Supporting Information

Formulation Effects and the Off-target Transport of Pyrethroid Insecticides from Urban Hard Surfaces

Brant C. Jorgenson and Thomas M. Young†*

** Agricultural and Environmental Chemistry Graduate Group, University of California – Davis, One Shields Avenue, Davis, California, 95616, USA*

† Department of Civil and Environmental Engineering, University of California – Davis, One Shields Avenue, Davis, California, 95616, USA

Number of pages: 10

Number of figures: 2

Number of tables: 1

EXPANDED EXPERIMENTAL SECTION.

Rainfall Simulations. Drop forming rainfall simulators were designed and calibrated to specifications outlined by Battany and Grismer (*1*). Needle panels loaded with 23-gauge hypodermic syringe needles (B-D Precision Glide) were elevated 1.6 meters above the target surface, producing a homogeneous drop pattern and drop size that impacted the target surface at approximately 60% of terminal velocity (*2*). Simulators used a local treated groundwater supply (average hardness: 120 ppm) which was dechlorinated by granulated activated carbon filtration. Temperature of simulated rainfall averaged 19°C over the course of the study.

Surface runoff from simulations was collected as timed volume intervals, allowing for the measurement of both average runoff rate and total volume of simulated runoff (Table S1). Simulations were designed to control for five variables, including rainfall intensity, slope, product set time, pyrethroid active ingredient, and formulation type. Slope was held constant at 4 degrees from the horizontal. Rainfall intensity was controlled at either 25 mm/hr or 50 mm/hr, and simulations were performed for 60 minutes. Product set times investigated were 1.5 hours, 24 hours, and seven days from the time of product application. On some surfaces, successive simulations were conducted without intervening product application, starting at 1.5 h, 7 d, 21 d and 49 d after the initial application (1.5h, 7d 2^{nd}, 21d 3^{rd}, 49d 4^{th}).

Ten 80x80 cm plywood forms were constructed and 5 cm concrete slabs poured (Quickrete 5000). The surface of the concrete was brushed perpendicular to the course of surface flow and sealed to the forms with self leveling crack sealent (Quickrete No 8640). Plywood forms extended 5 cm above the concrete surface on 3 sides. Runoff was directed over a galvanized sheet metal lip into an aluminum collection channel. Runoff was collected from the channel though a short length of flexible siloconized tubing into pre-cleaned amber glass bottles (I-Chem 200 Series). A galvanized sheet metal shield, connected to the plywood forms, covered the lip and collection channel. The concrete surface was allowed to cure and weather with repeated washings prior to use in simulations. Prior to each product application, concrete surfaces were washed with water to remove settled material then allowed to dry. Treated slabs were stored outdoors where they were exposed to natural sunlight.

Determination of Pyrethroid, Surfactants, Suspended Solids. Neat standards of pyrethroids and C_{10}-C_{16} LAS were obtained from ChemService, Inc. (West Chester, PA). It was determined by fast atom bombardment mass spectroscopy (FAB-MS) that three of the four products tested in this study contained LAS to varying degree, therefore LAS was selected as a model surfactant for experimentation purposes. The CMC of the LAS was determined to be 250 mg/L using a SensaDyne QC6000 surface tensiometer in static mode at a bubble frequency of 0.8 bubbles/minute. Tensiometer data was plotted as the log of LAS concentration against surface tension, where CMC was taken as the intersection of two distinctly linear portions of the plot (*3*).

Extraction for pyrethroids and surfactants occurred between 3 and 24 hours following sample collection. Samples for pyrethroids and surfactants were subsampled in the laboratory by shaking the container to resuspend settled material and immediately drawing sample from mid-depth through a large-bore graduated pipette. For this study, batch permethrin matrix spike surrogate recoveries averaged 93%, with relative standard deviation between matrix spike duplicates of 4.9%.

Separate extraction of both pyrethroid and LAS surfactant was accomplished using an octodecyl (C-18) solid phase extraction cartridge (Supelco ENVI-C18) with a 500 mg sorbent bed. Pyrethroids were eluted with 10 mL mixture hexane/ethyl acetate (50/50 v/v; Fisher, Optima) and concentrated to 1 mL by nitrogen evaporation, or diluted if necessary. Surfactant was eluted with 10 mL methanol (Fisher, Optima) and similarly concentrated to 1 mL by nitrogen evaporation.

Quantitative determination of pyrethroids in simulated stormwater runoff samples was accomplished using an Agilent 6890 gas chromatograph with electron capture detection. Through use of a J&D Scientific DB-5 column (30 m x 0.25 mm x 0.25 μm) and a slow thermal gradient (100°C to 200°C at 15°C/min; 200°C to 250°C at 5 °C/min; 250°C to 290°C at 7 °C/min and hold for 2.5 minutes), resolution of cis and trans isomers could be obtained for bifenthrin, λ cyhalothrin, β cyfluthrin, and esfenvalerate.

Quantitative determination of LAS surfactant and qualitative investigation of formulated pyrethroid pesticide product composition were accomplished using an Agilent 1200 liquid chromatograph with diode array detection measuring at a 230 nm wavelength and inline with an Agilent 1200 evaporative light scattering detector (ELSD). Individual surfactant homologues were partially resolved utilizing a Dionex Acclaim surfactant column (4.6 x 250 mm x 5 μm) and slow mobile phase gradient (acetonitrile:ammonium acetate buffered water; pH 5.4; 35% to 95% ACN over 25 minutes and hold for 5 minutes).

Negative and positive ion fast atom bombardment (FAB) mass spectra were obtained for all formulated products utilizing a JEOL MSroute JMS-600h double focusing mass spectrometer and surfactants identified by comparison to mass fragment tables presented in Ventura et. al. (*4*). The FAB matrix consisted of 3-nitro benzyl alcohol and the samples were bombarded utilizing a xenon gun set to 2 keV. Analysis was performed by Drs. Jennifer Field and Jeff Morre of Oregon State University.

Total suspended solids analysis was conducted using a Whatman glass fiber filter (Whatman 934AH) following standard protocol (*5*). After being sub-sampled for pyrethroid and/or surfactant analysis, the remainder of the sample up to 1 L was passed through a clean and pre-weighed glass fiber filter. Dried residue mass was measured and results reported as milligrams per liter.

Experiments with Formulated Products. Four off-the-shelf general-use formulated products with labels permitting application to foundations and patios were tested. Products were prepared and applied to concrete surfaces per label specification and at label rates. Product labels did not prescribe a specific mass-per-area application ratebut rather generally specified that the surface be thoroughly “wetted with a coarse spray but without soaking”. In order to normalize surface treatment, application was conducted so that the entire concrete surface was wetted (approximately 55-65 grams of formulated product measured gravimetrically), with actual application rate recorded. Although application of formulated products were conducted in a similar manner and a similar volume, differences in active ingredient weight percentages resulted in different application masses across products. In those cases where the product was sold ready-to-use (RTU), the supplied pump action hand sprayer was utilized. In those cases where the product was sold as a dilutable liquid concentrate, a separately purchased home-and-garden pump action hand sprayer was used (Delta Industries, PA). Nozzles were adjusted to deliver a visually similar circular spray pattern. Manufacturer supplied or aftermarket sprayers generated a consistent circular spray pattern but visually heterogeneous drop size.

Experiments with Neat Pyrethroids. To investigate wash-off of pyrethroids free of any influence from formulation inerts, neat pyrethroid wash-off experiments were conducted utilizing esfenvalerate and bifenthrin. Neat esfenvalerate and bifenthrin were dissolved in hexane and applied to clean concrete surfaces at similar mass rates of application to their corresponding esfenvalerate EC and bifenthrin CE products. The hexane carrier was allowed to evaporate followed by a 25 mm/hr simulation 1.5 hours after application.

Experiments with Neat Bifenthrin and LAS. To investigate the role of surfactants in the wash-off of pyrethroids, an experiment with neat bifenthrin and LAS was conducted. Bifenthrin was first applied to the concrete surface in hexane at a rate equivalent to the corresponding bifenthrin CE product. The hexane was allowed to evaporate upon which LAS dissolved in deionized water was then applied to the same surface. LAS was applied at a rate of 906 mg/m^2. The deionized water carrier was allowed to evaporate followed by a 25 mm/hr simulation 1.5 hours after application.

EXPANDED RESULTS SECTION.

Total Suspended Solids. Total suspended solids was collected on all sample intervals. No positive correlation was observed between pyrethroid mass totals and suspended solids mass totals for all products. Figure S1 compares average pyrethroid mass totals with event suspended solids totals at 10 L of total runoff for the β cyfluthrin SC product and esfenvalerate EC products. Results were similar for the bifenthrin CE and λ cyhalothrin EC products. Elevated suspended solids with increased set time is a product of concrete surfaces accumulating particulate matter during the outdoor storage period between rainfall simulations.

Concrete as a Long-Term Source. As a final experiment, a single concrete test slab initially treated with 30.2 milligrams of our 2007 bifenthrin CE product was periodically rained on over the course of the study. As shown in Figure S2, after an initial mass loss of nearly 2,500 micrograms on day 1, at day 238 approximately 2 micrograms of bifenthrin continued to leach from the surface demonstrating that post-construction structural pest control treatments of concrete can remain a source of pyrethroid for a prolonged period of time.

TABLE S1. Rainfall simulator performance

Intensity (mm/hr)	25	50
Average steady-state runoff rate (L/min)	0.24	0.47
Average cumulative runoff (L)	14.0	28.5
CV runoff rate	0.037	0.027
n replicates	38	14

CV: coefficient of variation

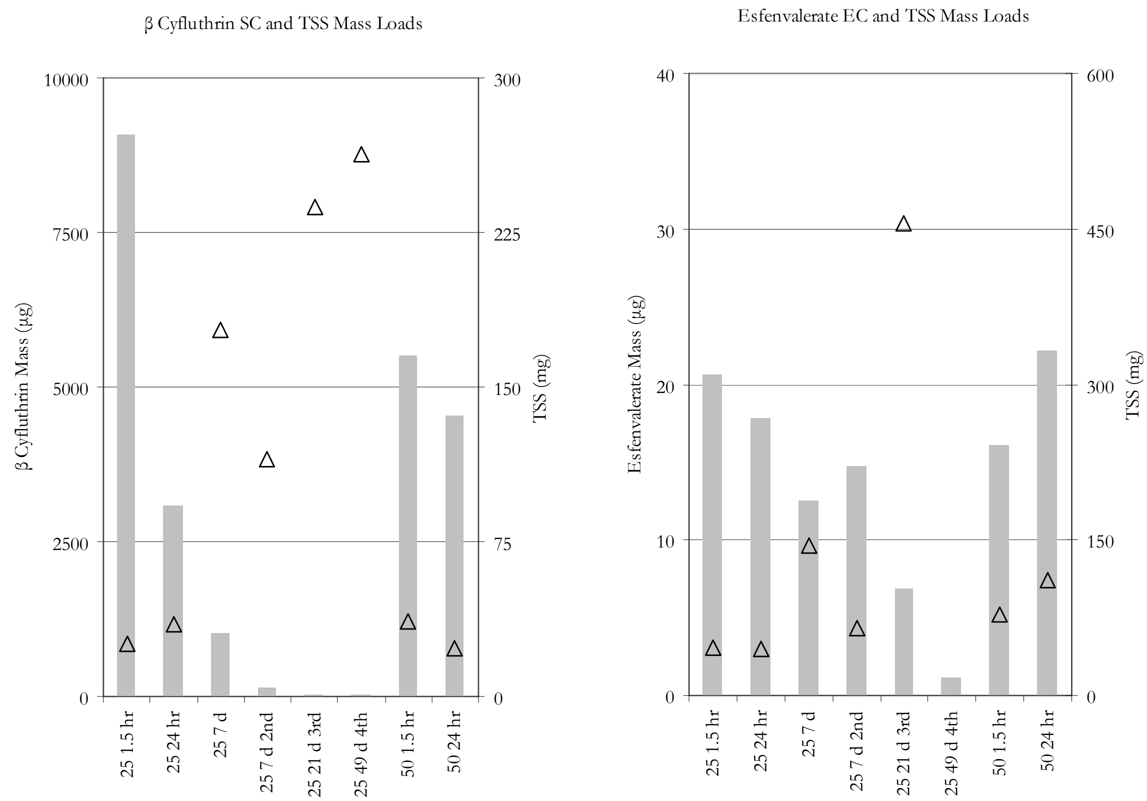

FIGURE S1. Pyrethroid and total suspended solids mass totals at 10 L of simulated runoff for β cyfluthrin and esfenvalerate products. Bars are average pyrethroid mass loadings and open triangles are average total suspended solid mass loading for the simulation listed (intensity and set time).

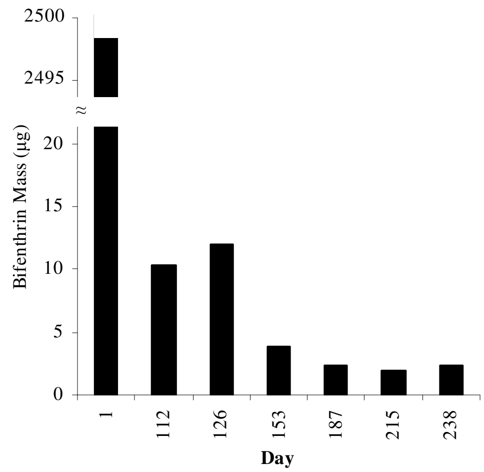

FIGURE S2. Bifenthrin mass in runoff collected from 2007 bifenthrin CE treated concrete over a 238 day study period.

SUPPORTING INFORMATION REFERENCES.

1 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.

2 Laws, J. O. Measurements of the fall-velocity of water-drops and raindrops. *Trans. Amer. Geophy. Union*. **1941**, *22*, 709-721.

3 Mukerjee, P.; Mysels, K., Eds. *Critical Micelle Concentrations of Aqueous Surfactant Systems*. NSRDS-NBS 36. United States Department of Commerce, National Bureau of Standards. Washington, D.C. 1971.

4 Ventura, F.; Caixach, J.; Figueras, A.; Espalder, I.; Fraisse, D.; Rivera, J. Identification of surfactants in water by FAB mass spectrometry. *Water Res.* **1989**, *23*, 1191-1203.

5 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.