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Occurrence, Fate and Transport Behaviors of Pesticides on Urban Impervious Surfaces

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Environmental Sciences

by

Weiying Jiang

June 2012

Dissertation Committee:

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The Dissertation of Weiyang Jiang is approved:

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ABSTRACT OF THE DISSERTATION

Occurrence, Fate and Transport Behaviors of Pesticides on Urban Impervious Surfaces

by

Weiying Jiang

Doctor of Philosophy, Graduate Program in Environmental Sciences

University of California, Riverside, June 2012

Dr. Jay Gan, Chairperson

Urban and residential areas are covered by impervious surfaces such as concrete. During rainfalls and irrigations, these surfaces transfer runoff directly to surface water through urban sewage. Impervious surfaces are highly possible to be contaminated with pesticides, through direct treatments or through indirect deposits from surrounding areas (e.g., lawns) via wind- or water-aided movements. Although pesticides have been widely found in urban watersheds, their persistence and runoff potential from impervious surfaces have been seldom studied.

This dissertation includes a series of lab and field scale experiments to assess pesticide contamination on concrete surfaces, as well as different environmental and application parameters that may affect their runoff potential.

The results showed pesticide wash-off potential from concrete rapidly decreased after treatments, but low levels were constantly detected in the water from concrete with extended outdoor exposure. Immediately after treatments with pesticides in liquid formulations, concrete surfaces were equilibrated with 30 mL CaCl_2 solution for 10 min to mimic runoff, and <25% of applied pesticides were recovered. The wash-off

percentage further decreased to <5% after 7-d. Higher wash-off potential was observed for solid formulated pesticides. The initial rapid loss of wash-off transferability was followed by a stage of sustained pesticide wash-off, which continued for over 112-d. The persistent wash-off potential was also observed for concrete repeatedly equilibrated with water once every 3-d. Most pesticides were still detectable after 10 times of washing-drying cycles.

To explain the observed wash-off patterns, sorption/desorption and degradation of permethrin on concrete were further studied using ¹⁴C-labeled permethrin. Although the sorption equilibrium was quickly achieved within 24-h, permethrin desorption continued for over 300-h, and around 20 % of applied ¹⁴C still remained on concrete after 300-h. If the desorption started 7-d after permethrin treatments, the amounts of desorbed permethrin decreased by 58 % compared the freshly spiked concrete.

Finally, field study was conducted to assess pesticide runoff following simulated and natural rainfalls. 80 % of runoff pyrethroids were found on suspended particles. Besides, a surface wiping method was developed to collect transferable particles from concrete and its potential to predict pesticide runoff prior to rainfall starts was demonstrated.

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CHAPTER 1

Introduction

Pesticide Use in Urban Environment

Pesticides are chemicals capable of repelling and killing unwelcome organisms, and are categorized into insecticides, herbicides, fungicides, etc. In United States, expenditures on pesticides for home and garden use increased from 1,108 to 2,664 million dollars during 1979-2007 (1). In 2010, 514,382 kg of pesticides were used by licensed California applicators for non-agricultural purposes, specifically structural pest control and landscape maintenance (2).

The heavy use of pesticides comes with concerns of their environmental contamination and risks to human and ecological health (3-6). For instance, the U.S. Environmental Protection Agency (EPA) sampled the indoor floors of 500 residential homes, and found pesticide residues nearly every residential home (4). Hintzen et al. found that 65 % of urban stream sediment samples contained insecticides beyond the lethal dose for a common toxicity test species *Hyalella azteca* (6).

The use of conventional organophosphate insecticides for residential pest control has been taken over by synthetic pyrethroids and fipronil in recent years, as they are selectively toxic to insects but safe to humans (7-9). During 2007 in U.S., pyrethroids were the second most commonly applied insecticides for home and garden uses (1). In California during 2010, licensed applicators used 17,391 kg fipronil and 152,990 kg pyrethroids for structural pest control and landscape maintenance in 2010 (2). While fipronil is sold only to professional applicators, pyrethroids are also contained in most of residential pest control products that are sold in retail stores (10).

Synthetic pyrethroids are chemicals with anthropogenic origins but structurally similar to pyrethrin extracted from *Chrysanthemum* flowers. This class of compounds blocks sodium channels along nerve cells and disrupts impulse transmission of target insects including ants and cockroaches (11-13). Since 1949, four generations of pyrethroids with over 10 different compounds have been introduced into market (14). In California, the most commonly used pyrethroids for non-agricultural purposes are permethrin, bifenthrin, cypermethrin and cyfluthrin. They accounted for 95% of total pyrethroid use in 2010, and were also the most commonly detected pyrethroids found in the environment and contributed most of the observed toxicities (7, 8, 15).

Fipronil, (±)-5-amino-1-(2,6-dichloro- α,α,α -trifluoro-*p*-tolyl)-4 [(trifluoromethyl)sulfinyl] pyrazole-3-carbonitrile, is a new phenylpyrazole insecticide first introduced to California in 1997 (2). Different from pyrethroids, fipronil binds to gamma-aminobutyric acid (GABA) of insects and disrupts their chloride uptake. In California, fipronil is almost exclusively used by professional applicators for structural pest control.

Both pyrethroids and fipronil are highly toxic to fish and invertebrates in surface water and sediments (16-21). For instance, the 48-h LC50 values of four pyrethroids (i.e., bifenthrin, cyfluthrin, lambda-cyhalothrin and tralomethrin) were 0.15-1.04 $\mu\text{g/L}$ for *Daphnia magna* and 0.07-0.30 $\mu\text{g/L}$ for *Ceriodaphnia dubia* (21). Pyrethroids and fipronil have been widely found in urban watersheds, and are the primary contributors to the observed toxicities (5-8, 15, 22-27). For instance, bifenthrin were detected in 94.1% of urban stream sediments sampled in Central Texas, and could account for 65% of sediment acute toxicities (6). In a 26-month monitoring study, the

median concentrations of fipronil and its degradates in the runoff from residential areas in Orange county, CA were 204–440 ng/L, which frequently exceeded the LC50 values to arthropods (24). In addition, both pyrethroids and fipronil are hydrophobic with octanol-water partitioning coefficient (K_{ow}) values over 10^4 , which increases their risk of accumulation in non-target organisms (28-31).

Although behaviors in urban environments are unknown, degradation of pyrethroids and fipronil in water, soils and sediments has been well studied. Depending on the environmental conditions, their degradation half lives may extend as long as years (32, 33). After sunlight exposure, fipronil is transformed to desulfinyl degradate (34-36). Fipronil degrades to fipronil sulfone in aerobic environments, but under anaerobic conditions, fipronil is transformed to fipronil sulfide (34, 35, 37, 38). The primary degradation pathway for pyrethroids is hydrolysis at the ester group, which forms alcohol and acid intermediates. Degradation products of pyrethroids and fipronil have been found to have greater environmental persistence and higher ecological toxicity than corresponding parent pesticides (34, 37, 39, 40, 41). For instance, under typical facultative conditions, the dissipation half lives of desulfinyl, sulfide and sulfone degradates of fipronil in urban stream sediments were 2.5-11.1, 3.9-7.7, and 5.5-18.9 times longer than the parent fipronil (34, 37). Tyler et al. found a common ester group cleavage degradate of pyrethroids, 3-phenoxybenzyl alcohol, has both estrogenic and antiandrogenic activities over 100 times greater than the parent permethrin (39).

Impervious Surfaces in Urban and Residential Areas

U.S. urban land areas increased by 56.7 % from 1982 to 2007 (42). Conversion of lands to urban and residential environments has significantly increased the areas of impervious surfaces, primarily concrete and asphalt (43). These materials are durable and water-resistant, and are widely used for streets, pedestrian sidewalk, parking lots and driveway, that may be directly connected to city hydraulic drainage systems (44). Depending on the site designs and land use type, impervious surfaces can account for up to 90% of total urban areas (44, 45). For instance, in residential areas, the percent of impervious coverage ranges from 12% to 65% (46). In commercial and business areas, the average coverage of impervious surfaces may be as high as 85% (46).

Concrete is a common anthropogenic material for surface pavements, and is prepared by mixing Portland cement and aggregates (sands and gravels) together, then added with water. The main minerals in hydrated concrete are amorphous calcium silicate hydrate (C-S-H) and crystalline calcium hydroxide, which may also incorporate foreign ions such as Mg^{2+} , Al^{3+} , K^+ and Na^+ (47-50). The space between solid materials is occupied by the continuous pore network. Depending on the initial water/cement ratio, voids can account for up to 50 % of total concrete volume (47, 50).

For urban and residential pest controls, pesticides may be directly applied on impervious surfaces (51). For instance, Flint reported 60% of California residential outdoor pesticide use is on impervious surfaces (52). In addition, wind, water and foot-tracking can also carry pesticides from lawns and turfs onto impervious surfaces. Although direct evidence is lacking, pyrethroids and fipronil are expected to sorb on

concrete due to their hydrophobicity, as pyrethroids were found quickly sorbed on glass, and the sorption may also take place in concrete porous structure (53). Besides sorption, concrete also contains great amounts of alkalinities and a large surface area, which provide various reaction sites for pesticide hydrolysis, and the rigid structure of concrete retained most treated pesticides in the surface layer making them easily to be oxidized and/or photolyzed (47, 48, 50, 54). Unfortunately, none of these processes have been studied.

Current Research Progress and Knowledge Gap

The percentage of impervious surface coverage is an important index to describe urbanization. The detection frequency and concentrations of pesticides and their degradates in the surface water have been found well correlated to the amounts of pesticide used and urbanization levels in the sampling areas (8, 24, 55). However, compared to the wealth of knowledge on pesticide behaviors in water, soils and sediments, information with regards to urban impervious surfaces is scarce, and most of existing studies stopped at the monitoring levels. This is primarily caused by the lack of standardized methods to directly quantify pesticide runoff potential, and the absence of analytical methods to accurately measure trace organic contaminants on impervious materials.

While behaviors of hydrophobic pesticides are not clear, a few studies have been conducted to assess runoff of hydrophilic herbicides from concrete and asphalt surfaces (56-59). Herbicide runoff decreased from 73 % to <10% with increasing K_{oc}

(soil organic carbon-water partitioning coefficient) values, and the runoff concentrations also rapidly decreased during a precipitation event (56, 59). Ramwell et al. furthermore found the equilibrium of herbicide sorption on concrete was quickly achieved within 2 h, and more diuron and diflufenican were found sorbed on concrete than on asphalt or soil (57, 58). This indicates other mechanisms independent of pesticide hydrophobicity were involved in their sorption on concrete. However, most of studied herbicides are water soluble (>1 mg/L), which makes it difficult to extrapolate the research conclusions to current use hydrophobic insecticides.

Studies on pyrethroid and fipronil runoff from concrete started until recent five years, and strong retention on concrete was observed as repeated runoff could not recover all treated pesticides (60, 61). Jorgenson et al. found that four-time repeated runoff could only account for 9.8% of β -cyfluthrin and 2.1% of esfenvalerate treated from concrete (60). They also found that same pesticide in different formulations showed different runoff potential, and the addition of surfactants (i.e., linear alkyl benzene sulfonate) enhanced pyrethroid runoff from concrete. Another reason for low recoveries of pesticides in the runoff water was transformation on concrete. For instance, fast photolysis of fipronil on concrete produced desulfinyl fipronil, which resulted in the detection of more desulfinyl degradate in the runoff than the parent fipronil 7 d after treatments (61). However, both studies were terminated within 50 d of pesticide treatments, and provided no information for pesticide and degradate runoff after extended outdoor exposure. Meanwhile, the effects of other factors, such as different precipitation intensities, water volumes, and various types of concrete surfaces, on the pesticide

amounts and concentrations in the runoff have not been weighted. The scarcity of information hampered the understanding of current urban pesticide contaminations, and decreased our ability to model, predict, regulate and mitigate these compounds.

Research Objectives

Concrete was selected as a model impervious surface to examine the runoff potential of pyrethroids and fipronil, two of the most commonly used hydrophobic pesticide classes in urban and residential areas. The general objective is to study the occurrence and behaviors of pesticide on concrete, which determine their potential of runoff contamination. A series of factors that may be encountered in the real environment were assessed to determine their effects on pesticide runoff potential. Due to the lack of reference research and standardized methods, the research objective was achieved following three progressive steps, and concrete surfaces in different dimensions were prepared correspondingly. Specifically,

(1) Design feasible bench-top methods to quantitatively assess pesticide wash-off from concrete after treatments, and explore possible factors that may influence the wash-off potential;

(2) Analyze sorption, desorption and degradation of pesticides on concrete, and evaluate their effects on amounts and rates of pesticide runoff from concrete;

(3) Expand the previous bench-top work to a field scale study in order to mimic the processes in the real environment.

For the first task, we prepared a concrete disk fixed into the bottom of a small glass jar, so only the top concrete surface could be in contact with water. Concrete surface was treated with different pesticides in different formulations. Four pyrethroids (i.e., bifenthrin, cyfluthrin, lambda-cyhalothrin and permethrin) and fipronil were selected and two formulations (liquid and solid) were investigated. The treated concrete was exposed to outdoor conditions for different periods, and the wash-off potential was expressed as the percentages of pesticides transferred into 30 mL calcium chloride solution to the applied amounts after vigorous shaking for 10 min. Pesticide removal following two types of wash-offs was assessed to represent two typical irrigation/rainfall scenarios, i.e. single-time wash-off after different periods of outdoor exposure or repeated wash-off every 3 days.

For the second task, we used permethrin labeled with ^{14}C to simplify chemical analysis, and its sorption, desorption and degradation were evaluated using small custom-made concrete cubes. During desorption, Tenax beads were added into water to trap all desorbed permethrin from concrete. Tenax also kept aqueous permethrin concentration at almost zero and simulated treated concrete flushed with continuous runoff. Besides measuring ^{14}C using liquid scintillation counter (LSC), we also employed gas-chromatography (GC) to identify parent permethrin from total ^{14}C wash-off. The combination of GC and LSC helped evaluate the consequences of permethrin degradation on the concrete and the occurrence of both parent and degradation compounds in the wash-off water.

For the third task, pesticide runoff following simulated and natural rainfalls was evaluated in a field-scale setup and large concrete slabs were constructed. Pesticide partitioning in aqueous and solid phases of the runoff water was investigated in order to determine their removal pathway from concrete and forecast their behaviors after entering the surface water. In addition to analyzing the runoff water, we also developed a surface wiping method to measure the portion of pesticides on concrete that are susceptible of runoff removal. The method provides an alternative solution to predict pesticide runoff before irrigation or rainfall actually occurs.

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CHAPTER 2

Wash-off Potential of Urban Use Insecticides on Concrete Surfaces

Abstract

Contamination of surface aquatic systems by insecticides is an emerging concern in urban watersheds, but sources of contamination are poorly understood, hindering development of regulatory or mitigation strategies. Hardscapes such as concrete surfaces are considered an important facilitator for pesticide runoff following applications around homes. However, pesticide behavior on concrete has seldom been studied, and standardized evaluation methods are nonexistent. In the present study, a simple batch method for measuring pesticide wash-off potential from concrete surfaces was developed, and the dependence of washable pesticide residues was evaluated on pesticide types, formulations, time exposed to outdoor conditions, and number of washing cycles. After application to concrete, the washable fraction of four pyrethroids (bifenthrin, permethrin, cyfluthrin, and cyhalothrin) and fipronil rapidly decreased, with half-lives ≤ 3 d, likely due to irreversible retention in micropores below the concrete surface. The initial fast decrease was followed by a much slower declining phase with half-lives ranging from one week to two months, and detectable residues were still found in the wash-off solution for most treatments after 112 d. The slow decrease may be attributed to a fraction of pesticides being isolated from degradation or volatilization after retention below the concrete surface. Wash-off potential was consistently higher for solid formulations than for liquid formulations, implying an increased runoff contamination risk for granular and powder formulations. Trace levels of pyrethroids were detected in the wash-off solution even after 14 washing–drying cycles over 42 d under outdoor conditions. Results from the present study suggest that pesticide residues remain on

concrete and are available for contaminating runoff for a prolonged time. Mechanisms for the long persistence were not clearly known from the present study and merit further investigation.

Keywords—Urban pesticides, Pyrethroids, Fipronil, Hardscapes, Pesticide runoff

Introduction

Insecticides are widely used in urban areas for control of vector, structural, and other insects. Owing to potential adverse health or ecological effects, many historically important pesticides, including many organochlorines and some organophosphates (e.g., diazinon and chlorpyrifos) have been discontinued for residential use in the United States (1,2). Consequently, the use of replacement insecticides such as pyrethroids and fipronil has increased in recent years. For example, most insecticides sold in retail stores for residential use in California, USA, contain pyrethroids as active ingredients ([3,4]; <http://www.up3project.org/documents/Final2005ShelfSurvey.pdf>). The total amounts of pyrethroids and fipronil reported by licensed applicators for structural pest control and landscape maintenance in California increased from 195,360 kg and 3,560 kg, respectively, in 2001 to 247,295 kg and 29,478 kg, respectively, in 2007 ((5); http://www.cdpr.ca.gov/docs/pur/pur07rep/07_pur.htm). In addition, surveys show that home owners also use significant amounts of pesticides, although the use is very poorly tracked or understood ((6); <http://www.tdcenvironmental.com/UP3%20Use%20Report%-202006.pdf>).

The widespread use of insecticides in urban areas has apparently contributed to contamination of urban streams, estuaries, and other surface water bodies, and resulted in sediment and water-column toxicities. Recent monitoring studies show almost ubiquitous contamination of urban bed sediments by pyrethroids in California, often at concentrations acutely toxic to benthic invertebrates (2,7,8). For instance, sediments and water sampled from mouths of urban drains verified their presence of various pyrethroids, and the concentrations were generally far beyond acutely toxic thresholds for aquatic invertebrates (9). Residues of pyrethroids were found in sediments of various urban creeks in other studies (1). In addition, fipronil and its metabolites have also been detected in urban streams (10).

Urbanized areas are distinguished by hardscapes, especially concrete surfaces that are generally termed impervious surfaces (11). Such hard surfaces are estimated to account for 20 to 90% of urban surfaces areas, depending on the site design (11,12; <http://www.cpesc.org/reference/tr55.pdf>, (13); <http://www.ci.olympia.wa.us/en/city-utilities/storm-and-surface-water/scienceandinnovations.aspx>). For instance, impervious surfaces comprise 25 to 60% of surfaces in a typical medium-density, single family home residential area (13). Urban hardscapes have low infiltration rates and are designed to facilitate surface runoff that may contain pollutants (11,14–16). Pesticides may be applied directly to concrete or similar hard surfaces, such as in treatments for ant trail eradication. A survey shows that 60% of residential outdoor pesticides used in regions such as California are for treatments on hard surfaces (3). In addition, drift during

application and wind/water-facilitated transport may also cause pesticides to deposit on hard surfaces (16–18).

Although pesticide fate and transport have been well studied in soil, very little is known about pesticide behavior on hardscapes such as concrete. Basic methods for evaluating pesticide persistence or runoff potentials on hard surfaces are lacking. The general paucity of research on pesticide fate and transport on urban hardscapes hampers accurate assessment of pesticide sources in urban watersheds and prevents development of scientifically sound regulatory and mitigation practices. Therefore, the objectives of the present study were to develop a simple batch method for quantifying the water wash-off potential of pesticides and to use the method to investigate the fate and persistence of common urban-use insecticides on concrete.

Materials and Methods

Chemicals

Bifenthrin, cyhalothrin, permethrin, cyfluthrin, and fipronil are among the most prevalent urban-use insecticides in regions such as California and were considered in the present study. Commercial formulations of these test compounds were purchased from various sources and used as received. Both solid and liquid formulations were included for bifenthrin, cyhalothrin, and permethrin to assess the effect of formulation. The solid formulations were wettable coarse granules for cyhalothrin, fine granules for bifenthrin, and dust for permethrin. The liquid formulations were ready-to-spray dilute solutions, except for permethrin and fipronil, which were concentrate solutions for permethrin and

suspended concentrate for fipronil. Before use, these products were analyzed and their actual active ingredient contents were found to be close to the labeled values. Chemical standards of the used pesticides were obtained from the manufacturers and Chem Service. Other chemicals and solvents were from Fisher Scientific and were of analytical grade or gas chromatograph (GC) grade. All glassware and sodium sulfate used were baked at 400 °C for 4 h before use to prevent possible cross contamination.

Preparation of concrete surfaces

Concrete disks were prepared in small glass jars (50mm inner diameter × 65mm height; Fisher Scientific) for use as the concrete surfaces throughout the present study. Briefly, a commercially available concrete mix (Pakmix[®]) from a local retailer was sieved (<5 mm) and mixed with water in a concrete mixer to form a cement slurry using a cement-to-water ratio of 5:1 (w/w). After mixing, 50 g (wet wt) of the concrete slurry was poured into a glass jar, and the jar was gently shaken by hand to allow the wet cement to form an even surface. The concrete jars were then kept in a greenhouse for at least 3 d to solidify. This preparation resulted in a concrete disk approximately 13mm thick, with the bottom and side surfaces fixated to the bottom and side walls of the jar. During solidification, a small amount of water was sprayed on the concrete surfaces three times a day. Before use, all dried concrete disks were conditioned by alternately rinsing with tap water and drying in the greenhouse for over 10 times to reduce the alkalinity. The conditioning procedure was repeated until the pH of 50 ml rinsing solution after 10 min mixing was under pH 9.0. The rinsing process, which took around two months, was

expected to complete the hydration of concrete and cure the product. All the conditioned concrete disks were saturated with deionized water overnight and air dried prior to use.

Pesticide treatment

The dry concrete disks were separated into multiple groups and spiked with different pesticides on the surface. The spiked amounts were based on the label recommendations and therefore the treatments represented direct application scenarios (Table 2-1). For liquid formulations, a pipette was used to uniformly apply the pesticide solutions onto the surface. For solid formulations, a given amount was weighed and then evenly transferred onto the surface, following by the application of a water mist (to hold the particles in place under windy conditions).

Measuring pesticide wash-off potential after outdoor exposure

After pesticide treatment, the concrete jars were transferred to outdoors under direct sunlight. On 0 (without outdoor exposure), 2, 7, 14, 28, 56, and 112 d after the treatment, three jars from each pesticide formulation as well as three control samples (no pesticide) were removed and immediately stored in a freezer at -18 °C until analysis. To simulate pesticide available for contaminating runoff water from a post application rainfall or irrigation, the treated concrete surfaces were subjected to 10-min washing with water. The fraction of pesticide transferred into the water phase was used to evaluate the washoff potential in the present study. For analysis, sample jars were transferred out of the freezer and equilibrated to room temperature, followed by addition of 30 ml 0.01M

CaCl₂ solution. The jars were screw-closed with Teflon-lined caps and were shaken on a horizontal shaker at 240 rpm for 10 min. Immediately after shaking, the overlying water solution from each sample was collected and extracted with 20 ml methylene chloride for three consecutive times in glass separatory funnels. The solvent extracts were combined and then concentrated to near dryness on a vacuumed rotary evaporator. Pesticide residues were recovered in hexane-acetone (9:1, v/v), and an aliquot was used for GC analysis to determine the pesticide concentration in the wash-off solution.

To determine the mass of pesticide remaining in the concrete after the washing step, concrete disks after 56 d were further subjected to solvent extraction. The washed concrete jars were extracted with 50 ml acetone for four consecutive times, using fresh solvent for each extraction. The extraction was carried out by sonicating the sample and solvent in a water bath (Fisher Scientific) at 42 kHz and room temperature for 5 min. The solvent extract from each extraction step was separately collected and concentrated to near dryness on a vacuumed rotary evaporator. The residues were redissolved in 1.0 ml hexane/acetone (9/1, v/v), from which an aliquot was analyzed by GC.

Measuring pesticide wash-off potential after repeated washings

In reality, a pesticide-contaminated concrete may be exposed to runoff water multiple times due to recurring irrigation or rain events. Another experiment was conducted in which the same concrete surfaces were repeatedly washed and dried when exposed to outdoor conditions. Seven pyrethroid formulations were included in this experiment (Table 2-1). After pesticide application, the concrete disks were placed

outside under direct sunlight. Concrete disks were subjected to a 10-min washing cycle 3 d after treatment, and the washed disks were again exposed to outdoor conditions. The same procedure as in the above single-washing experiment was used for washing and subsequent analysis of pesticide transferred into the wash-off solution. Washing and drying were repeated for a total of 14 times, when the same concrete disks were exposed to outdoor conditions for a cumulative 42 d.

Chemical analysis

Pesticide analysis was carried out using an Agilent 6890 GC (Agilent) equipped with a micro-electron capture detector. Samples were introduced through a splitless inlet. Separation was achieved by using a HP-5MS capillary column (30 m × 0.25 mm inner diameter × 0.25 mm film thickness; Agilent). The flow rate of carrier gas (helium) was 1.5 ml/min. The oven was initially set at 160 °C for 1.0 min, ramped to 260 °C at 3 °C /min, then ramped to 300 °C at 30 °C /min and finally held at 300 °C for 15 min. External calibration with standards of known concentrations was used to quantify pesticide concentrations in samples and 2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl were used as surrogates to determine extraction recoveries.

Results and Discussion

Pesticide wash-off potential under outdoor conditions

During the outdoor experiment, a light rain fell on day 50; however, the precipitation was small and no significant water accumulation occurred in the jars. From

records at a local climate station, during the exposure, it was mostly sunny with 29.7 °C average daily maximum temperature, 14.8 °C average daily minimum temperature, and 48 % mean relative air humidity (<http://www.cimis.water.ca.gov/>). The overall weather conditions during the outdoor experiment were therefore warm and dry, representing a typical summer in the arid southwestern region of the United States when the use of insecticides for control of insects such as ants is most common.

There was no standard method for measuring pesticide wash-off potential from landscape surfaces. In the present study, the wash-off potential of pesticides was operationally defined as the fraction of pesticide moved into water after the concrete disk was actively mixed in 30 ml CaCl₂ solution for 10 min. Pesticides in the wash-off solution as percentages of the initially spiked amounts are plotted against outdoor exposure time in Figure 2-1. In general, all of the test pesticides displayed a rapid decreasing trend initially. It is also clear that decrease of washable residues, except for permethrin solid formulation, did not follow simple first-order kinetics for the entire study duration (Fig. 2-1). For most treatments, there was an initial rapid decreasing phase, followed by a slower second phase. To account for the biphasic behavior, decrease of washable pesticide residues was evaluated by dividing the entire study duration into two phases, with 0 to 7 d for the first phase, and 14 to 112 d for the second phase. Data from both phases were separately fitted to a first-order decay model to derive the decrease rate constant k (d⁻¹) and half-decrease time (DT50, d) (Table 2-2). The fit to the first-order kinetics model was good for the first phase for all pesticide treatments, with R² value ranging from 0.71 to 0.99 (Table 2-2). For the slow phase, the fit was good for some

treatments, with R^2 ranging from 0.76 to 0.99, but were poor for solid formulation of lambda-cyhalothrin and liquid formulations of cyfluthrin and fipronil ($R^2 = 0.51 - 0.63$) (Table 2-2). The poor fit may be attributed to the insignificant differences in concentrations for samples from days 56 and 112, because measurements on these days contained relatively large standard deviations due to the very low concentrations. For treatments other than bifenthrin and permethrin solid formulations, the half-life (DT50) calculated for the second phase was longer than that for the first phase by 3.7 to 28 times for the same pesticide formulation (Table 2-2). For the solid formulations of bifenthrin and permethrin, the DT50s were almost identical for the two phases. With the exception for bifenthrin and permethrin solid formulations, the first-phase DT50s were only 0.9 to 3.3 d for the test products, suggesting a very rapid initial loss of the washable fraction once the pesticide came into contact with concrete under outdoor conditions. In comparison, decline of pesticides after 7 d significantly slowed, and DT50s for the second phase ranged from approximately one week to two months.

For the same pesticide, there were consistent differences between the solid and liquid formulations in the initial decreasing rate, with the solid formulations displaying slower decreases than the corresponding liquid formulations (Fig. 2-1). For example, for the first phase, DT50 of the solid formulation bifenthrin was 10 times of that of liquid formulation. After 7 d of exposure, approximately 35.3 ± 5.1 ppb of lambda-cyhalothrin was found in the wash-off from the solid formulation treatment, but only 1.5 ± 0.5 ppb was detected for the liquid formulation treatment. After 56 d of exposure, while the concentration of lambda-cyhalothrin in the wash-off from the solid formulation treatment

was 10.9 ± 3.1 ppb, it was below the detection limit (0.05 ppb) for the liquid formulation. The solid formulations also showed more persistence overall, with substantially higher residues detected in the wash-off solution after 56 or 112 d than the liquid formulations (Fig. 2-1). The slower pesticide decrease of solid formulations on concrete was likely due to the fact that the active ingredients in solid formulations were initially contained in solid carrier materials and partially shielded from direct exposure to the environment or penetration into the concrete. The above observations suggest that, under the same conditions, solid formulations of a pesticide are more likely to contaminate runoff water than liquid formulations, especially during the early stage after application.

For the different pesticides, the rates at which the wash-off potential decreased also differed, and the differences were more pronounced for the second phase. Among the four liquid formulated pyrethroids, the second-phase DT50s were longer for cyfluthrin, bifenthrin, and permethrin than for lambda cyhalothrin (Table 2-2). Compared to the liquid formulations of pyrethroids, the first-phase DT50 of fipronil was relatively long at 3.3 d (compared to 0.9 to 3.0 d for pyrethroids), while the second-phase DT50 (12.2 d) was within the range for pyrethroids (6.2 to 25.4 d) (Table 2-2). The relative stability of bifenthrin, permethrin, cyfluthrin, and fipronil on concrete surfaces may offer an explanation for their frequent detections in urban surface aquatic systems. For example, bifenthrin, permethrin, and cyfluthrin were among the most frequently detected compounds in surveys for sediment residues in California (1,2,7).

The prolonged persistence of pesticides on concrete surfaces was in a stark contrast with the rapid disappearance of washable residue immediately after pesticide

treatment. In particular, the 0-day samples were washed directly without ever being exposed to outdoor conditions, but the fraction of pesticide found in the wash-off solution ranged from only 4.3% for liquid formulation lambda-cyhalothrin to 35.9% for liquid formulation fipronil (Table 2-3). The low recoveries may not be attributed to solubility limitations, because commercial formulations containing carrier materials or surfactants were used. The rapid losses were likely due to irreversible retention of pesticides by the concrete. Although concrete is considered impermeable on the macroscale, it is known that the microstructure of concrete contains pores, including capillary pores and larger fractal pores derived from the hollow shell hydration mechanism (19–21). It is likely that the inner pores played an important role in the irreversible pesticide retention. In addition, pyrethroids are known to easily adsorb onto glass surfaces, and the sorption is so strong that exhaustive solvent extraction is often incapable of recovering the entire adsorbed fraction (22). Concrete has a similar chemical composition to glass, with calcium silicates as the main components of portland cement that bonds sand and other aggregates together in a concrete product (21,23). Therefore, it is probable that irreversible sorption of pyrethroids occurred below the surface of concrete, but this assumption needs to be further explored through controlled experiments.

Washable pesticide residues after long-time exposure

In areas such as California, pesticide use is most intense during the summer months when pest pressure is high, but precipitation usually does not occur until November. Therefore, washable pesticide residues on concrete surfaces after a prolonged

interval likely contribute the most to pesticide contamination in runoff during the first few storms. From Table 2-4, detectable residues were found for the liquid formulations of bifenthrin, permethrin, and cyfluthrin on days 56 or 112, although not for lambda-cyhalothrin. The relatively long persistence of fipronil was also evident from the fact that detectable levels of fipronil were found in the wash-off solution from both 56-d and 112-d samples (Table 2-4).

To determine the available residues after long-time exposure, the 56-d concrete disks, after washing with water, were further subjected to repeated acetone extractions after they underwent the water washing step (Table 2-5). It is evident that with the exception of liquid-formulated lambda-cyhalothrin and fipronil treatments, a significant fraction of pesticide residue still remained on the concrete after 56 d of exposure. In particular, a substantial fraction of the initially spiked pesticide was recovered after the first acetone extraction for the solid formulations of bifenthrin and lambda-cyhalothrin, and the liquid formulation of cyfluthrin (Table 2-5). Detectable residues were further found for most pesticides in the fourth (last) acetone extraction, suggesting that the remaining residues were not readily recovered by acetone and may be strongly retained at inner sites below the surface (Table 2-5). These observations suggest that pesticide residues on concrete may be available for transferring into runoff flow long after treatment. However, the mechanisms for the prolonged availability of pesticide residues on concrete were not investigated in the present study, and should be an important topic for further research.

Wash-off potential during repeated washings

Pesticides deposited onto concrete surfaces may be subject to washing by runoff water in a repeated fashion, as in prescheduled irrigation events or periodical rain storms. Concrete disks treated with pyrethroids were exposed to outdoor conditions, and wash-off potential was measured at 3-d intervals for the same disks when exposed to summer conditions. All pyrethroids displayed rapid losses of washable residues initially (Fig. 2-2). After 3 d of exposure, the wash-off fractions ranged from 0.023% for lambda-cyhalothrin liquid formulation to 26.7% for permethrin solid formulation, with solid formulations consistently showing higher wash-off potentials than the corresponding liquid formulations. The low recoveries and differences between formulations were in agreement with those observed in the above single-washing experiment.

Pyrethroids were consistently found in the wash-off solutions after multiple washing–drying cycles. Detectable residue was found in the 4th wash-off solution for the liquid formulation lambda-cyhalothrin and the 7th wash-off for liquid formulation cyfluthrin, while permethrin residue was found in the 10th (liquid) or 11th wash-off solutions (solid). The most persistent treatments were solid formulation of lambda-cyhalothrin, and liquid and solid formulations of bifenthrin, where detectable residues were present in the 14th (last) wash-off solution, when the disks had been washed 13 times or exposed to outdoor conditions for a cumulative 42 d (Fig. 2-2). Bifenthrin was found in the last set of wash-off solutions at $0.21 \pm 0.04 \mu\text{g/L}$ for the solid formulation, and $0.24 \pm 0.07 \mu\text{g/L}$ for the liquid formulation, levels sufficiently high to

cause mortality to aquatic invertebrates such as *Ceriodaphnia dubia* (LC50 = 0.078 µg/L) (24). The prolonged availability of bifenthrin was consistent with the single-washing experiment, and again may explain why bifenthrin has been found in urban surface streams at a much greater frequency than the other insecticides (24). The extended potential for pyrethroids to enter runoff water suggests that contaminated concrete may serve as a reservoir for pyrethroids during recurring irrigation or precipitation events, resulting in sustained levels of pyrethroids in urban streams that are recharged with residential runoff effluents.

Hardscapes such as concrete in urbanized areas are direct and indirect targets for insecticide application. However, although urban hardscapes are suspected to facilitate non-point source pollution through irrigation and rain-induced runoff, little is known about the fate and transport of pesticides after they come into contact with concrete surfaces. Results from the present study, although rather explorative in nature, showed for the first time, to our knowledge, that common urban-use insecticides may be available for contaminating runoff water long after their initial deposition onto a concrete surface. The persistence occurred despite the fact that the majority of the pesticide was not susceptible to removal by washing shortly after treatment. It appears that these pesticides were retained below the surface, likely in the micropores, due to physical trapping or chemical sorption. Differences were also seen between liquid and solid formulations for the same compound, with residues from solid formulations being more persistent. The long persistence of pesticides on concrete suggests that pesticides applied during the summer months may be available for contaminating runoff during the first few

winter storms in areas such as California. It also suggests that urban hardscapes, once contaminated by pesticides, may serve as a sustained source for pesticides in urban watersheds. The mechanisms for the prolonged pesticide persistence on concrete were not understood from the present study, and warrant further investigation.

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Table 2-1. Pesticide formulations and content of active ingredients

Pesticide	Formulation	Trade Name	Spiked amount per disk (μg)
Bifenthrin	granule	Ortho-Home Defense Max [®] , Scotts, Marysville, OH, USA	81.6
Bifenthrin	liquid	Ortho-Home Defense Max [®] , Scotts, Marysville, OH, USA	86.2
Lambda-cyhalothrin	granule	Spectacide Triazicide [®] , Spectrum Brands, Sandy Springs, GA, USA	132.6
Lambda-cyhalothrin	liquid	Spectacide Triazicide [®] , Spectrum Brands, Sandy Springs, GA, USA	142.8
Permethrin	dust	Ortho-BugBGon Max [®] , Scotts, Marysville, OH, USA	350.9
Permethrin	liquid	Spectracide Terminate [®] , Spectrum Brands, Sandy Springs, GA, USA	234.4
Cyfluthrin	liquid	Real-Kill [®] , Realex, St. Louis, MO, USA	70.0
Fipronil	liquid	Termidor [®] , BASF, Ludwigshafen, Germany	267.4

Table 2-2. Kinetic parameters of first-order decay models for the decrease of pesticides in wash-off from the concrete surface ^a

Pesticide	Formulation	Fast stage (0-7 d)			Slow stage (14-116 d)		
		k (d ⁻¹)	DT50 (d)	r^2	k (d ⁻¹)	DT50 (d)	r^2
Bifenthrin	granule	0.073	9.4	0.8	0.099	7	0.96
	liquid	0.764	0.9	0.75	0.027	25.4	0.76
Lambda-cyhalothrin	granule	0.34	2	0.97	0.019	35.7	0.55
	liquid	0.632	1.1	0.81	0.111	6.2	0.81
Permethrin	dust	0.104	6.7	0.93	0.075	9.3	0.99
	liquid	0.629	1.1	0.71	0.046	15.2	0.76
Cyfluthrin	liquid	0.229	3	0.99	0.01	66.6	0.51
Fipronil	liquid	0.212	3.3	0.88	0.057	12.2	0.63

^a k (d⁻¹) = the first-order rate constant; DT50 = the time at which 50% of the initial amount has decreased; r^2 = the coefficient of determination.

Table 2-3. Percentages of pesticides detected in wash-off water solutions from spiked concrete disks on 0 day (before outdoor exposure)

Pesticide	Formulation	Concentration ($\mu\text{g/L}$)	% ^a
Bifenthrin	granule	934.81 \pm 13.69	34.4 \pm 0.5
	liquid	705.88 \pm 16.95	24.6 \pm 0.6
Lambda-cyhalothrin	granule	348.70 \pm 25.71	7.9 \pm 0.6
	liquid	202.81 \pm 9.87	4.3 \pm 0.2
Permethrin	dust	3778.64 \pm 355.00	32.3 \pm 3.0
	liquid	2150.05 \pm 256.03	27.5 \pm 3.3
Cyfluthrin	liquid	461.07 \pm 4.32	19.7 \pm 0.2
Fipronil	liquid	3202.04 \pm 439.77	35.9 \pm 4.9

^a %, pesticide detected in the wash-off solution as percentage of initially spiked amount.

Table 2-4. Pesticide concentrations ($\mu\text{g/L}$, mean and standard deviation, $n = 3$) in wash-off solutions after long-time exposure to outdoors conditions ^a

Pesticide	56 d		112 d	
	Liquid	Solid	Liquid	Solid
Bifenthrin	0.14 \pm 0	3.44 \pm 1.68	0.06 \pm 0.03	12.3 \pm 4.6
Lambda-cyhalothrin	ND	10.9 \pm 3.1	ND	27.7 \pm 14.6
Permethrin	1.86 \pm 0.31	35.1 \pm 11.2	0.93 \pm 0.08	0.77 \pm 0.24
Cyfluthrin	55.0 \pm 18.9	NA	79.9 \pm 34.4	NA
Fipronil	1.01 \pm 0.58	NA	0.70 \pm 0.39	NA

^a NA=not applicable (solid-formulated cyfluthrin and fipronil were not included in this study); ND=not detected.

Table 2-5. Acetone-extractable pesticide residues from water washed concrete disks after 56 d of outdoor exposure ^a

Pesticide	Acetone-extractable residue after consecutive extractions (%) ^b			
	1st extraction	2nd extraction	3rd extraction	4th extraction
Bifenthrin (S)	2.63±0.91	0.18±0.07	0.15 ± 0.02	0.10 ± 0.04
Bifenthrin (L)	0.45±0.04	0.32±0.07	0.28 ± 0.07	0.17 ± 0.10
L-cyhalothrin (S)	11.0±1.77	1.37±0.30	0.78 ± 0.10	0.69 ± 0.08
L-cyhalothrin (L)	1.0±0.4×10 ⁻³	0.4±0.02×10 ⁻³	0.3±0.03×10 ⁻³	0.4 ± 0.09×10 ⁻³
Permethrin (S)	0.42±0.13	0.05±0.006	0.02 ± 0.002	0.01 ± 0.004
Permethrin (L)	0.22±0.04	0.09±0.04	0.06 ± 0.03	0.04 ± 0.03
Cyfluthrin (L)	4.58±1.12	0.09±0.03	0.05 ± 0.01	0.05 ± 0.009
Fipronil (L)	0.01±0.002	0.7± 0.1×10 ⁻³	0.3±0.2×10 ⁻³	ND

^a L=liquid; S=solid; L-cyhalothrin=Lambda-cyhalothrin; ND=not detected.

^b %=amount extracted by acetone as percentage of the initial spiked amount.

Figure 2-1. Changes of wash-off potential of residential use insecticides on concrete surfaces exposed under outdoor conditions: (a) bifenthrin, (b) lambda-cyhalothrin, (c) permethrin, (d) cyfluthrin, and (e) fipronil. Wash-off potential is presented as the percentage of pesticide transferred into water after mixing for 10 min to the initially spiked amount.

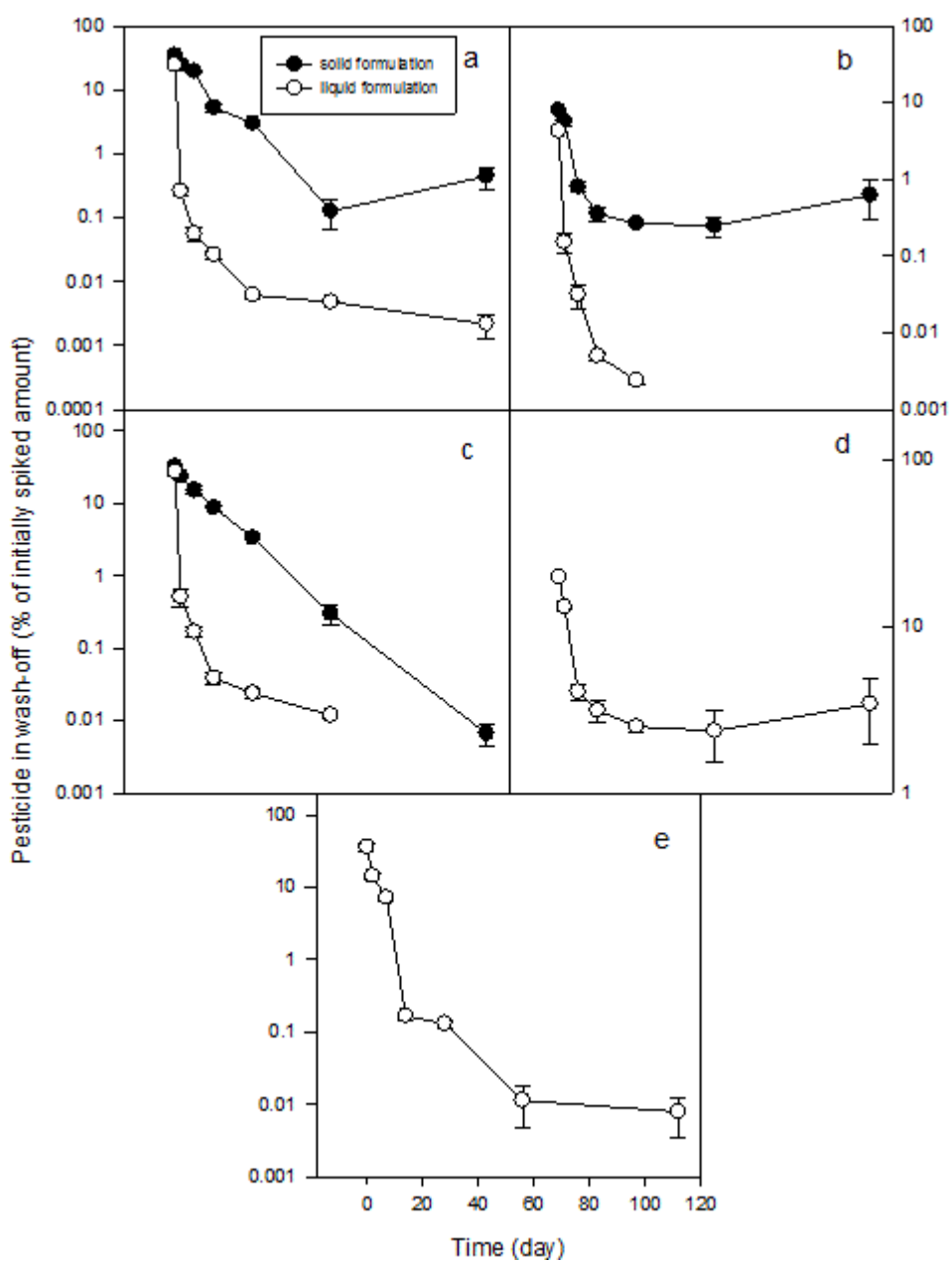
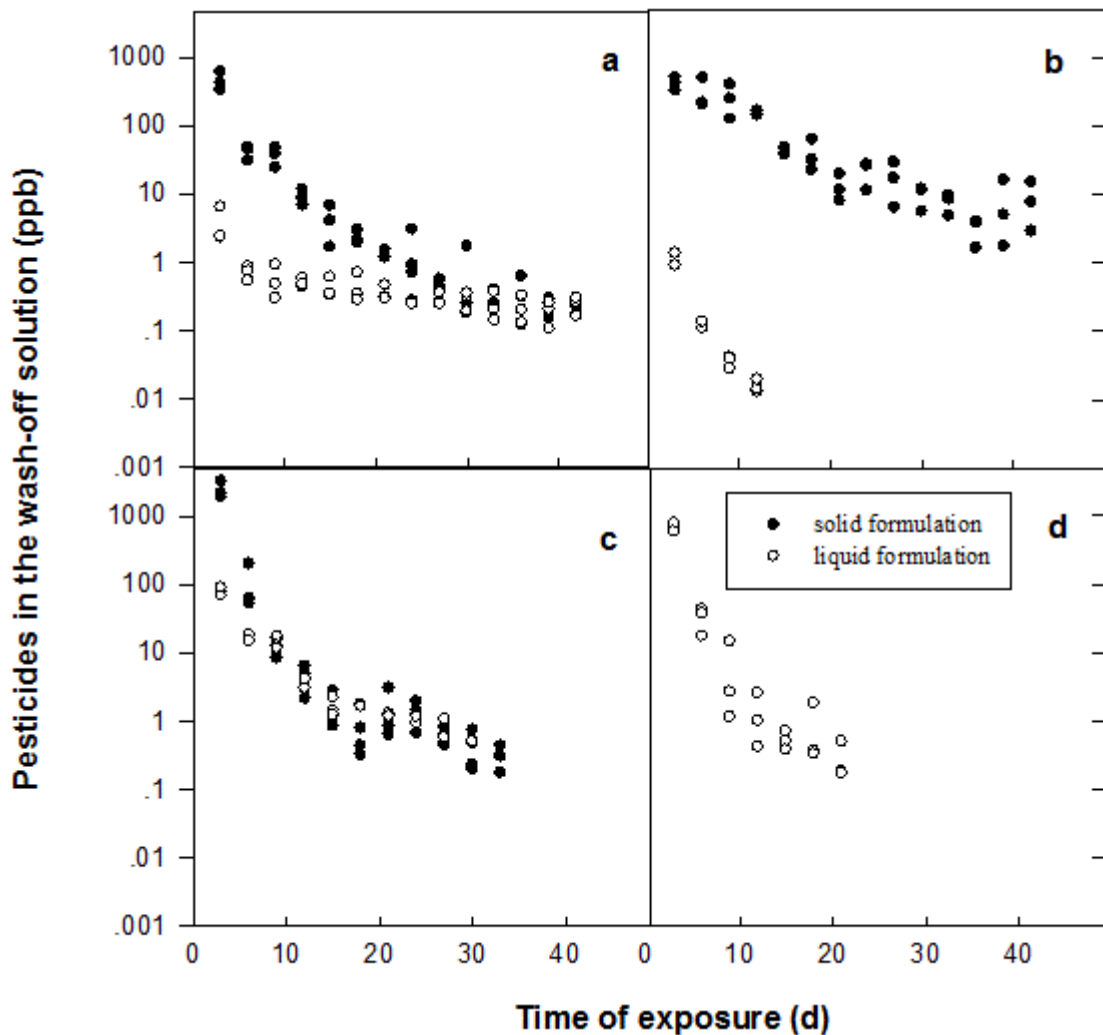


Figure 2-2. Changes of wash-off potential of insecticides on concrete surfaces exposed under outdoor conditions and periodic flush events: (a) bifenthrin, (b) lambda-cyhalothrin, (c) permethrin, and (d) cyfluthrin. Wash-off potential is presented as concentrations of insecticides in water mixed 10 min with the insecticide-contaminated concrete surfaces.



CHAPTER 3

Sorption and Desorption of Pyrethroid Insecticide Permethrin on Concrete

Abstract

Use of pesticides around residential homes is linked to contamination of urban waterways, where impervious surfaces like concrete are considered as sources or facilitators of the contamination. However, the fate of pesticides on urban hard surfaces is poorly understood. We characterized sorption and desorption of permethrin, the most used pyrethroid insecticide, on concrete surfaces, to understand its availability for contaminating runoff water. Sorption of ^{14}C -permethrin to concrete was rapid, and the sorption isotherm was linear, with surface area-normalized K_d of $1.91 \pm 0.1 \text{ mL/cm}^2$. When small permethrin-treated concrete cubes ($14 \times 14 \times 8 \text{ mm}$) were subjected to 300 h sequential desorption, both the parent compound and total ^{14}C showed an initial rapid desorption, followed by prolonged slow desorption. Meanwhile, permethrin became more resistant to desorption as the pesticide contact time on the concrete increased. When desorption was performed 1 and 7 d after the treatment, the desorbed permethrin after 300 h was $34.1 \pm 3.2\%$ and $23.7 \pm 1.1\%$ of the spiked amount, respectively, as compared to $56.2 \pm 6.1\%$ for the freshly spiked samples. The decreased desorption was partially attributed to permethrin decomposition on the alkaline concrete. However, even after 300 h, over 20% of the applied ^{14}C still remained in the concrete. Therefore, when pesticide-treated concrete surfaces come in contact with runoff water, elevated concentrations may be expected initially, while the extended desorption implies a potential for sustained contamination.

Introduction

Monitoring studies increasingly show prevalent contamination of urban streams with insecticides, and the contamination is linked to urban pesticide use (1-6). The finding of almost ubiquitous contamination of urban waterways by synthetic pyrethroids in areas such as California is of particular concern because of the broad spectrum acute toxicity of pyrethroids to water-column and sediment dwelling invertebrates (1-3, 6). For instance, pyrethroids were found in almost all urban runoff samples collected in Sacramento-San Joaquin delta of California (6). Holmes et al. found pyrethroids in urban sediments sampled throughout California, with bifenthrin and permethrin as the most frequently detected (3). In California, the total amount of pyrethroids used by licensed applicators for structural pest control and landscape maintenance increased from 30,730 kg in 1989 to 247,300 kg in 2007, and over 48% of the use was permethrin, an active ingredient found in numerous commercial formulations (7).

Although direct evidence is absent, impervious hard surfaces are considered a primary factor in urban contaminant transport. Urbanized areas are characterized by artificial impervious surfaces, such as concrete that may account for up to 90% of the total urban area in densely populated regions (8-10). Concrete pavements are often directly treated with insecticides for eradication of pests such as ants (11). Structural perimeter spray is commonly practiced by professional applicators for controlling ants, termites, spiders and other pests, where spray drift or subsequent water or wind aided movement may transfer pesticide residues onto the concrete surfaces. However, in contrast to the wealth of knowledge on contaminant behaviors in natural systems, such as

soils and sediments, similar information for artificial surfaces, such as concrete, is essentially nonexistent. In a recent study, we observed rapid initial decreases of water transferable residues when concrete surfaces treated with pesticides (bifenthrin, permethrin, cyfluthrin, cypermethrin, and fipronil) were exposed to outdoor conditions (12). Many of these pesticides also showed prolonged persistence as if some residues moved to sites below the surface. Jorgenson et al. (13) found that, after surface treatment, 0.8-60% of the initially applied pesticides entered the runoff water and that formulations and contact time greatly affected the off-site transport potential. These initial observations under simulated conditions highlighted the need to explore how pesticides are retained on and then released from concrete surfaces when exposed to water.

In the present study, we used permethrin as a representative urban-use insecticide and a combination of ^{14}C -labeling and gas chromatography (GC) analyses to evaluate its sorption and desorption on concrete. Results from this study will provide insights on the role of sorption in the availability of pesticide residues on concrete for contaminating runoff water. The methodology described herein may be also used for the evaluation of other contaminants or hard surface types.

Materials and Methods

Chemicals

^{14}C -Benzyl ring-labeled permethrin ((1RS)-cis-,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, 5.70×10^2 kBq/ μmol , 50% cis/50% trans) was obtained from FMC (Princeton, NJ) and purified before use. Nonlabeled permethrin

standard (97.0%) was obtained from Chem Service (West Chester, PA). Tenax TA beads (2,6-diphenylene-oxide polymer resin, 60-80 mesh) were purchased from Supelco (Bellefonte, PA). Solvents and other chemicals in pesticide or GC grade were obtained from Fisher Scientific (Pittsburgh, PA). All glassware was baked at 400 °C for 4 h before use to prevent cross contamination.

Preparation of concrete materials

Small concrete cubes in the size of 14 × 14 × 8 mm (8.4 cm² in exterior surface area) were prepared in the laboratory. Portland cement (ASTM C 150, Paragon, Norco, CA) was thoroughly mixed with sand (<2 mm, Paragon) and water at a 2:4:1 (w/w/w) ratio, and the paste was poured into a custom-made mesh template. The concrete cubes were allowed to harden for 24 h, and a small amount of water was periodically applied to keep the surface moist. The hardened concrete cubes were cured by immersion in deionized water for at least 28 d to complete the hydration process and to lower the alkalinity. Before use, the hydrated cubes were dried at room temperature. The void content and bulk density of concrete were determined to be 19.2 ± 0.4% and 2.10 ± 0.01 g/cm³, respectively, using modified ASTM C642-06 method (14).

Sorption of ¹⁴C-Permethrin by Concrete

The sorption experiment was carried out in 40-mL amber glass vials with PTFE-lined screw caps (I-Chem, Rockwood, TN). To determine the sorption kinetics, 60 µL of 1.55 ppm¹⁴C-permethrin was spiked into each amber glass vial, and 30 mL of

deionized water was added immediately after the solvent was evaporated. After the solution was homogenized by mixing, one preweighed concrete cube was added. The vials containing pesticide solution and the concrete cube were gently shaken end-over-end at 140 rpm in dark. Vials containing water and concrete cubes without ^{14}C -permethrin treatment were included as controls.

At different time intervals up to 3 d, three replicate vials together with controls were removed. Water and concrete were separated, and ^{14}C activities on the glass wall (including caps), in the concrete cube and in water were individually analyzed. The glass vial was extracted with 5 mL of acetone for four consecutive times, each time by mixing at 140 rpm for 1 h. The extracts were collected in a 20-mL glass scintillation vial (Fisher Scientific) and evaporated to near dryness in a fume hood. Each scintillation vial was then added 15 mL of UltimaGold liquid scintillation cocktail (PerkinElmer, Waltham, MA), and the ^{14}C -activity was measured on a PerkinElmer TriCarb liquid scintillation counter (LSC). The counting time was 6 min, and each sample was measured for 3 times. The chemiluminescence was eliminated by keeping the samples in dark for at least 5 h before the measurement. The water sample was transferred into a 40-mL glass vial and weighed and was extracted with 5 mL of hexane for four consecutive times by mixing at 140 rpm for 1 h each time. Preliminary experiments showed that the extraction recoveries for the empty glass vials and water were $92.2 \pm 1.6\%$ and $92.3 \pm 0.6\%$, respectively. The concrete cubes were weighed and then air-dried in a fume hood for 24 h. The amount of ^{14}C -permethrin sorbed on each concrete cube was quantified by combustion of the entire sample in a biological oxidizer at $900\text{ }^\circ\text{C}$ for 4 min (R. J. Harvey Instruments, Hillsdale,

NJ), followed by the measurement of radioactivity of the evolved $^{14}\text{CO}_2$. The recovery as determined by spiking a clean concrete cube with a known amount of ^{14}C -permethrin was $85.7 \pm 4.7 \%$ ($n = 13$).

The sorption isotherm was determined by treating 30 mL water with different amounts of ^{14}C -permethrin and equilibrated with concrete cubes. After 24 h of mixing at 140 rpm, three replicates for each concentration along with controls were removed and the distribution of ^{14}C -radioactivity on the glass surface, in water, and in concrete was analyzed using the same approach as above.

Desorption from Concrete.

To understand desorption of the sorbed permethrin from concrete, the concrete cubes were treated on one side with ^{14}C -permethrin (in 60 μL acetone) at 185 ng/cm^2 . After the solvent was evaporated, the treated samples were equilibrated with 30 mL of water containing 0.1 g of Tenax by mixing on a horizontal shaker at 140 rpm. The use of Tenax beads was to capture the desorbed ^{14}C -permethrin to minimize the resorption on glass walls, and to facilitate measurement. Preliminary experiments showed that $88.2 \pm 3.4\%$ of permethrin in water was trapped by 0.1 g Tenax in less than 10 min. After 1 h equilibration, the aqueous phase (along with the Tenax) was decanted and passed through a filter paper (Whatman #41, Maidstone, U.K.). The concrete cube was transferred into a new vial containing 30 mL of clean water and 0.1 g Tenax. This desorption step was repeated for a total of 11 consecutive times, with equilibration intervals of 2, 4, 8, 12, 24, 36, 60, 108, 156, 228, and 300 h from the onset of desorption. During the equilibration, to

minimize the base-catalyzed permethrin hydrolysis, 2% HNO₃ was added every 12 h to keep pH between 7.0 and 9.0.

After passing through the filter paper, 5.0 mL of the filtrate was mixed with 15 mL UltimaGold cocktail to measure ¹⁴C-radioactivity by LSC. The Tenax beads collected on the filter paper were rinsed with deionized water and extracted for four consecutive times, each time by sonication with 5 mL of acetone/hexane mixture (1/1, v/v) using a 20kHz ultrasonic processor (Fisher Scientific). The sonication was programmed for 5 min in the 2-s pulse mode. Preliminary test revealed that the extraction recoveries of Tenax were 91.4 ± 0.5%. The extracts were combined into a 20 mL glass scintillation vial and evaporated to near dryness, and the ¹⁴C activity was measured after addition of 15 mL of cocktail. The concrete cubes collected after the last desorption step were air-dried in a fume hood for 24 h, and combusted in the biological oxidizer to determine the amount of remaining ¹⁴C-residue.

To evaluate the effect of application rates, the same treatment was carried out with ¹⁴C-permethrin at two other rates (18.5 and 61.8 ng/cm²). The treated concrete cubes were sequentially desorbed, following the same protocol as described above.

Effect of Contact Time

After treatment, a pesticide may be in contact with concrete for different periods of time before exposure to runoff water. To evaluate the effect of pesticide residence or contact time on desorption, additional concrete cubes were treated with ¹⁴C-permethrin at 185 ng/cm² and kept in the dark at room temperature (21 ± 1 °C). After 0

(i.e., immediately after treatment), 1, or 7 d, six concrete cubes were removed and equally divided into two groups. Three concrete cubes were used to measure desorption following the same procedures as given above. The other three concrete cubes were also subjected to desorption, except that the desorption step was only repeated 1, 8, 24, 60, 156, and 300 h from the onset of the desorption sequence and the desorbed fraction was subjected to analysis by gas chromatography (GC). The Tenax extracts, after evaporation, were reconstituted into 1mL of ethyl acetate, and an aliquot was analyzed on GC for the concentrations of the parent compound permethrin to evaluate the decomposition of ^{14}C -permethrin during equilibration.

Chromatographic Analysis

The analysis of *cis*- and *trans*-permethrin by GC was carried out using an Agilent 6890 GC equipped with a microelectron capture detector (Agilent, Wilmington, DE). Samples were introduced into the inlet at 250 °C in a pulsed splitless mode and the separation was achieved on a VF-5MS capillary column (30 m × 0.25 mm × 0.25 μm film thickness, with 10 m EZ-Guard precolumn, Varian, Palo Alto, CA). The carrier gas was helium, and the flow rate was 1.5 mL/min. The oven program was initially set at 160 °C for 1.0 min, ramped to 260 at 3 °C/min, then ramped to 300 at 30 °C/min and finally held at 300 °C for 15 min. The detector temperature was set at 310 °C. The mean retention times of *cis*- and *trans*-permethrin were 31.27 and 31.71 min, respectively. The quantitation of *cis*- and *trans*-permethrin was through external calibration using standards

with known concentrations. The instrument detection limits were 0.5 ng/mL for both *cis*- and *trans*-permethrin.

Results and Discussion

Adsorption of ¹⁴C-Permethrin on Concrete

Mass balance after accounting for ¹⁴C in water and on concrete and glass surfaces of the container was $90.9 \pm 5.3\%$ for the sorption experiment. Because of the rigid structures, only the exterior surfaces and pores immediately beneath the exterior surfaces of the concrete cubes were likely involved in the interaction with permethrin. The concentration of ¹⁴C-permethrin on concrete was expressed in mass of ¹⁴C-permethrin per surface area (ng/cm²), instead of mass per mass (ng/g) as typically used in the expression of chemical sorption in soils or sediments. In general, rapid uptake of ¹⁴C-permethrin from the aqueous phase was observed, with apparent equilibrium reached in less than 24 h (Figure 3-1a). For instance, after 2 h equilibration, $20.0 \pm 0.9\%$ of the initially applied ¹⁴C-permethrin was detected on concrete. The maximum ¹⁴C-permethrin sorption on concrete was observed at 24 h of equilibration, when the ¹⁴C level (expressed as equivalent of permethrin) on concrete was 2.72 ± 0.2 ng/cm². After reaching the maxima, the amount of ¹⁴C sorbed on the concrete decreased slightly. The average ¹⁴C level on concrete was 2.18 ± 0.58 ng/cm² at 48 h and 2.20 ± 0.13 ng/cm² at 72 h. The gradual decrease of ¹⁴C on concrete after equilibrium may be attributed to permethrin decomposition. It is known that cured cement materials contain alkali chemicals such as calcium hydroxide formed during hydration (15, 16). Although the concrete cubes were

washed repeatedly before use, pH of the solution exceeded pH 9 after 24 h equilibration. Moreover, the alkalinity below the concrete surface was unknown but could be even higher than that in the bathing solution.

A hardened concrete paste is composed of various minerals, with calcium silicates as the main binding component (16, 17). Several studies showed strong sorption of pyrethroids on various mineral surfaces (18-21). For instance, Zhou et al. (18) measured sorption of pyrethroids on glass, montmorillonite, aluminum oxide and kaolinite and found that the sorption was dependent closely on the size of exposed surface areas. In the present study, the amount of ^{14}C -permethrin sorbed on glass surfaces was measured to be only $0.12 \pm 0.02 \text{ ng/cm}^2$, which was more than 20 times smaller than that on the concrete. Therefore, in addition to the exposed exterior surface, sorption of permethrin on concrete may have also involved sites below the exterior surface. This supposition was supported by a water permeability test, which revealed that after 48 h immersion in water, the concrete cubes accumulated water up to $19.18 \pm 0.42 \%$ of its bulk volume. Cured concrete is known to contain continuous porous structures, including capillary pores and larger fractal pores derived from the evaporation of water during the hydration process (16, 22, 23). Therefore, it is likely that ^{14}C -permethrin moved in water or by diffusion to the interior of the porous concrete matrix and became sorbed at some of the inner sites immediately below the exterior surface.

The sorption isotherm was linear within the range of aqueous concentrations of ^{14}C -permethrin (Figure 3-1b). The slope of the linear isotherm, or K_d , was $1.91 \pm 0.1 \text{ mL/cm}^2$. The linear isotherm suggested that sorption of ^{14}C -permethrin did not reach

saturation over the concentration range tested in the study. A K_d value of this magnitude, when measured for a soil or sediment, would suggest weak or moderate sorption capacity. However, because only the exterior surfaces and likely water-accessible micropores participated in the sorption, the derived K_d for concrete was not directly comparable to values for soils or sediments. To the best of our knowledge, this was the first time that K_d of a pesticide was measured and expressed using the surface area of concrete. It is therefore impossible to know how sorption of permethrin may be compared to other compounds. At equilibrium, the aqueous concentration of ^{14}C -permethrin was 49.6 ± 3.2 % of the initial concentrations. Considering the relatively small surface area of the concrete cubes (8.4 cm^2), the potential for permethrin to sorb onto the concrete was likely substantial.

Desorption from Concrete Surfaces

Following deposition onto concrete, subsequent desorption of pesticides to runoff water dictates the potential and pattern for off-site pesticide transport. In the present study, desorption of ^{14}C -permethrin from concrete cubes was measured by mixing with water containing Tenax (Figure 3-2a). Good mass balance ($91.8 \pm 2.7\%$, $n = 15$) was achieved when accounting for ^{14}C trapped on Tenax, dissolved in the solution and remaining on the concrete at the end of the 300 h sequential desorption. Tenax has been used in recent studies to evaluate sequential desorption of organic compounds from soils and sediments (24-26). As the desorbed ^{14}C -permethrin was expected to be quickly sequestered by Tenax, it was as if that the concrete were constantly exposed to pesticide-

free water, thus mimicking the scenario where the concrete surface is swept continuously by runoff water as during a rainfall event.

In general, rapid desorption during the first 24 h was observed for the freshly spiked concrete cubes. The amount of ^{14}C desorbed during the first 24 h was over 60 % of the total ^{14}C desorbed over 300 h. For instance, for concrete cubes treated at 185 ng/cm^2 , desorption within the first 24 h accounted for $68.2 \pm 1.86\%$ of the total desorbed ^{14}C (Figure 3-2a). In a stark contrast to the initial fast desorption, desorption became increasingly slower in the later phase of desorption. For instance, only $2.24 \pm 0.26 \%$ of the overall desorption was attributable to the desorption interval from 228 to 300 h. The decreased desorption was likely because of the distribution of a fraction of the applied ^{14}C -permethrin deeper into the concrete matrix with reduced desorption potential. To describe the desorption kinetics, desorption as a function of time was fit to a three-phase desorption model (24-26)

$$\frac{S_t}{S_0} = F_{\text{rapid}} \cdot e^{-k_{\text{rapid}} \cdot t} + F_{\text{slow}} \cdot e^{-k_{\text{slow}} \cdot t} + F_{\text{vs}} \cdot e^{-k_{\text{vs}} \cdot t} \quad (1)$$

where S_0 and S_t (ng) are the amounts of ^{14}C (equivalent to permethrin) on concrete initially applied and after desorption time interval t (h), respectively, F_{rapid} , F_{slow} , and F_{vs} are the rapid, slow, and very slow desorption fractions of the initially spiked amount, respectively, and k_{rapid} , k_{slow} , and k_{vs} (h^{-1}) are the rate constants for rapid, slow and very slow desorption fractions, respectively.

Desorption of ^{14}C from concrete was well described by the three-phase model ($R^2 = 0.99$). For the freshly spiked treatments, the estimated k_{rapid} was around 7 and 123

times greater than k_{slow} and k_{vs} , respectively, clearly suggesting a sharp decrease in the desorption rate in the late desorption phases. The rapid desorption fraction ($25.3 \pm 1.9\%$) was similar to the slow and very slow desorption pools ($26.0 \pm 1.6\%$ and $28.9 \pm 1.5\%$, respectively). Desorption followed similar trends when the concrete cubes were treated with ^{14}C -permethrin at two lower rates (61 and 18.5 ng/cm²) (Figure 3-2a and Table 3-1), where the corresponding k_{rapid} was about 6-7 and 125-150 folds of k_{slow} and k_{vs} , respectively. This observation suggested that under the tested conditions, application rates had little effect on desorption or the potential for permethrin to contaminate runoff water.

Effects of Contact Time on Desorption Kinetics

A separate experiment was carried out to understand the effect of contact time (i.e., the time elapsed from pesticide treatment) on desorption kinetics. As the contact time increased from zero (freshly spiked treatment) to 1 d and to 7 d, ^{14}C -permethrin on concrete became progressively more resistant to desorption (Figure 3-2b). For instance, when the desorption was initiated 1 d after pesticide application, desorption over the first 24 h accounted for $50.7 \pm 2.2\%$ of the overall desorption, as compared to $68.2 \pm 1.9\%$ for the freshly spiked treatment. When the contact time was 7 d, this ratio decreased to $49.6 \pm 1.3\%$. Fit of data to the three phase model showed that as the contact time increased, F_{rapid} decreased to <50 % of that for the freshly spiked concrete (Table 3-1). For the 7 d contact time treatment, F_{rapid} decreased to only $8.7 \pm 0.9\%$ (from $25.3 \pm 1.9\%$

for the 0 d treatment), clearly demonstrating a pronounced effect of contact time or aging on permethrin desorption potential (Table 3-1).

As desorption was measured from the ^{14}C -activity trapped on Tenax, the reduced desorption could be attributed to decomposition of permethrin or the retention of ^{14}C on the concrete at the end of the 300 h desorption experiment. Combustion of the desorbed concrete cubes showed that $18.2 \pm 1.8 \%$ of the applied ^{14}C remained in the concrete for the freshly spiked treatment. This fraction slightly increased to $21.6 \pm 1.8 \%$ for the 1 d contact time treatment, and $28.5 \pm 1.9 \%$ for the 7 d contact time treatment. The chemical composition of the retained ^{14}C , however, was not further explored in this study.

Two parallel measurements suggested occurrence of abiotic transformations, with the extent of decomposition increasing with contact time. Analysis of ^{14}C activity in the aqueous phase (i.e, not recovered on Tenax) showed that more ^{14}C appeared in the aqueous solution as the contact time was prolonged (Figure 3-3a). At the end of the desorption experiment, $27.0 \pm 1.1 \%$ of the initial applied ^{14}C was found in the water phase for the 7 d contact time treatment, while only $6.8 \pm 0.8 \%$ was detected for the freshly spiked treatment (Figure 3-3a). This observation suggested that as ^{14}C -permethrin stayed on the concrete, it underwent transformations leading to the formation of polar degradation products that were not sorbed by the concrete nor sequestered by the nonpolar Tenax polymer.

To further evaluate decomposition of ^{14}C -permethrin on concrete, GC was used to quantify the parent compound in the ^{14}C recovered by Tenax. Desorption in the form

of permethrin decreased with increasing contact time. For instance, 63.4 ± 13.6 ng permethrin was desorbed after 1 h from the freshly spiked concrete, whereas this amount decreased to 33.6 ± 4.0 ng for the 1 d contact time treatment and only 15.4 ± 2.8 ng for the 7 d contact time treatment. Cumulatively, a total of 239.9 ± 25.8 ng permethrin was desorbed from the freshly spiked concrete cubes, while 145.4 ± 13.7 and 101.2 ± 4.8 ng were desorbed from the 1 and 7 d contact time treatments, respectively. The simultaneous analysis of permethrin and ^{14}C afforded the calculation of the contribution to the total ^{14}C -desorption by the parent compound (Figure 3-3b). For the 0 and 1 d contact time treatments, the majority of the desorbed ^{14}C was initially in the form of permethrin, with the fraction close to 1.0. However, this fraction decreased to 0.63 ± 0.06 at 24 h for the freshly spiked treatment, and 0.30 ± 0.03 for the 1 d contact time treatment. For the 7 d contact time treatment, permethrin accounted for only 0.16 ± 0.03 of the desorbed ^{14}C at 1 h, suggesting that extensive decomposition already took place prior to the desorption measurement. Interestingly, as the desorption progressed further, the fraction of permethrin again increased (e.g., after 24 h). This was likely caused by the fact that the polar ^{14}C degradation products were quickly depleted from the concrete cube, leaving only the parent compound and relatively nonpolar degradation products available for further desorption. In summary, permethrin contributed 76.8 ± 8.4 % of the entire ^{14}C desorbed from the freshly spiked samples during the 300 h cumulative desorption, whereas the contributions were 46.6 ± 4.6 % and 37.3 ± 2.0 % for the 1 and 7-d aged samples, respectively.

Environmental Implications

In this study, all of the desorbed permethrin may be assumed to be quickly trapped by Tenax. Correspondingly, the aqueous concentration of permethrin was constantly kept at a negligible level. This would simulate conditions when concrete surfaces are exposed to continuous runoff from recurring irrigation events or an extended episode of rainfall. Given the unchanged mixing speed, the sequential desorption experiment represented a scenario of runoff at a constant flow rate. Therefore, the cumulative runoff volume should be proportional to the cumulative desorption time. To visualize the potential permethrin loading as a function of runoff volume, the time dependent permethrin desorption was replotted as the percentage of the total desorbed amount (Figure 3-4). In general, permethrin loading displayed a convex temporal trend, with the potential for contaminating runoff the greatest during the initial stage. For instance, for the freshly spiked treatment, 75.1 ± 3.0 % of the total desorbed permethrin was released during the first 24 h. As the contact time increased, the 24 h desorbed fraction decreased to 56.3 ± 3.7 % for the 1 d contact treatment and to 47.4 ± 4.3 % for the 7 d contact time treatment. It has been reported that during an extended storm event, the first portion of runoff water, or “first flush”, usually contains much higher levels of contaminants (27). Therefore, management of the first flush would command special attention for pollution prevention. For instance, Soller et al. (28) showed that increased levels of dissolved metals were present in the first flush of urban runoff water. Findings from the present study agree with such previous research and suggest that relatively high levels of pesticides may be expected to appear in the first flush.

Following the initial rapid desorption, permethrin continued to desorb from the treated concrete, although at reduced rates, for a long time. Detectable permethrin residues were found on all Tenax samples collected at the end of the 300-h desorption cycle. For instance, 21.6 ± 4.7 ng of permethrin was desorbed over the 156-300 h desorption interval for the freshly spiked concrete, accounting for 9.0 ± 1.5 % of the entire permethrin desorption. This amount was 19.7 ± 6.5 ng (or 13.4 ± 3.2 %) for the 1-d contact treatment, and 19.6 ± 3.4 ng (or 19.3 ± 3.1 %) for the 7-d contact time treatments. The prolonged permethrin desorption from concrete is of great significance, as it suggests a possibility for the concrete to serve as a source for sustained runoff contamination. Therefore, permethrin applied early in the season may still be available for contaminating runoff during the rain events occurring later in the year. The mechanisms for the prolonged permethrin desorption from concrete and the effect of longer contact time warrant further investigation. In addition, the sorption and desorption behaviors of other urban-use pesticides on hard surfaces, and the effect of application variables such as formulations (13), also merit further research.

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Table 3-1. Model regression parameters of ^{14}C desorption from concrete subjected to different ^{14}C -permethrin treatments and different contact time before desorption^a

treatment rate ($\text{ng}\cdot\text{cm}^{-2}$)	contact time (d)	F_{rapid}	F_{slow}	F_{vs}	R^2
185.3	0	0.25 ± 0.02	0.26 ± 0.02	0.29 ± 0.02	0.998
61.8	0	0.22 ± 0.03	0.31 ± 0.03	0.25 ± 0.02	0.995
18.5	0	0.24 ± 0.02	0.27 ± 0.02	0.29 ± 0.01	0.997
185.3	1	0.20 ± 0.02	0.35 ± 0.01	0.34 ± 0.02	1.000
185.3	7	0.09 ± 0.009	0.25 ± 0.009	0.38 ± 0.01	0.998

Figure 3-1. Sorption behaviors of ^{14}C -permethrin on concrete. (a) Kinetic uptake of ^{14}C -permethrin from water onto concrete cubes; and (b) Sorption isotherm of ^{14}C -permethrin between concrete and water. Data points are given as means \pm standard deviations ($n = 3$).

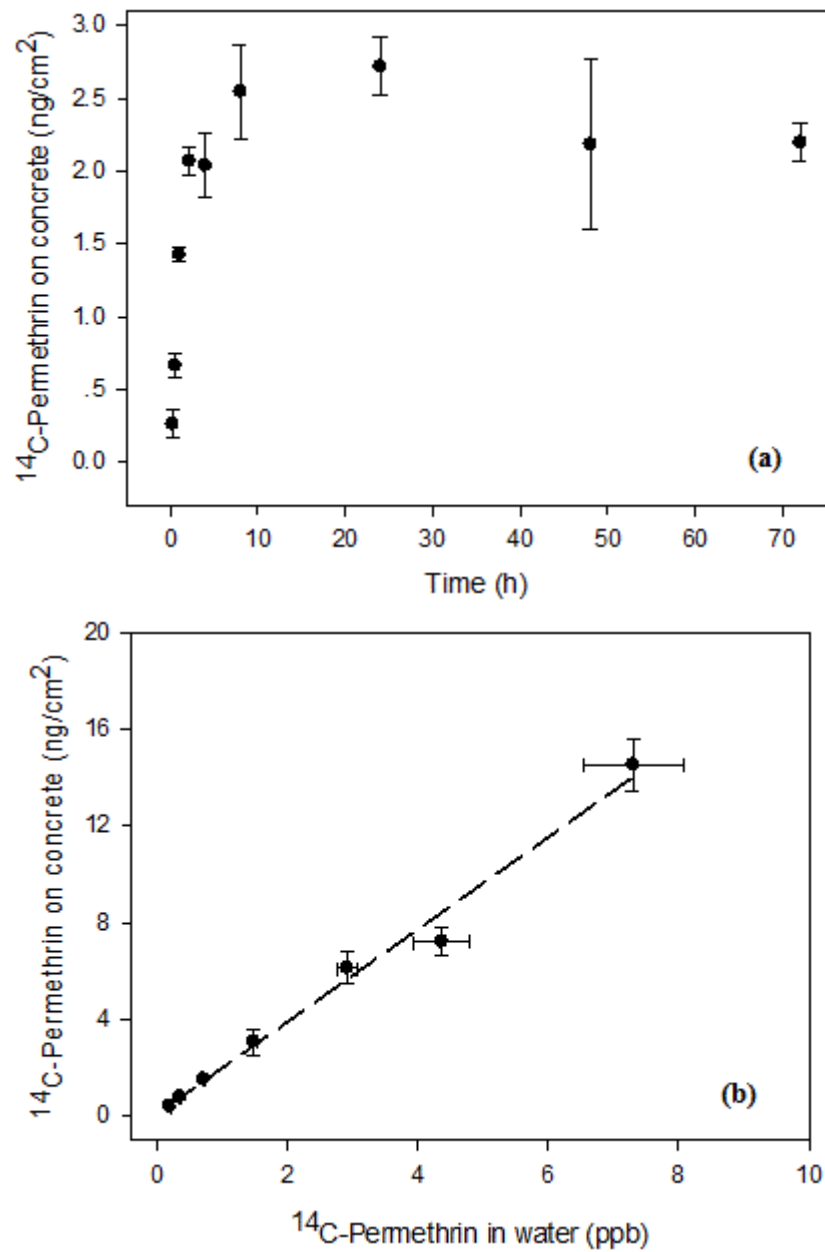


Figure 3-2. Sequential desorption of ^{14}C -permethrin from concrete cubes. (a) Desorption of ^{14}C -permethrin from small concrete cubes freshly treated with 185 (●), 61.8 (○), or 18.5 (▼) ng/cm^2 permethrin, respectively. (b) Desorption of ^{14}C -permethrin after 0 (●), 1 (○), or 7 (▼) d elapsed from the treatment. Data points are given as means \pm standard deviations ($n = 3$).

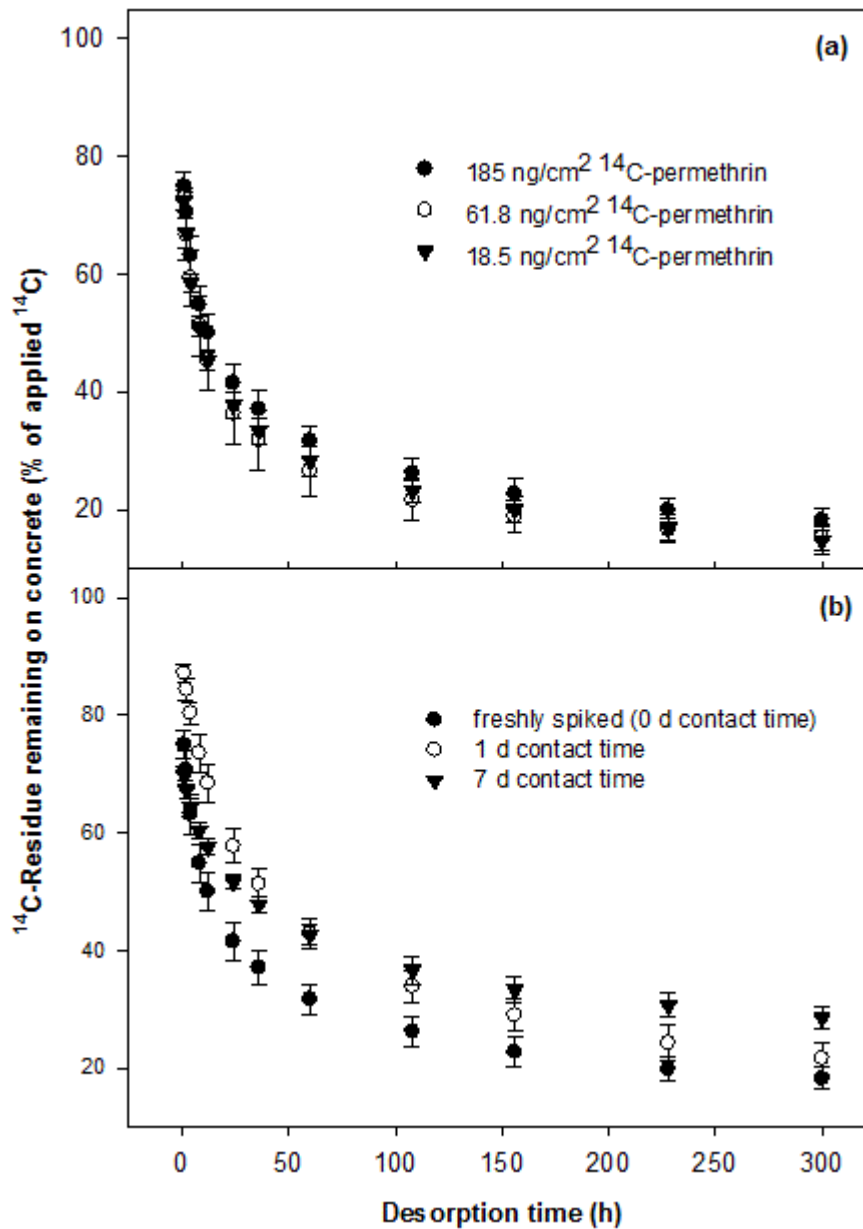


Figure 3-3. Desorption of ^{14}C -permethrin from concrete cubes after 0 (●), 1 (○), or 7 (▼) d elapsed from the treatment. (a) Accumulation of ^{14}C in the water phase and (b) fractions of permethrin to ^{14}C captured on Tenax. Data points are given as means \pm standard deviations ($n = 3$).

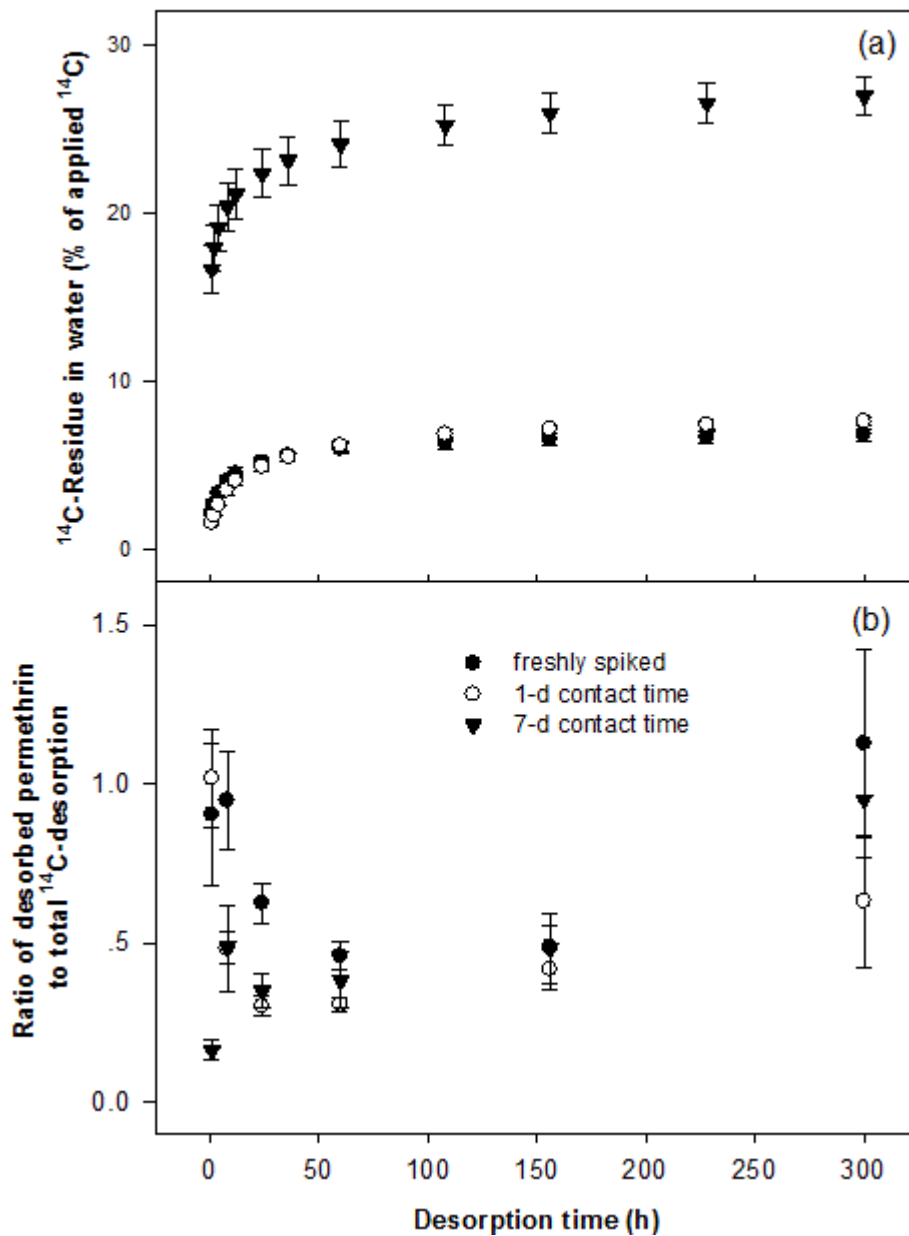
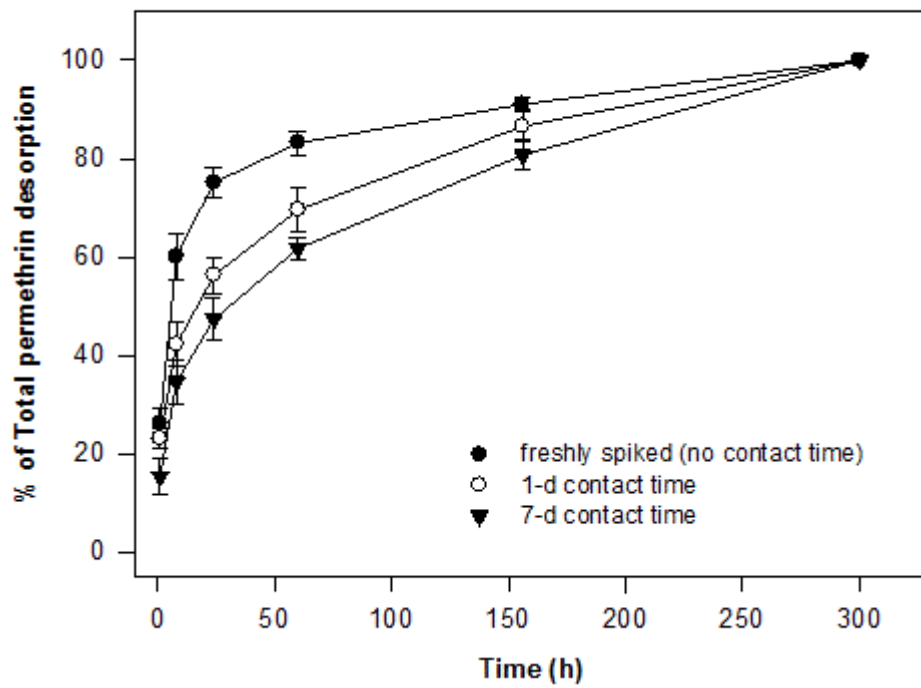


Figure 3-4. Estimated loading of permethrin into runoff from concrete after 0 (●), 1 (○), or 7 (▼) d elapsed from the treatment. Data points are given as means ± standard deviations (n = 3).



CHAPTER 4

Runoff of Pyrethroid Insecticides from Concrete Surfaces Following Simulated and Natural Rainfalls

Abstract

Intensive residential use of insecticides has resulted in their ubiquitous presence as contaminants in urban surface streams. For pest eradication, urban hard surfaces such as concrete are often directly treated with pesticides, and wind/water can also carry pesticides onto hard surfaces from surrounding areas. This study expanded on previous bench-scale studies by considering pesticide runoff caused by irrigation under dry weather conditions and rain during the wet season, and evaluated the effects of pesticide residence time on concrete, single versus recurring precipitations, precipitation intensity, and concrete surface conditions, on pesticide transferability to runoff water. Runoff from concrete 1 d after pesticide treatment contained high levels of bifenthrin (82 µg/L) and permethrin (5143 µg/L for cis and 5518 µg/L for trans), indicating the importance of preventing water contact on concrete after pesticide treatments. Although the runoff transferability quickly decreased as the pesticide residence time on concrete increased, detectable residues were still found in runoff water after 3 months (89 d) exposure to hot and dry summer conditions. ANOVA analysis showed that precipitation intensities and concrete surface conditions (i.e., acid wash, silicone seal, stamping, and addition of microsilica) did not significantly affect the pesticide transferability to runoff. For concrete slabs subjected to natural rainfalls during the winter wet season, pesticide levels in the runoff decreased as the time interval between pesticide application and the rain event increased. However, bifenthrin and permethrin were still detected at 0.15-0.17 and 0.75-1.15 µg/L in the rain runoff after 7 months (221 d) from the initial treatment. In addition, pesticide concentrations showed no decrease between the two rainfall events,

suggesting that concrete surfaces contaminated by pesticides may act as a reservoir for pesticide residues, leading to sustained urban runoff contamination.

Introduction

Insecticides such as synthetic pyrethroids are commonly used in residential areas for structural pest control and landscape maintenance, and this has been linked to sustained pesticide contamination and toxicity in urban streams and estuaries (Budd et al., 2007; Weston et al., 2009). For instance, residues of pyrethroids have been found in urban creeks and sediments in the United States, especially in California, often at levels exceeding the toxicity thresholds to native invertebrates (Amweg et al., 2006; Weston et al., 2009; Holmes et al., 2008; Hintzen et al., 2009; Ding et al., 2010; Weston and Lydy, 2010). In California, the total amount of pyrethroids used by licensed professional applicators for structural pest control and landscape maintenance was 138,000 kg in 2009 (CDPR, 2009), with bifenthrin and permethrin accounting for 16% and 54% of the total pyrethroid use, respectively. In addition, pyrethroids are also included in many pest control products that are designed for homeowners and available at retail stores, but the use of these products is poorly controlled or documented (Moran, 2006).

It is commonly suspected that transport of pesticide residues from urban hard surfaces via irrigation or rain-induced runoff is an important cause for downstream pesticide contamination. Unlike agricultural fields or natural ecosystems, residential areas usually contain artificial hard surfaces (e.g., concrete) that may account for up to 90% of the total surface area (Arnold and Gibbons, 1996; USDA, 1975; COPWD, 1994). To

control pests such as ants, hard surfaces may be treated directly with insecticides (e.g., structural perimeter spray and ant trail eradication), and spray drift and wind or water-aided movement may also transport pesticide residues onto hard surfaces. However, in contrast to the wealth of knowledge about the fate of pesticides in soil, pesticide behavior on urban hard surfaces is poorly understood. This lack of understanding hampers the development of effective regulatory and mitigation strategies.

In a bench-scale study, it was observed that after treatment on concrete, the transferability of pyrethroids into the washoff water rapidly decreased (Jiang et al., 2010.). However, it was also noted that pesticide residues remained on the concrete for an extended period of time, and even after 112 d under hot and dry summer conditions, pesticide residues were still detected in the runoff water. The persistence of pyrethroids was further validated through a study using ^{14}C -labeled compounds (Jiang et al., 2011), where ^{14}C -permethrin desorption was found to continue for over 300 h, and about 20% of the applied ^{14}C remained on the concrete at the end of the extended desorption procedure. Jorgenson and Young (2010) showed that runoff of pyrethroids from concrete surfaces was affected by formulations, especially surfactants, and also by the contact time between pesticides and concrete. These recent studies revealed that urban hard surfaces such as concrete should not be viewed as inert surfaces, and research is urgently needed to delineate the effect of common factors on pesticide transferability from hard surfaces to runoff water.

This study considered the effect of a number of application and environmental variables on pesticide runoff potential, including pesticide residence time on concrete,

precipitation intensity, concrete surface condition, single versus repeated runoff, and simulated versus natural rainfalls.

Materials and Methods

Chemicals

Bifenthrin and permethrin were used in this study as representative urban-use insecticides. Professional formulations of bifenthrin and permethrin were obtained from FMC (Philadelphia, PA) and United Phosphorus Inc (King of Prussia, PA), and the contents of active ingredients were determined to be $8.74 \pm 0.44\%$ and $35.1 \pm 1.2\%$, respectively. Chemical standards of bifenthrin (99%, Chem Service, West Chester, PA), permethrin (97%, 40% *cis*/60% *trans*, FMC), phenoxy $^{13}\text{C}_6$ -labeled *cis*-permethrin (^{13}C -permethrin, 99%, Cambridge Isotope Laboratories, Andover, MA), and decachlorobiphenyl (99.2%, Chem Service) were obtained from different sources. All solvents and other chemicals in GC/MS or pesticide grade were purchased from Fisher Scientific (Pittsburgh, PA). All glassware was baked at $400\text{ }^\circ\text{C}$ for 4 h before use to prevent cross contamination.

Preparation of concrete slabs and pesticide treatment

Concrete slabs in the dimension of $60 \times 40 \times 9\text{ cm}$ (L \times W \times H) were prepared by pouring a fresh mixture of Portland cement, sand, and gravels (1:3:3 ratio) in water into wooden frames. The concrete slabs were allowed to cure under outdoor conditions for at least 6 months before use to ensure the completion of concrete hydration.

All concrete slabs were placed lengthwise on a $2.7 \pm 0.5^\circ$ slope. The surface of each slab was finished with a V-shaped indentation at the lower end before the concrete became hardened, and a brass-tubing was attached to allow the runoff water to drain into a glass sample bottle secured in the ground.

Pesticides were applied using a Marson MC air-brush sprayer (Swingline, Lincolnshire, IL) at 40 psi. The professional formulations of bifenthrin (0.91 mL) and permethrin (16 mL) were mixed together with 500 mL water, and 50 mL of the mixed solution was applied evenly onto each concrete slab. The actual application rates were determined at $3.2 \mu\text{g}/\text{cm}^2$ for bifenthrin and $233.3 \mu\text{g}/\text{cm}^2$ for permethrin, which were consistent with label instructions for these products. All treatments were completed within a 12-h time window to assure similar environmental conditions.

Measurement of pesticide runoff from concrete

Runoff from concrete slabs was generated by an automated rainfall simulator (Ghodrati, 1989). To understand the effect of different environmental conditions and application factors on pyrethroid runoff transferability, the concrete slabs were treated with the same amounts of bifenthrin and permethrin and then subjected to the following different precipitation or sampling schemes. For each precipitation/sampling scheme, four replicates together with one control were included to assess the variance.

Pesticide residence time: To evaluate the effect of pesticide residence time on concrete, five groups of concrete slabs were exposed to outdoor conditions for 1, 7, 20, 47 or 89 d after treatment, and then received a single precipitation at $26.2 \pm 2.7 \text{ mm}/\text{h}$.

Repeated wash-off: Another group of concrete slabs were subjected to repeated wash-off at 1, 7, 20, 47, and 89 d after treatment, with the precipitation rate at 26.2 ± 2.7 mm/h, to evaluate changes in pesticide transferability with recurring irrigation or rainfall events.

Precipitation intensities: Three groups of concrete slabs received repeated precipitations at three different rates, i.e., 19.3 ± 1.7 , 26.2 ± 4.2 , and 32.6 ± 4.2 mm/h, on day 1, 7, 20, 47, and 89 after pesticide treatment. To collect a similar runoff volume for each treatment group, the precipitation continued for 10 (32.6 mm/h), 15 (26.2 mm/h), or 20 (19.3 mm/h) min, depending on the precipitation intensity.

Concrete surface modifications: At the time of concrete slab construction, the surface of some slabs was modified to mimic common practices. The surface modifications included acid washing and silicone coating (sealing) 3 months after the concrete slabs were constructed, stamping before the concrete hardened, and addition of microsilica before pouring. Details about concrete modifications are available in the Supporting Materials. After pesticide treatment, these slabs were subjected to repeated precipitations at 26.2 ± 2.7 mm/h on day 1, 7, 20, 47 and 89 after pesticide treatment.

Natural rainfalls: Five other groups of concrete slabs were treated with pesticides at different times in the year and did not receive any simulated precipitation. Runoff water from the first and second natural rainfalls in the wet season (November 8 and November 20, 2010) was separately collected and analyzed for pesticide residues. This treatment was designed to investigate the relationship between pesticide application

time and runoff contamination from wet season rain events that typically occur at the end of the year.

Pyrethroid analysis and instrument quantification

The runoff water from simulated or natural precipitation events was collected in amber glass bottles and the samples were transported to the laboratory within 4 h of collection. If the runoff samples were not analyzed immediately, each amber bottle was added with 60 mL methylene chloride and then stored at 4 °C before extraction.

Analysis of pyrethroids in the runoff water was carried out using liquid-liquid extraction (LLE) following the modified EPA method 3510C. The extracts were subjected to Florisil cleanup (modified EPA method 3620C), and analysis was carried out using gas chromatography/tandem mass spectrometry (GC-MS/MS). More details about pesticide extraction and instrument analysis are available in the Supporting Materials.

Quality assurance and data analysis

Several practices were used to assure the accuracy and reproducibility of sample analysis. First, method recoveries and detection limits (MDLs) of pyrethroids were determined through preliminary experiments following EPA protocol 40 CFR, Part 136, Appendix B (n = 4) (Table S1). Second, surrogate and isotope-labeled internal standards were used in all samples to correct for extraction efficiency and calibrate for instrument response variations. The surrogate recoveries were $74.3 \pm 13.0\%$ for all

samples analyzed. Third, potential laboratory cross-contamination was assessed by including one laboratory blank for every 20 samples.

Effects of different variables on pesticide transferability from concrete surfaces to runoff water were evaluated by analysis of variance (ANOVA). Factors considered in ANOVA include pesticide residence time on concrete before the onset of precipitation, precipitation intensity, and concrete surface conditions. Statistical comparisons were carried out using Tukey test with the significance level set at 0.05. Normality and equal variance tests were performed before analysis to validate the statistical hypotheses.

Results and Discussion

Runoff from simulated single-time and repeated precipitations

The pesticide-treated concrete slabs were generally exposed to warm and dry weather conditions, with an average daily air temperature of 19.4 °C and maximum daily air temperature exceeding 30 °C for 22 out of 89 days. No measurable natural rainfall occurred during the 89 d simulated precipitation study (CIMIS, 2010). An average $56.9 \pm 8.3\%$ of the applied precipitation water was recovered as runoff water.

When the treated concrete slabs received precipitation 24 h after treatment, concentrations of bifenthrin ($81.9 \pm 46.0 \mu\text{g/L}$) and permethrin ($5143 \pm 2604 \mu\text{g/L}$ for *cis* and $5518 \pm 2896 \mu\text{g/L}$ for *trans*) were very high in the runoff water. These levels were above their respective water solubility limits (14 ng/L for bifenthrin and 5.5 $\mu\text{g/L}$ for permethrin, Laskowski, 2002), suggesting that surfactants in the formulations and fine particles from the concrete surfaces may have contributed to the enhanced transferability.

However, when expressed as percentage of the active ingredients applied, the total amount of chemicals transferred into the 1-d runoff water accounted for only 0.84 ± 0.46 , 2.67 ± 1.33 , and $1.11 \pm 0.57\%$ of the initially applied bifenthrin, *cis*-permethrin and *trans*-permethrin, respectively. After 20 d of outdoor exposure, pyrethroid concentrations in the runoff were lower than those in the 1-d runoff by at least one order of magnitude (Figs. 4-1 and 4-2). However, despite the initial rapid decrease, bifenthrin and permethrin residue displayed great persistence on the concrete, and bifenthrin, *cis*-permethrin and *trans*-permethrin were found at 0.59 ± 0.18 , 17.8 ± 3.0 and 30.0 ± 5.5 $\mu\text{g/L}$ in the 89-d runoff water. To better understand the decline of pyrethroid runoff transferability over time, pyrethroid concentrations in runoff water from the single-time precipitation treatments were fitted to a first-order decay model. Good model fitting was observed for all compounds ($p < 0.001$), and the estimated half-lives for runoff transferability were 15.3, 12.8, and 11.6 d for bifenthrin, *cis*-permethrin, and *trans*-permethrin, respectively. From the estimated k values, under the test conditions, it would take at least 117 d for the bifenthrin level to decrease to 0.1 $\mu\text{g/L}$. Therefore, considering the extremely low aquatic toxicity thresholds (10th centile of LC50 to all tested organisms: 15 ng/L for bifenthrin and 180 ng/L for permethrin, Solomon et al., 2001), runoff of pyrethroids such as bifenthrin and permethrin from concrete may be of significant environmental concern even long after the initial pesticide treatment.

Similar to simulated single-time precipitation treatments, pyrethroids on concrete also displayed long persistence following repeated precipitation simulations (Figs. 4-1 and 4-2). After 4 repeated precipitation events, both bifenthrin and permethrin

were still detectable in the runoff generated from the day 89 precipitation, at concentrations of 0.64 ± 0.09 , 12.44 ± 2.58 , and 19.98 ± 3.91 $\mu\text{g/L}$ for bifenthrin, *cis*-permethrin, and *trans*-permethrin, respectively. However, when expressing pyrethroid runoff following each precipitation event as the percentage of the cumulative runoff loss, the runoff on day 89 only accounted for 0.88 ± 0.46 , 0.30 ± 0.18 and $0.44 \pm 0.24\%$ of the total runoff loss of bifenthrin, *cis*-permethrin, and *trans*-permethrin, respectively (Table 4-1). In contrast, the corresponding fractions for the Day 1 runoff were 83.3 ± 5.8 , 93.1 ± 2.9 , and $90.8 \pm 3.7\%$. This indicates that to mitigate urban runoff contamination, it is critical to prevent the treated area from coming into contact with irrigation or rainfall shortly after pesticide treatments. On the other hand, low levels of pyrethroids may be available for transferring from concrete surfaces to runoff water for a prolonged time, contributing to sustained contamination of urban surface streams.

In a previous bench-scale study, pyrethroids, including bifenthrin and permethrin, also displayed an initial rapid loss of runoff transferability after treatments on concrete, followed by a stage of persistent pyrethroid runoff from concrete for an extended period of time (Jiang et al., 2010). This observation was attributed to pesticide retention in small pores below the concrete surface. In another experiment, when small concrete cubes were spiked with ^{14}C -permethrin, slow ^{14}C desorption from concrete was still observed at the end of the 300 h study (Jiang et al., 2011). Even though cured concrete is considered to be impermeable, it is effectively composed of a porous matrix containing capillary pores and larger fractal pores derived from the concrete hydration process (Paria and Yuet, 2006; Diamond, 1999; Sosoro, 1998; Chen and Poon, 2009).

Consequently, sorption and/or trapping of pesticide residues in these pores may contribute to the extended runoff transferability by shielding pesticides from fast runoff loss (Jiang et al., 2010).

Effect of precipitation intensity

To evaluate the effects of precipitation intensity on pesticide runoff transferability, concrete slabs treated with bifenthrin and permethrin received repeated precipitations at 19.3 ± 1.7 , 26.2 ± 4.2 or 32.6 ± 4.2 mm/h, and the precipitation durations were adjusted for the different intensities to achieve similar precipitation volumes. As shown in Fig. 4-3, precipitation intensities appeared to have little effect on pyrethroid runoff transferability from concrete, and both the temporal trend and actual concentrations of pyrethroids in the runoff water were similar. All pyrethroids displayed high runoff transferability from the concrete 1 d after the treatment, but detectable residues were found in the runoff for all treatments even after 89 d of exposure. For instance, on day 89, bifenthrin concentrations in the runoff water were 0.57 ± 0.08 , 0.64 ± 0.10 , and 0.75 ± 0.16 ppb for 19.3 ± 1.7 , 26.2 ± 2.7 , and 32.6 ± 4.2 mm/h respectively, which are not statistically different at the 95% confident level.

Enhanced runoff of nutrients and herbicides from soil surfaces at increased rainfall intensities has been reported in previous studies (Shigaki et al., 2007; Kleinman et al., 2006; Müller et al., 2004; Berger et al., 2010; Revitt et al., 2002), and the increased runoff transport was attributed to higher extraction efficiency and/or enhanced soil erosion at higher rainfall intensities. However, this conclusion may not be applicable to

concrete surfaces. Similar to findings from this study, Jorgenson and Young (2010) also noticed that increasing the intensity of simulated rainfalls did not necessarily increase pyrethroid concentrations in the runoff from concrete. Unlike soils which are composed of erodible aggregates, hardened concrete is cured to form a solid integrity and designed to resist water erosion. Therefore, increased precipitation intensity will not necessarily enhance pesticide removal from concrete. It must be noted that in this study, the lowest precipitation rate (19.3 ± 1.7 mm/h) is already higher than the intensity of most natural rainfalls, which may have contributed to the absence of discernable effect by different precipitation intensities.

Impact of concrete surface conditions

In residential areas, concrete surfaces are often subject to surface or ingredient modifications to achieve specific esthetic or functional purposes. Common modifications include acid washing, surface sealing, stamping, and others. For instance, a freshly prepared driveway is often acid washed before use to remove milky stains and obtain a uniformly darker color. Silicone sealants are often applied to protect concrete surfaces against water and extend the lifetime of the concrete. These modifications may change the surface texture or porosity of concrete materials, which will probably lead to differences in pesticide persistence and runoff transferability.

To evaluate the effects of concrete modifications on pesticide runoff potential, concrete slabs with different surface conditions were treated with pyrethroids and subjected to repeated precipitations at 26.2 ± 2.7 mm/h. As shown in Fig. 4-4 for

bifenthrin, different surface treatments showed similar decreasing trends in runoff transferability. For instance, in the day 1 runoff, $0.85 \pm 0.38\%$ of bifenthrin applied on the concrete with acid-washing (AW) was recovered, which was not statistically different from $1.33 \pm 0.37\%$ for concrete with silicone sealing (SC). In addition, extended persistence of pyrethroid runoff was observed for all concrete surface types. Following repeated precipitations, the bifenthrin concentration in the day 89 runoff from AW treatments was $0.24 \pm 0.08 \mu\text{g/L}$, which was close to $0.10 \pm 0.05 \mu\text{g/L}$ for SC concrete treatments. The overall statistical analysis showed that the only difference frequently observed was the reduced bifenthrin runoff from the stamped concrete (SS). For instance, only $0.21 \pm 0.07\%$ of the applied bifenthrin on the SS concrete was found in the day-1 runoff water, which was smaller than the $0.85 \pm 0.38\%$ for the AW treatment and $1.33 \pm 0.37\%$ for the SC treatment. In the day-89 runoff, the bifenthrin concentration from the SS treatment was $82.4 \pm 21.9 \text{ ng/L}$, which was lower than 236.4 ± 84.6 and $212.4 \pm 47.8 \text{ ng/L}$ for AW and SC treatments respectively. The decreased pyrethroid transferability may be due to the increased surface roughness after stamping and/or enhanced physical trapping of loose particles that may contain pyrethroids. As mentioned before, given the relatively high precipitation rate used in the experiment, more pronounced effects of surface conditions may be observed if reduced precipitation intensity was used.

Pesticide runoff through natural rainfalls

In regions such as California, rainfalls events are normally concentrated in the winter months, whereas pesticides are usually applied in the summer when the greatest

pest pressure occurs. Previous studies show that runoff from winter rainfalls is the primary source for pollutant loadings into urban watersheds, even though irrigation-induced runoff continues for months before the first winter rainfall (Pedersen et al., 2006; Schiff and Sutula, 2004; Bailey et al., 2009; Amweg et al., 2006; Weston et al., 2005). For instance, Weston et al. (2009) estimated that in residential areas, one intense 3-h rainfall may result in bifenthrin runoff comparable to over 6 months of irrigation runoff under dry weather conditions. Therefore, it is important to determine the availability of pesticides applied early in the year to contaminate rainfall runoff in the winter months. Such information may also be used to mitigate rain-induced pesticide runoff by determining better timing for pesticide applications.

In this study, five sets of concrete slabs were treated with pyrethroids at the same rates, but in different months of the year ahead of the winter raining season. Runoff water from concrete surfaces was sampled during the first two natural rainfall events (Fig. 4-5). In general, pyrethroid concentrations in the rain-induced runoff always decreased as the time interval between pesticide treatment and the rain event increased. For instance, for the July concrete treatments, the event mean concentrations (EMCs) of bifenthrin in runoff water were 1.41 ± 0.28 and 2.10 ± 0.35 $\mu\text{g/L}$ for the first and second rain events, respectively. These values were about 10 times smaller than 13.08 ± 5.67 and 18.91 ± 5.16 $\mu\text{g/L}$ for the November treatments, for which the pesticides were applied only 7 d before the first rainfall event. The average concentrations of pyrethroids in the two runoff events were further plotted as a function of the elapsed time after treatments and fitted to a first-order decay model to derive the dissipation rate constant (k , d^{-1}) and half lives ($T_{1/2}$,

d) (Table 5-2). In general, good model fitting was observed for both bifenthrin and permethrin, with R^2 values ranging from 0.90 to 0.94 (Table 5-2). Both pyrethroids displayed long runoff transferability, and the estimated $T_{1/2}$ values were greater than 20 d in all cases. The extended availability of pyrethroid residues for runoff contamination was further evident from the earliest treatment made on April 1, 2010, which was 221 d prior to the first winter rainfall. For this treatment, the pesticide-treated concrete slabs received three significant rain showers (3.6, 24.9, and 7.1 mm, respectively) during the month of April (CIMIS, 2010). However, pyrethroid residues were still detected in the runoff from two monitored winter rainfalls. The EMCs were 0.15 ± 0.06 and 0.17 ± 0.06 $\mu\text{g/L}$ for bifenthrin, 0.87 ± 0.49 and 0.75 ± 0.21 $\mu\text{g/L}$ for cis-permethrin, and 1.15 ± 0.69 and 0.87 ± 0.30 $\mu\text{g/L}$ for trans-permethrin, respectively.

The two winter rainfalls monitored in this study occurred two weeks apart. The first rainfall was small, with a 16-h cumulative precipitation rate of only 2.3 mm, and the maximum hourly intensity was 0.24 mm/h. In comparison, the second rainfall lasted for 32 h with 12.4 mm total precipitation, and the recorded maximum hourly intensity was 4.1 mm/h (CIMIS, 2010). Correspondingly, greater amounts of pyrethroids were recovered in the runoff from the second rainfall. For instance, for the July treatment, 657 ± 166 ng of bifenthrin was transferred from each concrete slab to the runoff water during the first rainfall event, which was much smaller than 3256 ± 691 ng for the second one. The increased pesticide runoff loss during the second rainfall was primarily attributed to the much larger runoff volume collected, because pesticide EMCs were often similar between the two rainfall events. For instance, for the September treatment, runoff EMCs

of bifenthrin following the first and second rainfalls were 14.0 ± 5.1 and 16.0 ± 2.4 $\mu\text{g/L}$, respectively. This observation showed that the rainfall intensity did not necessarily influence pesticide transferability from concrete. The lack of variation in pesticide levels between the first and second rainfalls further highlighted the role of concrete surfaces as a reservoir of pesticide residues, contributing to sustained contamination of urban runoff through recurring rainfall events.

Conclusions

This study showed that the transferability of pyrethroid residues to runoff water after applications on concrete was initially high, but decreased quickly over time. However, runoff from concrete contaminated by low levels of pyrethroid residues was also observed for an extended duration of time. For concrete slabs repeatedly subjected to simulated precipitations, pyrethroid residues were found in runoff even after 3 months of exposure to outdoor summer conditions, and pyrethroids could be found in rain-induced runoff after more than 7 months. Precipitation intensities and concrete surface conditions did not appear to greatly affect the runoff transferability of pyrethroid residues from concrete. Findings from this study validated, under more realistic field conditions, the conclusions previously derived from bench-scale studies. The initial high transferability would suggest that water contact with freshly treated concrete surfaces should be prevented (e.g., no pesticide treatment before pressure washing of concrete, no perimeter pesticide treatments on concrete around lawns with impending irrigation events), and that pesticides should not be applied before a rain event. The long persistence of transferable

pesticide residues on the concrete implies that pesticide treatments made early in the year can be a significant source for contamination of rain-induced runoff in the winter months.

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Table 4-1. Relative contributions of pyrethroid runoff from each simulated precipitation event to the total cumulative pyrethroid runoff loss. Results are given as mean \pm standard deviation (n = 4).

Precipitation (days after treatment)	% of Total cumulative runoff loss		
	Bifenthrin	<i>cis</i> -Permethrin	<i>trans</i> -Permethrin
1	83.29 \pm 5.75	93.10 \pm 2.94	90.10 \pm 2.94
7	12.08 \pm 3.88	4.81 \pm 2.11	6.29 \pm 2.54
20	2.32 \pm 0.75	1.25 \pm 0.51	1.80 \pm 0.67
47	1.43 \pm 1.10	0.53 \pm 0.32	0.71 \pm 0.46
89	0.88 \pm 0.46	0.30 \pm 0.18	0.44 \pm 0.24

Table 4-2. First-order rate constant k (d^{-1}) and half-life (DT50, d) values describing the decline of pyrethroid transferability to runoff from concrete.

Precipitation Type	Parameters	Bifenthrin	<i>cis</i> -Permethrin	<i>trans</i> -Permethrin
Simulated single-time precipitation	k ($\times 10^{-2}$, d^{-1})	4.53 ± 0.82	5.41 ± 0.52	5.97 ± 0.48
	DT50 (d)	15.3	12.8	11.6
	R^2	0.64	0.86	0.87
	p	<0.0001	<0.0001	<0.0001
Natural rainfall	k ($\times 10^{-2}$, d^{-1})	2.30 ± 0.14	3.10 ± 0.24	3.24 ± 0.25
	DT50 (d)	30.1	22.4	21.4
	R^2	0.94	0.91	0.90
	p	<0.0001	<0.0001	<0.0001

Figure 4-1. Levels of bifenthrin in the runoff following simulated single-time or repeated precipitations at 26.2 ± 2.7 mm/h ($n = 4$). The results are expressed as bifenthrin concentration ($\mu\text{g/L}$) in the runoff water and percentage of the initial application rate.

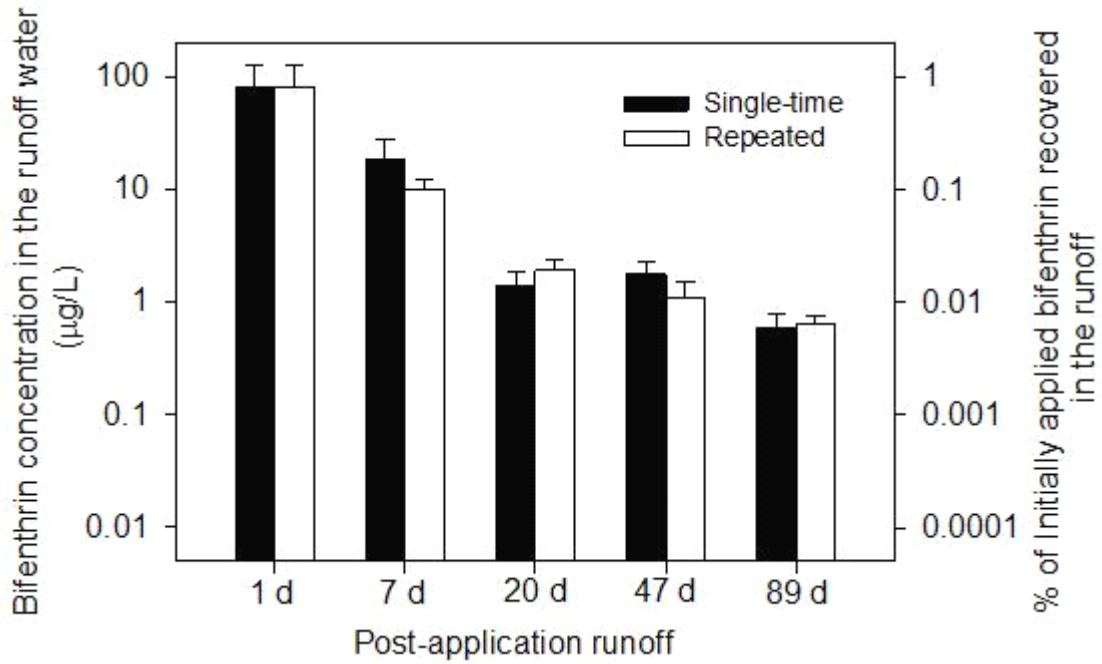


Figure 4-2. Levels of (A) *cis*-permethrin and (B) *trans*-permethrin in the runoff following simulated single-time or repeated precipitations at 26.2 ± 2.7 mm/h ($n = 4$). The results are expressed as permethrin concentration ($\mu\text{g/L}$) in the runoff water and percentage of the initial application rate.

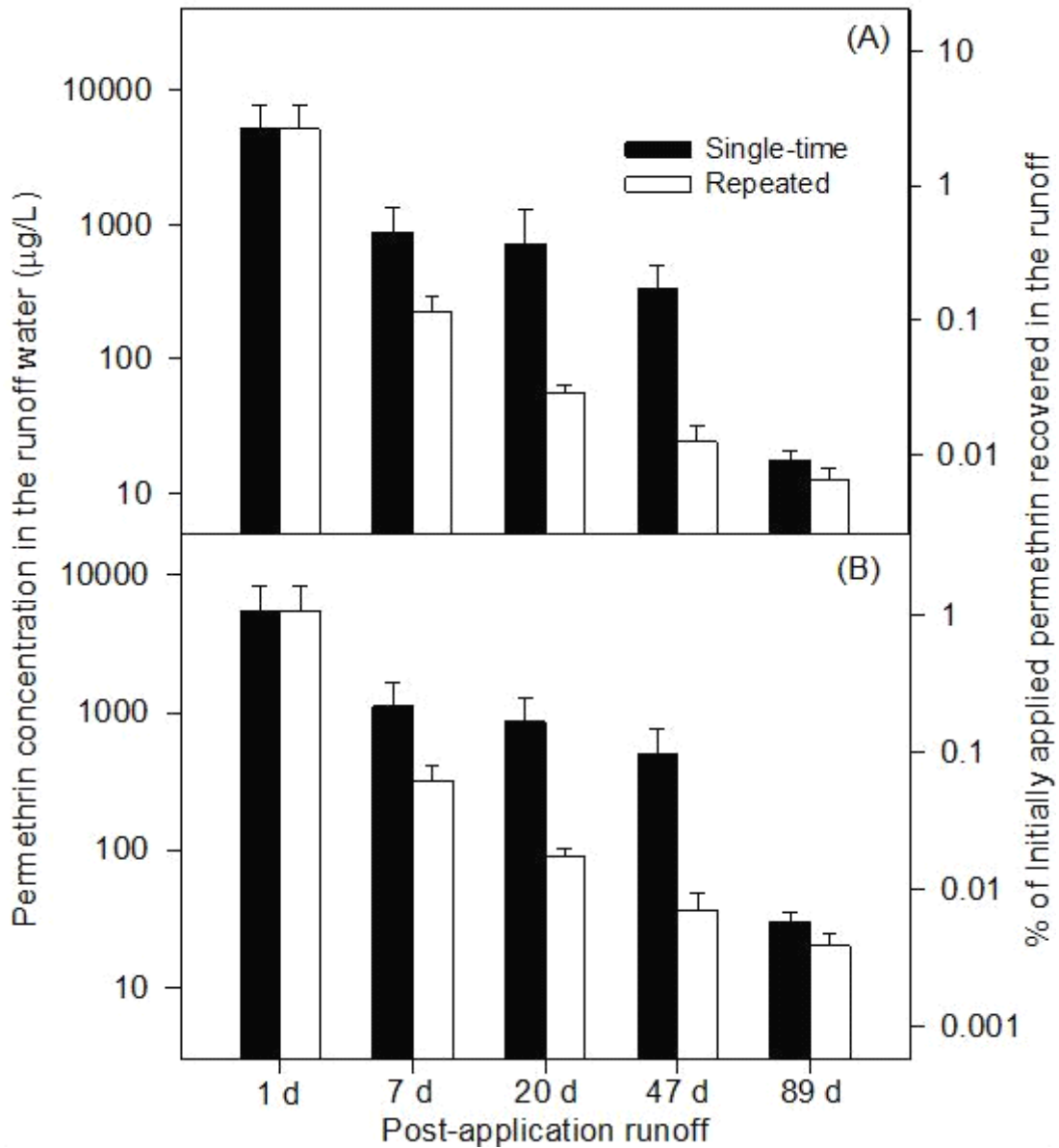


Figure 4-3. Levels of *cis*-permethrin in the runoff water from concrete slabs receiving repeated precipitations at 19.3 ± 1.7 , 26.2 ± 2.7 , or 32.6 ± 4.2 mm/h (n = 4)

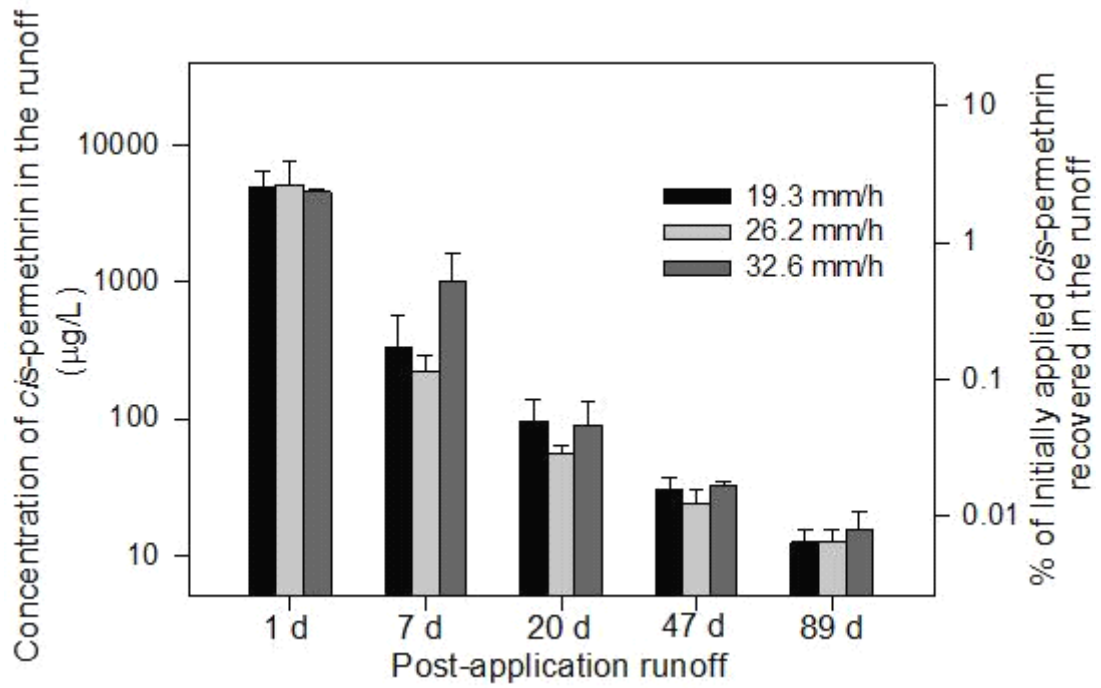


Figure 4-4. Levels of bifenthrin in the runoff water from different concrete surfaces after repeated precipitations (n = 4).

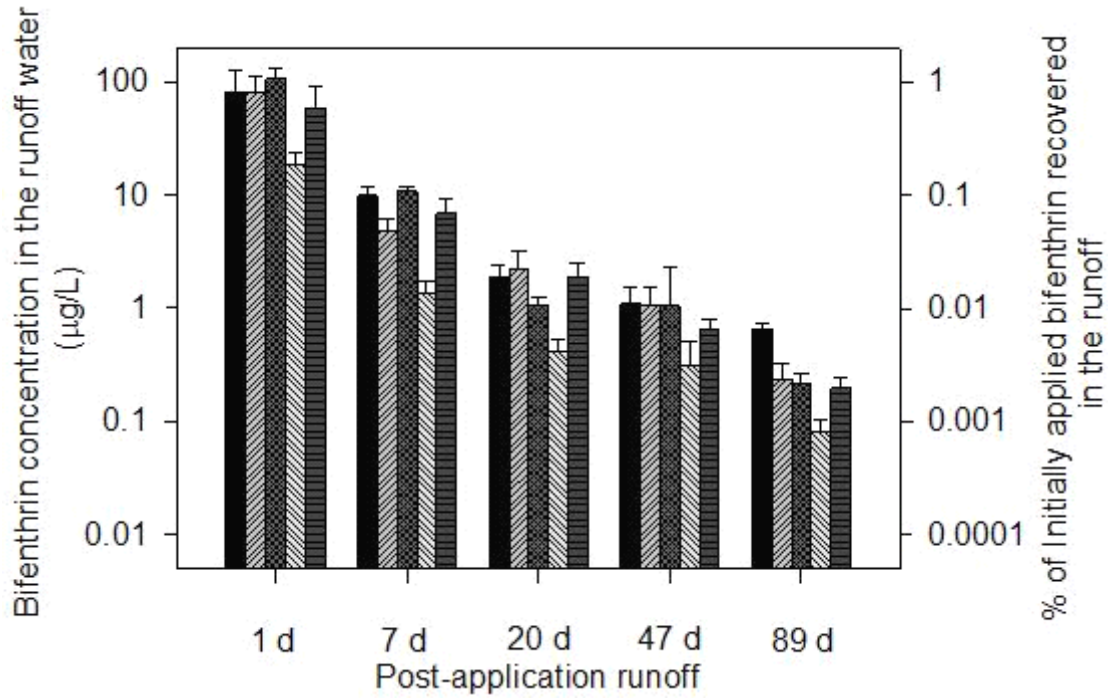
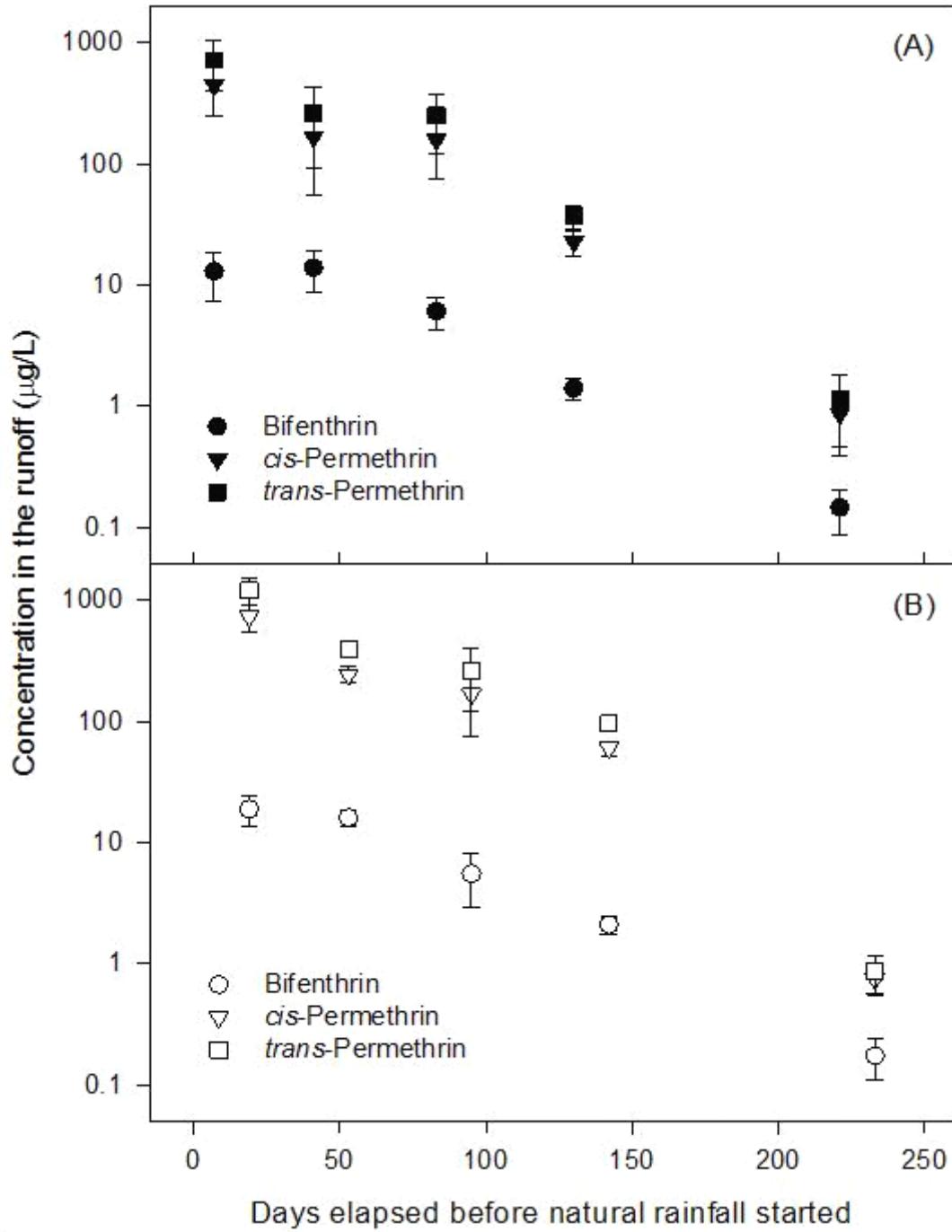


Figure 4-5. Concentrations of bifenthrin and permethrin in the runoff water from two winter rainfalls. (A) first rainfall; (B) second rainfall (n = 4).



Supplementary Materials

Concrete modification

Four sets of concrete slabs were subjected to surface or ingredient modifications to simulate common practices. These modifications includes microsilica addition during concrete slab preparation, surface stamping before concrete hardened, and acid wash or silicone sealing 3 months after the concrete slabs were constructed.

Acid wash: After curing for 3 months, the concrete surfaces were soaked with 10% muriatic acid until bubbling stopped (~10 min). The concrete surface was then dusted with sodium bicarbonate and washed with tap water to remove the remaining acid residues.

Silicone seal: After curing for 3 months, the concrete surface was evenly brushed with a water-based silicone sealant (BEHR, Santa Ana, CA) until saturation. To prevent contact with water, the sealed concrete surfaces were covered with a plastic film for 3 days.

Stamping: Immediately after smoothing the surfaces, the concrete surfaces were dusted with stamping releasing agents (Advanced Surfaces Inc., Margate, FL), followed by patting with a sheet of rubber map to achieve a slate texture. After removing the stamping mat, the concrete was allowed to cure for 24 h and then washed with tap water to remove the residues left on the concrete.

Microsilica addition: The concrete slabs modified by microsilica addition were prepared by replacing 10% sands with the same volume of Grade 965 microsilica (Elkem Silicon Materials, Kristiansand, Norway). The concrete slurry was then individually

poured into the frame templates and the slabs were prepared following the same practices as the other treatments.

Simulated precipitation system

The system was composed of a mobile spray panel driven by a 12V gear motor (Anaheim Automation, Anaheim, CA) and linear-moving on an elevated trail at a speed of 1.2 m/min. The spray panel was equipped with six Teejet 8002E even flat spray tip assemblies (Teejet Technologies, Springfield, IL). The nozzles were calibrated at 45 cm above the ground (34 cm above concrete surface) to achieve uniform precipitation over the concrete slabs. Precipitation intensity was controlled by pre-setting the hydraulic pressure gauge at 20, 40, or 55 psi, and the resulting precipitation rates were 19.3 ± 1.7 , 26.2 ± 2.7 , 32.6 ± 4.2 mm/h. The distribution uniformity (DU) measured by the catch cup method was 89.2% (20psi), 89.9% (40psi), and 84.6% (55psi).

Chemical Analysis

Pyrethroids in the runoff water were solvent extracted following modified EPA Method 3510C, sample cleanup with Florisil following modified EPA Method 3620C, and analyzed by gas chromatography/tandem mass spectrometry (GC-MS/MS). Briefly, the water sample was transferred to a 2-L glass separatory funnel preloaded with 40 g sodium chloride and spiked with 200 μ L of 2 ppm decachlorobiphenol as a surrogate. Pyrethroids were extracted for four consecutive times using 60 mL methylene chloride each time. The extracts from the four extractions were combined and then passed through

40 g anhydrous sodium sulfate to remove the residual water, followed by concentration to near dryness, and then reconstituted in ethyl acetate/hexane (3/7, v/v). The clean-up was carried out by loading the extract onto a 150-mg Florisil cartridge (Grace, Deerfield, IL) preconditioned with 5 mL ethyl acetate/hexane (3/7, v/v), and eluting with 10 mL ethyl acetate/hexane (3/7, v/v). The eluted fraction was further concentrated to near dryness under nitrogen, spiked with 10 μ L 1.2 ppm ^{13}C -permethrin as the internal standard and then reconstituted to 1 mL with hexane/acetone (9/1, v/v). An aliquot of the final extract was injected for GC-MS/MS analysis.

Pyrethroid quantification was carried out using a 3800 GC (Varian Instruments, Sunnyvale, CA) coupled with a Varian 1200 triple-quadrupole mass spectrometer and a CombiPal autosampler (CTC Analytics, Zwingen, Switzerland). Samples were introduced into the inlet at 260 $^{\circ}\text{C}$ and the separation was achieved on a DB-5ms capillary column (30m \times 0.25 mm \times 0.25 μm , Agilent, Wilmington, DE). The carrier gas was helium (99.999%) and the flow rate was set at 1.0 mL/min. The column temperature was initially programmed at 80 $^{\circ}\text{C}$ for 1.0 min, then ramped to 300 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C}/\text{min}$, and held at 300 $^{\circ}\text{C}$ for 5 min.

The triple-quadrupole mass spectrometer was operated in EI selected reaction monitoring mode at 70 eV. The transfer line, ion source, and manifold temperatures were set at 300, 170, and 40 $^{\circ}\text{C}$, respectively. Argon (99.999%) in 2.0-2.1 mTorr was used as the collision gas, and a 7 min solvent delay and extended dynamic range (EDR) were enabled for the detector. The EI-MS-MS profile was obtained by injecting individual analyte under the experimental conditions to determine the parent ion, collision energy

and daughter ion (Table S1). The quantification was through injection of chemical standards containing known concentrations of target analytes and internal standards.

Table 4-S1. Method detection limits (MDLs) and conditions of mass spectrometer for pyrethroid quantification. Recovery results are given as mean \pm standard deviation (n = 4).

Chemical	Recovery (%)	MDL ^a (ng/L)	Retention (min)	Parent ion (<i>m/z</i>)	Daughter ion (<i>m/z</i>)	Collision energy (eV)
Bifenthrin	83.7 \pm 5.9	4.5	14.85	181	166	10
<i>cis</i> -Permethrin	99.0 \pm 9.1	6.9	16.08	183	153	12
<i>trans</i> -Permethrin	97.1 \pm 9.1	10.4	16.16	183	153	12
¹³ C- <i>cis</i> -permethrin			16.08	189	174	14
Decachlorobiphenyl			17.12	498	426	30

^a MDL: method detection limit.

CHAPTER 5

Importance of Fine Particles in Pesticide Runoff from Concrete Surfaces and Its Prediction

Abstract

Pesticides such as pyrethroids have been frequently found in runoff water from urban areas and the offsite movement is a significant cause for aquatic toxicities in urban streams and estuaries. To better understand the origination of pesticide residues in urban runoff, we investigated the association of pyrethroid residues with loose particles in runoff water from concrete surfaces after treatment with commercial products of bifenthrin and permethrin. In runoff water generated from simulated precipitations after 1 to 89 d exposure under dry outdoor conditions, over 80% of the pesticides was found on particles $>0.7 \mu\text{m}$ for most treatments. The solid-water partitioning coefficient (K_d) on day 1 was estimated to be 2.4×10^3 - 1.1×10^5 L/kg for permethrin and bifenthrin on these solids. Except for solid formulations, the pesticide-laden particles likely originated from dust particles preexisting on the concrete before treatment and the disintegration of the surficial concrete matter through weathering. We consequently tested a simple sponge-wipe method to collect and analyze the loose particles on concrete. Concurrent analyses ($n = 30$) showed an excellent linear correlation between the amount of pesticides transferrable to runoff water and that on the wipe ($R^2 = 0.78$, slope = 1.13 ± 0.11 , $P < 0.0001$). The fact that the linear relationship has a slope close to 1.0 suggests that this method may be used to predict pesticide residues available for contaminating runoff water before runoff actually occurs. The importance of loose particles should be considered when developing practices to mitigate pesticide runoff contamination from urban residential areas.

Introduction

Widely used for urban structural and landscape pest control, pesticides such as pyrethroids have been identified as a primary cause for invertebrate toxicities in water and sediments of urban streams and estuaries around the United States, especially in California (1-5). The source of pesticide contamination in urban watersheds has been attributed to the offsite movement of pesticide residues from urban hard surfaces such as concrete via irrigation and rain-induced runoff (6-9). In highly urbanized areas, hard surfaces such as concrete may account for up to 90% of the total urban area (10-12). Pesticides may be intentionally applied on concrete to eradicate pests such as ants and termites, or indirectly reach concrete surfaces via wind or water-aided movement from other treated areas such as lawns or around the foundation of houses. A survey showed that 60% of pesticide use in residential outdoor environments in California is on impervious surfaces (13).

Although environmental fate of pesticides has been generally well studied in matrices such as soil and water, it was not until recent years that researchers attempted to understand pesticide behaviors on concrete and the transferability of pesticide residues from concrete surfaces to runoff water (6-9). In previous studies, we observed that after treatment, pesticides such as pyrethroids were rapidly sorbed onto the concrete surface, causing an initial sharp decrease in their transferability to water. However, low levels of pesticide residues remained available for contaminating water long after the initial treatment, even when the concrete surfaces were exposed to harsh summer conditions for several months and subjected to many rounds of water wash-off (6, 9). It is well known

that owing to their high K_{ow} and hydrophobicity, pyrethroids have a strong affinity to solid surfaces and particles, and attachment to loose soil or sediment particles is the main form by which their offsite movement takes place in soil-water or sediment-water continuums (14, 15). Therefore, it is reasonable to hypothesize that fine particles also play a critical role in the offsite transport of runoff-borne pyrethroid residues from concrete surfaces. Furthermore, if loose particles are the main carrier of pyrethroid residue in urban surface runoff, then collection and measurement of these particles before a runoff event would provide a good prediction of pesticide runoff potential from concrete areas.

The primary objective of this study was to test the assumption that particles are the primary form by which pyrethroid residues move from concrete surfaces into runoff water. To address this objective, we treated concrete surfaces with different formulations of bifenthrin and permethrin and exposed them to outdoor conditions up to 89 d. Precipitation water was applied in a recurring fashion to the treated surfaces and pesticide association with suspended particles $> 0.7 \mu\text{m}$ was quantified in the runoff water. In addition, we tested a simple sponge wipe method to measure the amounts of pesticides in the dislodgeable particles on concrete for predicting pesticide availability for contaminating runoff water. The safety, portability and simplicity of this method make it an easy tool for estimating pesticide runoff potential before the offsite contamination actually occurs.

Materials and Methods

Chemicals. Bifenthrin and permethrin were selected as the representative urban-use pyrethroids. While permethrin has been the most heavily used pyrethroid in regions such as California, bifenthrin is often the compound detected most frequently in urban water and sediments (16). Three commercial formulations of bifenthrin and permethrin, i.e., ready-to-use (RTU) solid formulation, RTU liquid formulation, and professional concentrate, were purchased from various sources. The concentrations of bifenthrin and permethrin were determined to be $0.15 \pm 0.01\%$ and $0.22 \pm 0.01\%$ in the RTU solid formulation, $0.06 \pm 0.01\%$ and $0.20 \pm 0.02\%$ in the RTU liquid formulation, and $8.74 \pm 0.44\%$ and $35.1 \pm 1.2\%$ in the professional formulation, respectively. Chemical standards of bifenthrin (99%, Chem Service, West Chester, PA), permethrin (97%, 40% *cis*/60% *trans*, FMC), phenoxy $^{13}\text{C}_6$ -labeled *cis*-permethrin (^{13}C -permethrin, 99%, Cambridge Isotope Laboratories, Andover, MA), and decachlorobiphenyl (99.2%, Chem Service) were obtained from different sources. All solvents and other chemicals in GC/MS or pesticide grade were purchased from Fisher Scientific (Pittsburgh, PA). All glassware was baked at $400\text{ }^\circ\text{C}$ for at least 4 h before use to prevent cross contamination.

Preparation of Concrete Slabs. Details on the preparation of large concrete slabs used in this study were described elsewhere (9). The concrete slabs in the dimension of $60 \times 40 \times 9\text{ cm}$ (L \times W \times H) were prepared according to product instructions. Each slab was set on a $2.7 \pm 0.5^\circ$ slope, and the surface was finished with a V-shaped indentation at the lower end and attached with a brass tubing to allow the drainage and collection of runoff water. Before pesticide treatment, all concrete slabs were allowed to

cure under outdoor conditions for almost 6 months to complete cement hydration and mimic natural aging of concrete surfaces. The average temperature within this period was 20.7 °C, and natural precipitation was observed on 20 days (17).

Pesticide Treatment and Runoff Water Generation. The concrete slabs were divided into three groups and thoroughly washed with a hose the day before pesticide treatment. The washed slabs were treated with the different formulations at comparable rates following the label instructions. For RTU solid formulations, bifenthrin and permethrin were mixed together and uniformly dusted onto concrete surfaces. For RTU liquid formulations, pesticides were applied onto the concrete surfaces directly using a Marson MC air-brush sprayer (Swingline, Lincolnshire, IL). For professional formulations, 0.91 mL of the bifenthrin concentrate and 16 mL of the permethrin concentrate were added to 500 mL water, and 50 mL of the mixed solution was applied evenly onto each concrete slab by setting the air pressure at constant 40 psi. The actual application rates of bifenthrin and permethrin were 3.80 and 175.5 $\mu\text{g}/\text{cm}^2$ for RTU solid, 3.48 and 248.3 $\mu\text{g}/\text{cm}^2$ for RTU liquid, and 3.2 and 233.3 $\mu\text{g}/\text{cm}^2$ for professional formulations, respectively. All pesticide treatments were completed within a 12-h time window to assure similar environmental conditions.

After pesticide treatment, the concrete slabs were exposed to outdoor summer conditions and simulated precipitation was applied repeatedly on day 1, 7, 20, 47, and 89. A rainfall simulator was used to apply the precipitation water at 26.2 ± 2.7 mm/h (9, 18). Catch cups were randomly placed in the precipitation zone and the precipitation distribution uniformity was estimated to be about 90%. For each precipitation, . 1572 \pm

162 mL water was applied onto each concrete slab, of which $56.9 \pm 8.3\%$ was collected as runoff water.

Sample Preparation and Chemical Analysis. The runoff water collected in the amber glass bottles were transported to the laboratory within 4 h and stored at 4 °C before analysis. Before extraction, the runoff water was filtered, under vacuum, through a GF/F glass filter paper (0.7 μm , Whatman, Florham Park, NJ) to separate fine particles from the water phase. The amounts of pyrethroids in the filtrate and on the filter paper were quantified separately. The filtrate samples were extracted using liquid-liquid extraction (LLE) following a modified EPA method 3510C, and the extract was loaded onto a Florisil cartridge (150 mg, Grace, Deerfield, IL) for cleanup following a modified EPA method 3620C. The filter paper (along with the retained particles) were extracted with methylene chloride/acetone (1:1, v/v) in a sonication bath using a modified EPA method 3550, followed by clean up using a Florisil cartridge. Bifenthrin and permethrin in the extracts were analyzed on a gas chromatography/tandem mass spectrometry (GC-MS/MS). More details of pesticide extraction and instrument analysis may be found in the Supporting Materials and in a previous publication (9).

Development of a Surface Wiping Method for Predicting Runoff Potential.

Although not for runoff prediction, surface wiping has been often used to assess the risk of human exposure to pesticide residues in a variety of settings (19, 20). For instance, wiping with cotton fabrics are commonly used to estimate pesticide residues transferrable from residential floors in indoor exposure assessment (21, 22). Using a similar concept, Li et al. analyzed pesticide accumulation on protective gloves to evaluate occupational

exposure of fruit-harvesting workers (23). We tested a similar method by using a 10 × 10 cm Versalon™ nonwoven sponge (4-ply, Kendall Healthcare, Mansfield, MA) pre-wet with 10 mL isopropanol to wipe a given area of concrete surface. For each pesticide formulation, parallel to the above runoff experiment, two additional concrete slabs were similarly treated with the pesticides and subjected to recurring precipitations. However, right before the onset of each precipitation event, a 20 × 20 cm area on the concrete surface was wiped with the sponge, following a side-to-side S-pattern motion in both right-left and top-bottom directions. The sponge was firmly pressed against the concrete surface during wiping but without causing tears to the sponge textile. After wiping, the sponge was stored in a glass jar containing 80 mL methylene chloride/acetone (1/1, v/v) and stored at 4 °C before analysis.

The sponge samples and methylene chloride/acetone solution were transferred to a 250-mL glass beaker and spiked with 200 µL 2 ppm decachlorobiphenol as the recovery surrogate. The samples were then placed in an ultrasonic bath (Fisher Scientific, Pittsburgh, PA) for extraction for 15 min at 42 kHz. The extract was passed through 30 g anhydrous sodium sulfate into a 500-mL round bottom flask. The extraction was repeated for three additional times using fresh solvent each time, and the extracts were combined. The sample extracts were concentrated to near dryness on a vacuumed rotary evaporator at 42 °C, and the residue was reconstituted in 1 mL hexane/ethyl acetate (7/3, v/v). The extract was subjected to further cleanup by elution through a Florisil cartridge and an aliquot of the final sample was analyzed by GC-MS/MS.

Quality Assurance. Several practices were used to assure the accuracy and reproducibility of analytical results. Extraction recoveries and method detection limits (MDLs) of bifenthrin and permethrin from filtrate, filter paper and wiping sponge were determined through preliminary experiments following EPA method 40 CFR Part 136, Appendix B and the results are shown in Table S1. Isotope-labeled internal standard (i.e., ^{13}C -*cis*-permethrin) was spiked into the final sample extract before instrumental analysis to correct for instrument response variations. In addition, a surrogate standard (i.e. decachlorobiphenyl) was spiked individually to all samples before extraction to determine recoveries, and the recoveries were $78.4 \pm 15.5\%$, $91.4 \pm 25.0\%$, and $70.0 \pm 30.7\%$ for filtrate, filter paper, and wipe samples, respectively. Lastly, one laboratory blank was included for every 20 samples and extracted using the same methods to assess potential cross-contamination. The target analytes were not detected in any of the blank samples.

Results and Discussion

Association of pesticides with fine particles in runoff. The concrete slabs were treated at the beginning of summer on July 1, 2010, and then sat under direct sunlight until September 28, 2010. No rain occurred during this period, and the average daily maximum air temperature was $26.1\text{ }^{\circ}\text{C}$, suggesting warm and dry weather conditions (17). In the runoff water collected 1 d after treatment, the highest levels of pesticides were found from concrete treated with the RTU solid formulations, even though the application rates were similar among the different formulations (Table 5-1). On the average, 36.8-62.0%

of the initially applied bifenthrin or permethrin was found in the 1-d runoff water for the RTU solid formulations, which were 1-3 orders of magnitude greater than those for the professional formulation (0.84-2.67%) or RTU liquid formulation treatments (0.1-10.7%) (Figures 5-1 and 5-2). Relatively high levels of pesticides were also found in the runoff from the RTU solid formulation treatments in the subsequent runoff samples. For instance, after 89 d, bifenthrin was detected in the runoff water at $15.50 \pm 7.35 \mu\text{g/L}$ for the RTU solid formulation treatments, which was over 20 times higher than that from the professional formulation treatment ($0.64 \pm 0.10 \text{ ppb}$) or the RTU liquid formulation treatment ($0.76 \pm 0.07 \text{ ppb}$) (Table 5-1). The higher transferability of pesticides from solid formulations (e.g., dust, granules) to runoff water was observed also in a previous study, and was attributed to reduced retention of the pesticide ingredient in the solid carrier by concrete and the inhibited degradation due to shielding provided by the solid carrier from environmental factors (e.g., sunlight) (ϕ).

To evaluate the role of fine particles in pesticide runoff, all water samples were filtered through a 0.7- μm membrane to separate particle and dissolved phases. The majority of bifenthrin or permethrin in the whole runoff water was consistently found on particles regardless of formulations, indicating that particles were the primary carrier for pyrethroid residues leaving the concrete surfaces (Table 5-2). For example, 85.1-92.0% of the total bifenthrin concentration was from particles in runoff samples from concrete surfaces treated with the professional formulation, and the fraction was 88.1-97.6% for *cis*-permethrin and 87.7-96.5% for *trans*-permethrin (Table 5-2). The particle-associated fraction similarly dominated the amounts transferred to the runoff water for the RTU

liquid formulation treatments, with the exception of the 1-d samples where the fractions were smaller (48.8% for bifenthrin and 71.5% for *trans*-permethrin) (Table 5-2). The relatively smaller contribution from particles in the 1-d runoff samples was likely due to surfactants or solvents present in the RTU liquid formulations, which may have enhanced the apparent partition to the water phase (δ). The particle fraction was even greater for runoff samples from the RTU solid formulation treatments (Table 5-2), where it accounted for 94.4-99.9% of the total bifenthrin concentration, 96.8-99.9% of the total *cis*-permethrin concentration, or 96.1-99.9% of the total *trans*-permethrin concentration.

Unlike RTU solid formulations, RTU liquid formulations and professional concentrates used in this study were all liquid products and contained no visible solid materials. The RTU liquids of bifenthrin and permethrin were registered as solutions or liquids with diluted concentrations of active ingredients (24). The bifenthrin professional formulation was a suspended concentrate, while the permethrin professional formulation was an emulsifiable concentrate, i.e., an organic solution containing pesticide and emulsifying agents (24, 25). Therefore, while the dominant association with particles may be attributed to the solid carrier contained in the RTU solid formulations, the particles on the concrete surfaces treated with the liquid formulations had different origins, including likely soil or dust particles previously deposited on the concrete that were not removed by the pre-treatment washing, soil or dust particles deposited onto the concrete by wind after the treatment, and small concrete aggregates formed from concrete weathering. Given that the concrete slabs were situated in an unplanted field away from residential homes, the soil particles deposited after the pesticide treatment should contain little bifenthrin or

permethrin. Therefore, while it was impossible to physically distinguish the different origins, the pesticide-laden particles on the concrete slabs were either solids that were not removed from the concrete surface by the pre-treatment washing, or from the disintegration of surficial concrete matter, or both. Particles present on the concrete prior to the treatment could come into contact with high levels of pesticides as the application solution was sprayed onto the surface. It is also known that when exposed to different environmental factors (e.g., atmospheric carbon dioxide, temperature cycles, wetting/drying cycles, aggressive chemicals), concrete undergoes structural deterioration, especially on the exposed surface, which may gradually produce scalings, fractures and efflorescence, and finally result in mass loss from the bulk (26-31). For instance, after 130 wetting-drying cycles in CaCl₂ solutions, concrete lost about 2% of its original mass (32). Therefore, it is likely that upon treatment, the outmost thin layer of concrete contained very high levels of the applied pesticides, and that the gradual disintegration of the concrete matter at the exposed surface over time acted as a constant source supplying pesticide residues transferrable to runoff water.

The amount of fine particles >0.7 μm was measured for the 1-d runoff samples by drying the filter paper in a desiccator for 24 h. As expected, the amount of solids from the RTU solid formation was very large (Table 5-3). In comparison, only about 0.39-0.54 g of dry solids was found in the 1-d runoff water from those concrete slabs treated with the liquid formulations (Table 5-3). The apparent sorption coefficient K_d was estimated using the concentration on the particles and that in the filtrate. Very large K_d values were obtained. For instance, K_d values ranged from 3.1×10^4 to 1.1×10^5 L/kg for the

professional formulation treatments, and 2.4×10^3 to 4.0×10^4 L/kg for the RTU liquid formulation treatments (Table 5-3). These values were over 1 order of magnitude higher than those for soil or sediment phases that were typically measured under equilibrium conditions (33-35). The much larger K_d values observed in this study provided further evidence that dislodgeable particles on concrete surfaces were likely pre-deposited dust particles that became heavily dosed with pesticides during treatment and fragments from the disintegration of the outmost layer of concrete containing high levels of pesticides.

The mass of fine particles was not determined for runoff samples collected beyond the 1-d interval, as deposition of soil or dust particles by wind was expected to become an increasingly important source over time. However, the fact that pesticide levels in the runoff water decreased exponentially as a function of time (Figure 5-1) suggested that extraneous soil or dust particles containing high levels of pyrethroids were quickly depleted, and that the subsurface layer of concrete containing exponentially lower levels of pesticides became exposed. The disintegration of the subsurface layer of concrete matter resulted in the transfer of low levels of pyrethroids to the runoff water in a sustained fashion. Future studies should investigate the vertical penetration patterns of pesticides in concrete and influences of factors such as pesticide formulations (e.g., surfactants) (δ), concrete texture and age, and concrete surface modifications (e.g., sealants, acid wash).

Estimation of runoff-transferrable pesticide residues. The observation that dislodgeable particles contributed the most to the pesticide levels in the runoff water implies that a method that quantitatively recovers and analyzes the loose particles would

provide an estimate of pesticide runoff potential from concrete surfaces. The surface-wiping method tested in this study is a simple, non-invasive method that is capable of capturing the loose particles from concrete surfaces. The concurrent analysis showed a consistently good agreement between the amounts of pesticides detected in the runoff water and those found on the sponge wipes for the same treatment and at the same elapsed time interval. For instance, $35.0 \pm 7.2 \mu\text{g m}^{-2}$ of bifenthrin was found in the 7-d runoff water from the concrete slabs treated with the professional formulation, and similar amounts ($24.8 \pm 6.6 \mu\text{g m}^{-2}$) were simultaneously found on the sponge wipes. Likewise, the amounts of permethrin ($1929.4 \pm 570.3 \mu\text{g m}^{-2}$ in the runoff and $1982.1 \pm 342.5 \mu\text{g m}^{-2}$ on the wipes) from the same treatment were also statistically identical. When pesticide amounts in the runoff water and those recovered on the sponge wipes, after normalization over the surface area of concrete slabs, were plotted against each other, a very good linear correlation was observed (Figure 5-3). The correlation was statistically significant at $P < 0.0001$, with R^2 of 0.78. Furthermore, the slope of the linear regression was 1.13 ± 0.11 , statistically similar to 1, suggesting that the sponge wiping method accurately predicted the runoff potential of these pesticides from concrete surfaces. It must be noted that the correlation included data points for both bifenthrin and permethrin, and concrete slabs treated with all different formulations. The good linear regression highlights the validity to estimate pesticide runoff potential based on the collection of loose particles as well as the rigorousness of this method.

To our knowledge, this study was the first attempt to develop a method for predicting the offsite transport potential of pesticides from concrete via surface runoff.

Although not tested in this study, the underlying principle of the surface wiping method should be similarly applicable for other hydrophobic contaminants, including other hydrophobic pesticides, and PAHs, and likely other urban hard surfaces (e.g., asphalt) as well. The simplicity, portability, and minimal time or material demand make the surface wipe method particularly suitable for use in quick surveys in residential areas. Such surveys may be used to identify “hot spots” around individual homes to delineate the causes of pesticide runoff contamination on the individual residence level, or to compare different neighborhoods, urban watersheds, or different cities to achieve a better understanding of the influences of pest management practices, and soil, landscape and environmental conditions. Such information will be valuable for devising lot- or neighborhood scale mitigation options to minimize pesticide runoff contamination from urban residential areas.

The finding that particles on concrete were likely the primary carrier of hydrophobic pesticide residues in offsite transport from concrete underlines the importance to decrease loose particle movement as a critical step to mitigate urban non-point pollution. It must be noted that in practice, concrete surfaces are not cleaned prior to a pesticide application. Therefore, the role of preexisting solids may play even a greater role in transporting pesticides offsite via surface runoff than that observed in this study. In addition, most residential areas have vegetated landscapes, as well as hardscapes, and contributions of pesticide-containing soil or dust particles from treated soil or planted areas to the overall pesticide residues available for contaminating runoff water may be also significant. The probable mitigation practices include the use of

barriers such as curbs and vegetated swales to prevent solids from leaving the home site, baffles to trap solids before the runoff water enters the drainage system, and small settling ponds or wetlands at the drainage outfalls to decrease the levels of solids reaching downstream creeks or streams. In addition, practices such as street sweeping, especially before the onset of a rainy season, may help to reduce the amount of pesticides entering rain-induced surface runoff.

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Table 5-1. Total concentrations of pyrethroids ($\mu\text{g/L}$) in the runoff water ($n = 4$). The concrete was treated with pyrethroids in ready-to-use (RTU) solid, RTU liquid or professional formulations.

<i>Bifenthrin</i>			
Runoff (d)	RTU solid	RTU liquid	Professional
1	$3.89 \pm 0.42 \times 10^3$	7.88 ± 4.07	$8.19 \pm 4.60 \times 10^1$
7	$1.78 \pm 0.38 \times 10^2$	1.54 ± 0.39	9.91 ± 2.14
20	$6.06 \pm 1.32 \times 10^1$	0.74 ± 0.10	1.91 ± 0.50
47	$2.77 \pm 1.35 \times 10^1$	0.86 ± 0.06	1.09 ± 0.42
89	$1.55 \pm 0.74 \times 10^1$	0.76 ± 0.07	0.64 ± 0.10
<i>cis</i> -Permethrin			
Runoff (d)	RTU solid	RTU liquid	professional
1	$1.00 \pm 0.07 \times 10^5$	$2.56 \pm 0.45 \times 10^4$	$5.14 \pm 2.60 \times 10^3$
7	$6.86 \pm 1.32 \times 10^3$	$8.50 \pm 5.33 \times 10^2$	$2.23 \pm 0.66 \times 10^2$
20	$1.91 \pm 1.06 \times 10^3$	$5.98 \pm 1.64 \times 10^1$	$5.60 \pm 0.79 \times 10^1$
47	$6.91 \pm 4.87 \times 10^2$	$3.66 \pm 1.70 \times 10^1$	$2.41 \pm 0.62 \times 10^1$
89	$2.15 \pm 0.76 \times 10^2$	$2.29 \pm 0.67 \times 10^1$	$1.24 \pm 0.30 \times 10^1$
<i>trans</i> -Permethrin			
Runoff (d)	RTU solid	RTU liquid	professional
1	$1.46 \pm 0.11 \times 10^5$	$5.77 \pm 1.11 \times 10^3$	$5.52 \pm 2.90 \times 10^3$
7	$9.20 \pm 1.50 \times 10^3$	$1.63 \pm 0.27 \times 10^2$	$3.23 \pm 0.93 \times 10^2$
20	$2.96 \pm 1.64 \times 10^3$	$2.73 \pm 0.52 \times 10^1$	$8.91 \pm 1.26 \times 10^1$
47	$1.05 \pm 0.81 \times 10^3$	$2.10 \pm 0.46 \times 10^1$	$3.53 \pm 0.98 \times 10^1$
89	$3.58 \pm 1.37 \times 10^2$	$2.24 \pm 0.34 \times 10^1$	$2.00 \pm 0.45 \times 10^1$

Table 5-2. Percent of pyrethroids attached on particles (>0.7 μm) in the runoff water (n = 4). The concrete was treated with pyrethroids in ready-to-use (RTU) solid, RTU liquid or professional formulations.

Bifenthrin			
Runoff (d)	RTU solid	RTU liquid	Professional
1	99.9 \pm 0.1	48.8 \pm 17.7	92.0 \pm 5.7
7	98.3 \pm 1.0	90.6 \pm 1.7	89.9 \pm 1.7
20	97.6 \pm 0.4	83.4 \pm 2.2	91.9 \pm 2.6
47	94.5 \pm 2.2	80.0 \pm 7.0	85.1 \pm 4.0
89	97.2 \pm 1.8	88.8 \pm 0.6	87.4 \pm 2.8

<i>cis</i> -Permethrin			
Runoff (d)	RTU solid	RTU liquid	professional
1	99.9 \pm 0.1	94.0 \pm 2.9	97.6 \pm 1.1
7	99.1 \pm 0.7	96.0 \pm 2.1	93.9 \pm 2.3
20	98.8 \pm 0.5	92.7 \pm 1.6	92.1 \pm 2.6
47	96.8 \pm 1.2	94.1 \pm 1.9	90.1 \pm 2.8
89	97.5 \pm 1.5	92.2 \pm 1.3	88.1 \pm 5.3

<i>trans</i> -Permethrin			
Runoff (d)	RTU solid	RTU liquid	professional
1	99.9 \pm 0.0	71.5 \pm 12.5	96.5 \pm 1.2
7	98.9 \pm 0.7	92.4 \pm 2.3	91.2 \pm 1.0
20	98.6 \pm 0.4	85.4 \pm 3.9	91.9 \pm 2.9
47	96.1 \pm 1.6	87.6 \pm 3.3	88.4 \pm 3.2
89	97.3 \pm 1.6	89.9 \pm 1.5	87.7 \pm 5.2

Table 5-3. Partitioning coefficient (K_d) of bifenthrin, *cis*-permethrin and *trans*-permethrin in the 1 d runoff water (n=4). The concrete was treated with pyrethroids in ready-to-use (RTU) solid, RTU liquid or professional formulations.

Formulation	Weight of particles (g)	Partitioning coefficient (K_d , $\times 10^3$ L/kg)		
		Bifenthrin	<i>cis</i> -Permethrin	<i>trans</i> -Permethrin
RTU solid	63.07 \pm 8.96	30.2 \pm 28.3	39.1 \pm 34.7	33.6 \pm 28.8
RTU liquid	0.54 \pm 0.15	2.4 \pm 1.5	39.5 \pm 21.3	6.5 \pm 4.0
Professional	0.39 \pm 0.12	31.4 \pm 12.6	108.4 \pm 62.9	71.9 \pm 39.9

Figure 5-1. Bifenthrin levels in runoff water from concrete slabs after simulated precipitation events (as % of the initially applied amount). The concrete slabs were treated with ready-to-use solid (RTU Solid), ready-to-use liquid (RTU Liquid), or professional concentrate (Professional) formulations (n = 4).

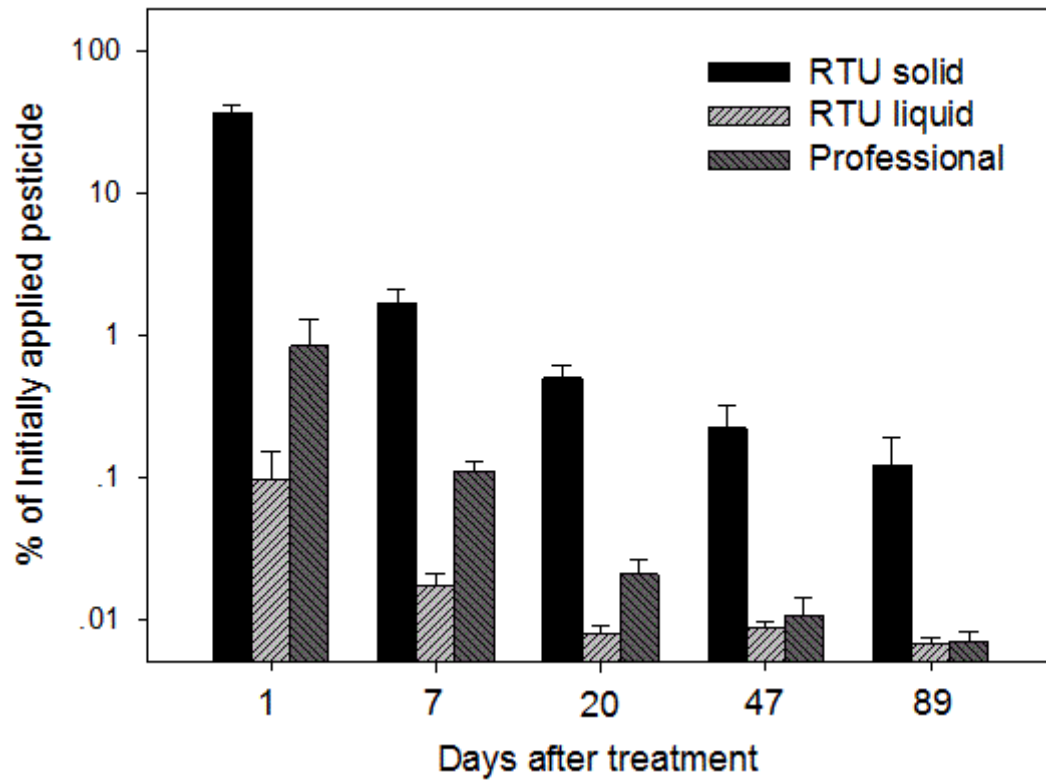


Figure 5-2. Levels of (A) *cis*-permethrin and (B) *trans*-permethrin in runoff water from concrete slabs after simulated precipitation events (as % of the initially applied amount). The concrete slabs were treated with ready-to-use solid (RTU Solid), ready-to-use liquid (RTU Liquid), or professional concentrate (Professional) formulations (n = 4).

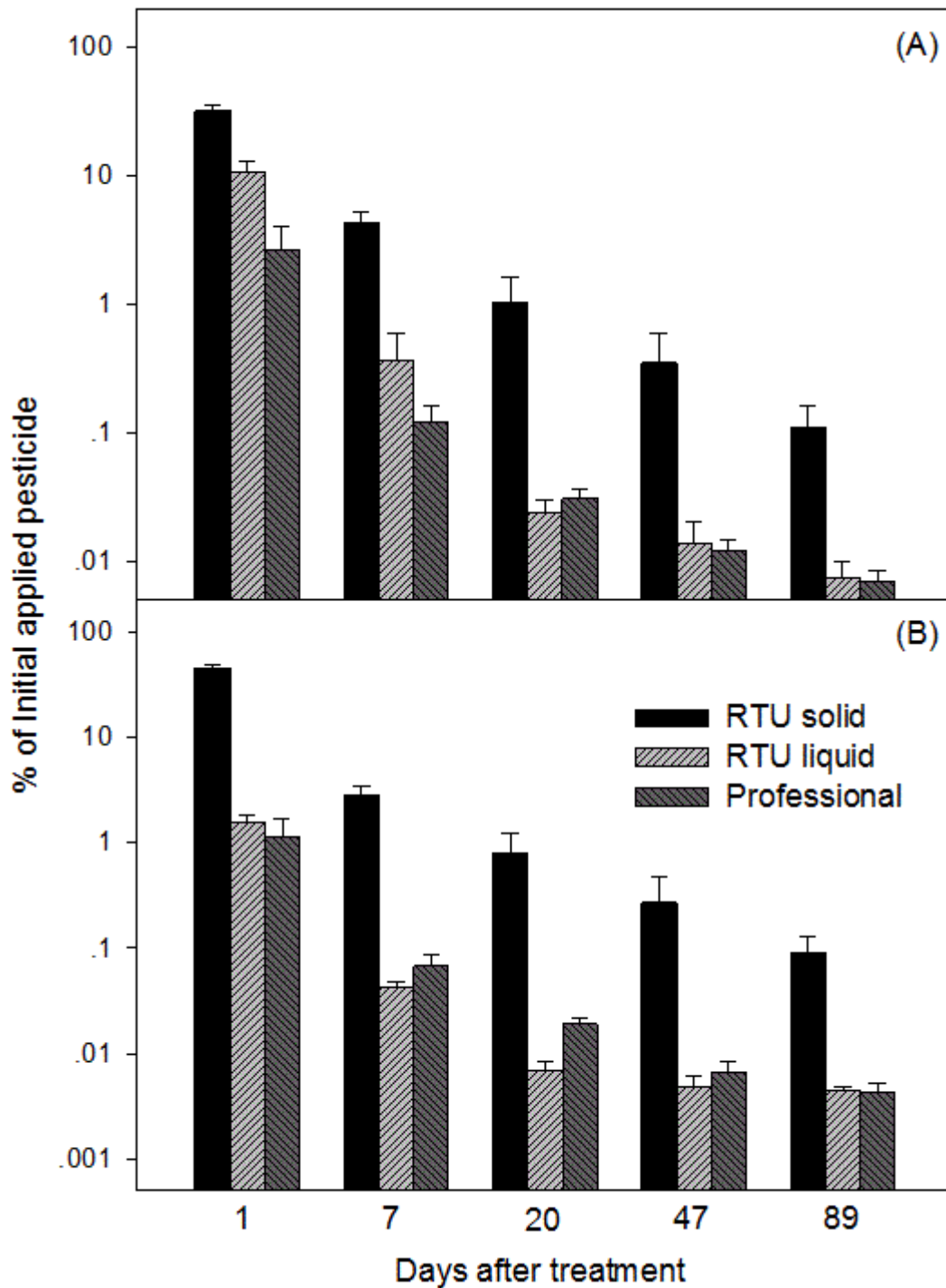
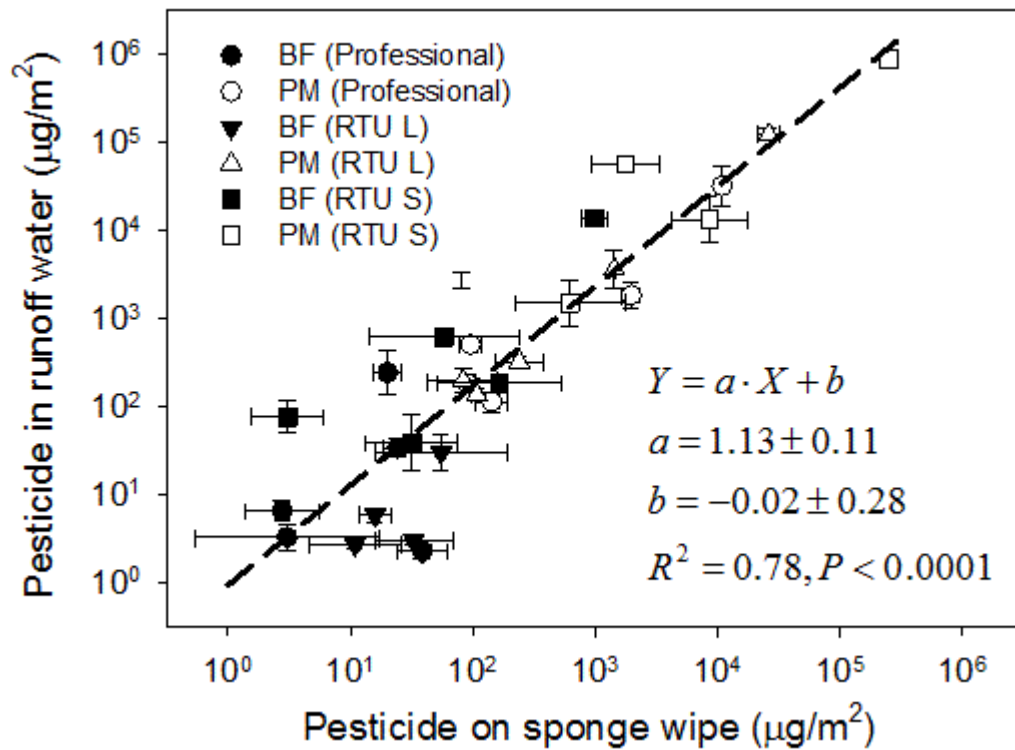


Figure 5-3. Linear correlation of bifenthrin (BF) and permethrin (PM) amounts in runoff water and their corresponding amounts on sponge wipes (after normalization over concrete surface area). The concrete slabs were treated with pesticides in ready-to-use solid (RTU S), ready-to-use liquid (RTU L), or professional concentrate (Professional) formulations.



Supplementary Materials

Chemical Analysis

Filtrate. The pyrethroids in the filtrate ($<0.7\ \mu\text{m}$) was extracted using modified EPA method 3510C for liquid-liquid extraction and cleaned-up following modified EPA method 3620C using florisil cartridges (150 mg, Grace, Deerfield, IL). The filtrate was transferred into a 2-L separatory funnel and spiked with 200 μL 2 ppm decachlorobiphenol as surrogate. The filtrate was extracted for four consecutive times using 60 mL methylene chloride each time. The extracts were passed through 40g anhydrous sodium sulfate, condensed to dryness, and reconstituted in 1 mL ethyl acetate/hexane (3/7, v/v). The extract was further loaded onto a Florisil cartridge preconditioned by 5 mL ethyl acetate/hexane (3/7, v/v), and eluted by 10 mL ethyl acetate/hexane (3/7, v/v) solution. The elution was concentrated to dryness under nitrogen and reconstituted into 1 mL hexane/acetone (9/1, v/v) spiked with 10 μL 1.2 ppm ^{13}C -permethrin as internal standard. An aliquot of the final extract were taken for gas chromatography/tandem mass spectrometry (GC-MS-MS) analysis.

Filter paper. Pyrethroids associated with suspended particles and retained on the filter paper were extracted following modified EPA method 3550 using an ultrasonic bath (Fisher Scientific, Pittsburgh, PA) and cleaned-up using florisil cartridges following modified EPA method 3620C. The GF/F filter paper was transferred into a 250 mL glass beaker and spiked with 200 μL 2 ppm decachlorobiphenol. Each filter paper was extracted by adding 60 mL methylene chloride/acetone (1/1, v/v) and sonicating at 42

kHz and room temperature for 15 min. The extraction was repeated for another three consecutive times and the extracts were passed through a Whatman #41 filter paper filled with 30 g anhydrous sodium sulfate, condensed to dryness, and reconstituted in ethyl acetate/hexane (3/7, v/v). The extract was subject to further florisil cleanup using the same method as mentioned above and the pyrethroid amounts in the final extracts were analyzed by GC-MS-MS.

Table 5-S1. Method detection limits (MDLs) and extraction recoveries of pyrethroids in the filtrate, filter paper and wiping sponge (n = 4).

Chemical	Filtrate		Filter paper		Wiping sponge	
	Recovery (%)	MDL ^a (ng/L)	Recovery (%)	MDL (ng/L)	Recovery (%)	MDL (ng)
Bifenthrin	85.6 ± 3.1	2.4	87.4 ± 8.1	6.1	109.9 ± 22.2	5.0
<i>cis</i> -Permethrin	110.7 ± 6.3	4.7	95.5 ± 7.6	5.8	127.7 ± 25.4	5.8
<i>trans</i> -Permethrin	108.2 ± 4.6	5.2	91.9 ± 8.7	9.9	99.4 ± 11.9	2.7

^a MDL: method detection limit.