Survey of Pesticide Residues in Loose Particles on Hardscape Surfaces

Loose particles on impervious surfaces are an important carrier to transfer pesticides into residential runoff water and subsequently contribute to contamination of urban streams and estuaries by urban-use pesticides. However, data regarding levels of pesticide contamination in the runoff-transferable dusts are scarce and their runoff potential and toxicity impacts to urban watersheds still remains poorly understood. In this study, a surface vacuuming method was used to collect dusts from residential outdoor impervious surfaces and samples were analyzed for concentrations of 14 legacy and current-use pesticides including pyrethroids, fipronil, fipronil metabolites, chlorpyrifos and diazinon. A total of 360 dust samples from curbside gutter, sidewalk and street surfaces were collected from 40 residential homes belonging to two residential communities in southern California. Each house was sampled three times in the year of 2011, i.e., May, July and September.

For dust collection, an average of 0.56 m$^2$ concrete/asphalt surface (median 0.56 m$^2$, range 0.34-0.81 m$^2$, N=360) was sampled, and the dust amounts ranged from 0.03 to 28.12 g/m$^2$. Pesticides were found in almost all dust samples (358 out of 360), and 75.8% samples were detected with at least 5 pesticides (Table 1). For samples collected from different locations, pesticide concentrations varied orders of magnitude from less than detection limits to thousands of micrograms per kg of dusts. The highest detection frequencies were found for synthetic pyrethroids. For example, 5 out of 9 target pyrethroids were detected in over 68% of dust samples, and bifenthrin was found in almost every sample with concentrations up to 6407 μg/kg. Simple model calculations predicted that during the two rainfalls after the sampling dates, 42.5% and 64.6% of the dust could be washed off, and the estimated bifenthrin runoff concentrations would be 54.6 and 109.1 ng/L, close to monitoring findings of bifenthrin concentrations in residential runoff water. Bifenthrin was observed with the highest runoff potential and the predicted runoff amounts were 9170.0 μg and 26544.8 μg respectively.

This study confirms the contamination of various pesticides on residential outdoor impervious surfaces and the findings support the hypothesis that dust from impervious surfaces constitutes an important source of pyrethroids and other pesticides in residential runoff.

Table 1. Detection frequencies and concentrations of pesticides in dust on pavement (μg/kg).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>N</th>
<th>D%</th>
<th>median</th>
<th>75th</th>
<th>90th</th>
<th>Min</th>
<th>Max</th>
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</thead>
<tbody>
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<td><strong>Organophosphate</strong></td>
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<tr>
<td>diazinon</td>
<td>360</td>
<td>6.7</td>
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<td>&lt;RL</td>
<td>&lt;RL</td>
<td>&lt;RL</td>
<td>87.2</td>
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<tr>
<td>chlorpyrifos</td>
<td>360</td>
<td>11.4</td>
<td>&lt;RL</td>
<td>&lt;RL</td>
<td>1.6</td>
<td>&lt;RL</td>
<td>113.0</td>
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<tr>
<td><strong>Pyrethroids</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fenpropathrin</td>
<td>360</td>
<td>1.4</td>
<td>&lt;RL</td>
<td>&lt;RL</td>
<td>&lt;RL</td>
<td>&lt;RL</td>
<td>23.6</td>
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</table>
Transformation of Pesticides to Biologically Active Products on Urban Concrete Surfaces

This study aims to demonstrate the transformation of two urban-use pesticides to biologically active products when present on concrete surfaces. Under outdoor conditions, permethrin quickly formed 3-phenoxybenzoic acid (3-PBA); 3-PBA is known to have endocrine disruption activity. Similarly, fipronil is quickly transformed to its desulfinyl and sulfone derivatives, which are known to have biological activity similar or even greater than fipronil itself. The rapid pesticide transformations were likely caused by the high alkalinity and metal oxides in concrete and the conducive photolytic conditions on the concrete surface, although the specific mechanisms are unknown and merit further investigation.

Degradation of permethrin and fipronil was evaluated using large concrete slabs located in a field away from residential structures. The concrete slabs were divided into three groups and treated with the different formulations (solid, liquid and professional concentrates). The treatment rates were similar to the label instructions. Runoff water from the concrete slabs was generated by applying water using a rainfall simulator on day 1, 7, 20, 47, and 89 after pesticide treatment.

In general, the amounts of permethrin transferred into the runoff water decreased quickly over time, and the decrease was especially pronounced immediately after the treatment. However, detectable levels were found in the runoff water even at the end of the 89-d exposure. In the 1-d runoff, 3-PBA was found at 142.5 ± 57.7, 41.5 ± 18.2, and 390.9 ± 19.5 µg/L for the professional, liquid, and solid formulations, respectively. Although the level of permethrin parent decreased quickly over time, concentrations of 3-PBA in the runoff water were relatively constant in the runoff water from recurring precipitation events (Figure 1). Starting from the 20-d precipitation event, the 3-PBA concentrations were higher than the parent compound for professional and liquid formulations. Given that 3-PBA is an acid and should be easily removed from the concrete
slab during each simulated precipitation, its sustained occurrence in the runoff water suggests continuous transformation from permethrin to 3-PBA.

The amount of fipronil parent transferred into the runoff water also quickly decreased. Simultaneously, all three fipronil degradates, desulfinyl fipronil, fipronil sulfone and fipronil sulfide, were immediately found in the runoff water. The highest concentrations of these degradates appeared in the 1-d runoff water, when desulfinyl, sulfone and sulfide derivatives were found at 360.3 ± 96.0, 62.4 ± 19.8, and 30.3 ± 5.6 µg/L, respectively. Fipronil sulfone was consistently detected at the highest concentrations, followed by fipronil desulfinyl. Unlike 3-PBA, the levels of fipronil derivatives in the runoff water consistently decreased over time, and this difference was attributed to the lower hydrophobicity of fipronil (log Kow = 4.01). Fipronil degradates in the runoff water were present predominantly in the dissolved form. For instance, in the 1-d runoff, the concentrations of desulfinyl, sulfone, and sulfide derivatives in the aqueous phase (<0.7 μm) were 339.9 ± 82.6, 50.8 ± 13.3, and 25.9 ± 3.4 µg/L, respectively, which accounted for 86-93% of their total concentrations in the runoff water. The limited association of fipronil degradates with fine particles is in contrast to pyrethroids that are preferentially sorbed to suspended particles.

Results from this study and the neighborhood dust survey clearly show that pesticides are unstable on urban hard surfaces such as concrete and may be readily transformed to biologically active degradates. Therefore, management of pesticide risks should take into consideration of biologically active transformation products.

![Figure 1. Constant appearance of 3-PBA from permethrin-treated concrete](image)

**A simple surface wipe method for dust sampling and runoff prediction**

This study considered the association of pyrethroid residues with loose particles in runoff water from concrete surfaces after treatment with commercial products of bifenthrin and permethrin. A simple sponge-wipe method was developed and tested for collecting and analyzing the loose particles on concrete. This method may be used to predict pesticide residues available for contaminating runoff water before runoff actually occurs. Different formulations of permethrin and bifenthrin were applied in three groups of large concrete slabs. 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 10 × 10 cm Versalon nonwoven sponge prewet with 10 mL of isopropanol was used 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.

The majority of bifenthrin or permethrin in the whole runoff water was consistently found on particles regardless of formulations. 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. The apparent sorption coefficient Kd was estimated using the concentration on the particles and that in the filtrate. Very large Kd values were obtained. For instance, Kd values ranged from $3.1 \times 10^4$ to $1.1 \times 10^5$ L/kg for the professional formulation treatments, and $2.4 \times 10^3$ to $4.0 \times 10^4$ L/kg for the RTU liquid formulation treatments.

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 ± 7.2 μg 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 ± 6.6 μg m$^{-2}$) were simultaneously found on the sponge wipes (Figure 2).

![Figure 2](image-url)  

**Figure 2.** Correlation between amounts of pyrethroids in runoff water and those collected on surface wipes (BF: bifenthrin; PM: permethrin)

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

This study considered pesticide runoff caused by irrigation under dry weather conditions and rain falls during the wet season, and evaluates the effects of pesticide residence time on
Professional formulations of bifenthrin and permethrin were mixed together with water. The mixed solution was applied evenly onto each concrete slab. The actual application rates were determined to be 3.2 mg/cm² for bifenthrin and 233.3 mg/cm² for permethrin, which are consistent with label instructions for these products. 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. Another group of concrete slabs were subjected to repeated wash-off at 1, 7, 20, 47, and 89 d after treatment, to evaluate changes in pesticide transferability with recurring irrigation or rainfall events. To assess the influence of rainfall intensity, three groups of concrete slabs received repeated precipitations at three different rates, i.e., 19.3, 26.2 and 32.6 mm/h, on day 1, 7, 20, 47, and 89 after pesticide treatment. Some slabs were modified to mimic common practices. The surface modifications included acid washing and silicone coating, stamping before the concrete hardened, and addition of microsilica before pouring. 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.

When the treated concrete slabs received precipitation 24 h after treatment, concentrations of bifenthrin (81.9 mg/L) and permethrin (5143 mg/L for cis and 5518 mg/L for trans) were very high in the runoff water, although only accounting for 0.84, 2.67, and 1.11 % of the amount initially applied. 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. 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, 17.8 and 30.0 mg/L in the 89-d runoff water.

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.

Different surface treatments showed similar decreasing trends in runoff transferability. For instance, in the day 1 runoff, 0.85% of bifenthrin applied on the concrete with acid-washing was recovered, which was not statistically different from 1.33% for concrete with silicone sealing. In addition, extended persistence of pyrethroid runoff was observed for all concrete surface types.

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 of bifenthrin in runoff water were 1.41 and 2.10 mg/L for the first and second rain events, respectively. These values were about 10 times smaller than 13.08 and 18.91 mg/L for the November treatments, for which the pesticides were applied only 7 d before the first rainfall event.

Findings from this study validated, under realistic field conditions, the conclusions previously derived from laboratory experiments. 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.

Publications: