

# Conversion of Pyrethroid Insecticides to 3-Phenoxybenzoic Acid on Urban Hard Surfaces

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**Supporting Information** 

**ABSTRACT:** The urban use of pyrethroids has been associated with the contamination and toxicity of urban surface water. A less considered phenomenon is that many pyrethroids may be transformed to a common intermediate, 3-phenoxybenzoic acid (3-PBA), that is an endocrine-disrupting compound. Here we examined the conversion of five common pyrethroids, permethrin,  $\lambda$ -cyhalothrin, deltamethrin, fenpropathrin, and esfenvalerate, to 3-PBA on concrete. Formation of 3-PBA was almost instantaneous, reaching up to 3% of the initial level of pyrethroids within hours of exposure, and was caused mainly by hydrolysis, likely enhanced by the strong alkalinity of concrete. The accumulation of 3-PBA on concrete was transient, with half-lives of 4.2–6.7 h depending on the treatment. Low levels (nanograms per liter) of 3-PBA were frequently found in urban streams draining residential neighborhoods, validating the off-site



transport potential of 3-PBA from urban hard surfaces. Findings from this study suggested that urban hardscapes such as concrete pavement are reactive surfaces, conducive to the formation of biologically active transformation products.

# INTRODUCTION

Urban pesticide use, including structural pest control and landscape maintenance, is an important contributor to total pesticide use. For example, in 2014, urban consumption in California was 1.8 million kg of active ingredients for structural pest control alone.<sup>1</sup> Pyrethroids are among the most popular insecticides used in urban settings because of their high insecticidal potency and low mammalian toxicity.<sup>2,3</sup> This intensive use has led to ubiquitous occurrence of pyrethroids in urban environments<sup>4–9</sup> and toxicity in urban surface aquatic systems.<sup>10–12</sup> While contamination of urban surface water by pyrethroids has been extensively studied in recent years, little attention has been given to their transformation products.

Transformation of pyrethroids is well-understood in agricultural environments;<sup>13,14</sup> however, relatively little is known about their fate in urban settings. The urban environment is characterized by hard surfaces,<sup>15</sup> especially concrete pavement that has properties distinctively different from those of soil. For example, the pH of fresh concrete is ~13, and as it cures, the pH decreases to ~8.5.<sup>16,17</sup> A recent study showed conversion of permethrin to 3-phenoxybenzoic acid (3-PBA) on concrete slabs; 3-PBA was found in wash off water even 3 months after the treatment.<sup>18</sup> 3-Phenoxybenzoic acid exhibits anti-estrogenic activity with a lowest observed inhibition concentration of 2.6 ± 1.5 mg L<sup>-1</sup>.<sup>19</sup> anti-androgen activity at 0.1 mM,<sup>20</sup> and cardiac toxicity at 10  $\mu$ M.<sup>3,21</sup> Moreover, 3-PBA is a common degradation product of multiple pyrethroid insecticides, including permethrin, deltamethrin,

fenpropathrin, cyhalothrin, and esfenvalerate.<sup>22,23</sup> However, it is unclear whether the other commonly used pyrethroids may also be susceptible to -conversion to 3-PBA on hard surfaces.

The objectives of this study were to discern mechanisms for pyrethroid dissipation on concrete, to explore the kinetics of formation of 3-PBA from commonly used pyrethroids, and to test if 3-PBA contamination is detectable in ambient urban streams. The findings will complement our current understanding of the fate and risk of pyrethroids and potentially heighten the importance for considering biologically active degradation products in urban settings.

# MATERIALS AND METHODS

Pesticide Treatment and Monitoring on Hard Surfaces. Details of chemicals and their purities and sources are given in the Supporting Information (Text S1). Small concrete cubes with dimensions of 14 mm × 14 mm × 8 mm were prepared and cured for 10 days according to the method described by Jiang et al.<sup>24</sup> These surfaces, along with borosilicate glass disks (20 mm in diameter), were treated using a 0.5 mL syringe to apply 0.5 mL of an acetone solution containing fenpropathrin,  $\lambda$ -cyhalothrin, permethrin, esfenvalerate, and deltamethrin, each at 100 µg mL<sup>-1</sup>. The solution

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spread over the entire surface evenly. The concrete and glass surfaces (96 samples in total) were exposed to irradiation or dark conditions. For the radiation treatment, samples were placed on the roof of a building  $(33^{\circ}58'26.0''N 117^{\circ}19'33.8''W)$  and exposed to natural sunlight from April 27 to June 26, 2016. The daytime length ranged from 12.9 to 14.4 h during this period. For the dark treatment, samples were wrapped in aluminum foil and placed on the same roof. Thus, the two treatments underwent similar temperature regimes. Meteorological conditions during the experiment are listed in Tables S1 and S2. The samples were removed after being exposed to light for 1, 3, 6, 12, 24, 48, 168, and 336 h (accumulated hours with natural light from sunrise to sunset) after the treatment.

**Deduction of Contributing Mechanisms.** Dissipation of pyrethroids on concrete surfaces may be attributed to volatilization, irreversible binding, hydrolysis, and photolysis. Hydrolysis, photolysis, and subsequent oxidation may lead to 3-PBA formation. The inclusion of non-irradiated glass (NG), non-irradiated concrete (NC), irradiated glass (IG), and irradiated concrete (IC) treatments allowed the estimation of rate constants, as follows:

$$\ln C_t = \ln C_0 - k_{\text{volatilization}} t_{\text{total}} \tag{1}$$

$$\ln C_t = \ln C_0 - k_{\text{volatilization}} t_{\text{total}} - k_{\text{binding+hydrolysis}} t_{\text{total}}$$
(2)

$$\ln C_t = \ln C_0 - k_{\text{volatilization}} t_{\text{total}} - k_{\text{photolysis-G}} t_{\text{light}}$$
(3)

$$\ln C_t = \ln C_0 - k_{\text{volatilization}} t_{\text{total}} - k_{\text{binding+hydrolysis}} t_{\text{total}} - k_{\text{photolysis-C}} t_{\text{light}}$$
(4)

where  $C_t$  and  $C_0$  are pyrethroid concentrations in micrograms per square meter on impervious surfaces at times t and 0, respectively;  $k_{\text{volatilization}}$ ,  $k_{\text{binding+hydrolysis}}$ ,  $k_{\text{photolysis-G}}$ , and  $k_{\text{photolysis-C}}$  are first-order rate constants in inverse hours for volatilization, binding and hydrolysis, photolysis on glass surfaces, and photolysis on concrete surfaces, respectively; and  $t_{\text{total}}$  and  $t_{\text{light}}$ are times in hours for the entire reaction and exposure to natural sunlight, respectively. It must be noted that in  $k_{\text{binding+hydrolysis}}$ , hydrolysis and irreversible binding were combined, as the experimental design would not allow the distinction between these two processes on concrete surfaces. The non-irradiated glass treatment was used to obtain  $k_{\text{volatilization}}$  (eq 1), while the volatilization rates were assumed to be similar between concrete and glass surfaces. Therefore,  $k_{\text{binding+hydrolysis}}$  could be calculated using eqs 1 and 2, while  $k_{\rm photolysis-G}$  may be calculated using eqs 1 and 3. Binding and hydrolysis on the glass surfaces were assumed to be negligible because of the high recoveries of all pyrethroids. Finally,  $k_{\text{photolysis-C}}$  may be determined using eqs 2 and 4.

To differentiate irreversible binding and hydrolysis,  $100 \ \mu L$  of [<sup>14</sup>C]permethrin in acetone (specific radioactivity of  $1.0 \times 10^4$  dpm mL<sup>-1</sup>) was added to concrete surfaces and incubated in dark for 28 days. The <sup>14</sup>C radioactivity of the extract and extracted concrete cubes (after combustion) was measured on a liquid scintillation counter.<sup>24</sup>

**Sampling of Urban Surface Water.** Grab water samples were taken monthly for five consecutive months from two small urban streams in Orange County, California. Salt Creek 3 (SC 3, 33°30′43.02″N 117°41′49.55″W) was located in Laguna Niguel, CA, and Wood Creek 2 (WC 2, 33°34′53.70″N

117°44′44.65″W) in Aliso Viejo, CA. These two surface streams drain primarily runoff from the surrounding neighborhoods.<sup>25</sup> The Wood Creek site received runoff from the nearby residential areas; however, the runoff flowed through a wetland prior to the sampling point. Neither site received water directly from any wastewater treatment plant. For sampling, 1 L amber glass bottles were submerged in the water and filled. Duplicate samples were taken at each site, with different bottles being collected for the determination of the levels of pyrethroids and 3-PBA.

**Chemical Analysis.** Pyrethroids and 3-PBA were analyzed according to previously published methods.<sup>18</sup> Briefly, concrete cubes and glass discs were sonicated with 30 mL of an acetone/ dichloromethane solvent [1:1 (v/v)] for 15 min. For pyrethroids and 3-PBA in the field-collected water samples, samples were extracted using liquid—liquid extraction and solid phase extraction, respectively. A Waters Acquity ultraperformance liquid chromatography—tandem mass spectrometry instrument (Waters, Milford, MA) was used for analysis of 3-PBA in the urban streamwater samples; an Agilent (Wilmington, DE) model 6890N gas chromatography—mass spectrometry instrument was used for all other samples. Details of chemical analysis are given in Text S2.

Quality Control and Data Analysis. Reagent blanks, field blanks, recovery surrogates, internal standards, and replicates were used when applicable to ensure the quality of the analysis. During extraction, one reagent blank was extracted every 10 samples to check for cross-contamination. All glassware, sodium chloride, sodium sulfate, and the impervious surfaces were baked at 400 °C for 4 h before use. Samples were analyzed in duplicate (water samples) or triplicate to ensure reproducibility. Samples were spiked with either  $d_5$ -bifenthrin,  $\begin{bmatrix} 13 \\ C \end{bmatrix}$ -3-PBA, or both before extraction to determine the extraction efficiency. Recoveries of  $d_5$ -bifenthrin were 75  $\pm$  19 and 91  $\pm$  30% for the water samples and impervious surface samples, respectively. Recoveries of  $[^{13}C]$ -3-PBA were 63 ± 19 and 83 ± 30% for the water and impervious surface samples, respectively. Instrumental controls consisted of the use of [<sup>13</sup>C]permethrin as an internal standard for all samples analyzed by gas chromatography and mass spectrometry and construction of an eightpoint calibration curve with concentrations ranging from 1 to 500  $\mu$ g L<sup>-1</sup> before every analytical run and after analysis of every 50 samples.

Statistical analysis was performed using PC SAS version 9.4 (SAS Institute, Cary, NC). Analysis of variance was performed with PROC GLM. Planned comparisons of two different surfaces over time were further evaluated with a PDIFF option in a LSMEANS statement if analysis of variance proved to be significant.

#### RESULTS AND DISCUSSION

**Pyrethroid Dissipation on Concrete and Mechanisms.** Fitting decreases in concentration to the first-order decay model yielded half-lives (hours) for the different treatments (Table S3). Overall, rapid disappearance of pyrethroids was observed on the concrete irradiated with sunlight (Figure 1), but different pyrethroids displayed significant differences in their stability. Of the five compounds, permethrin was the most stable, with a half-life of 30 h, while  $\lambda$ -cyhalothrin was the least stable with a half-life of only 3 h (Table S3). The other experimental conditions were included to uncover potential contributions by volatilization, photolysis, and binding and hydrolysis. The first-order rate constants describing these loss



**Figure 1.** (A) Dissipation of pyrethroids and (B) formation and dissipation of 3-BPA under different conditions. Note that the initial concentrations of  $\sum$  pyrethroids on concrete and glass surfaces were 128 and 80  $\mu$ g cm<sup>-2</sup>, respectively.

processes were further calculated using eqs 1-4 (Table S3), from which the relative contribution of each loss process on irradiated concrete was estimated (Figure S1).

In general, volatilization was a minor loss pathway for  $\lambda$ cyhalothrin and fenpropathrin (Figure S1). However, despite their low vapor pressures,<sup>26</sup> the relative contribution of volatilization was significant for esfenvalerate (20%), permethrin (25%), and deltamethrin (39%) (Figure S1). The significant contribution of volatilization may be due to the high ambient temperature during the experiment.

Photolysis was the dominant loss pathway for permethrin, contributing 75% to its total loss, while it was also substantial for fenpropathrin and deltamethrin. The photolysis half-lives of pyrethroids on concrete were much shorter than half-lives previously reported for soil or water (Table S3). It was interesting to note that similar first-order rate constants were derived for both concrete and glass surfaces, indicating that the surface properties of concrete did not inhibit pyrethroid photolysis.

Binding and hydrolysis were not distinguished in the outdoor experiment and were found to be an important mechanism for the loss of the selected pyrethroids except for permethrin (Figure S1). The importance of hydrolysis in pyrethroid dissipation was likely due to the high pH of concrete promoting ester hydrolysis.<sup>23,27</sup> The reduced role for permethrin may be attributed to the fact that permethrin is more stable at higher pH than the other pyrethroids are (Table S3).<sup>27</sup> The recalcitrance of permethrin to base-catalyzed hydrolysis may be due to the lack of a cyano group next to the ester bond in its structure.<sup>22,23</sup> In the dark incubation treatment with [<sup>14</sup>C]permethrin, <3% of <sup>14</sup>C was found to be irreversibly bound to the concrete during the initial 24 h (Figure S2). Thereafter, the irreversibly bound fraction gradually increased to  $\sim$ 40% at 7 days and remained at  $\sim$ 40% until 28 days. Therefore, irreversible binding was not likely to be an important

irreversible binding was not likely to be an important contributor to the overall loss at least during the initial stage, and the rapid loss was likely due to evaporation, hydrolysis, and photolysis. Overall, these results illustrated that hydrolysis is an important degradation pathway for pyrethroids on concrete surfaces, highlighting that urban surfaces are capable of converting pyrethroids to hydrolysis intermediates.

Formation of 3-PBA on Concrete Surfaces. More 3-PBA was formed in the treatments with higher pyrethroid dissipation rates (Figure 1). For example, the rate of formation of 3-PBA in the IC treatment was much higher than that in the NG treatment, while pyrethroids dissipated much faster in the IC treatment. After 3 h, the residual amounts of total pyrethroids for the IC and NG treatments were  $52 \pm 12$  and  $105 \pm 5\%$  of the initial applied amount, respectively, while the quantities of 3-PBA for these treatments were 5.1  $\pm$  0.2 and 0.095  $\pm$  0.006  $\mu g$  cm<sup>-2</sup>, respectively (Figure 1). This relationship suggested that as pyrethroids disappeared on the concrete, 3-PBA was concurrently formed. However, this relationship was not stoichiometric, and the highest 3-PBA occurrence accounted for only 3% of the initially applied amount. In a previous study, 3-PBA formation was found to range from 1.6  $\pm$  0.1 to 17  $\pm$ 1% of the initially applied permethrin over 7 days.<sup>18</sup> The low yields implied that other degradation products were likely also produced, although they were not targeted for detection in this study. Compared to glass surfaces, considerably more 3-PBA was formed on concrete. There was generally little difference between the dark and irradiation treatments on concrete, implying that hydrolysis, rather than photolysis, contributed primarily to 3-PBA formation on concrete. These results together suggested that base-catalyzed hydrolysis dictated the formation of 3-PBA on concrete.

It must be noted that 3-PBA did not accumulate on the concrete surface over time. The fit of 3-PBA levels on concrete surfaces to first-order decay resulted in half-lives of only 4.2-6.7 h in the different treatments, suggesting that 3-PBA was further transformed to other products. As the levels of 3-PBA were similar between the IC and NC treatments (Figure 1), photolysis did not affect the fate of 3-PBA on concrete.  $Katagi^{28}$ measured photolysis of 3-PBA on soil ( $t_{1/2}$  = 47 days), clay ( $t_{1/2}$ = 29 days), and silica gel ( $t_{1/2}$  = 17 days) and showed that 3-PBA was generally resistant to photolysis. The vapor pressure of 3-PBA is  $3.2 \times 10^{-6}$  mmHg, and therefore, there may be potential loss of volatilization, especially at elevated temperatures (Table S1).<sup>29</sup> The  $pK_a$  value of 3-PBA is 3.95, suggesting that 3-PBA may be deprotonated and react with calcium hydroxide or calcium carbonate in the concrete.<sup>30</sup> The level of degradation of 3-PBA was previously found to increase with pH in soil.<sup>31,32</sup>

The results of this study suggested that the occurrence of 3-PBA on concrete may be transient and off-site transport to surface waters is likely within the first 24 h of pesticide application. However, even after 336 h, the quantities of 3-PBA extracted from concrete cubes ranged from  $0.11 \pm 0.02$  to  $1.0 \pm 0.15 \ \mu$ g, which equaled  $0.55 \pm 0.11$  to  $5.1 \pm 0.77$  mg m<sup>-2</sup>, respectively. If extrapolated to a watershed scale, 3-PBA may behave as a pseudopersistent contaminant, because of the widespread and continuous use of pyrethroids.

**Occurrence in Urban Streams.** The total concentrations of the five pyrethroids ranged from  $47 \pm 16$  to  $865 \pm 130$  ng

 $L^{-1}$  at the Salt Creek site and from 27 ± 11 to 122 ± 38.4 ng  $L^{-1}$  at the Wood Creek site (Figure 2). Meanwhile, 3-PBA was



**Figure 2.** Concentrations of five target pyrethroids and 3-PBA in (A) Salt Creek (SC) and (B) Wood Creek (WC) located in Orange County, California.

also detected at lower concentrations, ranging from  $2.9 \pm 1.5$  to  $37 \pm 2.1 \text{ ng L}^{-1}$  and from  $0.20 \pm 0.01$  to  $12 \pm 3 \text{ ng L}^{-1}$  at the Salt Creek site and Wood Creek site, respectively. At the Salt Creek site, a positive correlation was observed between pyrethroid and 3-PBA concentrations (Pearson correlation coefficient of 0.963; p < 0.01). The elevated concentrations, especially from the June sampling time point, coincided with a rainfall event, which provided further evidence that 3-PBA may be transported from urban surfaces via runoff. However, this relationship was not observed at the Wood Creek site (p > p)0.05). This could be due to the fact that the Wood Creek site was located downstream from a treatment wetland. While degradation of 3-PBA in soil or sediment is not well understood, previous research suggested that adsorption of 3-PBA by soil or sediment may be a major removal pathway.<sup>33</sup> Therefore, it is likely that because of the decreased flow and hydraulic retention in the wetland, some of the suspended solids settled out of the flow, along with 3-PBA.<sup>34</sup> Another study showed that 3-PBA was susceptible to photolysis in water with half-lives of 2.6-3.6 days.<sup>28</sup> Therefore, it is also possible that 3-PBA was attenuated through a combination of adsorption, photolysis, and microbial degradation<sup>35</sup> in the wetland.

The occurrence of 3-PBA along with pyrethroids in urban streams suggested that urban surface streams in regions such as California may be ubiquitously contaminated with 3-PBA as a result of extensive use of pyrethroids. Even though concentrations of 3-PBA were much lower than the known toxicity threshold values,  $^{3,19-21}$  its effect on aquatic organisms, including small invertebrates, is essentially unknown. Future research should consider the potential adverse effects of 3-PBA on aquatic species from chronic exposure to low levels of 3-

Letter

PBA. Moreover, there is a clear knowledge gap regarding the environmental fate of 3-PBA, which needs to be addressed to improve our understanding of its potential environmental risk.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00466.

Additional methods and results, Texts S1 and S2, Tables S1–S3, and Figures S1 and S2 (PDF)

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#### Notes

The authors declare no competing financial interest.

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