did not occur at irrigation rates of 2.03 cm/h (0.8 in/h) but did occur when the irrigation rates were increased to about 3.81 cm/h (1.5 in/h), generating chemical losses in the first runoff event of up to 0.58 and 0.08% of applied for β-cyfluthrin and bifenthrin, respectively. Chemical runoff losses dropped significantly between over-irrigation events with the third over-irrigation event chemical runoff losses representing 0.026 and 0.015% of applied for β-cyfluthrin and bifenthrin, respectively. Runoff losses were generally less for liquid formulations than granular formulations but within a factor of three. Additionally, the study included a simulated winter rainstorm 8 wk after application. The low runoff losses from turf seen in this study suggest that other sources could be contributing to observed residues in urban streams. Other sources could include pyrethroids ending up on impervious surfaces, such as concrete driveways from off-target applications to turf, spills, and other poor handling practices, or pyrethroids applied directly to impervious surfaces for insect control.

Pyrethroids are a chemical class of insecticides used for control of a wide range of pests in agricultural and urban settings. Some pyrethroids with residential applications among their labeled uses have been detected in urban creek sediments (Weston et al. 2005). Also, pyrethroid residues tend to be detected in California's urban creeks more frequently and at higher concentrations during the winter wet season than in the dry summer season (R. Budd et al., 2007). How each of the labeled uses of these products contributes to detected pyrethroid residues is not well studied. Major residential uses of pyrethroid products include home perimeter treatments, lawn treatments, and treatment of ornamentals in landscapes. The California Department of Pesticide Regulation under California Notice 2006-13 required studies to be submitted to satisfy the need for data on the contribution from different pyrethroid uses, including lawn uses. Since a potential source of residues from lawns is in runoff water from over irrigation, the Pyrethroid Working Group, a group of pyrethroid manufacturers, conducted a study to determine the runoff losses from excessive lawn irrigation. Some researchers have suggested that some pyrethroid formulation types may be more vulnerable to runoff than others (Jorgenson and Young, 2010), so the study design included both liquid and granular formulations, as well as two different pyrethroid active ingredients. Additionally, the study included a runoff event representative of a winter rainfall storm.

Two representative pyrethroids, β-cyfluthrin and bifenthrin, were chosen so that two formulations could be tested on each plot to maximize the amount of information obtained. Beta-cyfluthrin is the active ingredient in the insecticides Advanced PowerForce Multi-Insect Killer and Tempo SC Ultra Insecticide. Bifenthrin is the active ingredient in the insecticides Talstar PL Granular and Talstar Professional. The Advanced PowerForce product is registered for use by homeowners in California and the other three products are registered for use by professional applicators in California.

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Abbreviations: CIMIS, California Irrigation Management Information System; DWR, Department of Water Resources; GC–MS, gas chromatograph/mass spectrometer; LOD, limit of detection; NI, normal irrigation; NID, Nevada Irrigation District; NIG, normal irrigation with granular bifenthrin/liquid β-cyfluthrin; NIL, normal irrigation with liquid bifenthrin/granular β-cyfluthrin; OI, over irrigation; OIG, over irrigation with granular bifenthrin/liquid β-cyfluthrin; OIL, over irrigation with liquid bifenthrin/granular β-cyfluthrin; TSS, total suspended solids.

Materials and Methods

The test site consisted of four 6.08-m (20-ft) by 12.16-m (40-ft) treated turf plots located on a residential lawn in Penryn, CA, located approximately 50 km northeast of downtown Sacramento. The turf was first established when the house was constructed more than 20 yr ago and was well maintained with uniform coverage. Each turfgrass plot was hydrologically isolated through installation of metal flashing around three sides of the plot perimeter to a depth of approximately 6.3 cm and a height above ground surface of approximately 6.3 cm. Pieces of flashing were pushed or pounded into the ground to create a continuous border around each study plot. An aluminum metal runoff collection gutter was positioned at the downslope end of each plot by excavating a trench across the plot bottom to a depth of approximately 15 cm. A flange on the uphill side of the gutter was inserted into the ground at the interface of the downslope end of the plot and the gutter. This 10.2-cm-deep flange ensured that runoff water flowing to the bottom of the plot could not flow under the gutter but was forced to flow across the 15.24-cm approach surface and drop into the V-channel gutter. To achieve a tight seal in the transitional area of the interface between turf, soil, and flange, a small amount of concrete crack filler was applied to every void to ensure no possibility of runoff loss under the gutter system.

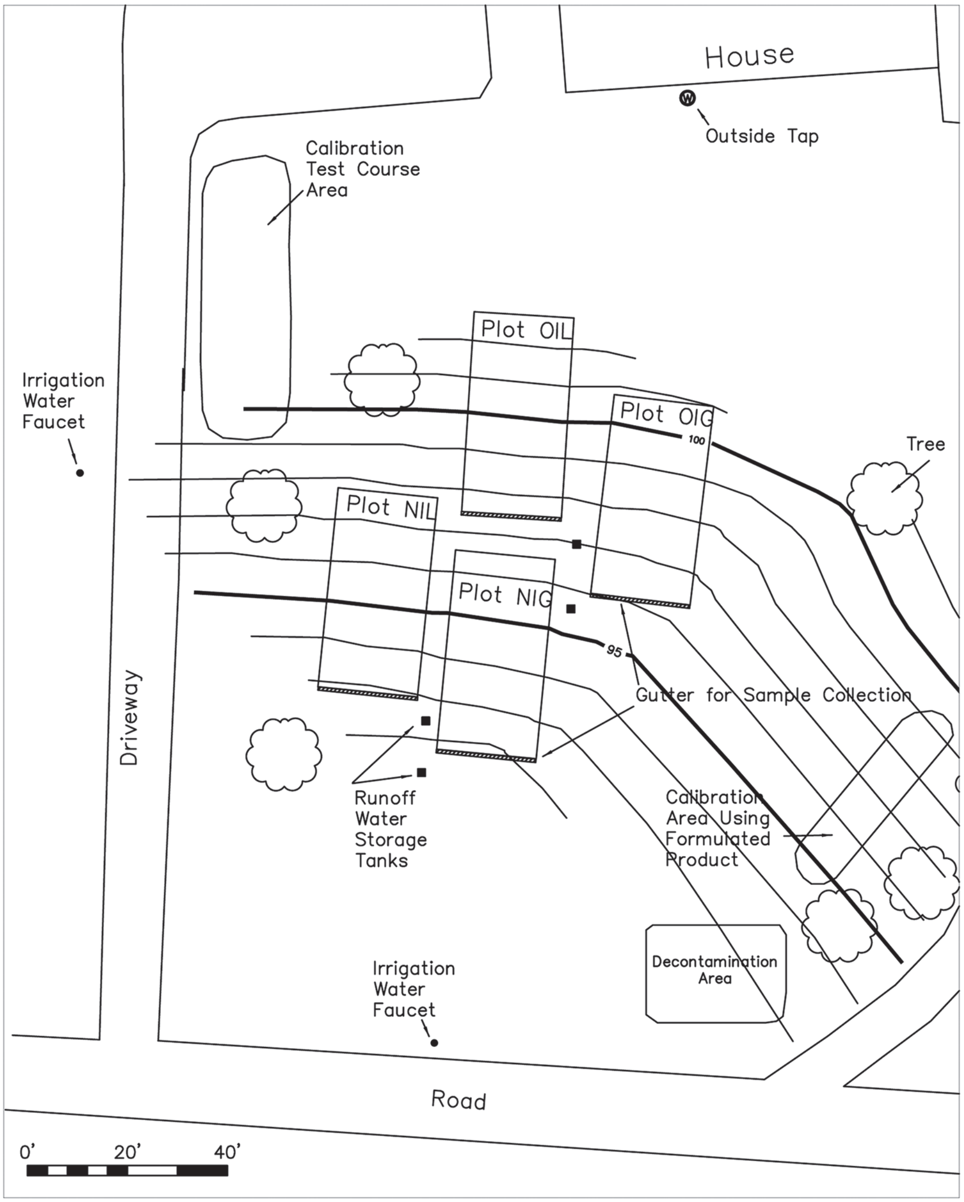

Fig. 1. Schematic of the plot layout on the residential lawn.

Runoff entering the gutter flowed down the sloping bottom toward an entrenched 18.9-L (5-gal) bucket. A bilge pump then transferred the runoff water from the bucket into a 264.6-L (70-gal) graduated tank for volume measurement. The gutter and 18.9-L bucket were covered to prevent direct interception of irrigation water. Samples for residue analysis were collected directly into two1-L amber glass jars at the end of the gutter from the runoff stream before it entered the 18.9-L bucket.

The plot identification consisted of the following (see Fig. 1): a designation for the type of irrigation, "OI" representing over irrigation, and "NI" representing normal (or best practice) irrigation; and a designation for the formulation of bifenthrin, "L," representing liquid bifenthrin, and "G," representing granular bifenthrin. The plot treatments were designated as follows:

Plot OIL—liquid bifenthrin/granular β-cyfluthrin with over irrigation

Plot OIG—granular bifenthrin/liquid β-cyfluthrin with over irrigation

Plot NIL—liquid bifenthrin/granular β-cyfluthrin with normal irrigation

Plot NIG—granular bifenthrin/liquid β-cyfluthrin with normal irrigation

Site Conditions

The study site was surveyed to provide accurate location and topographic data at a 0.3-m contour interval. Based on the site survey, the average slope in the area of the study plots was approximately 11%. The homeowner's irrigation system is fed by Nevada Irrigation District (NID) water. This water is collected by NID from mountain snowpack runoff and stored in a system of 10 reservoirs. Irrigation water is distributed through a series of canals and is then delivered to houses through a 15.24-cm (6-in) pipe. According to the USDA–NRCS Soil Survey of

Placer County (Soil Survey Staff, 2008), the soil at the site is Caperton–Andregg soil complex, a coarse sandy loam soil, 2 to 15% slopes. The Caperton series is a loamy, mixed, superactive, thermic, shallow entic haploxerolls, whereas the Andregg series is a coarse-loamy, mixed, superactive, thermic ultic haploxerolls. The capacity of the most limiting layer to transmit water is listed as very low to moderately low (0.00–0.15 cm/h). This soil is listed as a hydrologic group D and has shallow bedrock. Bedrock was encountered several times during instrumentation at a depth of approximately 46 to 61 cm. The homeowner did not apply pesticides or any other maintenance chemicals to the study plots during the study period. The only pesticide the homeowners applied to their lawn in the past several years had been Roundup Pro (Monsanto, St. Louis, MO), which was used as a spot spray for weed control. The study plots were mowed with a 56-cm (Toro, Bloomington, MN) mulching mower that finely ground grass clippings and left them in place on the plots. The mower was set to cut the grass to a height of approximately 7 cm. All plots were mowed every 7 d during the study period.

Weather Data

The California Irrigation Management Information System (CIMIS) is a program of the Office of Water Use Efficiency, California Department of Water Resources (DWR), which manages a network of more than 120 automated weather stations in the state of California. The CIMIS was developed in 1982 by DWR and the University of California, Davis to assist irrigators in managing their water resources efficiently. Weather data were obtained from CIMIS station #195 (Auburn, CA) for study period of 15 July to 10 Sept. 2008. These data were used to document natural rainfall, air temperature, solar radiation, and evapotranspiration during the study.

Pyrethroid Application

The timing of the pesticide application was planned for July based on information that peak use of pyrethroid products on lawns in California occurs from mid-June through July. On 15 July 2008, each study plot received an application of either Advanced PowerForce (granular formulation, active ingredient—β-cyfluthrin) (Bayer CropScience, Monheim, Germany) or Talstar PL (granular formulation, active ingredient—bifenthrin) (FMC Corp., Philadelphia, PA) at their respective maximum label rates. Each plot received an application of either Tempo SC Ultra (liquid formulation; active ingredient—β-cyfluthrin) (Bayer) or Talstar Professional (liquid formulation; active ingredient—bifenthrin) (FMC). Each liquid formulation was applied at an active ingredient rate equivalent to the rate used for the granular formulation that contains the same active ingredient. The test plots were treated as indicated in Table 1.

This application scenario resulted in each plot receiving two independent applications of test substance, one granular- and one liquid-formulated product. The applications were made separately using the appropriate application equipment for each formulation. All application equipment was calibrated on 14 July 2008, 1 d before application.

Spray applications were made using a 6.08-m-long (20-ft) handheld spray boom with two walking passes across each plot. Before application, plastic sheeting was used to cover the gutters and sampling areas at the downslope end of each plot to avoid application of the test substance onto these areas. For the eight passes made over the four plots, the average walking speed was 15.4 s and the maximum variation from the 15.1-s target rate was 1.2 s.

Granular applications were made using a drop spreader in 11 passes walking downslope through the test plots. Bifenthrin applications were made with a drop spreader (Accugreen 3000, The Scotts Co. LLC, Marysville, OH). The granular β-cyfluthrin applications were made with a drop spreader (Green Thumb model 7300GT).

Over-irrigation Setup and Runoff

Temporary, above-ground irrigation systems were built for the plots receiving over-irrigation runoff events. Originally, the system was designed to deliver a typical best-practice irrigation rate for a period of time that would also be sufficient to produce runoff. For each plot, the irrigation systems consisted of six sprinkler heads connected with rubber hose. The hose ran to an upper corner of the runoff plots and then divided into two lateral systems. Each lateral was positioned just outside the flashing down the 12.16-m sides of the plots. A sprinkler head with a 90° spray arc was located at each corner of the plot (four total) and a sprinkler head with a 180° arc was located in the middle of the 12.16-m sides of the plot (two total). Each sprinkler head was fitted with a Xerigation 206.7-kPa (30-psi) pressure regulator (Rain Bird, Tucson, AZ), which allowed for consistent pressure and flow at each sprinkler head.

Table 1. Target test substance application rates by study plot.

Plot	Test substance	a.i.	Formulation	Target application rate
OIL†	Talstar Professional	bifenthrin	liquid	2.18 g ai/92.9m^2
OIL	Bayer Advanced PowerForce	beta-cyfluthrin	granular	0.68 g ai/92.9m^2
OIG‡	Talstar PL	bifenthrin	granular	2.18 g ai/92.9m^2
OIG	Tempo SC Ultra	beta-cyfluthrin	liquid	0.68 g ai/92.9m^2
NIL§	Talstar Professional	bifenthrin	liquid	2.18 g ai/92.9m^2
NIL	Bayer Advanced PowerForce	beta-cyfluthrin	granular	0.68 g ai/92.9m^2
NIG¶	Talstar PL	bifenthrin	granular	2.18 g ai/92.9m^2
NIG	Tempo SC Ultra	beta-cyfluthrin	liquid	0.68 g ai/92.9m^2

† Over irrigation with liquid bifenthrin/granular β-cyfluthrin.

‡ Over irrigation with granular bifenthrin/liquid β-cyfluthrin.

§ Normal irrigation with liquid bifenthrin/granular β-cyfluthrin.

¶ Normal irrigation with granular bifenthrin/liquid β-cyfluthrin.

On 27 June 2008, which was mostly sunny, 33.5°C, with an evapotranspiration rate of 0.58 cm, all of the plots were over irrigated during the late afternoon. There was significant runoff from each plot within an hour. During this test, a standard irrigation nozzle configuration (Rainbird R17–24 series) was used. The irrigation rate of these nozzles was measured at 1.73 cm/h (0.68 in/h). During the preapplication saturation of the plots on 14 July 2008, after continuous irrigation for up to 7 h, runoff did not occur on three of the four plots. That day, the CIMIS station in Auburn, CA, recorded evapotranspiration of 0.68 cm, a maximum temperature of 34.6°C, solar radiation of 639 Ly/d, and an average soil temperature of 24.4°C. It was concluded that to generate runoff it would be necessary to install Rainbird 18 VAN series sprinkler heads (measured output of 3.71 cm/h [1.46 in/h]) to achieve a higher delivery rate of water to the plots. For the remainder of the experiment, if after 2 h the Rainbird R17–24 series did not generate adequate runoff to sample, it was then shut off and the 18 VAN series nozzles were turned on.

Three over-irrigation runoff events were conducted starting on the day after application of the test substances on 16 July 2008, and continuing every other day for 4 d, ending on 20 July 2008. The over-irrigation runoff events were conducted on plots OIL and OIG.

For all runoff events, the irrigation start and stop times, and the time when runoff started from each plot were recorded. While the over-irrigation event was in progress, the following data were recorded together with the time of the observation: (i) cumulative runoff volume (liters) in the collection tank and (ii) elapsed time to collect the 2 L of sample at each sample collection point (Fig. 2).

For each over-irrigation event on each plot, seven flow proportional samples of runoff were collected from the runoff stream at the end of the gutter. The collection of samples was based on the cumulative flow throughout each runoff event. For each treatment plot, two 1-L samples were collected in amber glass 1-L bottles at breakthrough of runoff and then at 18.9, 37.8, 75.6, 113.4, 151.2, and 189 L (5, 10, 20, 30, 40, and 50 gal) of cumulative runoff. It was determined that breakthrough of runoff had occurred when a consistent steady stream of flow was pouring from the gutter into the 18.9-L bucket. The timing of the collection of the sample at breakthrough and subsequent samples were recorded. Samples were placed on ice in field coolers before transfer to CRG Marine Laboratories, Torrance, CA, for sample analysis.

Simulated Rainfall Setup and Runoff

The 1-h rainfall depth with a 5-yr return interval (5-yr, 1-h rainfall) was chosen as the rainfall event to simulate. The depth of this rainfall event was determined using the NOAA Atlas 2 publication (Miller et al. 1973). The procedure involved determination of several rainfall frequency/duration depths from isopluvial maps contained in the publication, applying regression equations to calculate 2-yr 1-h and 100-yr 1-h depths, and use of a nomograph to finally determine the 5-yr 1-h rainfall depth. The 5-yr 1-h rainfall depth for the study site was determined to be 1.9 cm (0.75 in).

A rainfall simulator (Coody and Lawrence, 1994) was used to generate runoff from the turfgrass plots. This apparatus includes a system for continuously applying simulated rainfall having a droplet size spectrum, an impact velocity, a spatial uniformity, and an intensity-simulating natural rainfall. The rainfall simulator was assembled at the study site. The rainfall

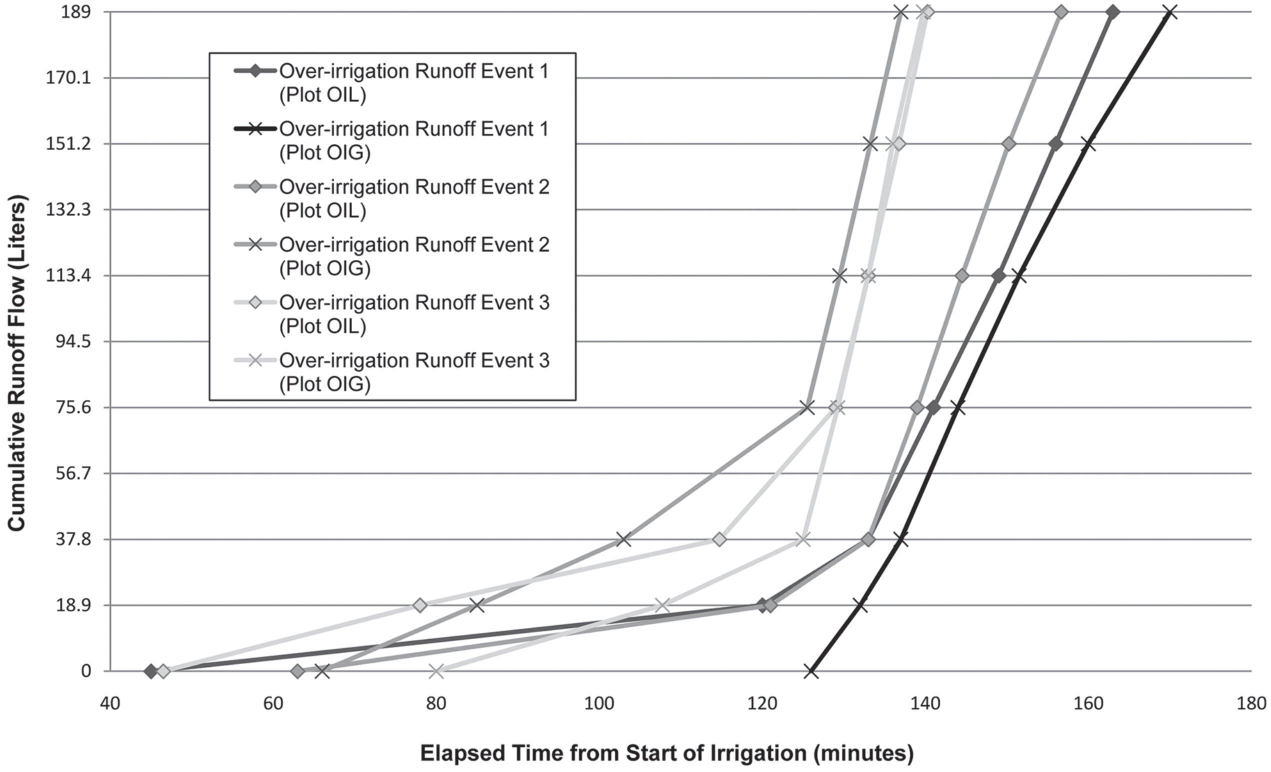

Fig. 2. Over-irrigation runoff event hydrographs. Each marker on the line represents a sample.

simulator was positioned around each of the test plots one at a time so that the plot was centered between the two 5.08-cm-diam (2-in) PVC laterals extending down the plot length. The laterals were approximately 16.4 m long and 6.4 m apart. The laterals were connected at the upslope end to a water main attached to the homeowner's irrigation system. Riser pipes were uniformly positioned every 4.05 m along the laterals, with five risers on the east lateral and four risers on the west lateral; these extended vertically to a height 2.84 m above the ground surface. Mounted on the top of each riser was a PC–S3000 irrigation head (Nelson Irrigation Corp. Walla Walla, WA) fitted with a #14 or #15 plastic nozzle, and a part circle spinner plate that sprayed the water in a 190° arc. The #14 and #15 nozzles were alternated on the risers down each lateral to best achieve the target delivery rate of 1.9 cm/h. Using a combination of the two nozzles achieved an average delivery rate of 1.96 cm/h. Each irrigation head contained a 103.35-kPa pressure regulator that provided a constant output rate from the nozzle irrespective of its position along the simulator lateral or the backpressure on the system. This served to maximize the uniformity of water distribution over the test plot. Each irrigation head irrigated a semicircular area with a radius of approximately 6.7 m (22 ft). The area irrigated by the rainfall simulator included the test plot area selected for each event. The simulated rainfall received outside the test plots was directed away from the sampling and flow monitoring locations, and did not contribute to the runoff volume measured or sampled.

Representative samples of runoff were collected on a flow proportional basis. Runoff samples were collected as the water moved out of the gutter system. Runoff water that was not sampled was then pumped into a graduated tank. Plot over-irrigation events were terminated when 189 L of runoff had been collected; some flow continued from the plots after the irrigation system had been shut off. The total amount of flow collected from each plot per event was documented.

On 10 Sept. 2008, the rainfall simulator was operated over each study plot. The sampling schedule for the simulated rainfall event for each plot was similar to the over-irrigation event. However, two criteria were specified for each event: (i) the duration of the storm had to equal at least 1 h in length and (ii) at least 189 L of runoff had to be generated from the plot. Therefore, sampling was continued at 37.8-L flow increments (after 189 L) until the duration of the simulation equaled 1 h in length or, alternatively, the simulation event could be continued until 189 L of flow had occurred.

Figure 3 shows the hydrographs for each simulated rainfall event. Plots OIL and NIG delivered approximately 189 L of runoff during the 1-h simulated event applied to the plots. Plot OIG required approximately 88 min of simulated rainfall to produce 189 L of runoff. Plot NIL delivered runoff at a higher rate than the other three study plots and produced >340 L of runoff within the 1-h simulation. All samples were placed on ice in field coolers before transfer to CRG Marine Laboratories for sample analysis.

Total Suspended Solids Sample Collection

At the conclusion of each over-irrigation event and the simulated rainfall event, the contents of the 264.6-L runoff collection tank were thoroughly mixed using a spiral-bladed, drywall mixing paddle powered by an electric drill. Once a visually homogeneous mixture of water and sediment was achieved, two 1-L subsamples were collected in 1-L high-density polyethylene bottles for total suspended solids (TSS) analysis. All samples were placed on ice in field coolers before transfer to CRG Marine Laboratories for sample analysis.

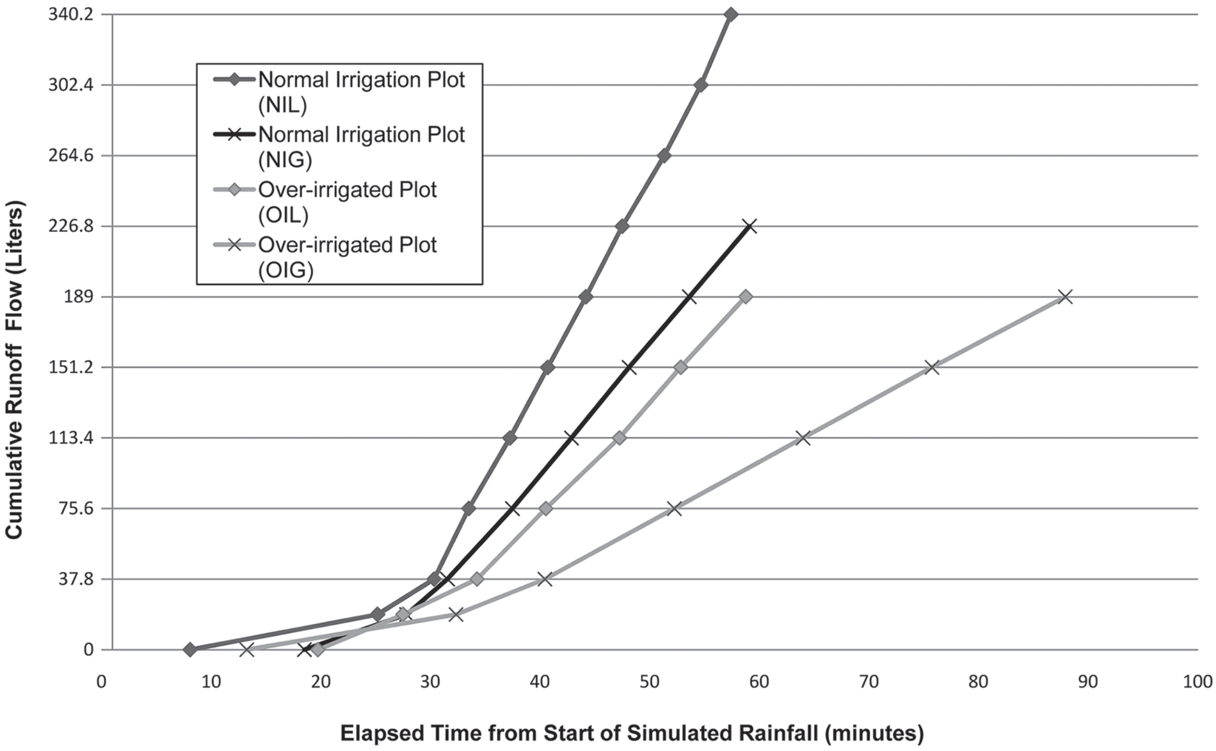

Fig. 3. Simulated rainfall runoff event hydrographs. Each marker on the line represents a sample.

Analytical Method

The analytical method used for this study was based on a modification of USEPA Method 625, "Base/Neutrals and Acids." Briefly, water samples are extracted with a nonpolar solvent (methylene chloride), concentrated, and analyzed by gas chromatography with a mass-selective detector. The modification of this method is described below.

Sample Handling and Processing

Approximately 2 L of water was collected for each sample in clean amber glass bottles with Teflon-lined caps. The samples were received at CRG Marine Laboratories and placed in a refrigerator at 4 ± 2°C until beginning the extraction procedure. All extractions were performed within 96 h of collection.

Sample Extraction

Each sample was extracted three consecutive times with 100 mL of pesticide-quality methylene chloride using a separatory funnel. In addition, for each extraction, the sample container was rinsed with methylene chloride and the solvent added to the separatory funnel to capture any pyrethroids in the glass container. The combined extracts were reduced in volume using a roto-evaporator and transferred into autosampler vials for analysis. Just before analysis, each autosampler vial containing the sample extract was spiked with an internal standard (1000 ng of 2,2′,5,5′-Tetrabromobiphenyl). Each sample batch included the analysis of a laboratory method blank (control sample), blank spike (fortification sample), and blank spike duplicate. The amount spiked into the 1-L fortified samples was 800 ng each for bifenthrin and β-cyfluthrin.

Sample Analysis

Sample analysis was accomplished using an Agilent 7890/5975N gas chromatograph/mass spectrometer (GC–MS) (Agilent Technologies, Santa Clara, CA) in the negative ion chemical ionization mode. The GC was equipped with a DB–5, 60-m, 0.25-mm ID, 0.25-µm film thickness chromatographic column purchased from J&W Scientific, Folsom, CA. Samples were injected using the splitless mode and the oven was temperature programmed from 45 to 200°C at 20°C/min, then to 285°C at 2.5°C/min, then held for 12 min. The helium carrier gas velocity was approximately 35 cm/s. The mass spectrometer was programmed in the full scan negative ion mode from 45 to 500 amu. Before analysis of the samples, the GC–MS was tuned via the GC–MS software in the chemical ionization mode. Methane was used for negative ion chemical ionization at 20 mL/min, resulting in a source pressure of approximately 0.0001 torr.

The stock calibration solution was made using neat (99% pure solid material) β-cyfluthrin and bifenthrin supplied by the product manufacturers. Before the analysis of each batch of samples, the GC–MS was calibrated using a five-point calibration curve based on the following amounts: 25 ng, 250 ng, 500 ng, 1000 ng, and 2000 ng. The calibration curves were based on a linear regression and the minimum acceptable correlation coefficient was 0.99. The calibration curve is based on the mass injected onto the GC–MS and are equivalent to the following sample concentrations: 12.5 ng/L, 125 ng/L, 250 ng/L, 500 ng/L, and 1000 ng/L. Fortification spikes were analyzed with each batch of samples using a solution purchased from a commercial supplier (AccuStandard, New Haven, CT) and is traceable to the National Institute of Standards Technology. The AccuStandard solution contained both α-cyfluthrin and β-cyfluthrin, and the supplier could not provide the actual concentration of each isomer, only the total concentration of both isomers combined. The solution used to calibrate the GC–MS was based on the neat compounds provided by the sponsors containing the β-cyfluthrin isomer only. In quantifying the fortified samples, the β-cyfluthrin results are less accurate due to the unknown concentration of these two separate isomers in the AccuStandard spiking solution and the recovery results appeared to be biased slightly low.

Laboratory Fortification Sample Results

For bifenthrin, laboratory fortifications (seven) of untreated blank samples ranged from 74 to 106%, with a relative percent difference ranging from 1 to 21 between the spike sample and its duplicate. For β-cyfluthrin, laboratory fortifications (seven) of untreated blank samples ranged from 72 to 101%, with a relative percent difference ranging from 0 to 6 between the spike sample and its duplicate.

Method Detection Limit Determination

Before analysis of the study samples, a method detection limit or limit of detection (LOD) study using the study matrix (site irrigation water) was performed according to USEPA 40 CFR, Part 136, Appendix B. The LOD was determined by spiking seven replicate samples with 5 ng/L (based on a 1-L sample volume) of each pyrethroid. The standard deviation of the seven spikes was calculated and multiplied by the t-score (n-1) for the 99% confidence interval (i.e., 3.14) to determine the LOD. The mean recovery of the seven bifenthrin-spiked samples was 109%, with a standard deviation of 0.19. The LOD for bifenthrin was determined to be 0.59 ng/L. The mean recovery of the seven β-cyfluthrin-spiked samples was 88%, with a standard deviation of 0.33. The LOD for β-cyfluthrin was determined to be 1.03 ng/L. The limit of quantitation for both pyrethroids was determined to be 10 times the LOD. All detectable results were reported to the LOD. The analytical results were not corrected for recoveries.

Field Fortification Samples

Four field-fortified samples were prepared for each pyrethroid at two levels—10 ng/L and 100 ng/L. These solutions were prepared by CRG Marine Laboratories personnel, in vials, and shipped to the study site. The vials were then uncapped in the field and each was dropped into a 1-L bottle of laboratory reagent water and shipped back to the lab using the same shipping and handling procedure for residue samples. Total sample volume from each bottle was measured at the lab. For the four 10 ng/L spikes, average recoveries were 83 and 92%, respectively, for bifenthrin and β-cyfluthrin. For the 100-ng/L spikes, the recoveries averaged 73 and 77%, respectively, for bifenthrin and β-cyfluthrin.

Analytical Method for Total Suspended Solids

Total suspended solids were measured following the USEPA Method 160.3 by passing a measured volume of sample through a preweighed glass fiber filter. The filter was dried at 105°C for 24 h and until a constant weight was achieved. The dried filter was weighed on an analytical balance and TSS calculated by dividing the net mass trapped by the filter by the exact volume filtered.

Results

Test Substance Application Results

Applications of bifenthrin to all plots are summarized in Table 2. Plots OIL and NIL were treated with a single batch of spray solution. Based on the calibration results, spray solution preparation and pass times, 1.82 g of bifenthrin or 104% of targeted rate, was applied to Plot OIL. Plot NIL received 1.78 g of bifenthrin or 102% of target. Table 3 summarizes the application of β-cyfluthrin to all four plots. Plots OIG and NIG were treated with a single batch of spray solution. Based on the calibration results and spray solution preparation and pass times, 0.550 g of β-cyfluthrin, or 101% of the targeted rate, was applied to plot OIG. Plot NIG received 0.559 g of β-cyfluthrin, or 103% of the target.

Overall, the data in Tables 2 and 3 indicate successful liquid applications of bifenthrin and β-cyfluthrin to the test plots at an application rate slightly greater than the targeted amounts.

Granular applications of bifenthrin to plots OIG and NIG are detailed in Table 2. The test substance weighback after application to plot OIG revealed that 18.3% of the target was delivered. Based on this low dose, it was decided to recalibrate the drop spreader. Three passes were made over the 12.16-m test course with blank material using the same settings from the original calibration. The yield of calibration confirmation resulted in 93.9% of the target delivery. This result was lower but similar to the original calibration runs of 108.7% of target. It was concluded there was a possibility the blank material had different flow characteristics through the spreader than the formulated product. It was decided to calibrate the drop spreader using the actual bifenthrin test substance. These

Table 2. Test substance treatment details. Bifenthrin applications by plot.

Parameter	Plot OIL†	Plot NIL‡	Plot OIG§	Plot NIG¶
Treatment date	15 July 2008	15 July 2008	15 July 2008	15 July 2008
Treatment time	1439 h	1446 h	1401 h	1144 h
Air temperature (°C)	30.8	30.8	28.1	28.6
Wind speed (km/h)	4	4.8	3.4	4.8
a.i./g of formulated product (g)	0.08	0.08	0.0019	0.0019
Target treatment rate (per plot)	1.74 g a.i.	1.74 g a.i.	1.74 g a.i.	1.74 g a.i.
Treatment rate based on tank mix and pass time# (per plot)	1.82 g a.i.	1.78 g a.i.		
Treatment Rate Based on weighback technique†† (per plot)			2.10 g a.i.	1.78 g a.i.
Target treatment rate	104%	102%	120%	102%

† Over irrigation with liquid bifenthrin/granular β-cyfluthrin.

‡ Normal irrigation with liquid bifenthrin/granular β-cyfluthrin.

§ Over irrigation with granular bifenthrin/liquid β-cyfluthrin.

¶ Normal irrigation with granular bifenthrin/liquid β-cyfluthrin.

Test substance application rate based on an 8.0% a.i. as determined by FMC Corp. calculations made with the formulated product assuming a specific gravity of 1.0.

†† Test substance application rate based on a 0.19% a.i. as determined by FMC Corp.

Table 3. Test substance treatment details. Beta-cyfluthrin applications by plot.

Parameter	Plot OIL†	Plot NIL‡	Plot OIG§	Plot NIG¶
Treatment date	15 July 2008	15 July 2008	15 July 2008	15 July 2008
Treatment time	0910 h	0941 h	1602 h	1606 h
Air temperature (°C)	Not recorded	25.3	33.6	33.6
Wind speed (km/h)	Not recorded	3.2	2.25	1.4
a.i./g of formulated product (g)	0.1135	0.1135	0.00046	0.00046
Target treatment rate (per plot)	0.544 g a.i.	0.544 g a.i.	0.544 g a.i.	0.544 g a.i.
Treatment rate based on tank mix and pass time# (per plot)	0.531 g a.i.	0.548 g a.i.		
Treatment rate based on weighback technique†† (per plot)			0.550 g a.i.	0.559 g a.i.
Target treatment rate	97%	101%	101%	103%

† Over irrigation with liquid bifenthrin/granular β-cyfluthrin.

‡ Normal irrigation with liquid bifenthrin/granular β-cyfluthrin.

§ Over irrigation with granular bifenthrin/liquid β-cyfluthrin.

¶ Normal irrigation with granular bifenthrin/liquid β-cyfluthrin.

Test substance application rate based on an 11.35% a.i. as determined by Bayer CropScience calculations made with the formulated product assuming a specific gravity of 1.0.

†† Test substance application rate based on a 0.046% a.i. as determined by Bayer CropScience.

calibrations were conducted at the northwest corner of the lawn, down gradient of the test plots. A total of 15 passes over a new 12.16-m course were made. The calibration runs were based on three passes over the course with the starting and ending weight of the test substance recorded for each three-pass test. Adjustments to the spreader setting were made as necessary at the beginning of the three-pass calibration run. The final two sets of three runs, with the slot opening set at 3.5, produced results of 95 and 110% of target.

It was decided to treat plot NIG with the new calibration settings, determine the application rate, and then proceed with efforts to deliver additional material to plot OIG, which received the low dose of bifenthrin. Table 2 indicates the treatment to plot NIG resulted in 1.78 g of bifenthrin, or 102% of the target dose. It was decided to retreat plot OIG using the new calibration settings on the drop spreader. It was anticipated that this would result in a higher application of bifenthrin to this plot due to the earlier low application. Table 2 indicates that, with both applications, plot OIG received 2.10 g bifenthrin, or 120% of the target application.

Granular applications of β-cyfluthrin to plots OIL and NIL are detailed in Table 3. The test substance weighback after application revealed that 97% of the target was delivered to plot OIL and 101% of the target was delivered to plot NIL. No anomalies were noted during these two applications.

Tank Mix Sample Residues

Two tank mix samples were collected for analysis from each application mixture of bifenthrin and β-cyfluthrin for a total of four samples. One sample was collected directly after the tank mix was prepared and thoroughly agitated, and the second sample was collected after the applications to each plot were completed. The purpose of the tank mix samples was to determine if mixing was adequate and if a homogenous proportion of the tank mix was delivered to the plots. The tank mix results were not used to make calculations of total mass applied to the plots. The average tank mix results for bifenthrin resulted in 121% of the target concentration. The average tank mix results for β-cyfluthrin resulted in 101% of the target concentration.

Over-irrigation Event Hydrology

For the over-irrigation events, there were significant differences (ranging from 45 to 126 min) in the timing of the first runoff sample between plots, as shown in Fig. 2. Each of the two plots was over irrigated individually, so the events took place at different times of the day and therefore ambient temperature, relative humidity, and evapotranspiration rate differed for each event. On all plots, runoff began in the middle of the plot and then expanded across the entire bottom of the plot as the full plot reached field saturation. There was no evidence of runoff pooling against the plot flashing.

At all over-irrigation events on all plots, the high flow system was switched on after 120 min because the runoff rate was deemed too low for timely sampling to occur. The rate of runoff quickly increased and stabilized. Figure 2 shows that the slope describing the flow rate (L/min) became consistent for all six of the events after the 120-min mark. Although there were differences in the timing of the start and end of runoff, the two plots appear to have replicated flow rates (slope) fairly consistently for each event.

Simulated Rainfall Event Hydrology

As Fig. 3 demonstrates, the hydrology of the 10 Sept. 2008-simulated rainfall events differed from the over-irrigation runoff events in July. Despite the fact that the rainfall simulator output (1.96 cm/h) was similar to that of the standard irrigation system (2.06 cm/h), each of the plots achieved a steady runoff rate within 30 min from the start of irrigation. Every plot reached or exceeded 189 cumulative L of runoff within 60 min, with the exception of plot OIG, which reached 189 L of runoff after 88 min. Plot NIG was directly downgrade from plot OIL and both plots responded comparably to the rainfall simulator. Plot NIL responded with the highest rate of runoff, accumulating 340 L during the 60-min simulation.

Irrigation and Simulator Source Water Residues

Water samples were collected for residue analysis from the homeowner's irrigation water source during the preapplication runoff event, each over-irrigation runoff event, and the simulated rainfall event, for a total of seven irrigation source water samples. No bifenthrin or β-cyfluthrin residues were detected in any source water sample.

Total Suspended Solids Residues

The TSS results are shown in Table 4. In general, the suspended solids in the runoff water from all plots were relatively low. Runoff from the over-irrigation for Events 1, 2, and 3 exhibited TSS ranging from 3.7 to 5.7 mg/L. Total suspended solids from the simulated rainfall were higher on all plots ranging from 10.3 to 17 mg/L. As expected, in no case was there any significant transport of sediment from this well-established turf.

Over-irrigation Event Residues

The total mass lost during the first over-irrigation event represented 0.081% of the mass applied for the liquid bifenthrin formulation and 0.052% of the mass applied of the granular formulation (Table 5). On the second and third irrigation events, the granular-treated plot exhibited higher mass transport compared with the plot treated with the liquid bifenthrin formulation. The mass of bifenthrin leaving the plots dropped

Table 4. Total suspended solids sample results (mg/L).

Event	Plot OIG†	Plot OIL‡	Plot NIG§	Plot NIL¶
Over-irrigation event 1	4.0	3.7	NR#	NR
Over-irrigation event 2	5.3	4.0	NR	NR
Over-irrigation event 3	4.5	5.7	NR	NR
Simulated rainfall event	14.0	12.5	10.3	17.0

† Over irrigation with granular bifenthrin/liquid β-cyfluthrin.

‡ Over irrigation with liquid bifenthrin/granular β-cyfluthrin.

§ Normal irrigation with granular bifenthrin/liquid β-cyfluthrin.

¶ Normal irrigation with liquid bifenthrin/granular β-cyfluthrin.

NR, no runoff.

Table 5. Mass loss from runoff events.

	Mass applied	Event 1		Event 2		Event 3		Simulated rain	
		Mass	Percent applied	Mass	Percent applied	Mass	Percent applied	Mass	Percent applied
	g	g	%	g	%	g	%	g	%
Bifenthrin treatment									
Plot OIG†-granular, over irrigation	2.10	1.1E-03	0.052	7.7E-04	0.037	3.1E-04	0.015	5.4E-05	0.003
Plot NIG‡-granular, best practice irrigation	1.78	NR#	NR	NR	NR	NR	NR	5.5E-05	0.003
Plot OIL§-liquid, over irrigation	1.82	1.5E-03	0.081	2.4E-04	0.013	1.1E-04	0.006	2.8E-05	0.002
Plot NIL¶-liquid, best practice irrigation	1.78	NR	NR	NR	NR	NR	NR	1.1E-04	0.006
Beta-cyfluthrin treatment									
Plot OIL§-granular, Over irrigation	0.531	3.1E-03	0.58	4.0E-04	0.075	1.4E-04	0.026	2.8E-05	0.005
Plot NIL¶-granular, best practice irrigation	0.548	NR	NR	NR	NR	NR	NR	6.0E-05	0.011
Plot OIG†-liquid, over irrigation	0.550	1.3E-03	0.23	3.5E-04	0.064	1.2E-04	0.021	3.2E-05	0.006
Plot NIG‡-liquid, Best practice irrigation	0.559	NR	NR	NR	NR	NR	NR	5.5E-05	0.010

† Over irrigation with granular bifenthrin/liquid β-cyfluthrin.

‡ Normal irrigation with granular bifenthrin/liquid β-cyfluthrin.

§ Over irrigation with liquid bifenthrin/granular β-cyfluthrin.

¶ Normal irrigation with liquid bifenthrin/granular β-cyfluthrin.

NR, no runoff.

significantly between over-irrigation events, with the third over-irrigation event runoff losses representing 0.015 and 0.006% of the applied granular and liquid formulations, respectively, as can be seen by the flattening of the curves on Fig. 4 and 5.

The total mass lost during the first over-irrigation event represented 0.58% of the mass applied for the granular β-cyfluthrin and 0.23% of the mass applied for the liquid formulation. The mass of β-cyfluthrin leaving the plots dropped significantly between over-irrigation events with the third over-irrigation event runoff losses representing 0.026% and 0.021% of the applied granular and liquid formulations, respectively. Line graphs displaying the cumulative total of residues from each plot for all runoff events are presented in Fig. 4 and 5.

This significant reduction in residues among runoff events is reflected in the concentration data as well. For the liquid formulation of bifenthrin, the concentrations in the seven samples collected from the 189 L of runoff in the first runoff event ranged from 5.4 to 17.4 μg/L, 0.89 to 1.6 μg/L in the second runoff event, and 0.41 to 0.91 μg/L in the third runoff event.

For the granular formulation of bifenthrin, the concentrations in the seven samples collected from the 189 L of runoff in the first runoff event ranged from 4.0 to 7.3 μg/L, 1.9 to 7.1 μg/L in the second runoff event, and 1.2 to 1.7 μg/L in the third runoff event.

For the liquid formulation of β-cyfluthrin, the concentrations in the seven samples collected from the 208 L of runoff in the first runoff event ranged from 4.0 to 13.0 μg/L, 1.3 to 2.5 μg/L in the second runoff event, and 0.40 to 0.79 μg/L in the third runoff event.

For the granular formulation of β-cyfluthrin, the concentrations in the seven samples collected from the 208 L of runoff in the first runoff event ranged from 7.39 to 20.2 μg/L, 1.2 to 2.5 μg/L in the second runoff event, and 0.25 to 0.97 μg/L in the third runoff event.

The maximum concentration for both formulations of bifenthrin and the granular formulation of β-cyfluthrin occurred in the first samples collected for the entire study. These samples were collected at the breakthrough of runoff. The maximum concentration of the liquid formulation of β-cyfluthrin occurred in the fourth sample collected after 75.6 L of flow had occurred.

Simulated Rainfall Event Residues

The residue data, mass export calculations, and percent of mass applied calculations for the simulated rainfall events for each sample and event totals are presented in Table 5. Mass transport was low for all plots during the simulated rainfall runoff events. The maximum loss was 0.011% of applied and came from the plot treated with granular β-cyfluthrin that was not over irrigated (NIL) before the simulated rainfall runoff event.

From the plots that were not over irrigated before the simulated rainfall runoff events, concentrations of bifenthrin from the liquid formulation in samples collected from the 453.6 L of runoff water ranged from 0.10 to 0.37 μg/L; concentrations of bifenthrin from the granular formulation in samples collected from the 260.8 L of runoff water ranged from 0.15 to 0.33 μg/L; concentrations of β-cyfluthrin from the liquid formulation in samples collected from the 260.8 L of runoff water ranged from 0.078 to 0.44 μg/L; concentrations of β-cyfluthrin from the granular formulation in samples collected from the 453.6 L of runoff water ranged from 0.0075 to 0.32 μg/L.

From the plots that were over irrigated before the simulated rainfall runoff events, concentrations of bifenthrin from the liquid formulation in samples collected from the 234.4 L of runoff water ranged from 0.088 to 0.18 μg/L; concentrations of bifenthrin from the granular formulation in samples collected from the 208 L of runoff water ranged from 0.19 to 0.49 μg/L; concentrations of β-cyfluthrin from the liquid formulation in samples collected from the 208 L of runoff water ranged from 0.10 to 0.31 μg/L; concentrations of β-cyfluthrin from the granular formulation in samples collected from the 234.4 L of runoff water ranged from 0.042 to 0.26 μg/L.

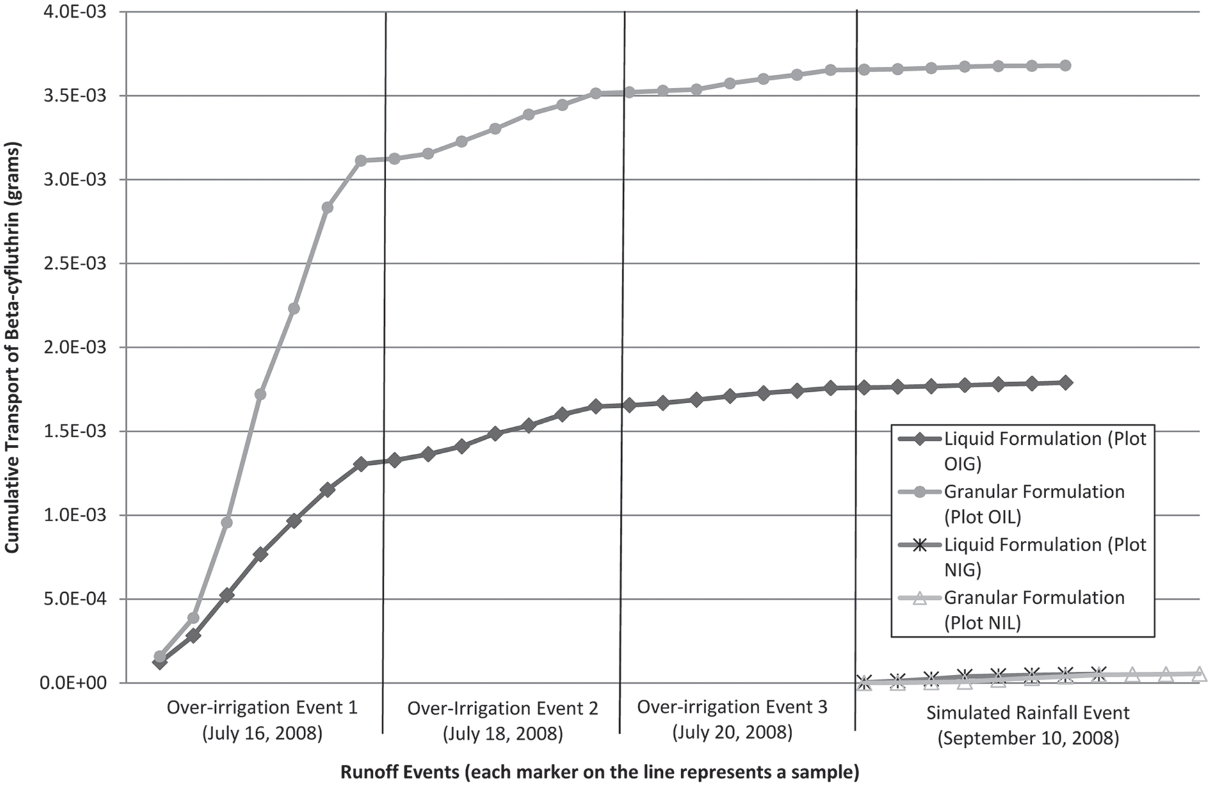

Fig. 4. Cumulative transport of bifenthrin in over-irrigation runoff and simulated rainfall runoff. For each event, the first sample represents the first 1.89 liters of runoff; the second sample represents 18.9 L, and all successive samples represent 37.8 L intervals.

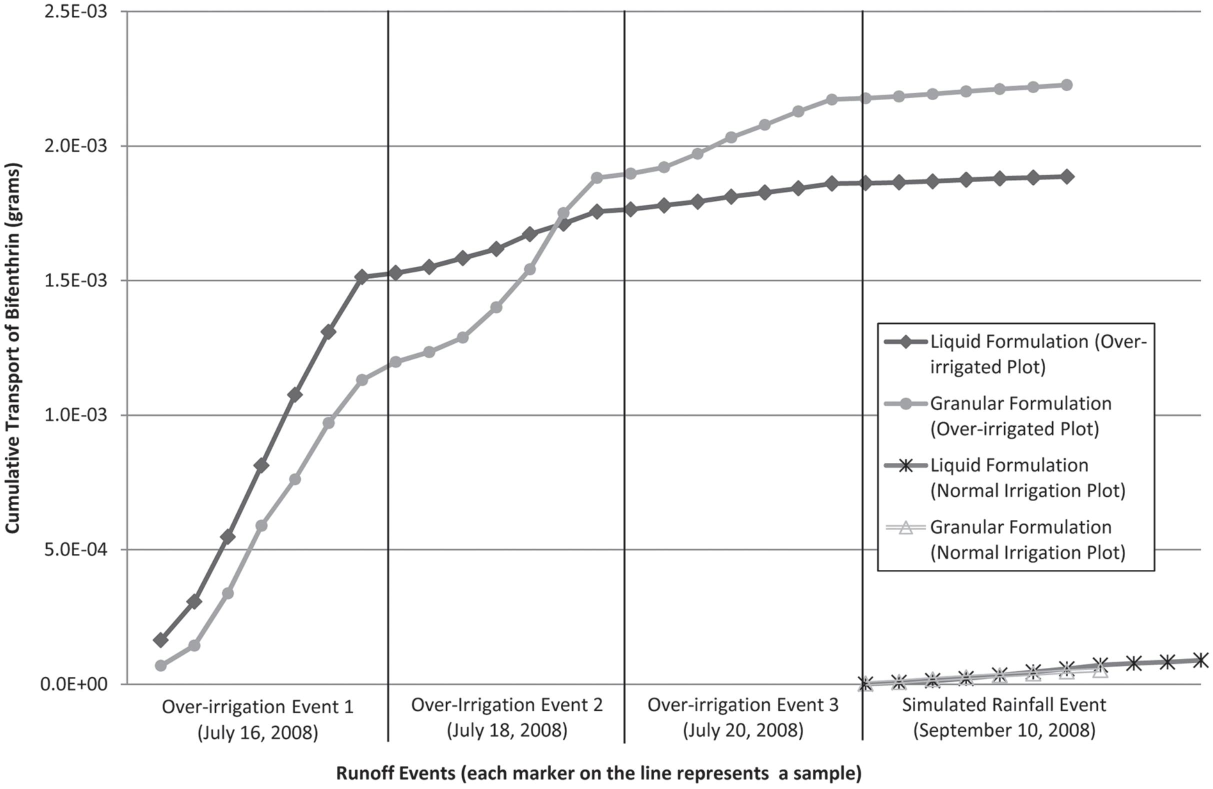

Fig. 5. Cumulative transport of β-cyfluthrin in over-irrigation runoff and simulated rainfall runoff. For each event, the first sample represents the first 1.89 L of runoff; the second sample represents 18.9 L, and all successive samples represent 37.8 L intervals.

Discussion and Conclusions

Plots irrigated without generating runoff (plots NIL and NIG) demonstrated very low losses of granular bifenthrin (0.003% of applied), liquid bifenthrin (0.006% of applied), granular β-cyfluthrin (0.011% of applied), and liquid β-cyfluthrin (0.010% of applied) in runoff water from a 1.9 cm/h simulated rainfall event that occurred 57 d after application. The data from this portion of the study indicate that continued education of the public on responsible irrigation practices in such programs as CIMIS and the California Urban Water Conservation Council could lead to significant reductions in overall losses of pyrethroid residues from lawns.

Mass transport in runoff for bifenthrin from the first over-irrigation event was 0.052 and 0.081% of applied granular and liquid formulations, respectively. Mass transport in runoff for β-cyfluthrin from the first over-irrigation event was 0.58 and 0.23% of applied granular and liquid formulations, respectively. These differences in losses of bifenthrin and β-cyfluthrin in irrigation runoff are likely the result of formulation differences rather than a reflection of the intrinsic properties of the two active ingredients.

The mass of β-cyfluthrin leaving the plots dropped significantly between over-irrigation events with the third over-irrigation event runoff losses representing 0.026 and 0.021% of the applied granular and liquid formulations, respectively. These decreasing runoff losses in successive irrigation events may indicate that the commonly used mitigation practice of "watering in" a pesticide application can reduce runoff loses. However, the study was not specifically designed to address this question, so, without further investigation, no firm conclusion can be made on the effect of this practice on pesticide loss.

The low runoff losses from turf seen in this study suggest that other sources could be contributing to observed residues in urban streams. Other sources could include pyrethroids inadvertently applied or over sprayed on impervious surfaces, such as concrete driveways from off-target applications to turf, spills, and other poor-handling practices, or pyrethroids applied directly to impervious surfaces for insect control.

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