WATER RESEARCH 46 (2012) 645–652

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Runoff of pyrethroid insecticides from concrete surfaces following simulated and natural rainfalls

Weiying Jiang [a,*], *Darren Haver* [b], *Michael Rust* [c], *Jay Gan* [a]

[a] *Department of Environmental Sciences, University of California, Riverside, CA 92521, USA*
[b] *University of California South Coast Research and Extension Center, Irvine, CA 92618, USA*
[c] *Department of Entomology, University of California, Riverside, CA 92521, USA*

ARTICLE INFO

Article history:
Received 24 May 2011
Received in revised form
28 October 2011
Accepted 8 November 2011
Available online 25 November 2011

Keywords:
Pyrethroid pesticides
Bifenthrin
Permethrin
Runoff
Urban hard surfaces
Concrete

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.

1. 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

* *Corresponding author*. Tel.: +1 626 376 0278; fax: +1 951 827 3993.
E-mail addresses: jiangwy85@gmail.com, wjian001@ucr.edu (W. Jiang).
0043-1354/$ – see front matter
doi:10.1016/j.watres.2011.11.023

(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 wash-off 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.

2. Materials and methods

2.1. 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 ± 0.44% and 35.1 ± 1.2%, respectively. Chemical standards of bifenthrin (99%, Chem Service, West Chester, PA), permethrin (97%, 40% *cis*/60% *trans*, FMC), phenoxy $^{13}C_6$-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 °C for 4 h before use to prevent cross contamination.

2.2. Preparation of concrete slabs and pesticide treatment

Concrete slabs in the dimension of 60 × 40 × 9 cm (L × W × 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 ± 0.5° slope. The surface of each slab was finished with a V-shaped indention 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 μg/cm^2 for bifenthrin and 233.3 μg/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.

2.3. Measurement of pesticide runoff from concrete surfaces

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.

2.3.1. 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 ± 2.7 mm/h.

2.3.2. 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.

2.3.3. *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.

2.3.4. *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.

2.3.5. *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.

2.4. *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.

2.5. *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 ± 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.

3. Results and discussion

3.1. *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 ± 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 ± 46.0 μg/L) and permethrin (5143 ± 2604 μg/L for *cis* and 5518 ± 2896 μg/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 μg/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 ± 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. 1 and 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 μg/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 μg/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

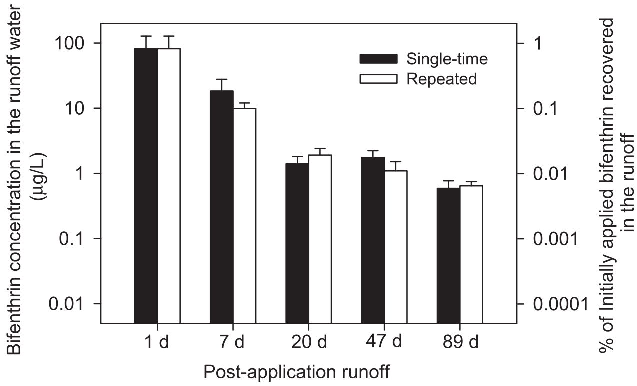

Fig. 1 – Levels of bifenthrin in the runoff following simulated single-time or repeated precipitations at 26.2 ± 2.7 mm/h ($n = 4$). The results are expressed as bifenthrin concentration (μg/L) in the runoff water and percentage of the initial application rate.

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. 1 and 2). After 4 repeated precipitation events, both bifenthrin and permethrin were still detectable in the runoff generated from

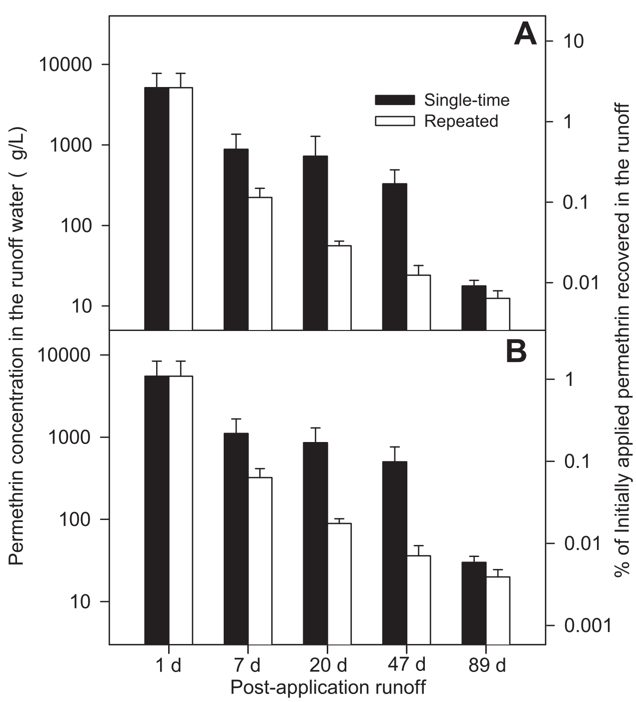

Fig. 2 – Levels of (A) *cis*-permethrin and (B) *trans*-permethrin in the runoff following simulated single-time or repeated precipitations at 26.2 ± 2.7 mm/h ($n = 4$). The results are expressed as permethrin concentration (μg/L) in the runoff water and percentage of the initial application rate.

the day 89 precipitation, at concentrations of 0.64 ± 0.09, 12.44 ± 2.58, and 19.98 ± 3.91 μg/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 ± 0.24% of the total runoff loss of bifenthrin, *cis*-permethrin, and *trans*-permethrin, respectively (Table 1). In contrast, the corresponding fractions for the Day 1 runoff were 83.3 ± 5.8, 93.1 ± 2.9, and 90.8 ± 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).

3.2. *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. 3, precipitation

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

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

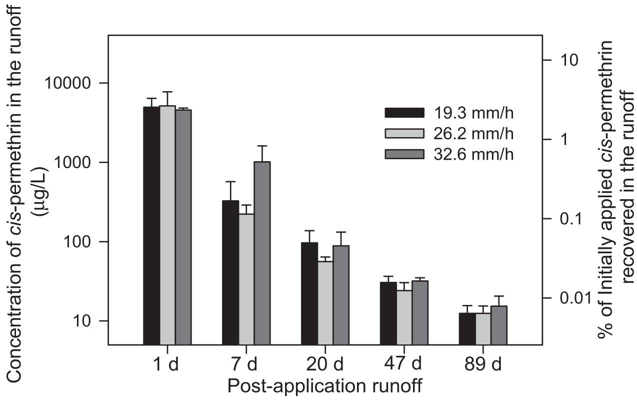

Fig. 3 – Levels of *cis*-permethrin in the runoff water from concrete slabs receiving repeated precipitations at 19.3 ± 1.7, 26.2 ± 2.7, or 32.6 ± 4.2 mm/h ($n = 4$).

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.

3.3. *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 for bifenthrin, different surface treatments showed similar decreasing trends in runoff transferability. For instance, in the day 1 runoff, 0.85 ± 0.38% of bifenthrin applied on the concrete with acid-washing (AW) was recovered, which was not statistically different from 1.33 ± 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 ± 0.08 µg/L, which was close to 0.10 ± 0.05 µg/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 ± 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 ± 0.38% for the AW treatment and 1.33 ± 0.37% for the SC treatment. In the day-89 runoff, the bifenthrin concentration from the SS treatment was 82.4 ± 21.9 ng/L, which was lower than 236.4 ± 84.6 and 212.4 ± 47.8 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.

3.4. *Pesticide runoff through natural rainfalls*

In regions such as California, rainfalls events are normally concentrated in the winter months, whereas pesticides are

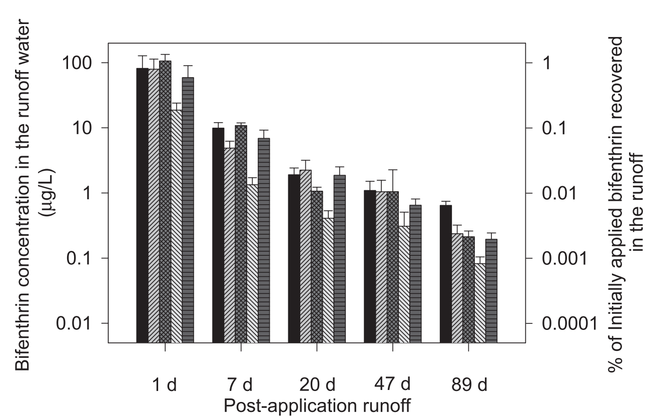

Fig. 4 – Levels of bifenthrin in the runoff water from different concrete surfaces after repeated precipitations ($n = 4$).

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. 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 μg/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 μg/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 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 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 μg/L for bifenthrin, 0.87 ± 0.49 and 0.75 ± 0.21 μg/L for cis-permethrin, and 1.15 ± 0.69 and 0.87 ± 0.30 μg/L for *trans*-permethrin, respectively.

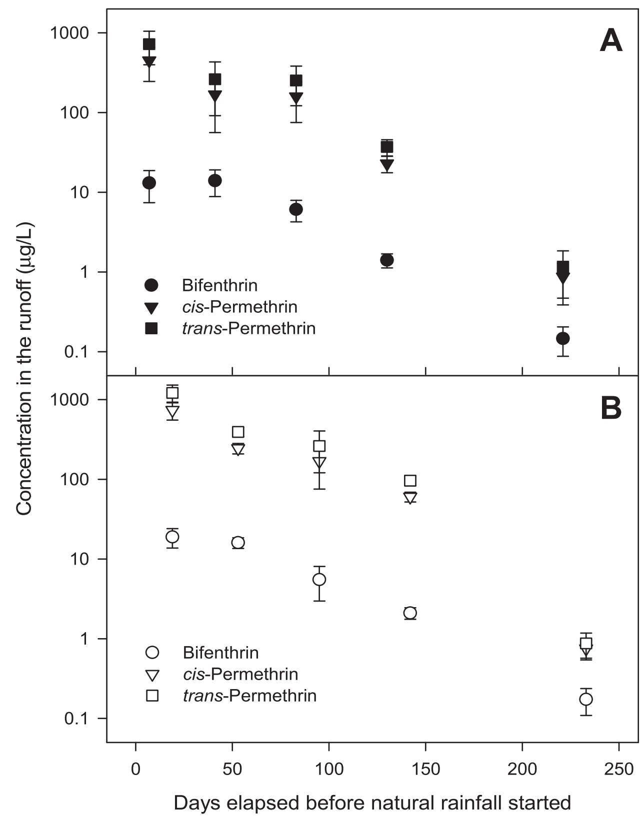

Fig. 5 – Concentrations of bifenthrin and permethrin in the runoff water from two winter rainfalls. (A) first rainfall; (B) second rainfall ($n = 4$).

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

Table 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	*cis*-Permethrin	*trans*-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

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 μg/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.

4. 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.

Acknowledgment

This research was funded by California Department of Pesticide Regulation. The authors thank Fredric Ernst, Katherine Thomason and Andy Lu for their help in sample collection and preparation.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2011.11.023. Details of concrete modifications, design of simulated precipitation system and chemical analysis is available in supplementary materials.

REFERENCES

Amweg, E.L., Weston, D.P., You, J., Lydy, M.J., 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. Environmental Science and Technology 40, 1700–1706.

Arnold, C.L., Gibbons, C.J., 1996. Impervious surface coverage – The emergence of a key environmental indicator. Journal of the American Planning Association 62, 243–258.

Bailey, H.C., Deanovic, L., Reyes, E., Kimball, T., Larson, K., Cortright, K., Connor, V., Hinton, D.E., 2009. Diazinon and chlorpyrifos in urban waterways in northern California, USA. Environ Toxicol Chem. 2009 (19), 82–87.

Berger, C., Schulze, M., Rieke-Zapp, D., Schlunegger, F., 2010. Rill development and soil erosion: a laboratory study of slope and rainfall intensity. Earth Surface Processes and Landforms 35, 1456–1467.

Budd, R., Bondarenko, S., Haver, D., Kabashima, J., Gan, J., 2007. Occurrence and bioavailability of pyrethroids in a mixed land use watersheds. Journal of Environmental Quality 36, 1006–1012.

California Department of Pesticide Regulation (CDPR), 2009. Summary of Pesticide Use Report. Sacramento, CA, USA. Available at: http://www.cdpr.ca.gov/docs/pur/pur09rep/09_pur.htm.

California Irrigation Management Information System (CIMIS). (2010) Available at http://wwwcimis.water.ca.gov/.

Chen, J., Poon, C.S., 2009. Photocatalytic cementitious materials: influence of the microstructure of cement paste on photocatalytic pollution degradation. Environmental Science and Technology 43, 8948–8952.

City of Olympia Public Works Department (COPWD), 1994. Impervious Surface Reduction Study: Technical and Policy Analysis-Final Report.

Diamond, S., 1999. Aspects of concrete porosity revisited. Cement and Concrete Research 29, 1181–1188.

Ding, Y., Harwood, A.D., Foslund, H.M., Lydy, M.J., 2010. Distribution and toxicity of sediment-associated pesticides in urban and agricultural waterways from Illinois. USA. Environmental Toxicology and Chemistry 29, 149–157.

Ghodrati M. (1989) A Field study of the effect of soil structure and irrigation method on preferential flow of pesticides in soil. A dissertation submitted in partial satisfaction of the requirements for the degree of PhD.

Hintzen, E.P., Lydy, M.J., Belden, J.B., 2009. Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. Environmental Pollution 157, 110–116.

Holmes, R.W., Anderson, B.S., Phillips, B.M., Hunt, J.W., Crane, D.B., Mekebri, A., Blondina, G., Nguyen, I., Connor, V., 2008. Statewide investigation of the role of pyrethroid pesticides in sediment toxicity in California's urban waterways. Environmental Science and Technology 42, 7003–7009.

Jiang, W., Lin, K., Haver, D., Qin, S., Ayre, G., Spurlock, F., Gan, J., 2010. Wash-off potential of urban use insecticides on concrete surfaces. Environmental Toxicology and Chemistry 29, 1203–1208.

Jiang, W., Gan, J., Haver, D., 2011. Sorption and desorption of pyrethroid insecticide permethrin on concrete. Environmental Science and Technology 45, 602–607.

Jorgenson, B.C., Young, T.M., 2010. Formulation effects and the off-target transport of pyrethroid insecticides from urban hard surfaces. Environmental Science and Technology 44, 4951–4957.

Kleinman, P.J.A., Srinivasan, M.S., Dell, C.J., Schmidt, J.P., Sharpley, A.N., Bryant, R.B., 2006. Role of rainfall intensity and

hydrology in nutrient transport via surface runoff. Journal of Environmental Quality 35, 1248–1259.
Laskowski, D.A., 2002. Physical and chemical properties of pyrethroids. Reviews of Environmental Contamination and Toxicology 174, 49–170.
Moran, K.D. (2006) Pesticides in Urban Surface Water: Urban Pesticides Use Trends Annual Report 2006.
Müller, K., Trolove, M., James, T.K., Rahman, A., 2004. Herbicide loss in runoff: effects of herbicide properties, slope, and rainfall intensity. Australian Journal of Soil Research 42, 17–27.
Paria, S., Yuet, P.K., 2006. Solidification-stabilization of organic and inorganic contaminants using Portland cement: a literature review. Environmental Reviews 14, 217–225.
Pedersen, J.A., Yeager, M.A., Suffet, I.H., 2006. Organophsphorus insecticides in agricultural and residential runoff: field observations and implications for total maximum daily load development. Environmental Science and Technology 40, 2120–2127.
Revitt, D.M., Ellis, J.B., Llewellyn, N.R., 2002. Seasonal removal of herbicides in urban runoff. Urban Water 4, 13–19.
Schiff, K., Sutula, M., 2004. Organophosphorus pesticides in storm-water runoff from southern California (USA). Environmental Toxicology and Chemistry 23, 1815–1821.
Shigaki, F., Sharpley, A., Prochnow, L.I., 2007. Rainfall intensity and phosphorus source effects on phosphorus transport in surface runoff from soil trays. Science of the Total Environment 373, 334–343.
Solomon, K.R., Giddlings, J.M., Maund, S.J., 2001. Probabilistic risk assessment of cotton pyrethroids: 1. Distributional analyses of laboratory aquatic toxicity data. Environ Toxicol Chem 20, 652–659.
Sosoro, M., 1998. Transport of organic fluids through concrete. Materials and Structures 31, 162–169.
U.S. Department of Agriculture (USDA) Soil Conservation Service, 1975. Urban Hydrology for Small Watersheds Technical Release No. 55.
Weston, D.P., Holmes, R.W., You, J., Lydy, M.J., 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. Environmental Science and Technology 39, 9778–9784.
Weston, D.P., Holmes, R.W., Lydy, M.J., 2009. Residential runoff as a source of pyrethroid pesticides to urban creeks. Environmental Pollution 157, 287–294.
Weston, D.P., Lydy, M.J., 2010. Urban and agricultural sources of pyrethroid insecticides to the Sacramento-San Joaquin delta of California. Environmental Science and Technology 44, 1833–1840.