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Occurrence, Fate, and Transport of Pesticides and Their Degradation Products in Urban Environments

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Occurrence, Fate, and Transport of Pesticides and Their Degradation Products in Urban Environments

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Jaben Ross Richards

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ABSTRACT OF THE DISSERTATION

Occurrence, Fate, and Transport of Pesticides and Their Degradation Products in Urban Environments

by

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Doctor of Philosophy, Graduate Program in Environmental Sciences
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Dr. Jay Gan, Chairperson

In highly urbanized areas, intensive use of pyrethroids has led to offsite transport to surface waters at concentrations known to cause toxicity to aquatic organisms. However, there is limited knowledge on the occurrence and distribution of pyrethroids in urban settings, or the role dust particles play in offsite transport of pyrethroids. Additionally, when pyrethroids enter the environment, they undergo transformation to form a common degradation product 3-phenoxybenzoic acid (3-PBA), which has been shown to cause endocrine disruption. However, little research has been conducted on the formation of 3-PBA in urban environments, its occurrence in urban streams, or its stability in different environmental matrices. Here we first evaluated the occurrence of particle-borne insecticides including pyrethroids in outdoor urban dust and studied their spatial and temporal distribution patterns and correlation with particle sizes. Temporally, particle-bound insecticides increased over the dry season and then significantly decreased after winter rains. Spatially, levels of pyrethroids in dust did not differ with distance from point of application, suggesting redistribution. Pyrethroids were found to associate predominantly with the smallest particle size fraction in dust. These findings suggest that loose particles are likely a significant source for offsite contamination of insecticides. In a subsequent study, we investigated pyrethroid transformation processes on concrete and 3-PBA formation. Pyrethroid degradation was rapid with hydrolysis being the most significant pathway, leading to rapid formation of 3-PBA. Low levels of 3-PBA were constantly detected in urban surface water, suggesting the need to understand chronic exposure and risk to aquatic species. In order to aid risk assessment of 3-PBA, in the last study we examined its stability in different environmental matrices. The half-life of 3-PBA in surface water and aerobic sediments was relatively short, while it was prolonged in soil and anaerobic sediments. These results further suggested that urban soil may be a source of 3-PBA to surface water or underlying groundwater, and due to the continuous input, additional research is needed to evaluate adverse effects on non-target organisms.

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Chapter 1 Introduction

1.1 Background

Pesticides are utilized in urban environments to control the populations of undesirable organisms such as ants, termites, and spiders. The most intensive urban pesticide use occurs in areas like Southern California with a large human population density and a climate that allows pest species to be active almost year-round. For example, over 6.4 million kg of pesticide active ingredients were applied to urban environments for structural pest control, landscape maintenance, and other non-agricultural uses in California during 2014 (CDPR, 2014). This is an increase of 1.7 million kg since 2009 (CDPR, 2014). Additionally, these numbers only consider the amount applied by professional pesticide applicators, indicating that the total may be much higher if homeowner usage is factored in (Budd, 2010).

Currently, the most commonly used insecticides in urban environments belong to one of two chemical families: the pyrethroids and the phenylpyrazoles. The pyrethroid group consists of 32 registered compounds, of which 8 are most commonly used (USEPA, 2011; CDPR, 2014). The pyrethroids account for up to 74% of urban pesticide use (Budd, 2010). Pyrethroids are composed of an acid moiety and an alcohol moiety, and are considered strongly hydrophobic with Log K_{ow} values ranging from 4.53 to 7.00 and very low water solubilities. (Laskowski, 2002; USEPA, 2011) (Table 1.1). Pyrethroids elicit neurotoxicity via inactivation of voltage-gated sodium channels within the cell membranes neurons (USEPA, 2011).

The phenylpyrazole group currently only has one compound (fipronil) registered by the USEPA. However, fipronil readily degrades by biotic or abiotic processes to form the primary metabolites fipronil desulfinyl, fipronil sulfide, and fipronil sulfone. Fipronil and its degradation products are more hydrophilic than the pyrethroids, with Log K_{ow} values ranging from 3.5-4.82. (Table 1.2). The mode of action for fipronil differs from that of the pyrethroids in that it affects γ -aminobutyric acid (GABA)-gated channels and disrupts the flow of chloride ions into neurons, causing paralysis and mortality (Gunasekara et al., 2007).

Pyrethroids and fipronil were originally developed as a solution to the problem of persistence posed by organochlorine (OC) insecticides and the wide spectrum potent acute toxicity posed by organophosphate (OP) insecticides. Pyrethroids and fipronil are more easily degraded than the OC compounds, are less acutely toxic to mammals than OPs, and often exhibit greater insecticidal activity (Elliot et al., 1978; van den Berg et al., 2012; Brander et al., 2016). For instance, the LD_{50} for acute 96 horal exposure of permethrin in rats is 2000 mg kg^{-1} (Elliot et al., 1978), while it is only 100 to 150 mg kg^{-1} for the OP diazinon (Bruce et al., 1955). Due to these properties, pyrethroids and fipronil have become widely adopted in urban settings and are seeing increased usage in agricultural settings as well (CDPR, 2012).

However, despite the benefits associated with the use of pyrethroids and fipronil compared to OCs and OPs, there are also some drawbacks. Although pyrethroids and fipronil have low potency in mammalian acute toxicity tests, they can cause non-target toxicity to invertebrates and fish in aquatic ecosystems, often at very low concentrations

(Weston et al., 2005; Amweg et al., 2006; Holmes et al., 2008; Phillips et al., 2012; Brander et al. 2016). Pyrethroids have been detected in residential areas at levels equivalent to 40 toxic units for *Hyallela azteca* in urban streams (Weston et al., 2005). Similarly, Amweg et al. (2006) found that 12 out of 15 creeks studied in California contained sediments that were acutely toxic to *H. azteca*, and this toxicity was due mostly to pyrethroid exposure. Holmes et al. (2008), observed pyrethroids in sediments from 30 urban streams, and when toxicity tests were conducted with these sediments, all 30 were found to be toxic to invertebrates. Similarly, pyrethroids can be up to 1000-fold more toxic to fish than mammals (Brander et al. 2016). Due to this concern, a great deal of research has been conducted over the last decade to understand the occurrence, fate, and transport of pyrethroids and fipronil into and within aquatic ecosystems.

1.2 Occurrence of Pesticides in Urban Environments

Since up to 90% of the surface area in urban environments is composed of impervious surfaces, the intensive use of pesticides in urban environments often leads to offsite transport through surface runoff. Numerous studies have been conducted to determine the occurrence of pyrethroids and fipronil in irrigation and rain-induced runoff as well as in aquatic systems across the United States, particularly in California (Gan et al., 2005; Amweg et al., 2006; Budd et al., 2007; Holmes et al., 2008; Hintzen et al., 2009; Weston et al., 2009; Ding et al., 2010; Lao et al., 2010; Gan et al., 2012; Ensminger et al., 2013). Gan et al. (2005) observed bifenthrin and permethrin concentrations ranging from 0.33 to 10.64 mg kg^{-1} and 0.20 to 6.10 mg kg^{-1}, respectively, in sediments receiving storm water from a nearby nursery. For streams receiving residential runoff, total pyrethroid concentrations as high as 0.5 mg kg^{-1} have been documented (Amweg et al., 2006). Similarly, Budd et al. (2007) observed pyrethroid sediment concentrations as high as 19 µg kg^{-1} in streams receiving runoff from residential neighborhoods, with freely dissolved concentrations as high as 27.7 ng L^{-1}. This value is six times higher than the concentration of bifenthrin necessary to cause 50% mortality of Hyallela azteca (LC_{50} = 4.23 ng L^{-1}) (Anderson et al., 2015). The presence of pesticides at toxic levels in urban streams is not limited to highly urbanized areas such as southern California or the Bay Area. For instance, Hintzen et al. (2009) found toxic unit measurements ranging from 0.03 to 7.99 in sediments of urban streams running through residential areas in Texas, with the majority of the toxicity being attributed to the pyrethroid bifenthrin. Similar observations were made in urban streams of Illinois, where sediments were more contaminated with pyrethroids and more toxic than those taken from streams in agricultural areas (Ding et al., 2010). These studies demonstrate that there is a widespread distribution of pyrethroids in aquatic environments within urban watersheds, and that the concentrations of pyrethroids in sediment and water often exceed levels acutely toxic to sensitive species such as *Hyallela azteca* (Holmes et al., 2008).

Although the presence of pesticides in urban watersheds has been linked to residential pesticide use (Gan et al., 2005; Jiang et al., 2010; Jiang et al., 2011; Gan et al., 2012; Jiang et al., 2012; Jiang and Gan, 2012; Ensminger et al., 2013), few studies have documented the occurrence of pesticides within residential areas, i.e., around homes. Mahler et al. (2009) measured concentrations of fipronil and its degradates in indoor and outdoor dust associated with an apartment complex in Texas. Jiang et al. (2016) measured the concentrations of 8 pyrethroids, fipronil, and three fipronil metabolites in outdoor dust in two neighborhoods in Riverside, CA. Both studies showed detectable levels of pesticides in nearly all of the outdoor dust samples. Furthermore, Jiang et al. (2016) found that pesticide loading through precipitation-induced runoff could be closely predicted from pesticide concentrations in outdoor dust samples by utilizing the SWMM model. These two studies provide preliminary data on pesticide occurrence within residential areas and highlight the importance of conducting sampling outside aquatic systems. However, more research is clearly needed to improve our understanding of the sources of pesticides in residential areas, their behavior on and interactions with impervious surfaces such as concrete (e.g., photolytic transformations, sorption), and the formation and down-stream fate of biologically active transformation products. This information may be used for improving risk assessment, risk management, and mitigation efforts.

1.3 Fate of Pyrethroids

After pesticides are applied in urban environments, their behavior is influenced by partitioning and transformation processes. These processes are in turn affected by their chemical properties and environmental factors such as temperature and the presence/absence of water, light, particles, organic matter, and microbial organisms. Based upon their large Log K_{ow} values, low water solubility, and low Henry's Law constants, it can be hypothesized that the fate of pyrethroids in urban environments is dominated by sorption to solids. This is confirmed by several monitoring studies where sediment concentrations were always found to be much higher than aqueous concentrations (Gan et al., 2005; Budd et al., 2007; Weston et al., 2009).

For biotic and abiotic transformation processes, pyrethroids have been observed to be relatively stable with regards to hydrolysis within environmentally relevant pH ranges (pH 5-7) (Laskowski, 2002). However, at higher pH values, which may be relevant for concrete surfaces, hydrolysis half-lives ranged from 1.84 d (cyfluthrin) to stable (bifenthrin) (Laskowski, 2002). For photolysis, pyrethroid half-lives ranged from 0.673 to 603 d in water and 3.87 to 104 d on soil surfaces (Laskowski et al., 2002). As for biotic transformation processes, most of the research to date is limited to aerobic and anaerobic conditions in soil or aquatic systems. For aerobic soil degradation, pyrethroid half-lives ranged from 27.4 to 330 d (Laskowski, 2002; Qin et al., 2006). For anaerobic soil degradation, pyrethroid half-lives ranged from 36.8 to 1280 d (Laskowski, 2002; Qin et al., 2006). In aquatic systems, the aerobic degradation half-lives were 10.6 to 189 d, while those for anaerobic degradation were 22.2 to 90.8 d (Laskowski, 2002). As can been seen from these results, persistence of pyrethroids varied greatly among compounds, with compounds from the newer generation of pyrethroids (e.g., bifenthrin) generally exhibiting longer persistence; and the persistence is further increased in sediments under anaerobic conditions. As shown above, transformation of pyrethroids is well understood for media present in agricultural environments (e.g., Schimmel et al., 1983; Lutnicka et al., 1999; Meyer et al., 2013). In contrast, relatively little is known about their fate and transformation processes in urban settings. The urban environment is characteristically covered by impervious surfaces, i.e., pavements and rooftops (Arnold and Gibbons, 1996). Concrete, the material used for most urban impervious surfaces, has distinct properties as compared to soil or sediment. For example, the pH of fresh concrete is about pH 13, and as the carbonic acid reacts with $Ca(OH)_2$ in the concrete (carbonation), pH of hardened concrete surfaces drops gradually to about 8.5 (McPolin et al., 2007). Calcium silicates and calcium aluminate are the major components of the concrete paste (Kurdowski, 2014). Concrete also has very low water permeability and contains little organic carbon. In addition, concrete surfaces are often exposed to direct sunlight due to the lack of vegetation, and its low heat capacity also leads to drastic variations in temperature, especially in regions such as California. These differences may lead to different transformation rates and pathways, but few studies to date have investigated insecticide transformation on urban surfaces.

As found for many other synthetic chemicals, the environmental fate of a compound may not be accurately reflected by the persistence of its parent form. For pyrethroids, many of the current-use products produce a common degradation intermediate, 3-Phenoxybenzoic acid (3-PBA) (Starr et al., 2008). Several studies have used concentrations of 3-PBA in human urine as biomarkers for measuring exposure to pyrethroids, but these studies were normally focused on occupational or indoor exposure scenarios (Leng et al., 1997; Hardt and Angerer, 2003). Additional studies showed detectable levels of 3-PBA in humans who were not directly exposed to pyrethroids, and it was attributed to dietary exposure where contamination of food by pyrethroids or metabolites might occur (Huedorf and Angerer, 2001; Schettgen et al., 2002).

A limited number of studies have found that 3-PBA exhibits endocrine disrupting activity (Tyler et al., 2000; Sun et al., 2007; Han et al., 2008; Xia et al., 2008). For instance, 3-PBA was found to have 10-100 times more endocrine activity than permethrin, fenpropathrin, and cypermethrin (Tyler et al., 2000). While in vivo studies take a long time and are costly, one study showed a link between urinary 3-PBA concentrations and altered semen quality in humans (Xia et al., 2008). Additionally, 3-PBA has been observed to cause protein damage in rat heart cells at concentrations of 2.1 to 4.4 mg L^{-1} (Vadhana et al., 2011), and earthworm toxicity with an LC_{50} of 49.81 ng cm^{-2}, which is 4 times more potent than the parent compound cypermethrin (Yao et al., 2015). These results suggest that the transformation of pyrethroids in the environment to 3-PBA may also alter the toxicity profile from one that specifically targets the arthropod nervous system to one that is broader spectrum, potentially affecting non-target groups such as mammals. Even though 3-PBA has been shown to have endocrine disrupting activity, no studies to date have been focused on the occurrence and formation of 3-PBA in urban environments. Likewise, few studies have been conducted on the fate of 3-PBA in the environment.

1.4 Transport of Pyrethroids

While pyrethroids are often applied near residences to control termites, ants, and other insect pests, their detection in urban waterways suggests that transport is readily occurring. Research to date has focused mostly on runoff as the major transport pathway. Water samples from storm drains which drained residential areas were monitored for one year in northern California, and discovered detection frequencies of 100% for bifenthrin, 50% for cyfluthrin, and 25% for both permethrin and cypermethrin during the dry season in which runoff was likely due to lawn irrigation events (Weston et al., 2009). Median and maximum concentrations of bifenthrin in the water samples during the dry season were above the LC_{50} values for the most sensitive organisms tested (Weston et al., 2009). During the wet season, detection frequencies increased to 100% for cyfluthrin and 88% for permethrin and cypermethrin each and median concentrations of cyfluthrin and cypermethrin were above LC_{50} values for sensitive species (Weston et al., 2009). In another study, Jiang et al. (2012) examined bifenthrin and permethrin concentrations in runoff water from consecutive precipitation events from 1 to 89 d after application. Runoff collected 1 d after application contributed to approximately 90% of the total bifenthrin and permethrin collected in runoff over the course of the experiment (Jiang et al., 2012). However, the most surprising finding is that bifenthrin and permethrin were both easily detected in runoff from concrete even 89 d after application and after four previous precipitation events (Jiang et al., 2012). These findings strongly suggest that pyrethroids are transported offsite due to either irrigation or rainfall events.

Because of their strong affinity for solid surfaces, the off-site transport of pyrethroids is expected to occur mainly through the movement of solid particulate matter containing sorbed pyrethroids. This movement may occur as suspended solids in runoff from irrigation or precipitation events or as dry particles that become suspended in the air due to wind or traffic (Jiang et al., 2016). These transport mechanisms have been partially confirmed in recent studies. Jiang and Gan (2012) found that over 80% of the pesticides in runoff water were associated with solid particles greater than 0.7 µm in diameter. Jiang et al. (2016) further demonstrated that modeled pesticide runoff concentrations based on particle-bound pesticide levels alone produced results similar to the measured values.

However, the role of dry-form transport of pesticide-laden dust has not been well studied. A recent study showed that pesticide concentrations associated with dust in an urban area of China varied seasonally based upon application and were within the same range as those seen near an agricultural area (Li et al., 2014). These studies illustrate that pesticide-laden particles do become suspended in the atmosphere and may be transported through wind. However, major knowledge gaps exist regarding how the dust becomes contaminated by pyrethroids, the occurrence of particle-bound pyrethroids in urban environments, and definitive evidence that the major pathway for off-site pyrethroid transport is through the movement of particle-bound pesticides.

1.5 Fate of Fipronil

Fipronil is transformed via photolysis, abiotically or biotically mediated oxidation, reduction, and hydrolysis to form three major metabolites (Table 1.2) (Gunasekara et al., 2007). These metabolites are fipronil desulfinyl (photolysis), fipronil sulfone (oxidation), and fipronil sulfide (reduction). These degradation products are important because they have similar or even higher biological activity to aquatic organisms when compared to the parent compound fipronil (Schlenk et al., 2001; Chandler et al., 2004; Maul et al., 2008). In a review paper, Gunasekara et al. (2007) summarized data from surface water samples taken by the USGS in which fipronil and its degradates were commonly detected, with the degradation products having detection frequencies equal to the parent fipronil. Gan et al. (2012), observed high levels of fipronil and its degradates in urban runoff samples, highlighting the fact that residential areas are a major source of fipronil to the environment and, subsequently, a potentially important cause of aquatic toxicity.

1.6 Transport of Fipronil

Due to the fact that fipronil and its degradation products have lower Log K_{ow} values and larger water solubility values than the pyrethroids, it can be hypothesized that sorption to solids may not dominate the fate of these compounds as it does for the pyrethroids. This is supported by the observation that fipronil is widely detected in runoff and water column samples (Gunasekara et al., 2007; Gan et al., 2012). In soils, fipronil was found to have low to moderate sorption capacity, suggesting that particle-bound fipronil may play a minor role in the overall environmental fate (Gunasekara et al., 2007). Further evidence was provided by Lao et al. (2010), who observed low detection frequency of fipronil and low concentrations of its degradates in sediments from an urban estuary. Fipronil and its degradates have low Henry's Law values, indicating that volatilization likely does not contribute significantly to the overall fate.

The transport of fipronil and its degradates may occur in the dissolved form or particle-bound form. Due to the fact that fipronil and its degradates are more water soluble than pyrethroids, it is suspected that transport of the dissolved fraction in runoff is the major transport pathway (Gunasekara et al., 2007; Gan et al., 2012). However, in regions such as California, rainfalls are limited to the winter months. It is likely that dry particles on impervious surfaces still play a significant role in the off-site movement of fipronil and metabolites in irrigation-induced runoff and in the “first-flush” of rain-induced runoff. At present, little is known about the prevalence of fipronil and its metabolites in loose dust particles, the relative composition of fipronil derivatives in dust particles, and seasonal and spatial patterns of particle-bound concentrations.

1.7 Problem Statement

The studies highlighted above have shown that insecticides are commonly found in surface waters and sediments in urbanized watersheds, that the concentrations of insecticides in these aquatic systems are often high enough to have an adverse effect on aquatic organisms, that residential areas are a major source of these insecticides, and that the transport of insecticides from residential areas to urban waterways is dominated by runoff. Similarly, past research suggests that the transformation of urban use insecticides may not reduce their toxicity because their degradation products are also biologically active. However, significant knowledge gaps exist that must be addressed before improved management and mitigation strategies can be devised to reduce the impacts that urban use of insecticides has on non-target organisms.

1.8 Research Objectives

The goal of this project was to fill some of the knowledge gaps listed above in order to improve fate and transport modeling of insecticides in urban environments as well as to provide data so that environmental risk assessments may be conducted on the pyrethroid degradation product 3-PBA.

Objective 1: If particle-bound insecticides compose the bulk of the insecticide mass that is transported off-site, the mechanisms behind the transport of particle-bound insecticides must be understood.

Hypothesis 1: Particle-bound insecticide concentrations will vary spatially in that they will be higher closer to residential houses and the point of application, while decreasing with distance from the house. Additionally, particle-bound insecticides in urban areas will decrease after winter rains.

In order to test this, dust samples were taken from the driveway, gutter, and street near 20 residences in Orange County, CA. The dust was then analyzed to determine whether any spatial, temporal, or physico-chemical relationships could be observed for particle-bound insecticides in urban environments.

Objective 2: Due to its endocrine activity, the mechanisms behind the formation of the pyrethroid degradation product 3-PBA on urban surfaces must be investigated, as well as its occurrence within urban streams.

Hypothesis 2: Rapid degradation of pyrethroids will occur due mostly to photolysis, and rapid and significant formation of 3-PBA will occur on urban surfaces. Similarly, 3-PBA will be widely detected in urban streams.

To test these hypotheses, the mechanisms behind the degradation of pyrethroids and the formation of 3-PBA on urban surfaces was investigated by spiking concrete cubes and glass surfaces and then exposing them to irradiation by natural sunlight, or to dark conditions. Additionally, two urban streams were sampled monthly for five months to quantify the occurrence of 3-PBA in the environment.

Objective 3: The environmental fate of the pyrethroid degradation product 3-PBA must be further evaluated due to its potential to cause endocrine disruption and other toxicological effects including chronic toxicity such as developmental toxicity.

Hypothesis 3: The degradation product 3-PBA will be rapidly degraded in different environmental compartments such as soil, water, and sediment.

This knowledge gap was filled by looking at the persistence of 3-PBA in various environmental media, including soil, water, and sediment. This information should help in the creation of environmental risk assessments for 3-PBA as well as help to inform regulators on whether or not it should be added to monitoring or emerging contaminant lists.

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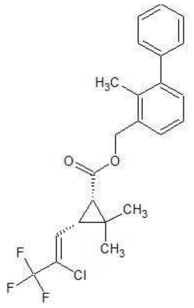
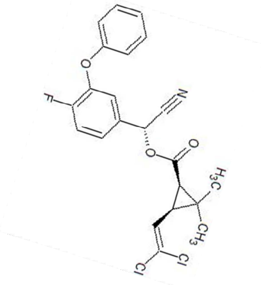
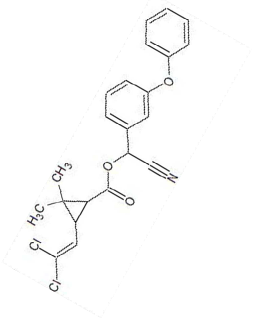
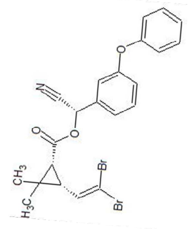
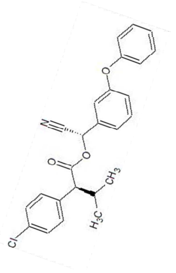
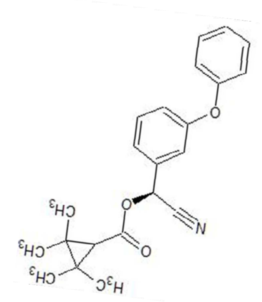
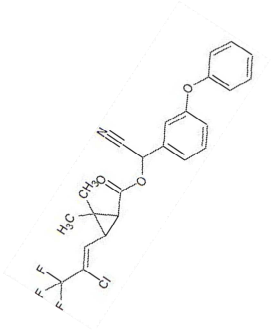
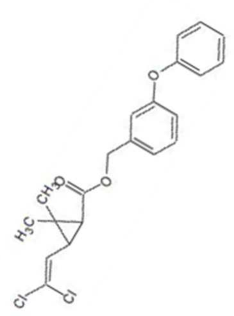
Table 1.1. Properties and structures of pyrethroids most commonly used in urban environments

Pesticide	**Log K_{ow}[a]**	**Solubility (mg L^{-1})[a]**	**Vapor Pressure (mm Hg)[b]**	**Structure**
Bifenthrin	6.4	1.4e-5	1.8 x 10^{-4}	
Cyfluthrin	5.97	2.3e-3	2.03 x 10^{-9}	
Cypermethrin	6.54	4.0e-3	3.07 x 10^{-9}	
Deltamethrin	4.53	2.0e-4	1.5 x 10^{-9}	

Esfenvalerate	5.62	6.0e-3	1.5 x 10^{-9}	
Fenpropathrin	6.00	1.03e-2	5.5 x 10^{-6}	
Lambda-cyhalothrin	7.00	5.0e-3	1.5 x 10^{-9}	
Permethrin	6.1	5.5e-3	2.2 x 10^{-8}	

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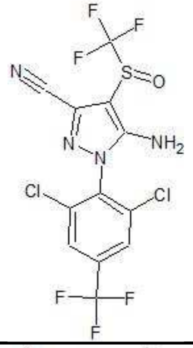
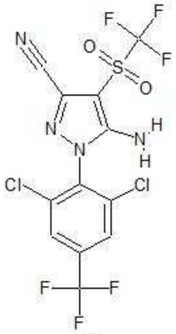
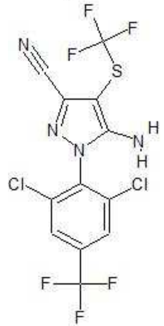
a Laskowski, 2002

b US Department of Health and Human Services, 2003

Table 1.2 Properties and structures of fipronil and its major degradation products.

Pesticide	Log K_{ow}	Solubility (mg L^{-1})	Vapor Pressure (mm Hg)	Structure
Fipronil†	3.5	1.9	1.13 x 10^{-9}	
Fipronil‡ Desulfinyl (Photolysis)	4.2	0.49	1.77 x 10^{-7}	
Fipronil Sulfone‡ (Oxidation)	4.4	0.13	5.8 x 10^{-10}	
Fipronil Sulfide‡ (Reduction)	4.8	0.09	1.79 x 10^{-8}	

†Values for fipronil are from Gunasekara et al. (2007)

‡Values for fipronil degradates estimated using USEPA's EPISuite

Chapter 2 Distribution of Pesticides in Dust Particles in Urban Environments

2.1 Introduction

Pesticides are used in urban environments to control undesirable pests such as ants, termites, and spiders. The most intensive urban pesticide use occurs in regions such as California that have highly urbanized populations and a conducive climate for pest activity year-round. For example, it was estimated that over 1.6 million kilograms of pesticide active ingredients were applied by professional applicators in urban settings in California in 2012 (CDPR, 2012). The actual pesticide consumption could be significantly larger if applications by homeowners are also considered (Budd et al., 2007).

Many studies in recent years have shown the occurrence of urban-use insecticides such as synthetic pyrethroids and fipronil in irrigation and rain-induced runoff and in urban streams (Gan et al., 2005; Amweg et al., 2006; Budd et al., 2007; Holmes et al., 2008; Hintzen et al., 2009; Weston et al., 2009; Ding et al., 2010; Lao et al., 2010; Gan et al., 2012; Jiang et al., 2012, Ensminger et al., 2013). In some cases, pesticide levels in the sediment or water of urban waterbodies exceed their acute toxicity thresholds for sensitive species such as *Hyallela azteca* (Holmes et al., 2008).

Due to their strong affinity for solid surfaces, it may be expected that after application, pesticides can contaminate surface soil in landscaped areas and dust on pavement. Wind, water or traffic may cause further movement and redistribution of these contaminated loose solids, depositing them onto paved surfaces. Irrigation or rain-induced surface runoff may subsequently carry these particles, along with the pesticide residues, to downstream water bodies. Due to the fact that up to 90% of the urban surface area may be comprised of impervious surfaces (e.g., pavement, roofs), pesticide-contaminated dust on hard surfaces can be a primary source for pesticide contamination of urban streams (USDA., 1996; Jiang et al., 2015). A recent study showed that concentrations of chlorpyrifos, cypermethrin, and permethrin in dust in an urban area of southern China varied seasonally based upon application and were within the same range as those seen near agricultural areas in the US, Malaysia, and Japan (Li et al., 2014). Mahler et al. (2009) measured concentrations of fipronil, fipronil sulfide, and fipronil desulfinyl in indoor and outdoor dust associated with an apartment complex in Texas and found that 100% of the samples contained at least one of the target compounds with outdoor concentrations ranging from <0.5-300, <0.5-8.42, and <0.5-120 $\mu g\ kg^{-1}$, respectively. A recent study by Jiang et al. (2015), found that 75.8% of outdoor dust samples contained 7 or more pesticides, and that pesticide concentrations in outdoor dust can be used to predict concentrations in runoff. These studies provide initial evidence of pesticide association with outdoor dust in urban residential areas. However, to date little effort has focused on identifying dust particles on urban pavement as a major contributor to pesticide contamination of urban surface water.

The main objectives of this study were to quantify the types and levels of pesticides in dust particles on urban pavement, determine whether spatial, temporal, or particle size distribution patterns exist, and evaluate contributions of urban pavement dust to off-site pesticide transport and surface water contamination in urban watersheds. This information may be used to improve the prediction of pesticide loadings to urban surface water bodies and to design more targeted mitigation measures to reduce the offsite transport of urban-use insecticides.

2.2 Materials and Methods

2.2.1 Chemicals

Twelve insecticide compounds in two classes were targeted for analysis in this study. These included 8 pyrethroids, i.e., fenpropathrin, lambda-cyhalothrin, bifenthrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate and deltamethrin; and the phenylpyrazole insecticide fipronil and its three primary transformation products desulfinyl fipronil, fipronil sulfide, and fipronil sulfone. The standards of pyrethroids were obtained from various chemical manufacturers, with purities from 97% to 99.9%. The deuterated bifenthrin (d5-bifenthrin) was provided by Toronto Research Chemicals (Toronto, Ontario, Canada), and phenoxy $^{13}C_6$-labeled *cis*-permethrin (^{13}C-permethrin, 99%) was obtained from Cambridge Isotope Laboratories (Andover, MA). Standards of fipronil (98.9%), desulfinyl fipronil (97.8%), fipronil sulfide (98.8%) and fipronil sulfone (99.7%) were obtained from the U.S. EPA's National Pesticide Standard Repository (Fort Meade, MD). Solvents used were in GC/MS or pesticide grade.

2.2.2 Sampling Locations

Twenty homes distributed throughout Orange County, CA were selected for sample collection. Orange County, CA was chosen because pesticide use records suggested that more urban use pesticides are often used in this area than elsewhere in

California (CDPR, 2012). The houses were selected with the help of Dr. Darren Haver of the South Coast Research and Extension Center in Irvine, CA, who had previous contact with the homeowners through the master gardener program. Geographically, the houses selected covered a distance of approximately 44 km from south to north and 17 km from east to west.

2.2.3 Sample Collection

At each house, triplicate dust samples were collected from the driveway directly against the garage door, curbside gutter, and middle of the street for a total of nine samples per house for each sampling event in August 2013, October 2013, and February 2014. The dust was collected using a handheld vacuum fitted with a metal housing and mesh that contained a pre-weighed 1.6 µm (pore size) Whatman GF/A glass-fiber filter paper (Maidstone, U.K.). The area vacuumed for each sample was fixed by using a 0.5 m^2 frame. If the amount of dust collected from one frame was small, the frame was moved to an adjacent area and the dust from an additional frame area was collected with the number of frames per sample being recorded. After collecting each sample, the filter paper was carefully removed and sealed in a glass vial for transport to the laboratory. The vacuum and housing were cleaned with isopropanol before collecting the next sample. Samples were transported in insulated containers to the laboratory on the same day of collection. The samples were stored at 4 ºC before analysis.

2.2.4 Sampling and Particle Size Fractionation

Dust samples in larger quantities were collected in April 2014 from three houses to characterize the dependence of pesticide distribution on particle sizes. These bulk dust samples were collected using a handheld vacuum with an attached 0.3 µm pore size vacuum bag and by vacuuming all surfaces (driveway, gutter, and street) at each house to get three representative samples. The bulk dust samples were loaded onto a stack of sieves (with decreasing mesh sizes from top to bottom) and mixed on a mechanical shaker. The fractionation resulted in the following particle size fractions: >2,000 µm, 2,000-425 µm, 425-250 µm, 250-149 µm, 149-45 µm, 45-38 µm, and < 38 µm. The mass of particles in each fraction was weighed to determine the particle size distribution of each dust sample. The fractionated particles were then analyzed individually for the target pesticides.

2.2.5 Sample Preparation

For the driveway, curbside gutter, and street dust samples, each filter paper with the associated particles was weighed again to determine the mass of collected dust particles. Centrifuge tubes containing the filter and dust particles were spiked with a surrogate (d5-bifenthrin) and extracted ultrasonically with 30 mL methylene chloride/acetone (1:1, v/v) for 15 min in a Fisher Scientific FS110H sonication water bath (Waltham, MA). After sonication, the samples were centrifuged at 2000 rpm for 10 min and the extract was passed through a layer of anhydrous sodium sulfate into a 250-mL glass round-bottom flask. The same extraction step was repeated a total of four times, and the organic solvent phase was combined. The extract was then evaporated under a gentle vacuum on a Büchi RE121 Rotavapor (Flawil, Switzerland) at 30 ºC to approximately 0.5 mL. The final extract was reconstituted in 5.0 mL of hexane/ethyl ether (7:3, v/v), and cleaned up by passing through a Florisil cartridge and eluting with hexane/ethyl ether (7:3, v/v). The clean extract was evaporated under a gentle nitrogen flow at 40 °C to near dryness and the residue was recovered in 1.0 mL hexane/acetone (9:1, v/v) for analysis.

For the bulk dust samples, a 2.0 g subsample from each size fraction was removed and extracted following the method as described above. The total organic carbon content (TOC) in each particle size fraction was determined by the loss on ignition method described by Gavlak et al. (2003). Briefly, duplicate 2.0 g subsamples from each particle size were removed and dried at 150 °C in a muffle furnace for 2 h. The dried samples were weighed and then heated in the muffle furnace at 425 °C for 2 h. After 2 h, the samples were removed and weighed again. The difference in mass was attributed to organic carbon and was used to calculate TOC. Reagent-grade calcium carbonate was included to determine if any losses of inorganic carbon would occur. Under the used conditions, calcium carbonate showed <0.05% loss.

2.2.6 Chemical Analysis

The target pesticides were identified and quantitatively analyzed on a Varian 3800 GC together with a Varian 1200 triple-quadrupole mass spectrometer (Varian Instruments, Sunnyvale, CA). The sample was injected into the 240 ºC GC inlet, and carried by helium (99.999%) at a flow rate of 1.0 mL min^{-1} to a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm, Agilent, Wilmington, DE) for separation. During separation, the oven temperature was 80 °C for 1.0 min, increased to 160 °C at 25 °C

min^{-1}, and then increased to 300 °C at 5 °C min^{-1} and held at 300 °C for 7 min. The sample then exited the column into the 300 °C transfer line and then entered the 250 °C ion source, followed by the triple-quadrupole mass spectrometer which was set in the EI selected reaction monitoring mode (SRM) which was operated at 70 eV. The manifold temperature was held at 40 °C throughout the analysis. The collision gas was argon (99.999%) at 2.0-2.1 mTorr. Individual standards of known concentrations were injected to determine retention times and optimize GC MS/MS parameters such as collision energy.

2.2.7 Quality Control and Data Analysis

Instrumental and procedural controls were used to ensure the integrity of sample analysis. Instrumental controls consisted of the use of the internal standard ^{13}C-permethrin in every sample, analysis of one calibration standard every 10 samples, and the construction of the entire 8-point calibration curve, which ranged from 1 to 500 ng g^{-1}, every 50 samples. Procedural controls included spiking each sample with 20 µL of 1.0 mg L^{-1} d5-bifenthrin before extraction to determine the method recovery, incorporating one method blank for every 15 samples to ensure that no cross contamination occurred, and collecting, analyzing samples in duplicate or triplicate, and baking all glassware and anhydrous sodium sulfate at 400 °C for 4 h before use to prevent cross contamination. Method extraction efficiency was determined by spiking quadruplicate dust samples with 100 ng g^{-1} of each of the analytes investigated in this study and comparing those results to unspiked dust. Extraction efficiencies for each compound were: fipronil desulfinyl 117 ± 24%, fipronil sulfide 83 ± 16%, fipronil 74 ±1 0%, fipronil sulfone 113±23%, bifenthrin

87 ± 15%, fenpropathrin 94 ± 21%, lambda-cyhalothrin 95 ± 20%, permethrin 120 ± 24%, cyfluthrin 101 ± 28%, cypermethrin 93 ± 20%, esfenvalerate 117 ± 22%, and deltamethrin 98±21%. The method detection limits (MDLs) were determined following EPA method 40 CFR, Part 136, Appendix B. Reporting limits were 3 times the MDLs, and are approximately 1 ng g^{-1} for all compounds except bifenthrin (0.5 ng g^{-1}).

Statistical analysis was performed using PC SAS v.9.4 (SAS Institute, Cary, NC). Analysis of variance was carried out with PROC GLM. Planned comparisons of the treatments (spatial, temporal, particle size) were further evaluated with a PDIFF option in an LSMEANS statement if ANOVA proved significant. Simple correlation was conducted on the bulk dust samples using a PROC CORR statement.

2.3 Results and Discussion

2.3.1 Concentrations and Detection Frequencies

To determine the potential contribution of dust-borne pesticides to the contamination of urban surface waters, dust samples were collected around single-family residences in a southern California community. The average surface area sampled for each dust sample was 0.95 m^2 and the average amount of dust collected per sample varied from 0.01 g to 9.58 g, with an average of 0.79 g. Recoveries of the d5-bifenthrin surrogate were 85 ± 40% during the course of the experiment. Among the 441 dust samples collected and analyzed, at least one target pesticide was found in 98.2% of the samples, while 16.8% of the samples contained all 12 target analytes above the detection limits. Additionally, 83.0% of the samples contained 7 or more pesticides at concentrations above the reporting limit (Table 2.1). Among the target pesticides, individual pyrethroids were detected at frequencies of 53.5 to 94.8% and the median concentrations ranged from 1 to 46 ng g^{-1}. Among the eight pyrethroid compounds, permethrin and bifenthrin were the most commonly detected with detection frequencies of 94.8 and 92.7%, respectively. These results were in agreement with pesticide use data, as permethrin and bifenthrin were among the most used pyrethroids in California (CDPR, 2012). For a specific example, 187.7 kg of bifenthrin and 283.2 kg of permethrin were applied by licensed applicators for non-agricultural uses in Orange County, CA during August 2013, while only a combined 106 kg of all the other pyrethroids investigated in this study were applied during this same time period based upon data from the California Pesticide Information Portal (CALPIP, http://calpip.cdpr.ca.gov/main.cfm). Likewise, these results agree well with those of Jiang et al (2015), who observed detection frequencies of 97.5% for bifenthrin in outdoor urban dust. These results also coincided with the monitoring results showing ubiquitous presence of permethrin and bifenthrin residues in sediments as well as water in urban areas of California (Holmes et al., 2008, Weston et al., 2009, and Ensminger et al., 2013, Budd, 2016, Ensminger, 2016), corroborating the connection between outdoor dust and pesticide contamination of surface streams in urban settings.

Occurrence of dust-borne fipronil and its derivatives was also widespread in the urban environment. Fipronil was detected in 52.4% of the dust samples collected, while its photolysis product desulfinyl fipronil was found in 75.5% and oxidation intermediate fipronil sulfone in 67.3% of the samples. The reduction product, fipronil sulfide, was found less frequently, in 50.6% of the samples. The median concentrations of fipronil, fipronil desulfinyl, fipronil sulfide, and fipronil sulfone were 1, 2, 1, and 2 ng g^{-1}, respectively. The degradation intermediates of fipronil are known to have similar or even greater biological activity to aquatic organisms when compared to fipronil (Schlenk et al., 2001; Chandler et al., 2004; Gunasekara et al., 2007; Maul et al., 2008). In a recent study, fipronil and fipronil degradates were consistently detected in runoff water draining urban neighborhoods, including those in the same general area where the dust sampling was conducted (Gan et al., 2012). The widespread occurrence of fipronil derivatives highlights the importance of considering degradation products as well as the parent to obtain a holistic understanding of pesticide fate and risk in the urban environment.

2.3.2 Spatial Patterns in Distribution

The spatial distributions of the target pesticides were examined to delineate the origin and movement of pesticide-laden dust particles. In this study, dust samples were taken from the driveway, the drainage gutter at the bottom of driveway and along the curb, and the middle of street (Figure 2.1). Pesticide applications are often made at the top of a driveway, because garage doors are a point of entrance for insects such as ants (Greenberg et al., 2014). On the other hand, no pesticide treatment would usually occur at the middle of a surface street.

For individual pyrethroids, average concentrations ranged from 2 ± 0.3 (cypermethrin, February 2014) to 696 ± 191 ng g^{-1} (permethrin, October 2013) for the driveway samples, 5 ± 1.6 (cypermethrin, February 2014) to 446 ± 75 ng g^{-1}

(cypermethrin, October 2013) for the drainage gutter samples, and 4 ± 1.2 (cypermethrin, February 2014) to 718 ± 120 ng g^{-1} (cypermethrin October 2013) for the middle of the street samples (Figure 2.2). When analyzed together, no clear spatial patterns existed among the different spatial locations at the same house (Figure 2.2). For example, concentrations of particle-borne lambda-cyhalothrin, bifenthrin, permethrin, esfenvalerate, and deltamethrin were not significantly different between the driveway and the middle of the street. Likewise, average bifenthrin concentrations were very similar at 79 ± 19, 43 ± 18 , and 64 ± 16 ng g^{-1} for the driveway, gutter, and street samples, respectively, in October 2013. In some cases, concentrations of pyrethroid insecticides were actually higher on the street than on the driveway. For instance, the average concentration of cypermethrin was significantly higher ($p<0.05$) on the street (343 ± 57 ng g^{-1}) than on the driveway (165 ± 25 ng g^{-1}) for the August 2013 sampling event. The absence of a clear pattern was further noticed at different sampling times. The relatively homogeneous distribution of pyrethroids around homes suggested that dust particles contaminated with pyrethroids were readily redistributed in the urban environment, likely due to movement aided by wind, water or traffic. The lack of a distribution gradient away from areas where pesticides are typically applied (driveways and lawns) also implied that pyrethroids in dust particles were relatively persistent and were able to survive movement leading to redistribution. The fact that pyrethroids were present in dust on the street surfaces emphasizes the non-point source nature of contamination and also challenges in mitigating runoff of such pesticides, particularly during rain events.

The average concentrations of total fipronils in the dust samples varied from 329 ± 183 (August 2013) to 458 ± 228 (October 2013), 25 ± 9 (February 2014) to 65 ± 23 (October 2013), and 15 ± 3 (February 2014) to 296 ± 235 (October 2013) ng g^{-1} for the driveway, curb gutter, and street samples, respectively. Unlike the pyrethroids, average particle-bound concentrations of fipronil desulfinyl, fipronil, and fipronil sulfone were significantly ($p<0.05$) higher in the driveway samples than in the samples from the curb gutter or street surfaces (Figure 2.3). The difference in spatial distributions among fipronils and pyrethroids may be attributed in part to their application practices in California. For instance, products containing fipronil can only be applied 0.3 m up and 0.3 m out from a structure, while many pyrethroid containing products can be applied further away from the structure (i.e., granular formulations can be spread onto lawns and hard surfaces). When the total concentration of fipronil and its degradates was considered, the driveway samples were significantly higher than those for the gutter or street samples in August 2013 ($p<0.01$), October 2013 ($p<0.05$), and February 2014 ($p<0.01$) (Figure 2.3). It is also probable that fipronil was more susceptible to abiotic transformations (e.g., photolysis and hydrolysis) than pyrethroids, and that fipronil underwent transformations to its degradation intermediates before moving away from the point of application. For instance, the photolysis half-life of fipronil is 0.33 d, while it is 110 and 408 d for permethrin and bifenthrin, respectively, and similar results have also been observed for hydrolysis (Laskowski, 2002; Gunasekara et al., 2007).

2.3.3 Temporal Trends in Distribution

Pesticide residues in dust were further evaluated to discern any temporal trends in their distribution. California has a Mediterranean climate, where precipitations occur mainly during the winter months from December to March. In this study, samples taken in August and October would represent the dry season, while the February sampling would be after several rainfall events. According to the local climate monitoring station (CIMIS station 075; Irvine, CA), 39 rainfalls were recorded during the sampling period and the total rainfall amount measured 92.9 mm, with 84.1 mm falling between the October 2013 and February 2014 sampling events. For the pyrethroids, lambda-cyhalothrin, esfenvalerate, permethrin, cypermethrin, and cyfluthrin displayed a clear trend of similar or increasing concentrations through the dry season, with significant ($p<0.05$) decreases in the rainy season (Figure 2.4). When the total concentration of all pyrethroids was considered, a similar trend was also observed and the trend was consistent among all sampling locations. For instance, the total pyrethroid concentrations increased from 716 ng g^{-1} ± 195 in the driveway samples in August 2013 to 1779 ± 401 ng g^{-1} in October 2013, and then significantly decreased ($p<0.01$) to 344 ± 126 ng g^{-1} in February 2014. The observation that rainfalls decreased pyrethroid levels in loose dust particles suggested that offsite movement of surface dust was likely an important contributor to pesticide contamination of downstream surface waterbodies during the raining season.

However, a similar temporal trend was not observed for several other pyrethroids, including bifenthrin, fenpropathrin, and deltamethrin. For example, dust-borne bifenthrin concentrations remained relatively constant on the driveway (80 ± 19 to 138 ± 58 ng g^{-1}), gutter (44 ± 18 to 64 ± 21 ng g^{-1}), and street (57 ± 13 to 96 ± 43 ng g^{-1}) surfaces throughout the temporal period examined. This could be due to the usage patterns of these specific pyrethroids. For instance, CALPIP data shows that monthly deltamethrin use ranged from 12.6 to 38.7 kg during the wet season, while it remained constant at approximately 11 kg per month during the dry season. However, the amount of bifenthrin applied each month by licensed applicators throughout the study period was similar. Therefore, the lack of temporal differences could be due to increased usage by homeowners or due to formulation differences between the pyrethroids applied. Lastly, it is likely that some loose particles were moved away from the driveway by low intensity rainfall, but did not leave the other locations. This may be seen by comparing the total pyrethroid concentrations among the three spatial locations over the three sampling times (Figure 2.4). For instance, samples from the driveway and gutter showed decreases in the total concentration of all pyrethroids of 80.6 and 82.2 %, respectively, from October 2013 to February 2014. However, the decrease in the total pyrethroid concentration in the street dust samples for the same period was only 70.1 %. This discrepancy implies that at least some of the particle-borne pyrethroids were likely transported to the street from the driveway and/or gutter surfaces, but were not carried away by surface runoff from the street. It may further be expected that a stronger rainfall would likely result in enhanced offsite movement of pyrethroid residues, contributing to elevated contamination of downstream surface water.

Temporal trends in particle-bound concentrations of fipronil and its degradation products varied with regards to one another and also when compared to pyrethroids (Figure 2.5). Fipronil showed a similar trend to pyrethroids with increasing particle-borne concentrations at all spatial locations through the dry season, followed by a decrease in particle-bound concentrations in the February samples which were taken after the winter rains (Figure 2.5). However, these decreases were only significant for the gutter (88.5% decrease, $p<0.05$) and street (97.5% decrease, $p<0.01$) samples. For the fipronil degradation products, on the other hand, dust-borne concentrations were statistically similar at all three spatial locations throughout the temporal duration considered (Figure 2.5). This suggests that the rain-induced movement of dust-borne pesticide residues may be less important for fipronil and its degradation products than for pyrethroids, or that the different application practices (fipronil 0.3m out from the structure compared to the broadcast application of pyrethroids) have an effect on the formation and transport of particle-bound insecticide concentrations. This observation suggested that fipronil was likely readily transformed on the hard surfaces and that conversion of fipronil to its degradation intermediates compensated for chemical losses facilitated by runoff water. It is also likely that owing to their lower hydrophobicity, fipronil and its degradation products were able to desorb from the concrete surface and became adsorbed by dust particles over time. Budd et al. (2015) found higher concentrations of fipronil in storm water runoff than in dry weather runoff, but did not see a similar trend for fipronil degradation products, suggesting that transformations likely influenced the offsite transport of fipronil degradation products in urban environments.

2.3.4 Particle Size Distribution

If dust-borne pesticides constitute a major offsite transport pathway in urban environments, it is important to understand how pesticides are distributed as a function of particle sizes. This may help identify the origins of dust particles on the hard surfaces. Moreover, fine particles are known to be able to travel over a longer distance than large particles in surface runoff, likely posing a greater risk for surface water contamination (Li et al., 2006). Three bulk dust samples were collected from different neighborhoods within the study area and analyzed for pesticide distributions among the different sizes of particles. Based upon the particle size analysis, weight based average particle size was found to be between 149-250 μm. This distribution was similar to that observed by Lewis et al. (1999) in indoor dust samples where 50% of the particles were finer than 150 μm on a weight basis. The organic carbon content of the different particle sizes varied greatly, ranging from 1.9 to 21.5 % with an average OC content of 8.3 ± 5.2%. For two of the samples, the OC content significantly ($p<0.01$) increased with decreasing particle size. However, this trend did not occur for the third sample due to the large amount of grass clippings that were visible in the sample and inseparable from sieving.

In general, pyrethroid concentrations increased with decreasing particle sizes (Figure 2.6). This relationship was significant ($p<0.05$) for bifenthrin, permethrin, esfenvalerate, and deltamethrin in samples taken from all three locations (Figure 2.6). This may be attributed to the fact that finer particles have larger surface areas, leading to enhanced sorption. For instance, if the particles are assumed to be spherical with a volume of 1 cm^3, the largest particle size examined in this study (2000 μm) has a total surface area of approximately 3.0 x 10^9 μm^3, while the surface area for the smallest fraction (38 μm) is two orders of magnitude larger at approximately 1.56 x 10^{11} μm^3. The high concentrations of total pyrethroids observed in the largest size fraction could have been due to the high OC content from grass clippings that made it through the sieve, or from the use of solid pyrethroid formulations by the homeowners, which are composed of coarse granules (Figure 2.6). Pyrethroid concentrations generally also increased with increasing organic carbon content. For instance, the relationship between total pyrethroids and OC content amongst all 3 samples was highly significant ($p<0.001$). The results of this study are in agreement with Lewis et al. (1999) who observed generally increasing concentrations of pesticides and PAHs in indoor and outdoor dust with decreasing particle size. However, a similar trend was not evident for fenpropathrin, lambda-cyhalothrin, cyfluthrin, or cypermethrin. This may be due to the low concentrations and/or infrequent detections for these compounds. This could also be due to the use of granular formulations of these compounds which could have been collected by the vacuum, causing larger particle-size fractions to have higher concentrations than from sorption alone.

Similar to the pyrethroids, dust-borne concentrations of fipronil, fipronil desulfinyl, fipronil sulfone, and fipronil sulfide showed a significant ($p<0.05$) increasing trend with decreasing particle sizes (Figure 2.6). For fipronil, the dust-borne concentration in the smallest size fraction (34 ± 1 ng g^{-1}) was significantly ($p<0.01$) higher than the larger size fractions (5 ± 0.1 to 11 ± 2 ng g^{-1}). The three fipronil degradation products also showed significantly higher concentrations in the smallest size fractions than the two largest size fractions ($p<0.05$). This is probably due to the increasing surface area of the smaller particle sizes, or could be due to the increasing OC content of the smaller size fractions. To investigate this further, the relationship between concentrations of particle-bound fipronils and OC content was examined. Significant ($p<0.05$) relationships existed between increasing concentrations of fipronil, fipronil sulfone, and fipronil sulfide and increasing OC content in the dust samples. Similarly, highly significant ($p<0.01$) relationships were observed between increasing concentrations of total fipronils and increasing OC content in the dust samples.

The finding that both pyrethroids and fipronils were enriched in fine particles have several implications. Fine particles are known to have a greater mobility in water or wind-facilitated transport (Addo et al., 1999; Li et al., 2006), and may therefore have a greater probability to enter downstream surface water. For the same reason, mitigation measures based on sedimentation (e.g., sediment traps) or filtration (e.g., vegetative filters) may be less effective than expected at reducing pesticide runoff in urban environments. On the other hand, fine particles are more likely to stay in the water phase, posing a greater exposure to water-column dwelling organisms, than coarse particles that tend to settle out quickly.

2.4 Conclusions

The results of this study show that there was widespread occurrence of urban-use insecticides in loose dust particles residing on paved surfaces around individual homes. The presence of pyrethroids was relatively uniform in areas around a house, suggesting long persistence and redistribution. Fipronil appeared to be quickly converted to its degradation intermediates on the pavement, highlighting the importance to consider biologically active metabolites to obtain a holistic risk assessment. Rainfalls exhibited a significant effect in decreasing pesticide levels in surface dust, implying that dust accumulation on urban surfaces during the dry season may constitute a significant source for contaminating surface water under wet conditions. Pesticides were generally concentrated in the fine particles, and therefore, fine dust particles may be considered as the primary carrier of pesticides into urban surface streams. If dust on paved surfaces is proven to be the primary contributor to pesticide contamination of urban surface water, surface runoff models may be modified to predict pesticide runoff loads within a given watershed. It is unclear from this study how the dust particles became contaminated with pesticides. It is unknown if pesticide-contaminated dust was from the surface soil treated with pesticides in the surrounding areas, or dust particles were directly contaminated with pesticides during applications. Future research is needed to understand the origin of such contamination, so that regulations and mitigation strategies may be implemented to minimize contamination of urban waterways by pesticides.

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Table 2.1. Occurrence of insecticides in outdoor urban dust, n=441.

Pesticide Class	**Percentile Distribution of Concentrations**							**Max**	**δ**	**Geomean**
Pyrethroids	10	25	33	50	67	75	90	(ng g^{-1})		(ng g^{-1})
Fenpropathrin	<RL	<RL	2	10	26	43	125	2384	124	47
Lambda-Cyhalothrin	<RL	1	2	3	8	13	35	696	56	25
Bifenthrin	2	7	11	24	43	60	170	2817	230	67
Permethrin	6	15	22	46	111	175	424	8852	603	132
Cyfluthrin	<RL	1	2	11	82	132	309	1474	183	53
Cypermethrin	<RL	1	2	13	233	314	592	2631	369	72
Esfenvalerate	<RL	<RL	<RL	1	3	9	92	523	32	22
Deltamethrin	<RL	<RL	<RL	11	36	53	133	6173	177	78
Phenylpyrazoles										
Fipronil	<RL	<RL	<RL	1	3	9	92	3664	320	60
Fipronil desulfinyl	<RL	1	1	2	3	4	22	5146	186	71
Fipronil sulfide	<RL	<RL	<RL	1	1	1	3	1069	19	32
Fipronil sulfone	<RL	<RL	1	2	3	5	21	6188	347	78

* Reporting Limit = 1 ng g^{-1} for all compounds except for bifenthrin where RL = 0.50 ng g^{-1}.

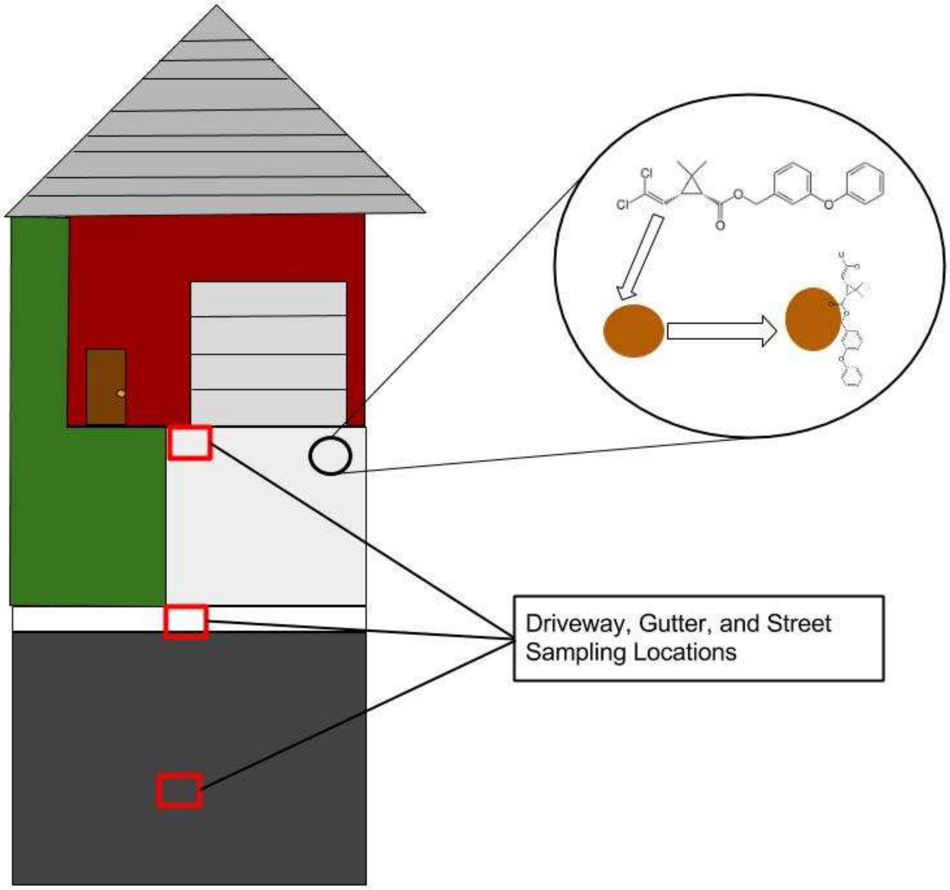

Figure 2.1. Conceptual model representing a typical residence where sampling took place in the driveway near the garage door, the gutter between the driveway and street, and within the street itself. The zoomed in portion shows permethrin becoming adsorbed to a dust particle.

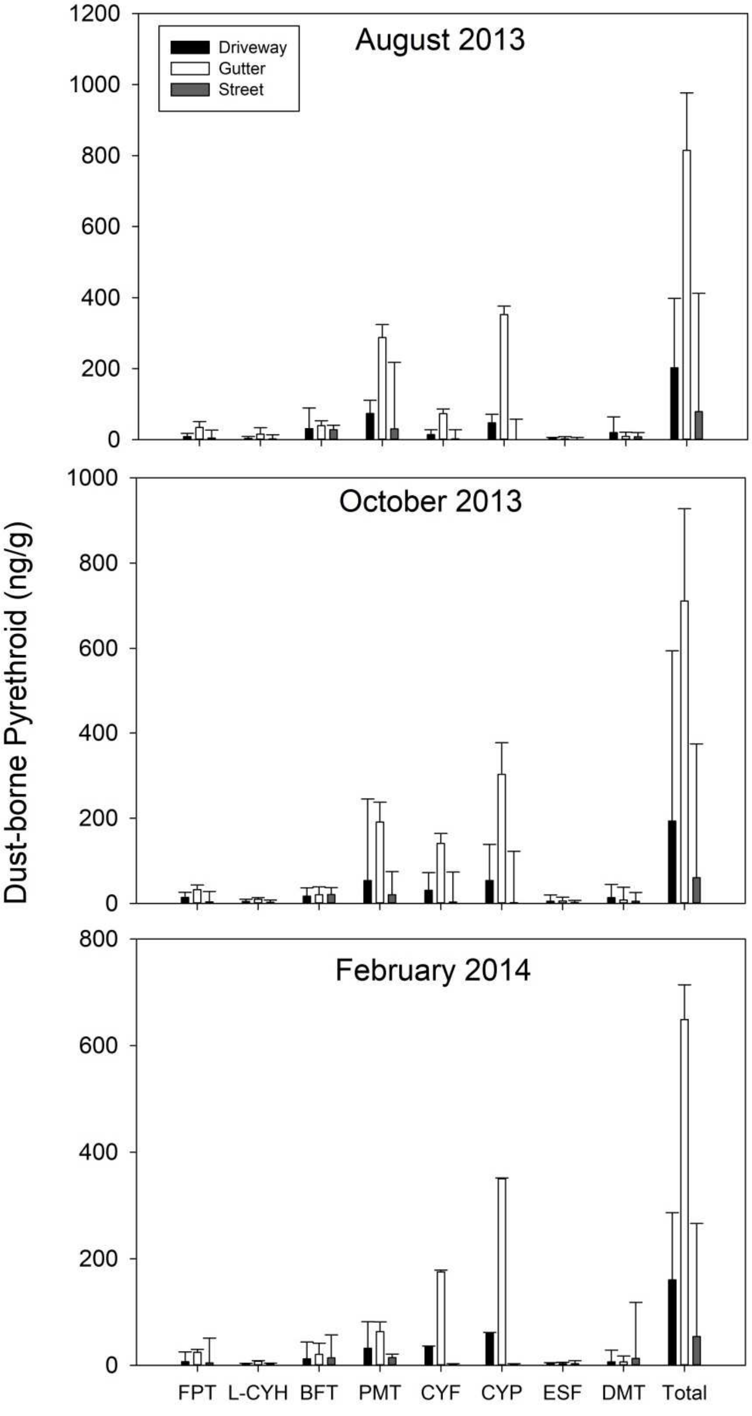

Figure 2.2 Spatial distribution of pyrethroid insecticides in urban dust by sampling month.

Pyrethroids: FPT=fenpropathrin, L-CYH=lambda-cyhalothrin, BFT=bifenthrin, PMT=permethrin, CYF=cyfluthrin, CYP=cypermethrin, ESF=esfenvalerate, and DMT=deltamethrin.

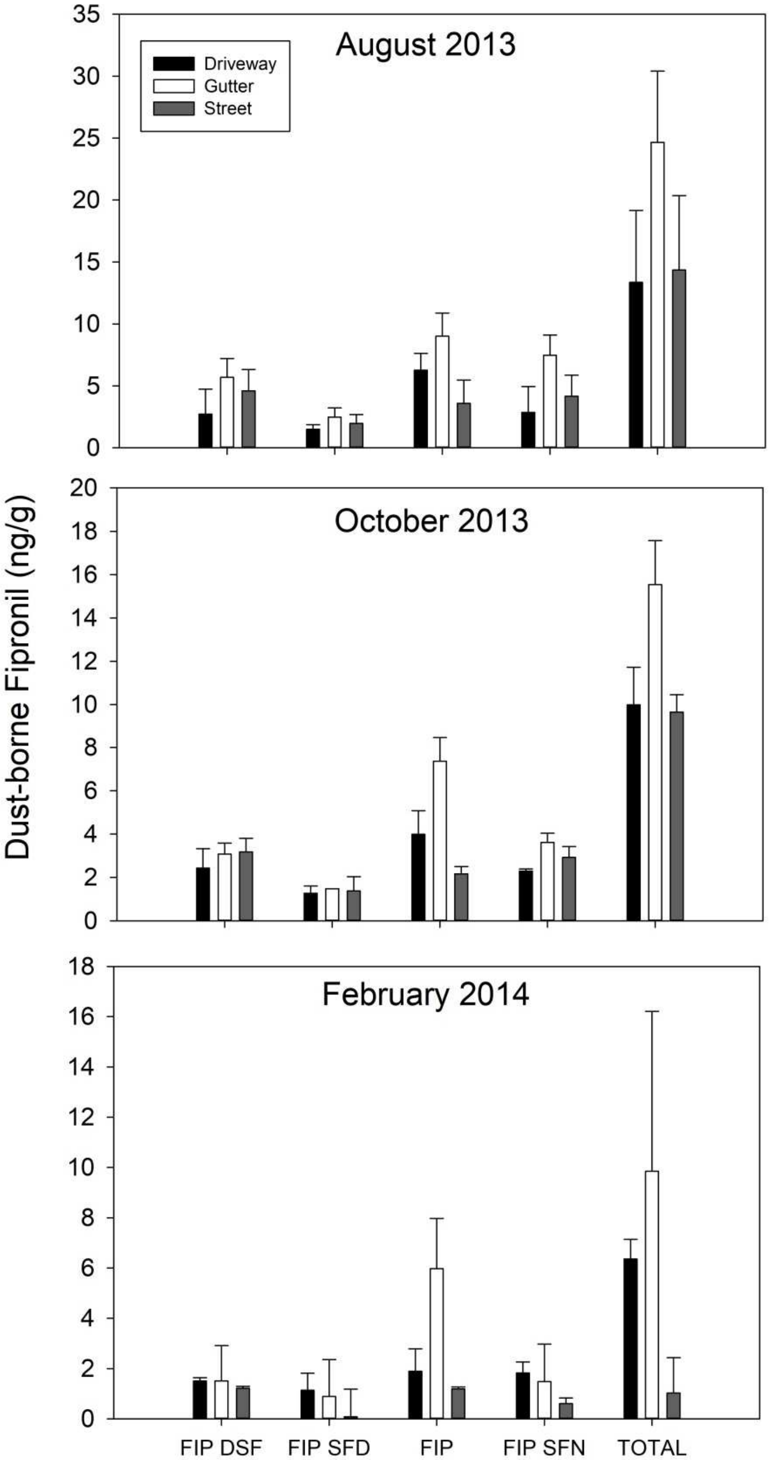

Figure 2.3. Spatial distribution of fipronil insecticides in urban dust by sampling month. FIP DSF=fipronil desulfinyl, FIP SFD=fipronil sulfide, FIP=fipronil, and FIP SFN=fipronil sulfone.

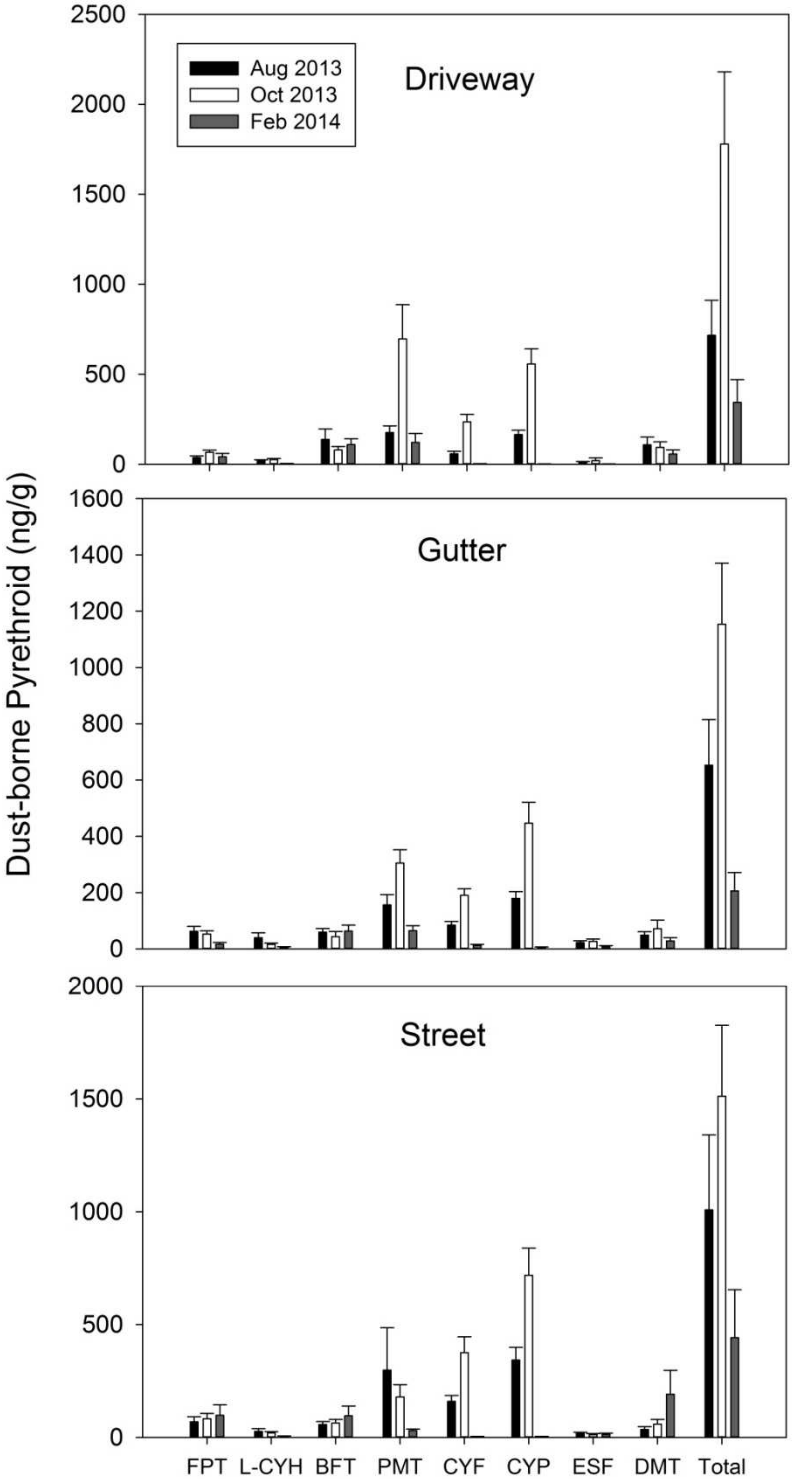

Figure 2.4 Temporal distribution of pyrethroid insecticides in urban dust by sampling location.

Pyrethroids: FPT=fenpropathrin, L-CYH=lambda-cyhalothrin, BFT=bifenthrin, PMT=permethrin, CYF=cyfluthrin, CYP=cypermethrin, ESF=esfenvalerate, and DMT=deltamethrin

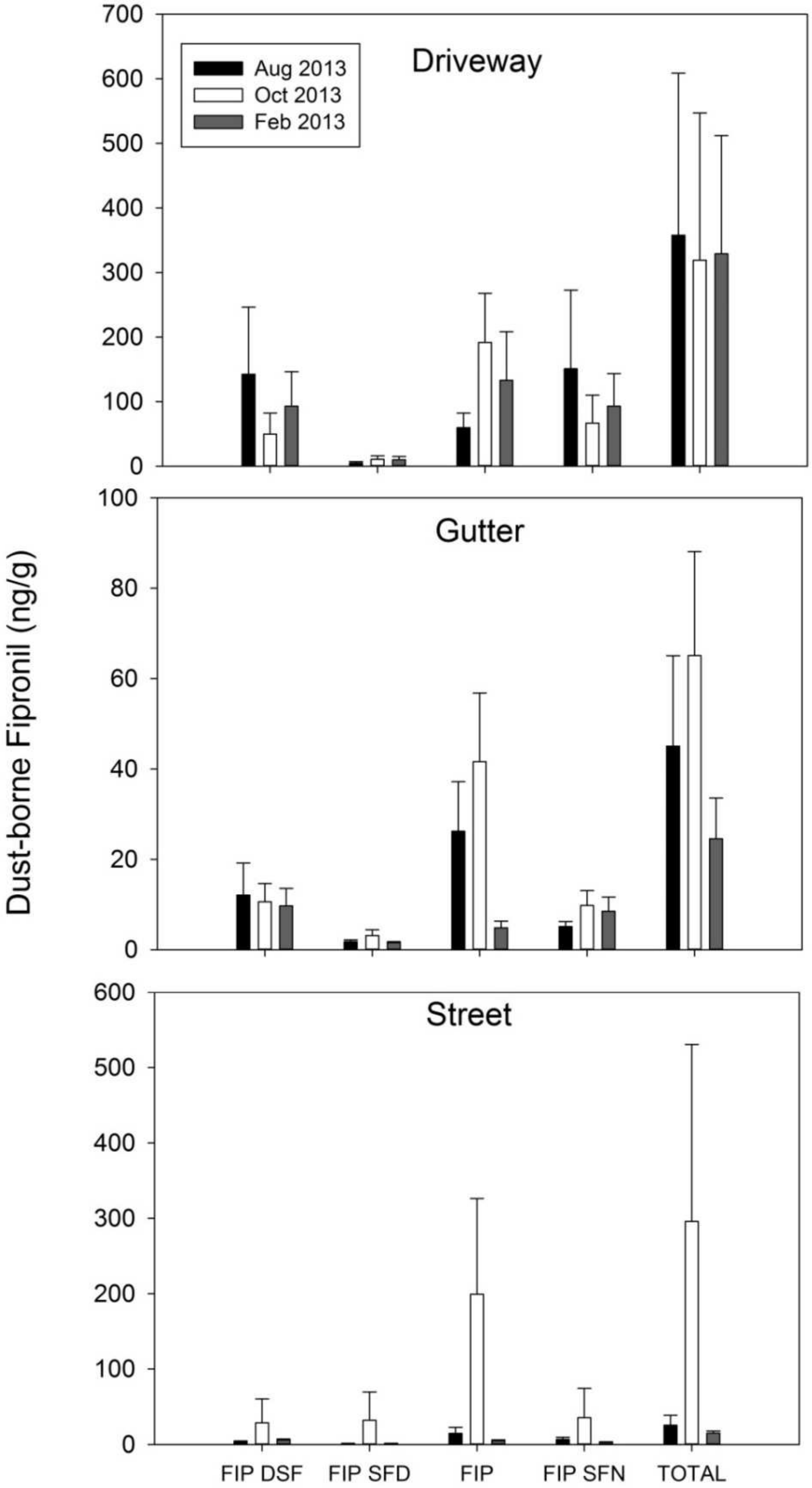

Figure 2.5. Temporal distribution of fipronil insecticides in urban dust by sampling location.

FIP DSF=fipronil desulfinyl, FIP SFD=fipronil sulfide, FIP=fipronil, and FIP SFN=fipronil sulfone.

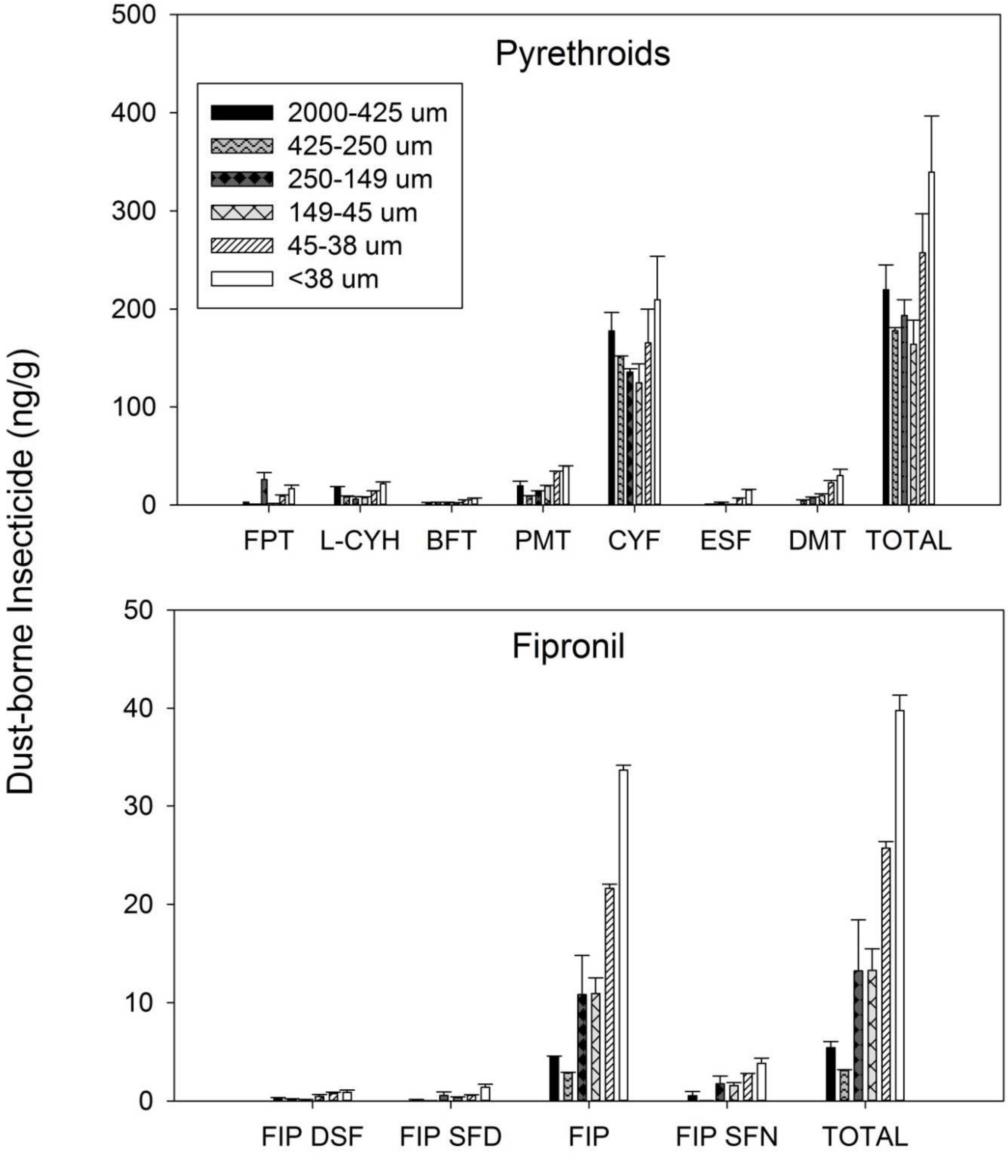

Figure 2.6. An example from one sample which shows the typical results of the distribution of particle-bound pesticide concentrations in different particle size fractions of outdoor residential dust. FPT=fenpropathrin, L-CYH=lambda-cyhalothrin, BFT=bifenthrin, PMT=permethrin, CYF=cyfluthrin, CYP=cypermethrin, ESF=esfenvalerate, and DMT=deltamethrin; FIP DSF=fipronil desulfinyl, FIP SFD=fipronil sulfide, FIP=fipronil, and FIP SFN=fipronil sulfone. Note that L-CYH and CYP were at concentrations below the detection limit.

Chapter 3 Degradation of Pyrethroids and Formation of 3-Phenoxybenzoic Acid on Urban Impervious Surfaces

3.1 Introduction

Urban pesticide use including structural pest control and landscape maintenance is an important contributor to the total pesticide use. For example, in the year of 2014, urban consumption in California was 1.8 million kg as active ingredients (a.i.) for structural pest control alone, of which the use of pyrethroids was 1.77×10^5 kg (CDPR, 2014). Pyrethroids are insecticides whose usage and popularity have been growing worldwide due to their high insecticidal potency and low toxicity to mammals(van der Berg et al., 2012; Brander et al., 2016). For instance, the total amount of pyrethroids used in urban areas of California by professional applicators increased from 1.43×10^5 to 1.77×10^5 kg (a.i.) between 2009 and 2014, representing a 25% increase (CDPR, 2014). The actual use could be substantially greater because homeowners also commonly use pyrethroid products. This intensive use in urban areas has led to widespread occurrence of pyrethroids in urban environments (Jiang et al., 2015; Jiang et al., 2016; Richards et al., 2016) and subsequent contamination and acute toxicity in urban surface aquatic systems (Weston et al., 2009). While the contamination of urban surface water by pyrethroids has been extensively studied in recent years, to date little attention has been given to their transformation products, including those retaining biological activity.

Transformation of pyrethroids is well understood for agricultural environments (Schimmel et al., 1983; Lutnicka et al., 1999; Meyer et al., 2013). In contrast, relatively little is known about their fate and transformation processes in urban settings. The urban environment is characterized with coverage of impervious surfaces, e.g., pavements and rooftops (Arnold and Gibbons, 1996). Concrete, the material used for most urban impervious surfaces, has distinct properties compared to soil or sediment. For example, pH of fresh concrete is about pH 13, and as the carbonic acid reacts with $Ca(OH)_2$ in the concrete (i.e., carbonation), pH of hardened concrete surfaces decreases gradually to about pH 8.5 (McPolin et al., 2007). Calcium silicates and calcium aluminate are the major components of the concrete paste (Kurdowski, 2014). Concrete also has very low water permeability and contains little organic carbon. In addition, concrete surfaces are often exposed to direct sunlight due to the lack of vegetation, and its low heat capacity leads to drastic variations in temperature, especially in regions such as California.

In a recent study, Jiang and Gan (2016) observed conversion of permethrin to 3-phenoxybenzoic acid (3-PBA) on concrete slabs under sunlight and 3-PBA was detectable in runoff water even 3 months after the initial treatment. Tyler et al. (2000) showed that 3-PBA exhibited anti-estrogenic activity in a yeast assay with an IC50 of 14 ± 5 mg L^{-1} and a lowest observed inhibition concentration (LOIC) of 2.6 ± 1.5 mg L^{-1}.[15] Further studies showed that 3-PBA may have endocrine disrupting activity (Sun et al., 2007; Brander et al., 2012) as well as protein damage capacity in rat heart cells (Vadhana et al., 2011; Brander et al., 2016). It must be noted that 3-PBA is a common degradation product of multiple pyrethroid compounds, including permethrin, deltamethrin, fenpropathrin, cyhalothrin and esfenvalerate (Starr et al., 2008; Liu et al., 2010). However, it is unknown whether the other commonly used pyrethroids may also be susceptible to conversion to 3-PBA on impervious surfaces. Moreover, it is unknown if formation of 3-PBA on impervious surfaces may lead to its contamination of surrounding surface streams.

The objectives of this study were to evaluate the formation of 3-PBA from different commonly used pyrethroid insecticides on concrete, explore potential mechanisms of the transformations and determine occurrence of 3-PBA in urban streams under ambient conditions. The findings from this study may add to a comprehensive understanding of environmental risks of synthetic pyrethroids by considering their biologically active degradation intermediates.

3.2 Materials and Methods

3.2.1 Chemicals

Standards of five pyrethroids (fenpropathrin, lambda-cyhalothrin, permethrin, esfenvalerate and deltamethrin) were obtained from various chemical manufacturers, with purities from 97% to 99.9%. Deuterated bifenthrin (d5-bifenthrin) was obtained from Toronto Research Chemicals (Toronto, Ontario, Canada), and phenoxy $^{13}C_6$ -3-phenoxybenzoic acid (^{13}C-3-PBA) was purchased from Cambridge Isotope Laboratories (Andover, MA). Phenoxy $^{13}C_6$- *cis*-permethrin (^{13}C-permethrin, 99%) was used as an internal standard and was obtained from Cambridge Isotope Laboratories (Andover, MA). A silylation reagent *n*-tert-butyldimethylsilyl-n-methyltrifluoroacetamide (MTBSFA) was obtained from Sigma Aldrich (St. Louis, MO) and used for derivatization of 3-PBA before instrumental analysis. Solvents used were in chromatography or pesticide residue grade.

Solutions containing individual pyrethroids at 100 μg mL^{-1} each, as well as a stock solution containing all five pyrethroids at a concentration of 100 μg mL^{-1} each (500 μg mL^{-1} total pyrethroid concentration) were prepared in acetone and stored at -20 °C before use. Concrete cubes with dimensions of 14 × 14 × 8 mm were prepared according to Jiang et al. (2011).[21] Briefly, Portland cement (ASTM C 150, Paragon, Norco, CA), sand, and water (2:4:1 w/w/w) were mixed, poured into forms, and left for 24 h. Curing was done by placing the concrete cubes in deionized water for 28 d. The void content and bulk density of the dried concrete cubes were determined by ASTM C642-06, and found to be 19.2 ± 0.4% and 2.10 ± 0.01 g/cm^3, respectively.[21] Borosilicate glass disks with a diameter of 20 mm were purchased from Thermo Fisher Scientific (Waltham, MA)

3.2.2 Batch Experiment Setup

Concrete and glass surfaces were spiked with 500 μL of the mixed pyrethroid stock solution, or 500 μL of individual pesticide solution. The treatment resulted in an initial concentration to 25.5 μg cm^{-2} for the concrete cubes and 15.9 μg cm^{-2} for the glass surfaces. These rates were similar to those used for urban residential pest control in California based upon pesticide labels.

The treated concrete and glass surfaces were subsequently exposed to irradiated or dark conditions. For the irradiated treatment, samples were placed on the roof of a three-story building (33°58'26.0"N 117°19'33.8"W) and exposed to natural sunlight from April 27 through June 26, 2016. Daytime lengths ranged from 12.9 to 14.4 h during this period. Meteorological conditions including temperature and light intensity were obtained from a California Irrigation Management Information System (CIMIS) station that was located about 200 m away (Table 3.4). For the non-irradiated treatment, samples were wrapped in aluminum foils and then placed on the same roof. Thus, the two treatments underwent similar temperature regimes, and differed only in sunlight exposure. Samples were removed at 1, 3, 6, 12, 24, 48, 168, and 336 light h after the treatment for analysis of remaining pesticide levels and appearance of 3-PBA.

3.2.3 Field Sample Collection

Grab water samples were collected monthly for five consecutive months from two 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) was located in Aliso Viejo, CA (Figure 3.1). These two surface streams drain primarily runoff from the surrounding neighborhoods and were previously included for urban pesticide monitoring in Southern California by the California Department of Pesticide Regulation (Budd, 2010). The Salt Creek site directly received rain and irrigation runoff from nearby housing developments (Figure 3.1). The Wood Creek site also received rain and irrigation runoff from nearby residential areas; however, the runoff was retained in a wetland above the sampling point. Neither site received water directly from any wastewater treatment plant. For sampling, 1 L amber glass bottles were submerged in the streams until approximately 1 L of water was collected. Duplicate samples were taken at each site, with different bottles being collected for the determination of pyrethroids and 3-PBA.

3.2.4 Sample Preparation

For extraction, concrete cubes or glass discs were placed in 40 mL amber glass vials and spiked with two surrogate standards (1 mL of 50 μg L^{-1} d5-bifenthrin for the pyrethroids and 20 μL of 2.5 mg L^{-1} ^{13}C-3-PBA for 3-PBA), followed by the addition of 30 mL acetone:dichloromethane (1:1 v/v). The mixture was sonicated for 15 min in a Fisher Scientific FS110H sonication water bath (Waltham, MA). The extract was then passed through 20 g anhydrous sodium sulfate (Na_2SO_4) into a 250-mL glass round bottom flask. The extraction was repeated a total of three times and the extracts combined. The samples were concentrated on a Büchi RE121 Rotavapor (Flawil, Switzerland) under vacuum at 30 °C to approximately 0.5 mL. The extract was then reconstituted in 15 mL of hexane/acetone (9:1, v/v) and was transferred to a 20 mL glass test tube. The extract was evaporated under a gentle nitrogen flow at 40 °C to near dryness, and the residue was reconstituted in 1.0 mL hexane/acetone (9:1, v/v). For analysis, an aliquot of 100 μL was taken from the sample and placed in a 250 μL glass insert inside a GC vial. An aliquot of 20 μL MTBSFA was added to the vial insert. These samples were placed in an oven at 60 °C for 1 h to silylate 3-PBA for GC analysis. Recoveries for fenpropathrin, lambda-cyhalothrin, permethrin, esfenvalerate, deltamethrin, and 3-PBA were determined through preliminary experiments to be 84 ± 19%, 82 ± 15%, 96 ± 19%, 104 ± 15%, 82 ± 11%, and 101 ± 14%, respectively.

A modified EPA Method 3510C was used to extract pyrethroids from the field collected water samples. Water samples (1 L) were transferred from the sample bottles to 2 L glass separatory funnels with 20 g sodium chloride (NaCl) and then shaken vigorously until the NaCl was completely dissolved. For extraction, 30 mL dichloromethane (DCM) was added to each sample bottle to thoroughly rinse the container and the rinsate was poured into the separatory funnel. The funnels were then mixed for 3 min each and allowed to settle for 1 h to allow for complete separation of the water and organic solvent phases. After phase separation, the DCM phase was drained through 20 g anhydrous Na_2SO_4 into a 500 mL glass round bottom flask. This process was repeated for a total of three times. The combined extract was evaporated, reconstituted, and evaporated again using the procedure as described above. Recoveries for fenpropathrin, lambda-cyhalothrin, permethrin, esfenvalerate, and deltamethrin were 88 ± 7%, 85 ± 17%, 96 ± 8%, 92 ± 17%, and 84 ± 15%, respectively, as determined through preliminary experiments.

Solid phase extraction was used to extract 3-PBA from the field collected water samples. Briefly, water samples (1L) were first filtered through GF/F glass fiber filter paper (0.7 µm, Whatman, Florham Park, NJ). The filtrate was then loaded onto an Oasis HLB SPE cartridge containing 150 mg sorbent that was pre-rinsed with 5 mL methanol and 5 mL ultrapure water. The cartridges were dried with a gentle air flow and then eluted with 15 mL methanol. The collected elute was evaporated to near dryness under a gentle nitrogen stream at 40 °C. The samples were then reconstituted in methanol to a final volume of 1 mL for analysis on an ultra-performance liquid chromatography - tandem mass spectrometer (UPLC-MS/MS). Recovery of 3-PBA as determined by spiking water was 94 ± 11% in preliminary experiments.

3.2.5 Chemical Analysis

For pyrethroids in both urban stream water and impervious surface samples and 3-PBA in the impervious surface samples, analysis was conducted using an Agilent 6890N Gas Chromatograph (GC) equipped with an Agilent 5973 mass selective detector (MS) (Agilent, Santa Clara, CA). The inlet temperature was 250 °C, and a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm, Agilent, Wilmington, DE) was used for separation. The oven temperature was held at 80 °C for 1.0 min, increased to 200 °C at 25 °C min^{-1}, and then increased to 300 °C at 5 °C min^{-1} and held at 300 °C for 9 min. Individual standards of known concentrations were injected to determine retention times and optimize the GC-MS parameters. The ion pairs utilized for quantification are listed in Table 3.5.

A Waters Acquity UPLC-MS/MS (Waters Milford, MA) was used for analysis of 3-PBA in the urban stream water samples.[14] Briefly, the sample was injected with two mobile phases consisting of water with 0.1% formic acid (A) and acetonitrile with 0.1% formic acid (B), respectively. The mobile phases were held with 70% A and 30% B for 3 min, then changed to 100% B over 3 min, held for 4 min, and then decreased back to 30% B over 3 min and held for 2 min. An UPLC BEH C18 column (2.1×100 mm, particle size at 1.7 μm, Waters) was used for separation at 0.2 mL min^{-1} flow rate and 40 °C column temperature. The MS was operated in the negative multiple reaction monitoring (MRM) mode, with the source temperature at 120 °C, and the capillary voltage at 3.2 kV.

3.2.6 Quality Control and Data Analysis

Reagent blanks, field blanks, recovery surrogates, internal standards, and replicates were used when applicable to ensure quality of analysis. During extraction, one reagent blank was extracted every 10 samples to exclude the presence of cross contamination. All glassware, sodium chloride, sodium sulfate, and the impervious surfaces were baked at 400 °C for 4 h before use. Samples were always analyzed as duplicates (water samples) or triplicates (impervious surface samples) to ensure reproducibility. Samples were spiked with either 20 μL of 1.0 mg L^{-1} d5-bifenthrin, 20 μL of 1.0 mg L^{-1} ^{13}C-3-PBA, or both, before extraction to determine the extraction efficiency. Recoveries of the d5-bifenthrin surrogate were 75 ± 19% and 91 ± 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 ^{13}C-permethrin as an internal standard for all samples analyzed by GC-MS and construction of an 8-point calibration curve with concentrations ranging from 1 to 500 μg L^{-1} before every analytical run and after every 50 samples analyzed.

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

Dissipation Mechanism Elucidation

Dissipation of pyrethroids on impervious surfaces may be attributed to volatilization, binding, hydrolysis, and photolysis. The degradation kinetics for non-irradiated (or dark) glass (NG), non-irradiated concrete (NC), irradiated glass (IG), and irradiated concrete (IC) treatments could be described using Equations 1-4, respectively:

$$\ln C_t = \ln C_0 - k_{volatilization} \bullet t_{total} \qquad [1]$$

$$\ln C_t = \ln C_0 - k_{volatilization} \bullet t_{total} - k_{binding+hydrolysis} \bullet t_{total} \qquad [2]$$

$$\ln C_t = \ln C_0 - k_{volatilization} \bullet t_{total} - k_{photolysis\text{-}G} \bullet t_{light} \qquad [3]$$

$$\ln C_t = \ln C_0 - k_{volatilization} \bullet t_{total} - k_{binding+hydrolysis} \bullet t_{total} - k_{photolysis\text{-}C} \bullet t_{light} \qquad [4]$$

where, C_t and C_0 are pyrethroid concentrations in μg m^{-2} on impervious surfaces at time t and 0, respectively; $k_{volatilization}$, $k_{binding+hydrolysis}$, $k_{photolysis\text{-}G}$, and $k_{photolysis\text{-}C}$ are the first-order rate constants in h^{-1} for volatilization, binding and hydrolysis, photolysis on glass and photolysis on concrete surfaces, respectively; and t_{total} and t_{light} are time in h for the entire reaction and exposure to natural sunlight , respectively. It must be noted that in $k_{binding+hydrolysis}$, losses due to 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 $k_{volatilization}$ (Eq. 1), while the volatilization rates were assumed to be similar between concrete and glass surfaces. Therefore, $k_{binding+hydrolysis}$ could be calculated using Equations 1 and 2, while $k_{photolysis\text{-}G}$ may be calculated using Equations 1 and 3. Binding and hydrolysis on the glass surfaces were assumed to be negligible due to the high recoveries of all pyrethroids from the glass surface in preliminary experiments. Finally, $k_{photolysis\text{-}C}$ may be determined using Equations 2 and 4.

3.3 Results and Discussion

3.3.1 Pyrethroid Dissipation

Pyrethroid dissipation occurred at different rates depending on the types of surfaces and presence or absence of sunlight (Figures 3.2 - 3.6). Fitting concentration declines to the first-order decay model yielded half-lives (h) for the different treatments, as shown in Table 3.2. Overall, rapid disappearance was observed on the sunlight irradiated concrete, but different pyrethroids displayed significant differences in their stability (Table 3.2). 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, followed by deltamethrin (Table 3.2).

The other experimental conditions (i.e., NC, IG, NG) were included in this study to uncover potential contributions by volatilization, photolysis, and binding/hydrolysis. For example, after 34 h the amount of fenpropathrin remaining on the surface decreased from 50.0 μg to 7 ± 1, 16 ± 7, and 19 ± 6 μg for the IC, NC, and IG treatments, respectively, but only to 35 ± 3 μg for the NG treatment (Figure 3.2). After 556 h, the extractable residual fenpropathrin was below 0.1 μg for the IC, NC, and IG treatments, while 26 ± 4 μg still remained for the NG treatment. These observations suggested that for fenpropathrin, binding/hydrolysis was likely the main cause for its dissipation on the concrete surfaces, while volatilization contributed insignificantly. Similar results were generally observed for lambda-cyhalothrin, deltamethrin, and esfenvalerate (Figure 3.3-3.6). However, there were several notable exceptions. For example, permethrin was relatively stable on non-irradiated concrete (Figure 3.4), suggesting a limited role of binding/hydrolysis, while lambda-cyhalothrin was relatively stable on non-irradiated glass, indicating minimal contribution from volatilization (Figure 3.3).

The dissipation of the total pyrethroid residues after application of the five pyrethroid mixture to the glass and concrete surfaces is shown in Figure 3.8. The rapid dissipation of pyrethroids on concrete observed in this study agreed well with that in Jiang and Gan (2016), where only 1.9 ± 0.9% of the initially applied permethrin was found in runoff from the concrete slabs after 24 h. The present study showed that 11 ± 2% of the initially applied pyrethroids was extractable with solvent after 24 h on the concrete under sunlight irradiated conditions (2016) (Figure 3.8). The larger percentage detected in this study was likely due to use of a solvent for the extraction of the concrete surface, as opposed to wash-off of water in the previous study.

The stability of pyrethroids on concrete surfaces has not been well studied. Half-lives estimated for irradiated concrete surfaces in this study were considerably shorter than those reported for the other media (Table 3.2). The half-lives were only 3 to 30 h for the five pyrethroids on concrete exposed to the sunlight. This illustrates the pronounced effect that both the concrete surface properties and sunlight had on the dissipation of pyrethroids on impervious surfaces. These findings further suggested that due to the relatively short persistence of pyrethroids on urban hardscapes such as concrete, using half-lives available from other media such as soil or water may lead to inaccurate estimates in predicting off-site transport of pyrethroids in urban settings. However, it is important to note that in this study, pure compounds were used for treatment, while commercial formulations containing emulsifiers and other additives are used in practice, which may lead to differences in their stability. Nevertheless, the contribution of photolysis and hydrolysis to the rapid dissipation of pyrethroids implies that degradation products may be concurrently formed on urban impervious surfaces under sunlight and should be considered.

3.3.2 Mechanisms of Pyrethroids Loss

The first order rate constants describing pyrethroid volatilization, photolysis, and binding/ hydrolysis losses were calculated using Equations 1-4 (Table 3.3). The relative contribution of each loss process to the overall loss on irradiated concrete was subsequently estimated (Figure 3.7). It should be noted that in order to make direct comparisons among different processes, photolysis rate constants in Figure 3.7 were adjusted to the actual daytime length recorded during the experiment.

In general, volatilization was a minor loss pathway for lambda-cyhalothrin and fenpropathrin (Figure 3.2 and Table 3.3). However, despite their low vapor pressures (USDHHS, 2003) (Table 3.1), the relative contribution of volatilization appeared to be significant for esfenvalerate (20%), permethrin (25%) and deltamethrin (39%) (Figure 3.7). This was in agreement with a previous study where 24% of deltamethrin was lost from soil due to volatilization (Boehncke et al., 1990). The significant contribution of volatilization for the pyrethroid loss may be partially due to the high temperature on the concrete surfaces exposed to direct sunlight.

The relative contribution of photolysis to the overall loss on concrete surfaces under sunlight also varied among the five compounds (Figure 3.7). Photolysis was the dominant loss pathway for permethrin, contributing 75% to its total loss, while it was also substantial for for fenpropathrin and deltamethrin (Figure 3.7). Photolysis rate constants on concrete ($k_{photolysis\text{-}C}$) were similar amongst the individual pyrethroids examined (Table 3.3). For instance, for concrete surfaces $k_{photolysis\text{-}C}$ values ranged from 0.008 ± 0.001 to 0.017 ± 0.002 h^{-1}, or a mere 2-fold difference, for the different pyrethroids (Table 3.3). This might be due to the structural similarity of these five pyrethroids (Table 3.1). The half-lives of pyrethroids due to photolysis on concrete were much shorter than photolysis half-lives previously reported for soil or water (Table 3.2). It was interesting to note that similar first-order rate constants were derived for both concrete and glass surfaces (Table 3.3), indicating that the surface properties of concrete did not inhibit pyrethroid photolysis as compared to the glass surface.

Binding and hydrolysis were undistinguished in this study and were found to be an important mechanism for the loss of the selected pyrethroids except for permethrin (Figure 3.7). For instance, binding/hydrolysis accounted for 75 ± 23, 97 ± 19, 73 ± 19, and 45 ± 23% of the total losses of fenpropathrin, lambda-cyhalothrin, esfenvalerate, and deltamethrin, respectively (Figure 3.7). The importance of hydrolysis in pyrethroid dissipation was likely due to the high pH of concrete for promoting ester hydrolysis (Table 3.2) (Laskowski, 2002; Starr et al., 2008). However, for permethrin, binding/hydrolysis was much less dominant. This might be due to the fact that permethrin is more stable at higher pH than the other pyrethroids. For example, the hydrolysis half-life of permethrin in water at pH 9 was 242 d, as compared to 2.15, 14.4, and 8.66 d for deltamethrin, fenpropathrin, and lambda-cyhalothrin, respectively (Table 3.2) (Laskowski, 2002). 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 (Table 3.1) (Starr et al., 2008). Overall, these results illustrated that hydrolysis may be an important degradation pathway for pyrethroids on concrete surfaces, further highlighting that urban concrete pavements are reactive surfaces capable of converting pyrethroids to degradation intermediates.

3.3.3 Formation of 3-PBA

The degradation product 3-PBA was detected in 100% of the samples following treating the surfaces with the pyrethroid mixture. Appearance of 3-PBA generally followed the opposite trends of the dissipation of the parent compound, i.e., more 3-PBA was detected for the IC, NC, and IG treatments while less 3-PBA was found for the NG treatment (Figure 3.3). For example, after 3 h, the amounts of residual lambda-cyhalothrin for the IC and NG treatments were 20 ± 7 and 47 ± 1.4 μg, respectively, while the quantities of 3-PBA for these treatments were 10 ± 0.4 and 0.3 ± 0.02 μg, respectively. This relationship suggested that as pyrethroids disappeared on the surfaces, 3-PBA was concurrently formed. However, the disappearance of the parent and accumulation of 3-PBA was far from being stoichiometric, and the highest 3-PBA occurrence in this study accounted for only 3% of the initially applied amount. In a previous study, 3-PBA formation was found to range from 1.6 ± 0.1 to 17 ± 1% of the initially applied permethrin over 7 d (Jiang and Gan, 2016). Furthermore, in the current study, the fraction of 3-PBA decreased rapidly after the first 3 h in all treatments, suggesting that 3-PBA was further transformed to other products (Figure 3.8). Compared to glass surfaces, considerably more 3-PBA was formed on the concrete surfaces, especially during the initial phase. There was also generally little difference between the dark and irradiation treatments on concrete, indicating that hydrolysis, rather than photolysis, contributed greatly to 3-PBA formation on concrete. Katagi (1991) investigated photodegradation of esfenvalerate on soil surfaces and observed indirect photolysis processes such as hydration of the cyano group followed by ether cleavage were the dominant reactions, leading to the formation of 3-PBA. However, concrete have very different physicochemical properties from a soil, e.g., absence of organic matter and high alkalinity. These results together suggested that differences in base-catalyzed hydrolysis may dictate the potential for the formation of 3-PBA among different pyrethroids on urban impervious surfaces.

Concrete surfaces were further treated with individual compounds and exposed to sunlight to evaluate differences in the production of 3-PBA among the different pyrethroids (Figure 3.9). The production of 3-PBA generally first increased and then decreased, following a similar trend to that for the mixture treatment. Among the five pyrethroids, a greater fraction of 3-PBA was formed from lambda-cyhalothrin, followed by esfenvalerate and deltamethrin, while the formation of 3-PBA from fenpropathrin or permethrin was consistently more limited (Figure 3.9). The elevated formation of 3-PBA from lambda-cyhalothrin was in agreement with its rapid binding/hydrolysis loss observed for lambda-cyhalothrin as compared to the compounds (Table 3.2). The least 3-PBA formation was observed with fenpropathrin (Figure 3.9). The $k_{\text{binding+hydrolysis}}$ measured from the mixture treatments for fenpropathrin was similar to that for esfenvalerate and deltamethrin. Therefore, the negligible production of 3-PBA from fenpropathrin on irradiated concrete suggested that fenpropathrin was lost mostly due to binding, rather than hydrolysis. The formation of 3-PBA was also relatively limited for permethrin, as compared to lambda-cyhalothrin, deltamethrin and esfenvalerate (Figure 3.9). In the previous mixture experiment, permethrin was found to be more recalcitrant to binding and hydrolysis, suggesting again that 3-PBA formation was attributable to hydrolysis on concrete.

It must be noted that after treatment in a mixture or individually, 3-PBA did not accumulate on the concrete surface over time. There could be several possible pathways for 3-PBA to dissipate on concrete surfaces exposed to sunlight, i.e., photolysis, volatilization, and acid-base reactions. As the levels of 3-PBA were similar between the IC and NC treatments (Figure 3.9), photolysis did not affect the fate of 3-PBA on concrete. Katagi (1992) measured photolysis of 3-PBA on soil ($t_{1/2}$ = 47 d), clay ($t_{1/2}$ = 29 d), and silica gel ($t_{1/2}$ = 17 d), and showed that 3-PBA was generally resistant to photolysis. The vapor pressure of 3-PBA is 3.2×10^{-6} mm Hg, and therefore, there may be potential volatilization loss, especially at elevated temperatures (USEPA, 2017). The pKa value of 3-PBA is 3.95, so at the high pH associated with concrete, it may be deprotonated and react with calcium hydroxide or calcium carbonate in the concrete (Rived et al., 1998). Evidence of this was observed by Chen et al. (2012), who found that higher pH increased 3-PBA degradation, while 3-PBA was more stable at lower pH values. Fit of 3-PBA levels on irradiated concrete surfaces measured in this study to the first-order decay model resulted in half-lives of only 4.2-6.7 h.

The results from the present study suggested that occurrence of 3-PBA on concrete surfaces may be transient and that the most important time window for 3-PBA off-site transport to surface waters is likely within the first 24 h after pesticide application. However, even after 336 h, the quantities of 3-PBA extracted from the concrete cubes ranged from 0.11 ± 0.02 to 1.0 ± 0.15 μg, which equaled to 0.55 ± 0.11 to 5.1 ± 0.77 mg m^{-2}. While these concentrations were low, they may lead to substantial levels of 3-PBA entering urban streams at the landscape scale, e.g., via precipitation-induced runoff. This was in agreement with the previous study, where the level of 3-PBA in wash-off water remained at over 100 ng L^{-1} even 3 months after the initial application of permethrin (Jiang and Gan, 2016). These results together suggested that 3-PBA forms rapidly on urban impervious surfaces and may follow similar transport routes (i.e., surface runoff) to urban waterways as pyrethroids.

3.3.4 Occurrence in Urban Streams

Both pyrethroids and 3-PBA were monitored in small surface streams draining urban neighborhoods in Southern California. The total concentrations of the five pyrethroids ranged from 47 ± 16 to 865 ± 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 3.10). Meanwhile, 3-PBA was also detected at lower concentrations, ranging from 2.9 ± 1.5 to 37 ± 2.1 ng L^{-1} and 0.20 ± 0.01 to 12 ± 3 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 occurrence and 3-PBA concentrations (Pearson's correlation coefficient 0.963, Figure 3.10). 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 surface runoff. However, this relationship was not observed at the Wood Creek site (Pearson's correlation coefficient -0.322). This could be due to the fact that the sampling location at the Wood Creek site was located below a storm water treatment wetland. While degradation of 3-PBA in soil or sediment is not well understood, previous research suggested that 3-PBA adsorption to soil or sediment may be a major removal pathway (Chen et al., 2011). Therefore, it is likely that due to the decreased flow and hydraulic retention in the wetland, some of the suspended solids settled out of the flow, along with some of the pyrethroids and 3-PBA (Budd et al., 2016). Another study showed that 3-PBA was susceptible to photolysis in water with half-lives of 2.6-3.6 d (Katagi, 1992). Therefore it is also possible that 3-PBA was attenuated through a combination of adsorption, photolysis, and microbial degradation in the wetland.

The frequent detection of 3-PBA in urban streams verified that surface streams in regions such as California are ubiquitously contaminated with 3-PBA as a result of extensive use of pyrethroids for pest control. However, the levels of 3-PBA are generally low. Future research should consider the potential adverse effects on aquatic species, including invertebrates, from chronic exposure to low levels of 3-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.

3.4 Conclusions

In this study, we explored environmental factors and processes contributing to pyrethroid dissipation on concrete surfaces and formation of the endocrine disrupting product 3-PBA. Rapid pyrethroid dissipation and 3-PBA formation was observed on concrete surfaces. On concrete, irreversible binding and hydrolysis contributed the most to the dissipation of fenpropathrin, lambda-cyhalothrin, esfenvalerate, and deltamethrin, while photolysis was more significant for the loss of permethrin. Hydrolysis of pyrethroids, likely enhanced by the strong alkalinity of concrete, was found to be primarily responsible for the production of 3-PBA, while photolysis played a limited role. The overall yield of 3-PBA on irradiated concrete surfaces was consistently low, and its formation further varied among the different pyrethroids. Trace levels of 3-PBA were constantly detected in surface streams draining urban communities, suggesting that the widespread use of pyrethroid products is resulting in contamination of urban surface water by 3-PBA. The environmental fate and ecotoxicological effects of 3-PBA are not clearly understood at present, and merit further investigation.

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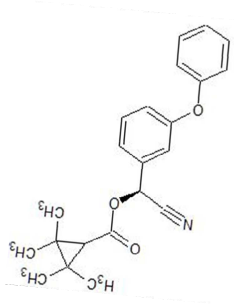
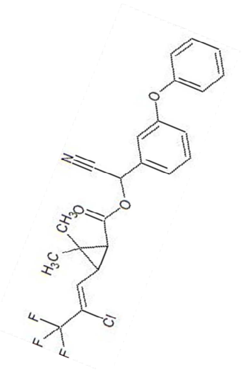
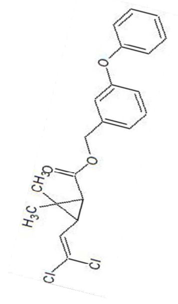
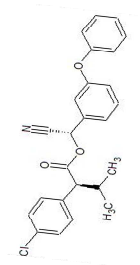
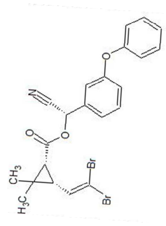
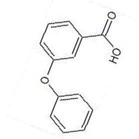
Table 3.1. Physicochemical properties and structures of selected pyrethroids and their degradation product 3-PBA

	Fenpropathrin	**Lambda-cyhalothrin**	**Permethrin**	**Esfenvalerate**	**Deltamethrin**	**3-PBA**
Log K_{ow}[a]	6.0	7.0	6.1	5.6	4.5	3.9[c]
Water Solubility (mg/L)[a]	1.0×10^{-2}	5.0×10^{-3}	5.5×10^{-3}	6.0×10^{-3}	2.0×10^{-4}	17[c]
Vapor Pressure (mm Hg)[b]	5.5×10^{-6}	1.5×10^{-9}	2.2×10^{-8}	1.5×10^{-9}	1.5×10^{-9}	3.2×10^{-6} [c]
Structure						

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[a] Laskowski, 2002

[b] US Department of Health and Human Services, 2003

[c] Predicted values from EPI Suite (USEPA, 2017)

Table 3.2. Half-lives (h) of combined and individual loss processes for five pyrethroids

	Fenpropathrin	**Lambda-cyhalothrin**	**Permethrin**	**Esfenvalerate**	**Deltamethrin**
			h		
IC	13 ± 3.5	3 ± 1	30 ± 5.2	11 ± 2.1	7 ± 1
NC	25 ± 7	5 ±1	347 ±104	11 ±1.4	13 ± 2.5
IG	110 ± 36	10 ± 3	17 ± 4	38 ± 13	14 ± 2
NG	NS[d]	NS[d]	277 ± 88.6	35 ± 15	22 ± 6.1
Volatilization	990 ± 424	NS[d]	231 ± 77	35 ± 17	23 ± 8
Photolysis glass	28 ± 9	35 ± 2	63 ± 12	41 ± 7	69 ± 7
Photolysis concrete	41 ± 3	63 ± 17	77 ± 9	87 ± 21	43 ± 11
Binding+hydrolysis	23 ± 8	4.6 ± 0.9	NS[d]	17 ± 4	35 ± 17
Soil photolysis	107[a], 24[b]	1289[a]	2496[a]	240[a]	833[a]
Water photolysis	14472[a]	588[a]	2640[a], 336[c]	413[a], 192[c]	1332[a]
Water hydrolysis (pH 9.0)	346[a]	208[a]	5808[a]	Stable[a]	52[a]

[a] Laskowski, 2002

[b] Takahashi et al., 1985

[c] Schimmel et al., 1983

[d] No significant relationship between concentration and time existed so kinetics could not be calculated.

Table 3.3. Degradation kinetics of five pyrethroids on concrete and glass surfaces.

	Fenpropathrin	**Lambda-cyhalothrin**	**Permethrin**	**Esfenvalerate**	**Deltamethrin**
		(h^{-1})			
$k_{volatilization}$	0.0007 ± 0.0003	NS[d]	0.003 ± 0.001	0.02 ± 0.01	0.03 ± 0.01
$k_{photolysis}$ glass	0.030 ± 0.002	0.020 ± 0.001	0.011 ± 0.002	0.017 ± 0.003	0.010 ± 0.001
$k_{photolysis}$ concrete	0.017 ± 0.002	0.011 ± 0.003	0.009 ± 0.001	0.008 ± 0.002	0.016 ± 0.004
$K_{binding+hydrolysis}$ concrete	0.03 ± 0.01	0.15 ± 0.03	Stable	0.04 ± 0.01	0.02 ± 0.01

Table 3.4. Temperature and light intensity over the course of the batch experiment.

Light Hours	Minimum Radiation (W m^{-2})	Maximum Radiation (W m^{-2})	Average Radiation (W m^{-2})	Minimum Temperature (°C)	Maximum Temperature (°C)	Average Temperature (°C)
1	665	840	753	15.7	17.1	16.4
3	665	993	858	15.7	19.3	17.6
6	665	993	852	15.7	20.8	18.8
12	143	981	763	21.1	24.0	22.9
24	55	885	577	17.9	34.0	28.8
48	22	885	547	16.7	34.0	27.4
168	16	1064	530	13.3	37.3	23.5
336	9	1064	513	13.3	42.2	25.9

Table 3.5. Ion pairs and retention times utilized for GC-MS and UPLC-MS quantification.

Compound	Ions	Retention Time (min)
Fenpropathrin	181, 152	18.1
Lambda-cyhalothirn	181, 152	19.6
Permethrin	183, 153	21.3
Cypermethrin	163, 127	22.7
Esfenvalerate	167, 125	24.9
Deltamethrin	181, 152	25.9
3-PBA (with MTBSFA on GC)	271, 227	10.7
3-PBA (UPLC)	213,93	6.6
Surrogate Standards		
d5 Bifenthrin	186, 171	17.7
^{13}C-3-PBA (with MTBSFA)	277, 233	11.7

Figure 3.1. Field sampling locations in Orange County, CA.

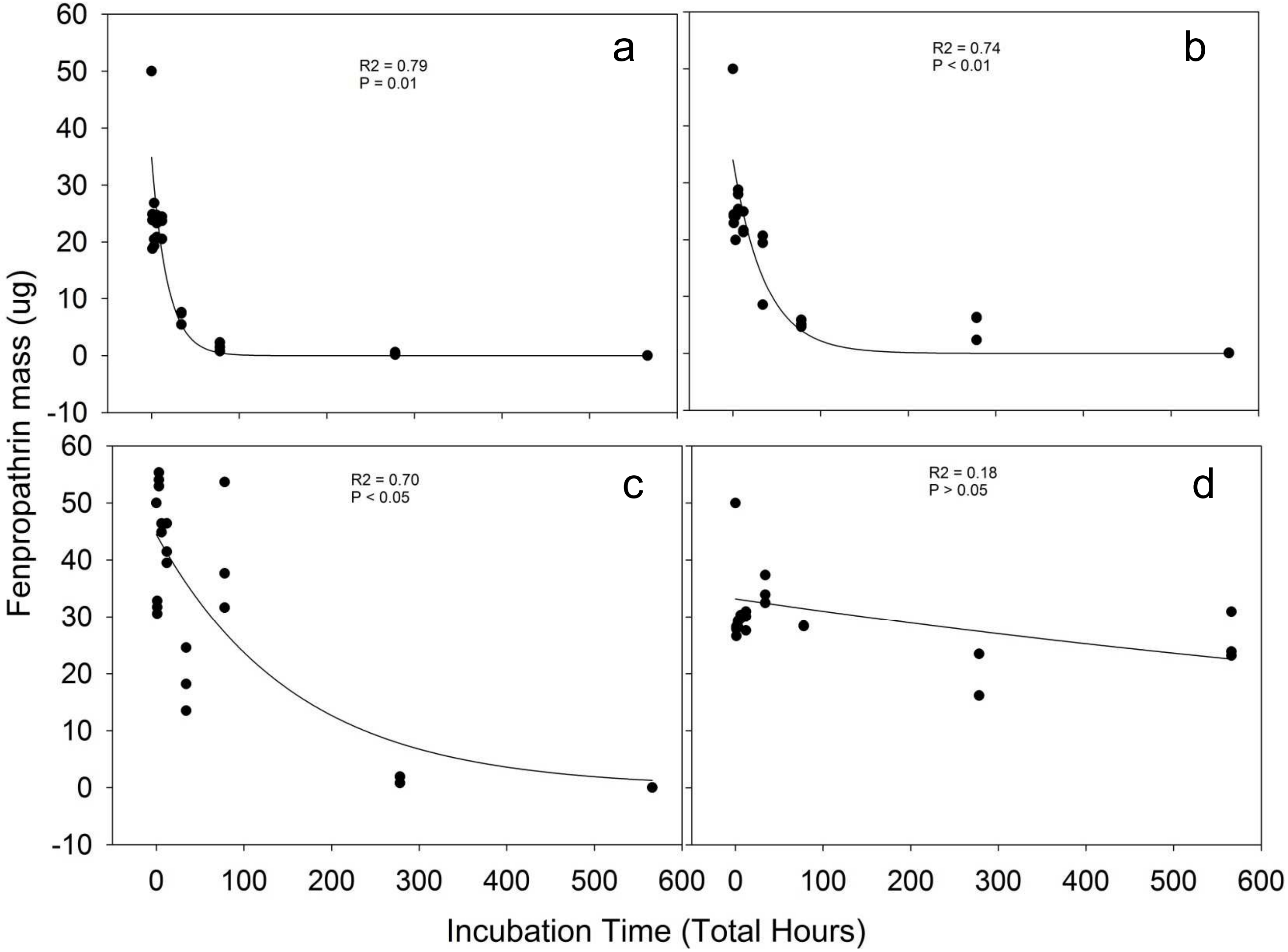

Figure 3.2. Exponential decay of fenpropathrin under different treatments. (a) Irradiated concrete. (b) Non-irradiated concrete. (c) Irradiated glass. (d) Non-irradiated glass.

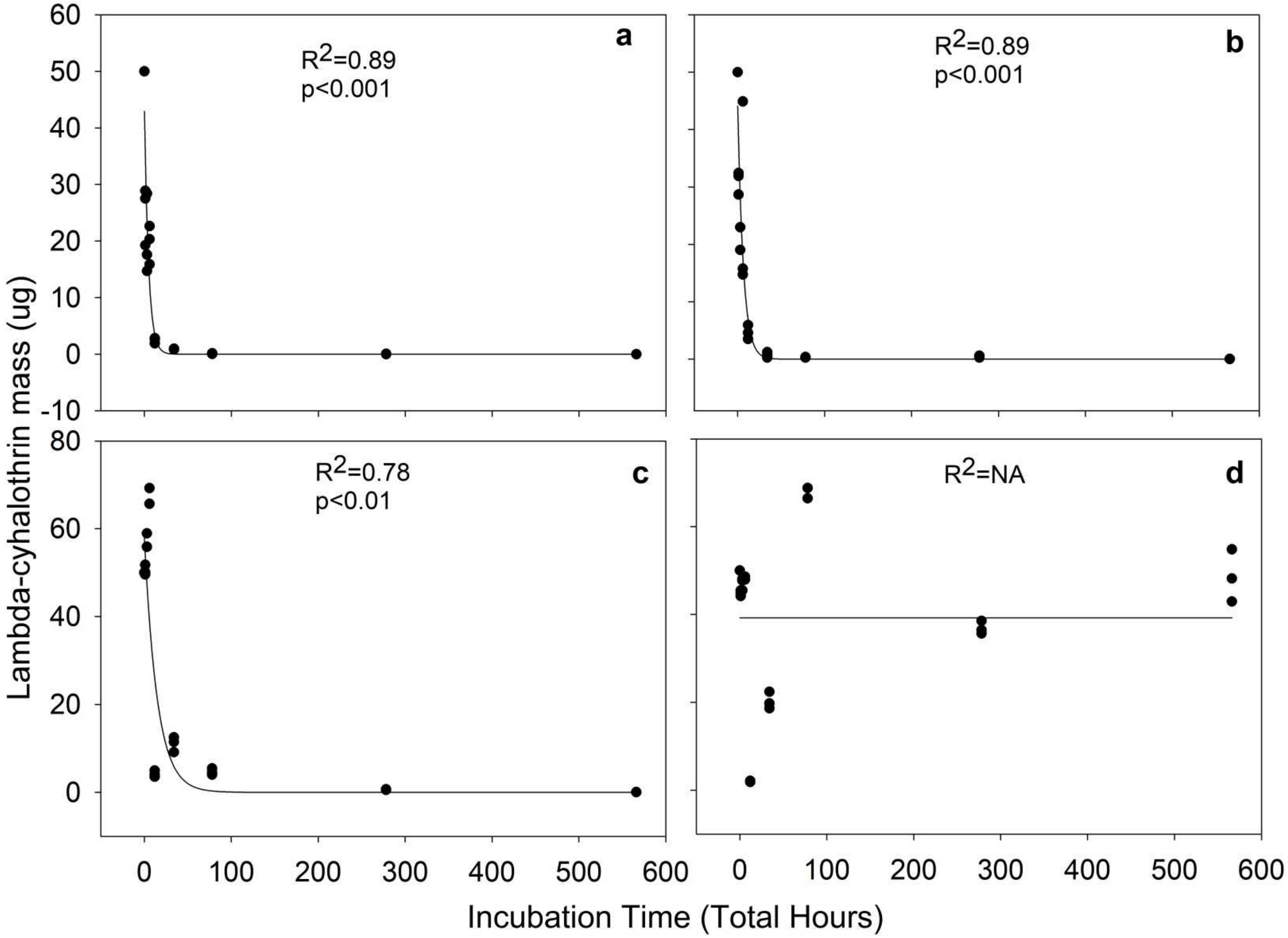

Figure 3.3. Exponential decay of lambda-cyhalothrin under different treatments. (a) Irradiated concrete. (b) Non-irradiated concrete. (c) Irradiated glass. (d) Non-irradiated glass.

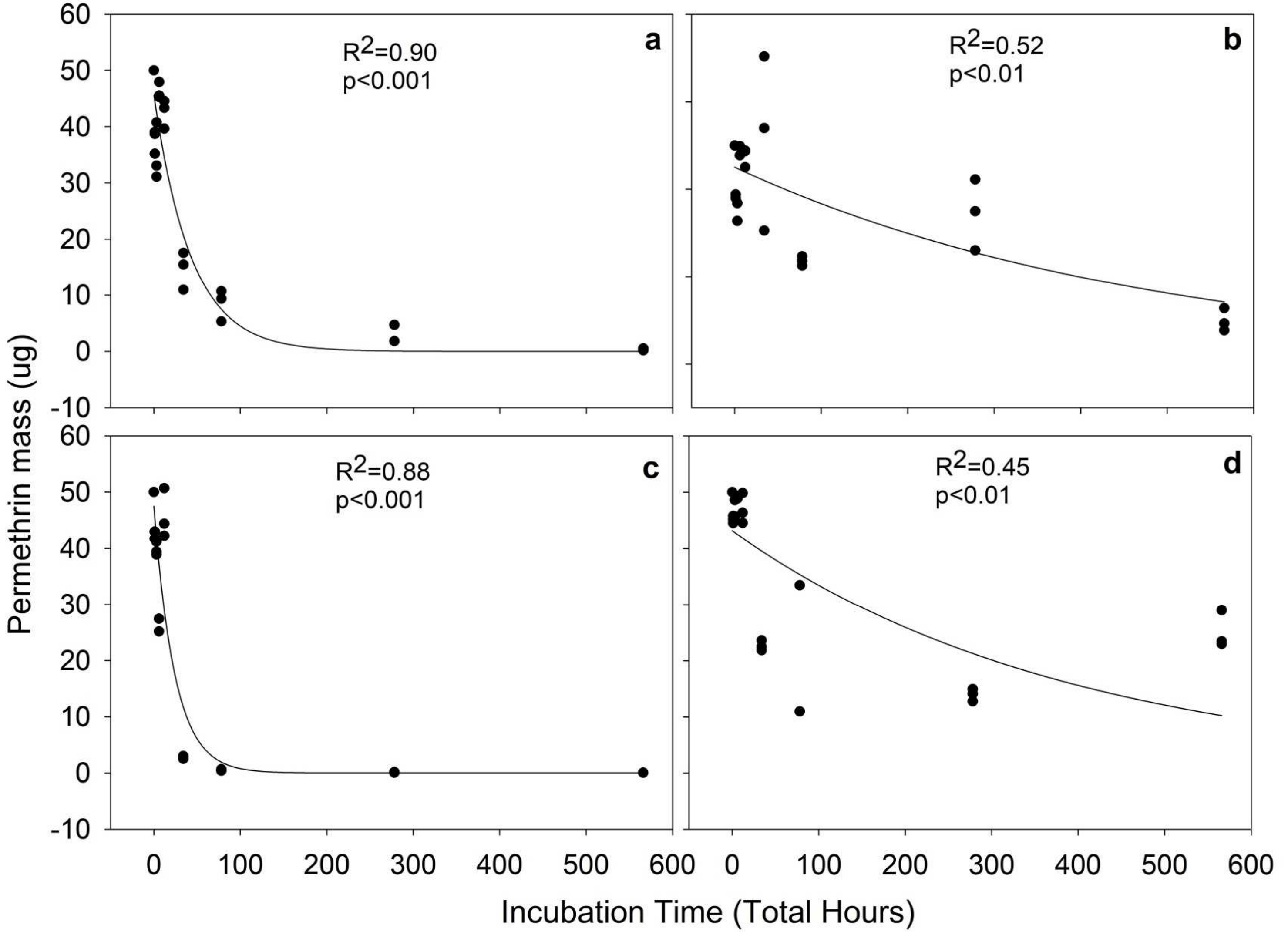

Figure 3.4. Exponential decay of permethrin under different treatments. (a) Irradiated concrete. (b) Non-irradiated concrete. (c) Irradiated glass. (d) Non-irradiated glass. l

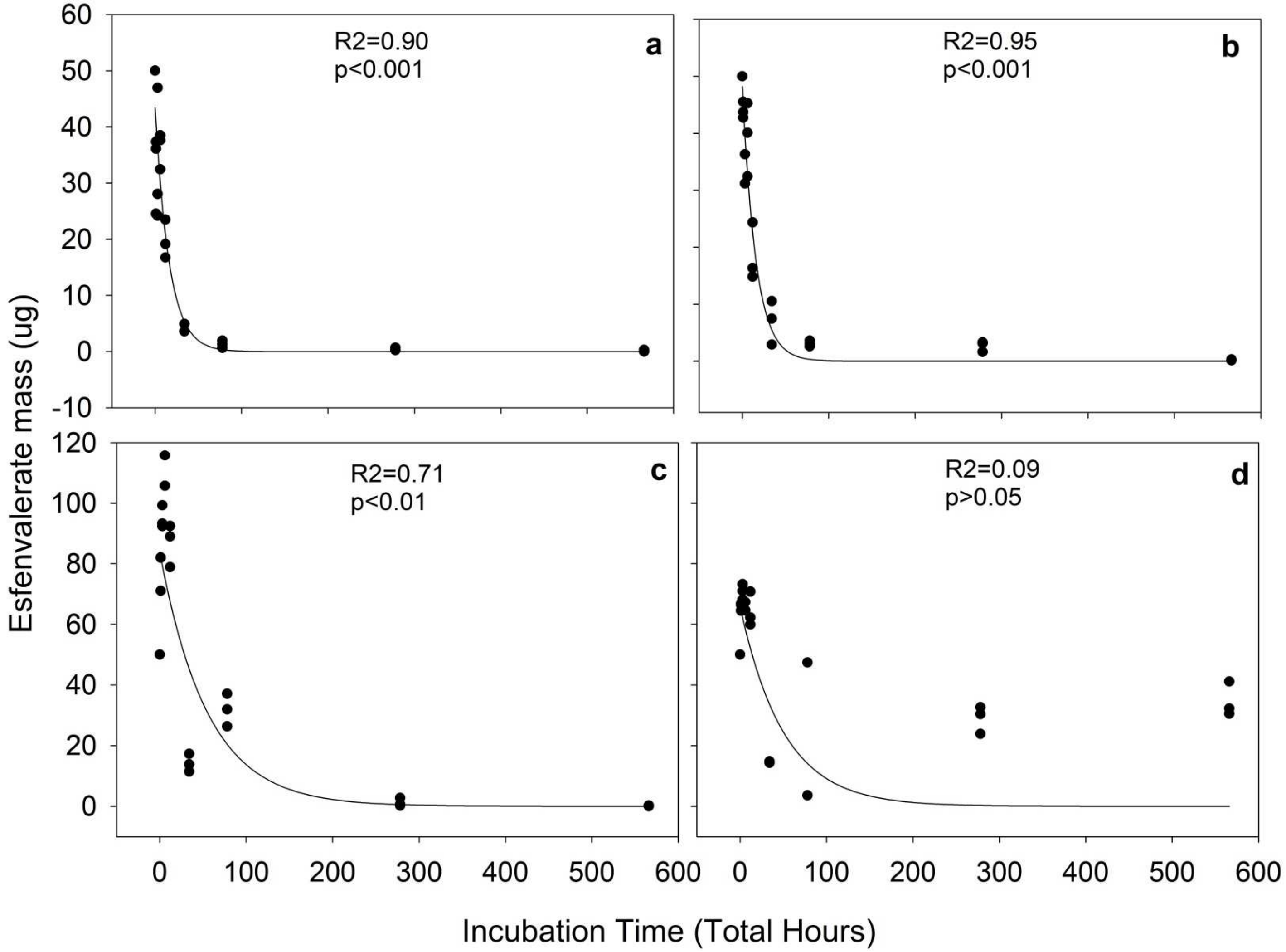

Figure 3.5. Exponential decay of esfenvalerate under different treatments. (a) Irradiated concrete. (b) Non-irradiated concrete. (c) Illuminated glass. (d) Non-irradiated glass.

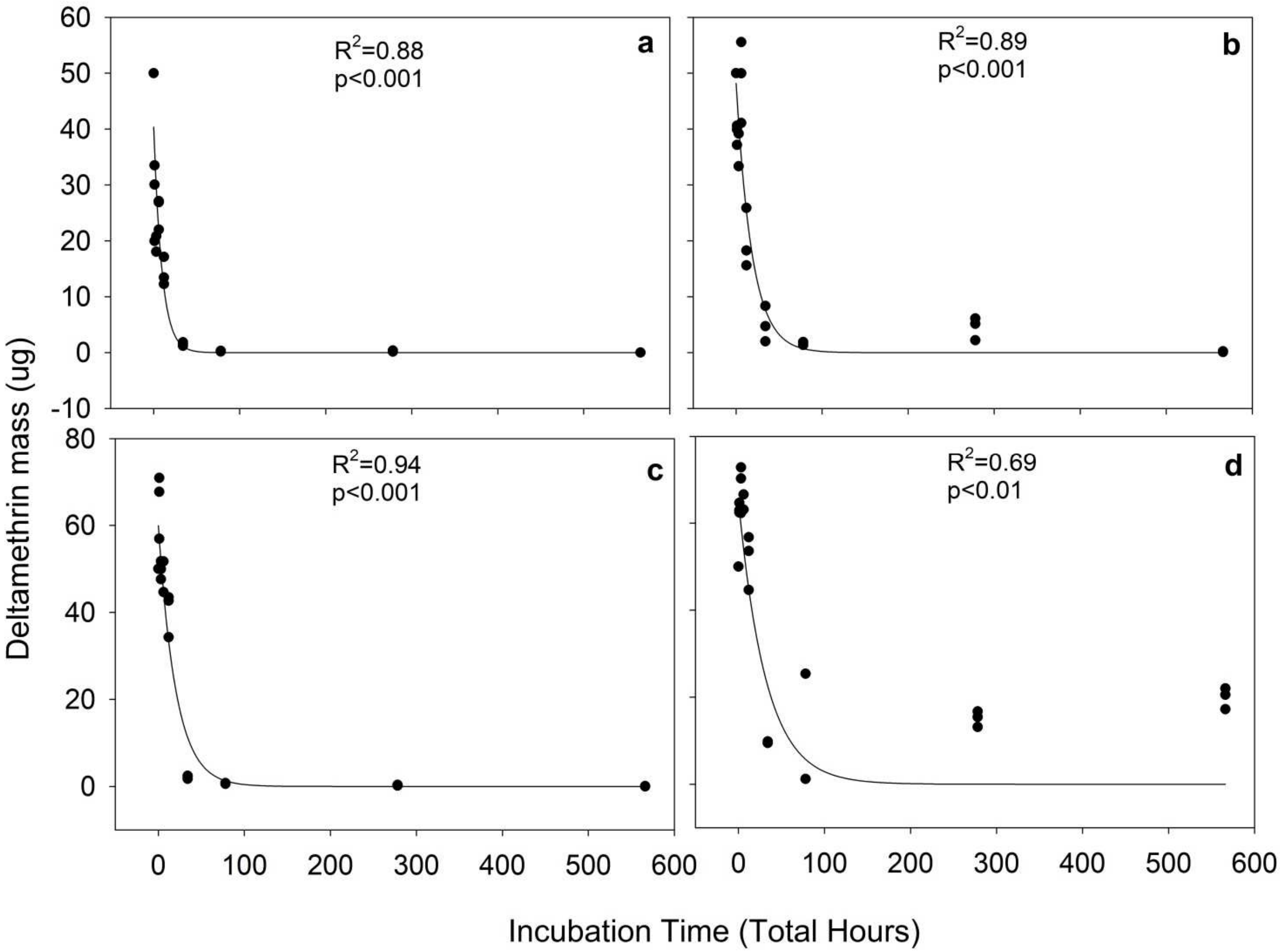

Figure 3.6. Exponential decay of deltamethrin under different treatments. (a) Irradiated concrete. (b) Non-irradiated concrete. (c) Irradiated glass. (d) Non-irradiated glass.

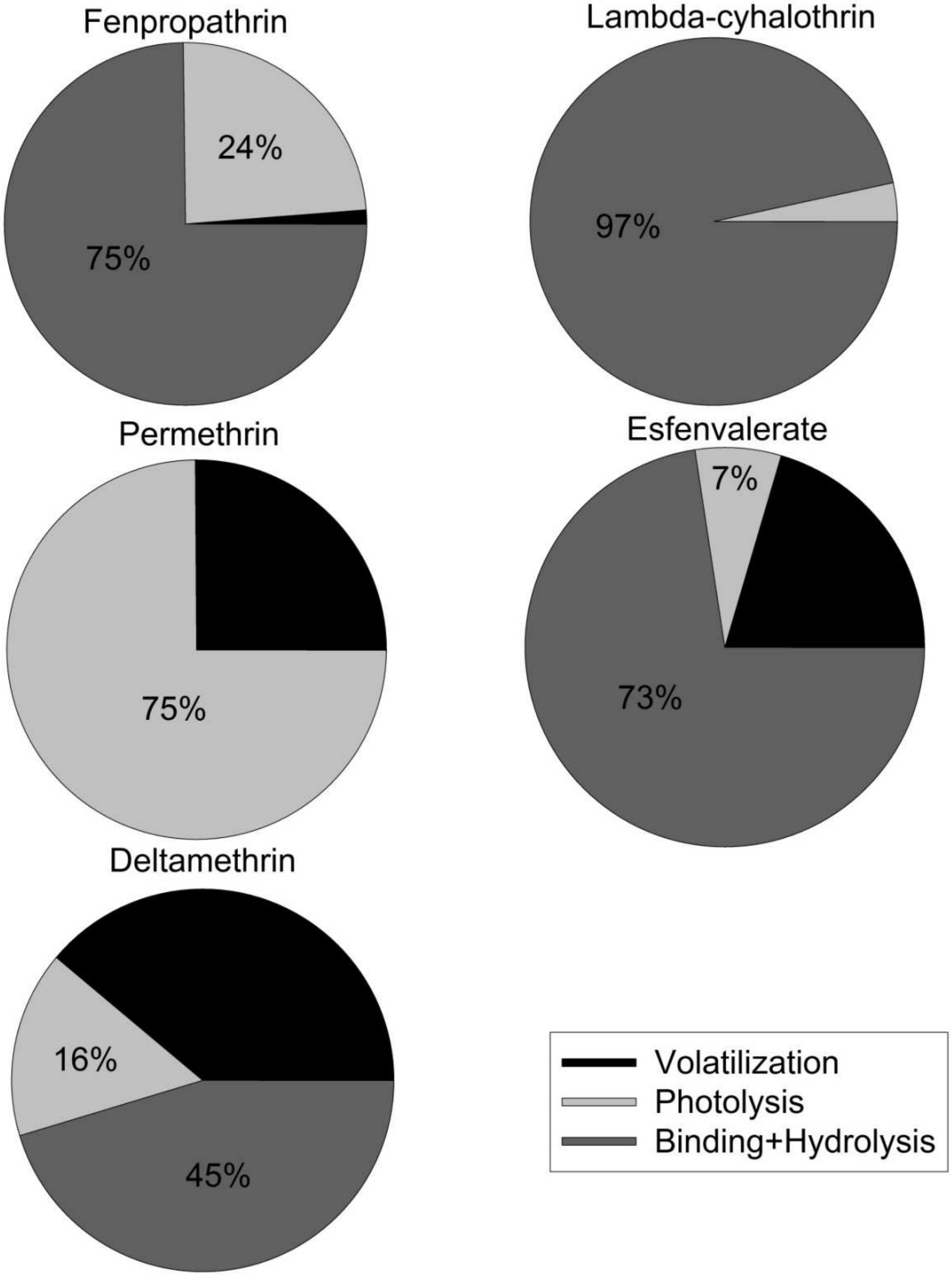

Figure 3.7. Contribution of volatilization, photolysis, and binding and hydrolysis to the loss of fenpropathrin, lambda-cyhalothrin, permethrin, esfenvalerate, and deltamethrin on concrete surfaces exposed to sunlight for 14 d.

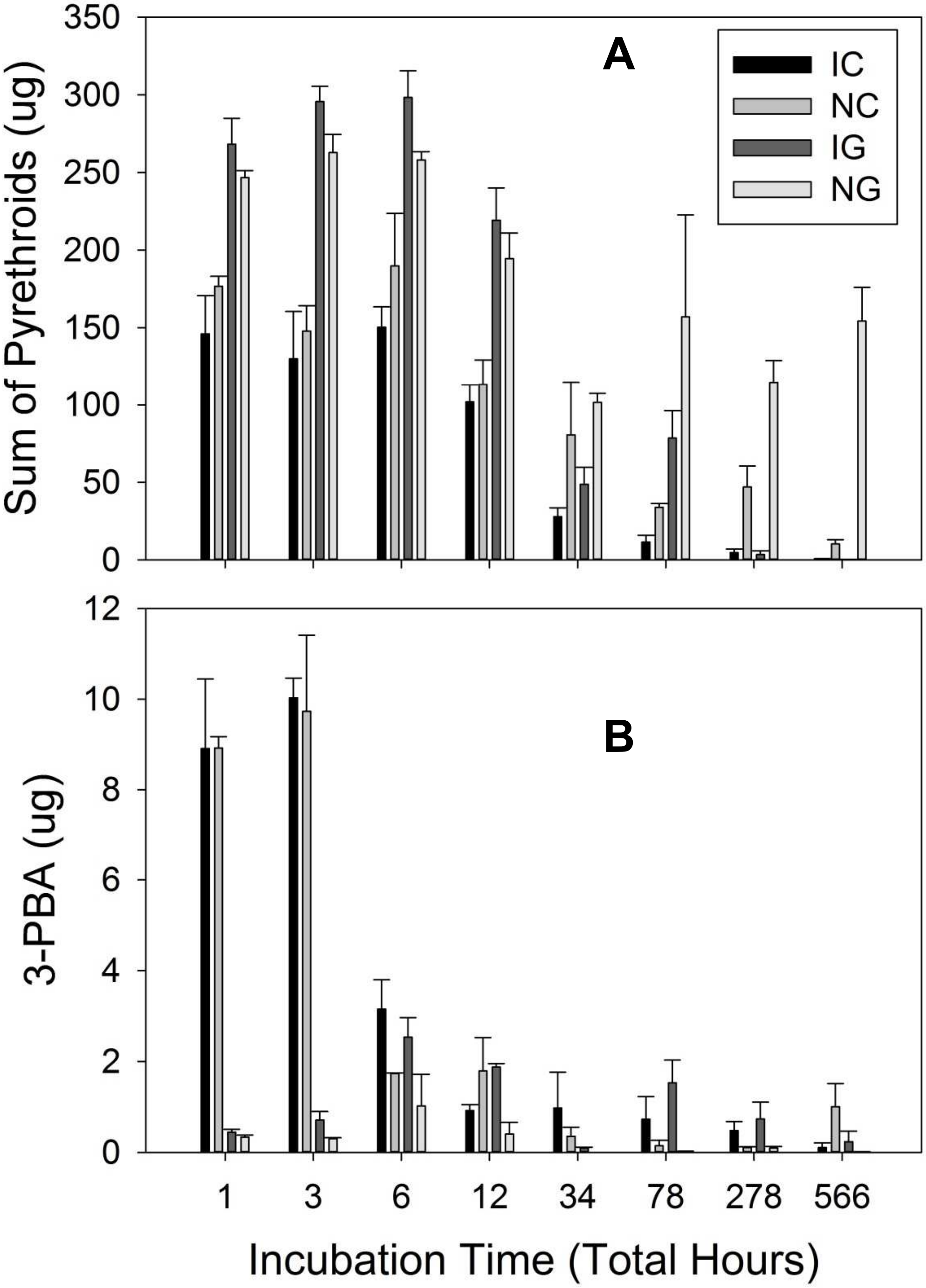

Figure 3.8. (a) Dissipation of pyrethroids and (b) formation and dissipation of 3-BPA under different treatments.

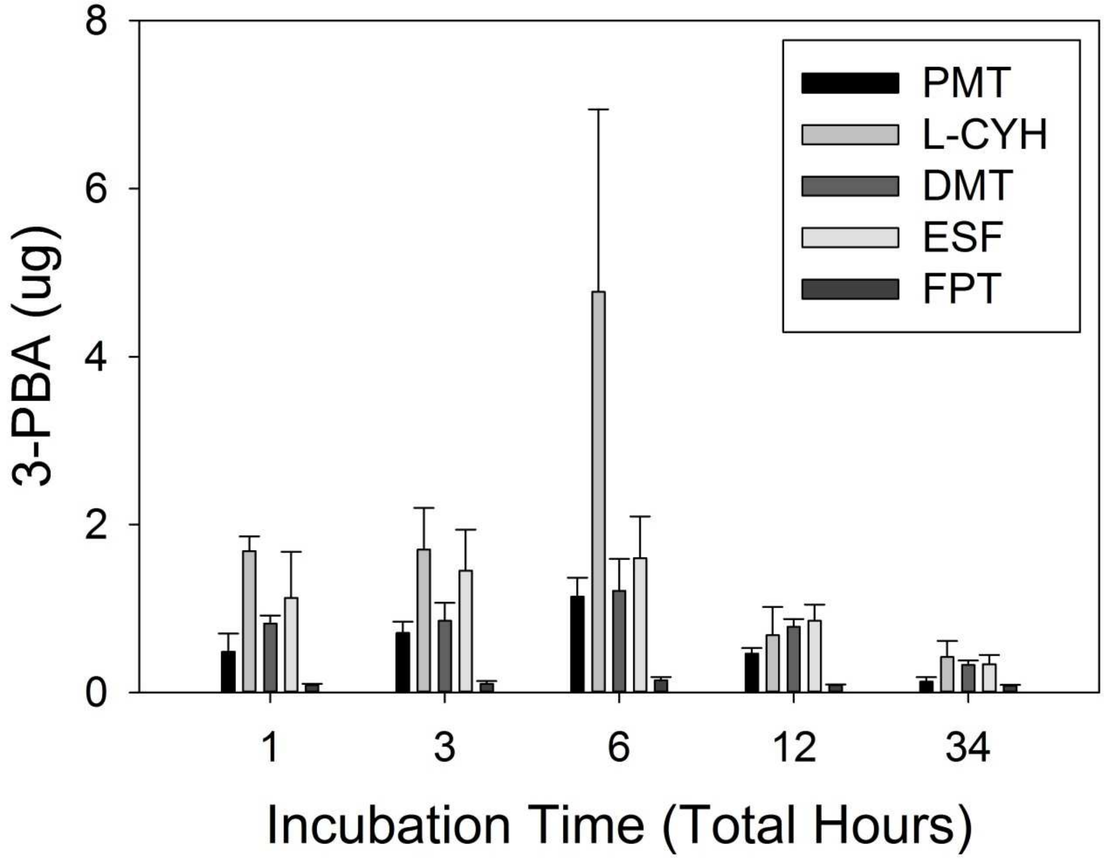

Figure 3.9. Amount of 3-PBA formation from individual pyrethroids on concrete under irradiated conditions

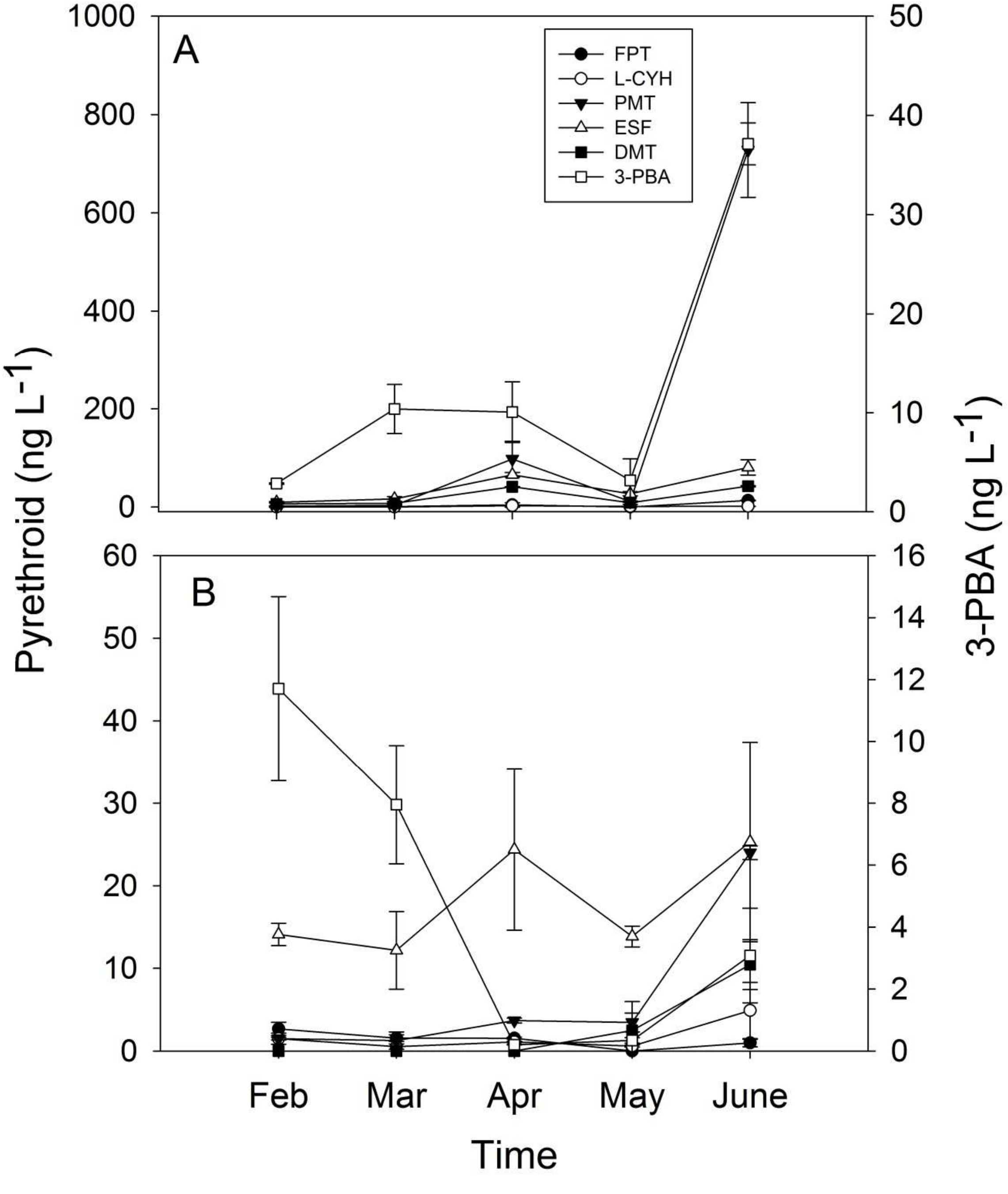

Figure 3.10. Concentrations of the five pyrethroids and 3-PBA in Salt Creek (SC) (a) and Wood Creek (WC) (b) located in Orange County, CA

Chapter 4 Persistence of 3-Phenoxybenzoic Acid in Soil, Sediment, and Water

4.1 Introduction

Previous research has shown that the use of pyrethroids has led to their occurrence in urban and agricultural runoff at levels toxic to arthropods and fish (Holmes et al., 2008; Weston et al., 2009; Ensminger et al., 2013; Brander et al., 2016). Further research has been subsequently conducted to focus on the sources of contamination, as well as the factors influencing the fate and transport of pyrethroids. For instance, Jiang et al. (2012) found detectable levels of bifenthrin and permethrin in runoff water from concrete surfaces even 7 months after the initial application. Similarly, Gan et al. (2012) measured insecticide runoff concentrations from six large neighborhoods and directly linked residential areas as the major source of insecticides to urban surface water. Additionally, pyrethroids have been detected in outdoor urban dust (Jiang et al., 2016), where no apparent spatial difference in particle-bound pyrethroid levels between the point of application and offsite areas, suggesting redistribution (Richards et al., 2016.) These studies highlight the ubiquitous occurrence of pyrethroids throughout urban areas including impervious surfaces as well as surface water and sediment of urban streams as contamination receptors.

However, when pyrethroids enter the environment they can undergo transformation via hydrolysis, photolysis, and chemical or biological oxidation to form different products (Demoute, 1989; Katagi, 1991; Katagi, 2004, Liu et al., 2010). While transformation is often beneficial and decreases the toxicity of man-made organic compounds, this is not always the case. For instance, Cwiertny et al. (2014) showed that bioactive structures of molecules are often conserved in transformation, or that the parent molecule is altered in such a way that the resulting transformation products may react with biological receptors different from the parent compound. This has been shown to be true for a common transformation product of pyrethroids: 3-phenoxybenzoic acid (3-PBA) (Starr et al., 2008; Brander et al., 2016). While the parent pyrethroids target the sodium channels of neurons (USEPA, 2011), 3-PBA has shown to interact with receptors of the endocrine system (Tyler et al., 2000). Specifically, anti-estrogenic activity by 3-PBA was observed in a yeast assay with a concentration showing inhibition in 50% of the population (IC_{50}) at 14 ± 5 mg L^{-1} and a lowest observed inhibition concentration (LOIC) at 2.6 ± 1.5 mg L^{-1} (Tyler et al., 2000). Similarly, Sun et al. (2007) tested the anti-androgenic activity of 3-PBA and found an IC_{20} of 258 mg L^{-1}. Further studies have also shown that 3-PBA may have endocrine disrupting activity (Brander et al., 2012) as well as protein damage capacity in rat heart cells (Vadhana et al., 2011; Brander et al., 2016). Therefore, due to the prevalence of pyrethroid use in urban areas, it is important to understand the formation and persistence of 3-PBA in these systems in order to ascertain risks.

Previous research has shown that the formation of 3-PBA on urban surfaces is rapid. Jiang and Gan (2016) observed 3-PBA concentrations in runoff water from concrete slabs spiked with permethrin ranging from 41.5 to 391 μg L^{-1} one day after application and 114 to 170 μg L^{-1} 89 d after application. This suggests that urban surfaces may be a significant source of 3-PBA to urban streams long after pyrethroid application has occurred. In a recent study, Richards et al. (under review) found that hydrolysis was the major process contributing to the formation of 3-PBA on urban surfaces. More importantly, this study confirmed the presence of 3-PBA in urban streams, although the concentrations were generally lower than the parent pyrethroids (Richards et al., under review). Studies to date have confirmed that urban areas are likely a major source of 3-PBA to surface waters, and that there is a potential risk to aquatic organisms due to exposure to 3-PBA.

However, in order to determine the risk 3-PBA poses, its persistence in the various environmental compartments must be known. However, at present relatively little is known about the fate of 3-PBA in different environmental media. Katagi (1992) investigated photodegradation of 3-PBA in water and on soil and silica gel surfaces. The half-life of 3-PBA in water ranged from 2.6 to 3.6 d at pH 7.0 and decreased to 0.2 d at pH 2, while the addition of hydrogen peroxide or dissolved organic matter (DOM) had little effect on the rate of photodegradation. A few studies have considered 3-PBA degradation in soil, but these studies focused primarily on specific isolated microbial strains and thus would not represent real-world situations. For instance, half-lives of 3-PBA in bioaugmented soil ranged from 2 to 4 d (Halden et al., 1999; Chen et al., 2012). However, these studies generally lasted for a short duration (e.g., 7 d), and little to no degradation of 3-PBA was observed by native soil microbes over the short time period. Additionally, little research has been done on the stability of 3-PBA in stream water or sediments, even though surface water is likely to a sink of 3-PBA from agricultural fields and urban areas. Therefore, the aims of the present study were to determine the persistence of 3-PBA in soil, sediment, and water and to evaluate the properties affecting the persistence of 3-PBA in these environmental matrices.

4.2 Materials and Methods

4.2.1 Chemicals

Standards of 3-phenoxybenzoic acid (98% purity) and ^{13}C 3-phenoxybenzoic acid (Phenoxy-^{13}C6, 99%) (^{13}C 3-PBA) were obtained from Cambridge Isotope Laboratories (Andover, MA). Sodium azide (99%) and calcium chloride (98%) were obtained from Fisher Scientific (Waltham, MA). Methanol was in HPLC grade or higher and dichloromethane was GC/MS grade or higher.

4.2.2 Soil, Sediment, and Surface Water Collection

Two agricultural soils were utilized in this study. The soils were chosen for their different physicochemical characteristics; specifically, soil texture, pH, and organic matter content. A sandy loam soil was collected from South Coast Research and Extension Center in Irvine, CA. The clay soil was collected in the Imperial Valley, CA. These two soils were sieved through a 2 mm sieve and stored at 4 °C.

Sediment samples and surface water samples were collected at three separate streams in southern California. These sites were Salt Creek, Wood Creek, and San Diego Creek. Water samples were collected by placing plastic buckets in the stream and allowing water to flow into the bucket. Care was taken not to disturb the sediment during the water sampling. After the water sampling at each site, sediment samples were collected with a shovel and placed in separate plastic buckets. The surface water and sediment samples were then transported back to the laboratory and stored at 4 °C before use. The sediments were wet sieved through a 2 mm mesh and the water content of the sieved portion was determined by weighing triplicates of each sediment and then drying at 85 °C overnight and weighing again before calculating the weight difference.

4.2.3 Batch Experiment Setup

For the soil incubation experiment, 5.0 g (dry weight) of soil was weighed and placed into 40 mL amber vials. For the unsterilized treatment, deionized water was added so that the soils were at 90% water holding capacity (approximately 1 mL for the sandy loam and 2 mL for the clay) and mixed by vortexing. The vials were allowed to sit uncovered for 3 d in order for microbial activity to resume and stabilize (Lu and Gan, 2014). For the sterilized treatments, the samples were autoclaved over 3 consecutive day for 20 min each day. After autoclaving, the soils were brought to 90% water holding capacity with a solution of 200 mg L^{-1} sodium azide in deionized water. All the soils were then spiked with 50 μL of a 1,000 mg L^{-1} 3-PBA solution, and vortexed for homogenization. The samples were then loosely covered with aluminum foil to allow air exchange, but prevent light from entering the sample vial. The soil samples were incubated at room temperature. Whole samples were removed at 0.5, 1, 3, 7, 14, 21, and 35 d post 3-PBA addition for extraction and analysis.

The sediment incubation experiment was setup following Lu and Gan (2014). Briefly, 10 g (dry weight) sediment was added to either 150 mL flasks for the aerobic treatment or 40 mL vials for the anaerobic treatment. For the unsterilized treatment, 5 mL of 0.01 mol L^{-1} calcium chloride was added to each sample. The samples were then vortexed, with the aerobic samples loosely covered with foil and allowed to sit for 3 d while the anaerobic samples were held under a nitrogen stream for 5 minutes, securely capped, and placed in a nitrogen filled glove chamber and allowed to sit for 10 d in order for anoxic conditions to form. Confirmation of the formation of anoxic conditions was conducted by measuring the oxidation/reduction potential (Eh) with a platinum electrode (Thermo Fisher, Waltham, MA). After this time period, the samples were spiked with 100 µL of 1,000 mg L^{-1} 3-PBA solution, vortexed, and loosely covered with foil (aerobic), or held under nitrogen for 5 min, capped, and placed in a nitrogen filled glove chamber (anaerobic). The sediment samples were then incubated at room temperature and whole samples were taken at 0.5, 1, 3, 7, 14, 21, and 35 d for extraction and analysis.

For the surface water incubation samples, 10 mL of either the Salt Creek, Wood Creek, or Sand Diego Creek stream samples was added to 20 mL glass vials. These samples were allowed to sit for 3 d for microbial activity to resume after refrigeration (unsterilized) or were autoclaved and amended with 1 mL of 200 mg L^{-1} sodium azide was added (sterilized). Next, 100 µL of a 1,000 mg L^{-1} 3-PBA solution was added to each vial. The vials were then placed on the roof of a building (33°58'26.0"N, 117°19'33.8"W) and were either left uncapped and uncovered to receive natural sunlight irradiation or were uncapped but covered loosely in aluminum foil to prevent sunlight irradiation. The water samples were then incubated and whole samples were sacrificed at 0.04, 0.25, 0.5, 1, 3, and 7 light d or 0.04, 0.25, 0.9, 1.4, 4.9, and 11.8 total d of exposure. The samples were refilled daily to account for water loss due to evaporation.

4.2.4 Soil, Sediment, and Water Properties

In order to determine factors influencing the persistence of 3-PBA, physicochemical properties of the different matrices (soil, sediment, and surface water) were quantified. Soil and sediment texture was determined by the hydrometer method (Gavlak et al. 2005). Organic carbon content for the sediment and soils was determined by the loss on ignition method (Gavlak et al., 2005). For the water samples, dissolved organic carbon (DOC) was determined by filtering 20 mL of the different surface water samples with a Whatman 0.45 μm filter. After filtration, the samples were acidified with 5 mL of 0.1 N HCl in order to remove inorganic carbon. The DOC was then quantified by a Shimadzu TOC-V CSH total organic carbon analyzer (Shimadzu, Tokyo, Japan). The pH of the water, sediment, and soil samples was measured using a Fisher Scientific Accumet pH meter (Waltham, MA).

4.2.5 Sample Preparation

Soil and sediment samples were extracted in the same manner following a modified version of Halden et al. (1999) that was first described by Xie et al. (2008). Briefly, 20 mL of methanol:dichloromethane 5:1 (v/v) was added to each vial. The vials were then sonicated for 15 min in a Fisher Scientific FS110H sonication water bath (Waltham, MA). The particles were allowed to settle and the extract was passed through a Whatman Grade 42 paper filter and collected in an 80 mL test tube. This process was then repeated two more times for a total of 3 extractions and the solvent phase from each extraction was combined. The extract was evaporated under a gentle stream of nitrogen at 35 °C to near dryness and reconstituted in 1.0 mL methanol. Recoveries were determined through preliminary experiments to be 77 ± 9, 64 ± 8, 63 ± 6, 51 ± 7, and 88 ± 12% for the sandy loam soil, clay soil, and Wood Creek, Salt Creek, and San Diego Creek sediments, respectively.

For the water samples, a 1 mL aliquot of each sample was removed and 20 μL of a 1 mg L^{-1} ^{13}C 3-PBA solution was added to the aliquot, which was then filtered with a 0.45 μm Whatman syringe filter. The filtrate was collected and injected directly into an HPLC-MS/MS for analysis.

4.2.6 Chemical Analysis

For all samples, 3-PBA analysis was performed on a Waters ACQUITY ultra-performance liquid chromatography (UPLC) combined with a Waters Micromass Triple Quadrupole mass spectrometer (qQq) equipped with an electrospray ionization (ESI) interface (Waters, Milford, MA). Separation was achieved using an ACQUITY UPLC C18 column (2.1 mm × 100 mm, 1.7 μm, Waters.) at 40 °C. A binary gradient system was used to separate analytes comprising of mobile phase A, DI water (18 Ω) acidified using 0.1% FA, and mobile phase B composed of MeOH. The solvent gradient program, in terms of mobile phase A, was as follows: initial condition began with 50% (A) for 1 min, decreased linearly to 30% for 1.5 min, further decreased to 10% for 0.5 min, decreased linearly to 0% for 0.5 min, increased linearly to 10% for 1 min, and finally it was increased to 50% and equilibrated for 1 min. The flow rate was 0.3 mL min^{-1} and the injection volume was set to 10 µL. Mass data were acquired using Intellistart® (Waters) in the multiple reactions monitoring (MRM) mode and product ion scan in the negative ESI mode. The specific instrument settings were as follows: capillary source voltage 1.20 kV, dwell time 0.247 s, source temperature 150 °C, desolvation temperature 500 °C, desolvation gas 900 L h^{-1} and cone gas 50 L h^{-1}. The collision gas was argon (99.9%). Cone voltage, collision voltage, and quantification ion were generated using IntelliStart software (Waters) and were 32 (V), 20 (V), and 93.0949 (m/z), respectively.

4.2.7 Quality Control and Data Analysis

Reagent blanks, recovery surrogates, and replicates were used to ensure quality of analysis. During extraction, one reagent blank was extracted every 10 samples to exclude the presence of cross contamination. All glassware was baked at 400 °C for 4 h before use. Samples were always analyzed in triplicate to ensure reproducibility. Similarly, samples were spiked with 20 µL of 1.0 mg L^{-1} ^{13}C-3-PBA before extraction to determine the extraction efficiency for individual samples. Recoveries of ^{13}C-3-PBA were 74 ± 19% for the soil and sediment samples and 93 ± 8% for the water samples, respectively. Instrumental controls consisted of construction of an 8-point calibration curve with concentrations ranging from 5 to 1000 μg L^{-1} before every analytical run and after every 50 samples analyzed.

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

4.2.8 Dissipation Mechanism Elucidation

Dissipation of 3-PBA in urban streams may be attributed to volatilization, hydrolysis, biotic degradation, and photolysis. The degradation kinetics for dark, dark-sterile, irradiated, and irradiated-sterile treatments could be described using Equations 1-4, respectively:

$$\ln C_t = \ln C_0 - k_{hydrolysis+\mathrm{volatilization}} \bullet t_{\mathrm{total}} \qquad [1]$$

$$\ln C_t = \ln C_0 - k_{hydrolysis+\mathrm{volatilization}} \bullet t_{\mathrm{total}} - k_{\mathrm{biotic}} \bullet t_{\mathrm{total}} \qquad [2]$$

$$\ln C_t = \ln C_0 - k_{hydrolysis+\mathrm{volatilization}} \bullet t_{\mathrm{total}} - k_{\mathrm{photolysis}} \bullet t_{\mathrm{light}} \qquad [3]$$

$$\ln C_t = \ln C_0 - k_{hydrolysis+\mathrm{volatilization}} \bullet t_{\mathrm{total}} - k_{\mathrm{biotic}} \bullet t_{\mathrm{total}} - k_{\mathrm{photolysis}} \bullet t_{\mathrm{light}} \qquad [4]$$

where, C_t and C_0 are 3-PBA concentrations in μg mL^{-1} in surface water at time t and 0, respectively; $k_{hydrolysis+\mathrm{volatilization}}$, k_{biotic}, and $k_{\mathrm{photolysis}}$ are the first-order rate constants in h^{-1} for hydrolysis and volatilization, biotic degradation, and photolysis and t_{total} and t_{light} are time in h for the entire reaction and exposure to natural sunlight, respectively. It must be noted that in $k_{hydrolysis+\mathrm{volatilization}}$, losses due to hydrolysis and volatilization were combined, as the experimental design would not allow the distinction between these two processes. The sterilized dark treatment was used to obtain $k_{hydrolysis+\mathrm{volatilization}}$ (Eq. 1). Therefore, k_{biotic} could be calculated using Equations 1 and 2, while $k_{\mathrm{photolysis}}$ may be calculated using Equations 2 and 4.

4.3 Results and Discussion

4.3.1 Persistence in Soil

Since pyrethroids are often applied to agricultural areas as well as directly to lawns in urban areas, it is likely that they will be transformed into 3-PBA in soils. Similarly, soil has been shown to be an important source of organic compounds to streams, as well as a source for dust mediated transport (Jones and de Voogt, 1999; Richards et al., 2016) Previous research has shown little degradation of 3-PBA in soil, but these studies generally adopted short time durations and focused on specific microbial strains that may or may not occur under natural conditions (Halden et al., 1999; Chen et al., 2012). However, significant degradation has been observed for other benzoic acid compounds in soil. For instance, Siciliano and Germida (1998) observed 27% and 37% decreases of 3-chlorobenzoic acid and 2,3-dichlorinated benzoic acid, respectively, after 28 d in a sandy loam soil without microbial inoculation.

Surprisingly, even after 35 d incubation, no significant degradation of 3-PBA was observed in either of the two soils, with 97 ± 3 % and 73 ± 12 % of the initially spiked amount remaining in the clay and sandy loam soils, respectively (Figure 4.1). Because of the slow dissipation, half-lives could not be accurately calculated for either soil (Table

4.3). In Siciliano and Germida (1998), the relatively rapid degradation was likely due to the use of water for extraction, where sorption may have contributed to the observed declines in remaining concentrations. In the present study, the use of polar organic solvents afforded more exhaustive extraction and thus the findings were likely reflective of the actual degradation stability. The results of the present study were in agreement with a previous study where the half-life of 3-PBA in soil was estimated to be 180 d (Halden et al., 1999). However, the soil used in the Halden et al. (1999) study was composed of 95% sand and contained only 0.5% organic matter. Therefore, it could be hypothesized that the half-life of 3-PBA in other soils with properties supporting more diverse microbial populations would be shorter. The present study utilized a clay soil composed of 70% clay and 4.2% organic matter, as well as a sandy loam soil composed of 66% sand and 1.1% OM (Table 4.1). The limited difference in 3-PBA persistence between these two soils suggested that soil properties did not play a significant role in regulating 3-PBA degradation (Figure 4.1).

These results suggest that once formation of 3-PBA occurs in soil, it is quite persistent. This is concerning because the log K_{ow} of 3-PBA (3.9) is much lower than the parent pyrethroids (4.53 to 7.00). Therefore, 3-PBA is likely more susceptible to offsite transport to surface or groundwater than the parent pyrethroids (Kaufman et al., 1981; USEPA, 2017). The relatively long persistence of 3-PBA in soil increases the risk of exposure, not just to soil organisms but also likely to aquatic organisms in nearby surface water systems.

4.3.2 Persistence in Sediment

Previous research has suggested that 3-PBA may be rapidly formed on urban impervious surfaces, easily transported through runoff, leading to contamination of 3-PBA in urban surface water (Jiang and Gan, 2016; Richards et al., under review). The current study examined dissipation of 3-PBA in three different sediments from urban streams under aerobic or anaerobic conditions over the course of 35 d.

The properties of the three different sediments varied widely, especially with regards to OC content (Table 4.1). This is likely due to differences in water input sources in addition to differences in river morphology. For instance, the sediment at the Wood Creek site was collected from a constructed wetland, whereas the sediment from the San Diego Creek was collected from an area where the channel had been covered with concrete. In order to ensure that aerobic and anaerobic conditions were achieved, the oxidation-reduction potential of the sediments was monitored, with the anaerobic treatments ranging from -364 to -249 mV and the aerobic treatments ranging from 55 to 159 mV.

For the sediment under aerobic conditions, 3-PBA degradation was relatively rapid with half-lives of 4.6 ± 1.0, 9.1 ± 3.9, and 6.1 ±1.7 d for the Wood Creek, Salt Creek, and San Diego Creek sediments, respectively (Table 4.3). Previous research has shown aerobic degradation of 3-PBA by isolated microorganisms and suggested that the first and major stage in this degradation is oxidation followed by cleavage of the diaryl ether (Chen et al., 2012). Therefore, the degradation of 3-PBA in sediment likely followed this pathway as no abiotic degradation was observed in the sterilized control and 3-PBA levels in the non-sterilized treatments were significantly lower than in the sterilized controls at all time points after 7 d (Figure 4.2). At the end of 35-d incubation, less than 1% of the initial 3-PBA still remained in the sediments (Figure 4.2).

Anaerobic degradation experienced a lag phase in comparison to aerobic degradation, with unsterilized samples being significantly different from the sterilized control after 14 d. The half-lives of 3-PBA in sediment under anaerobic conditions were 36.3 ± 11.8, 18.7 ± 6.2, and 51.7 ± 26.2 d for the Wood Creek, Salt Creek, and San Diego Creek sediments, respectively (Table 4.3). These values were 2.1-8.5 fold that in the aerobic sediments. It should also be noted that the regression relationship between 3-PBA and incubation time for the San Diego Creek sediment was not significant at the $P = 0.05$ level, suggesting that the actual half-life could be even longer (Table 4.3). Overall, 3-PBA was considerably more stable under anaerobic conditions, and 44 ± 1% to 75 ±8% of the initially spiked chemical remained in the sediment at the end of incubation. Additionally, 3-PBA appeared to be more persistent in the San Diego Creek sediment, while it was relatively less stable in the Salt Creek sediment (Figure 4.2). The differences were likely due to differences in the sediment properties. For instance, the Salt Creek sediment contained much higher organic matter than the San Diego Creek sediment (Table 4.1). Therefore, it is likely that the Salt Creek sediment contained a larger and more diverse indigenous microbial population, leading to more active microbial transformations of 3-PBA. Additionally, irreversible binding of 3-PBA to the large amount of organic matter in the Salt Creek sediment may have also occurred over time, as the sterilized treatment also showed decreases in 3-PBA concentrations over time.

The results of the sediment incubation experiment showed that 3-PBA was easily degraded under aerobic conditions, but was more persistent under anaerobic conditions. However, it should be noted that 3-PBA is likely pseudo-persistent in the urban environment due to continuous inputs from irrigation and rain-induced runoff (Postigo et al., 2010). Therefore, exposure to low levels of 3-PBA may be present in impacted urban streams. Research to date on 3-PBA has focused mostly on the acute exposure effects of 3-PBA (Tyler et al., 2000; Sun et al., 2007). Future research on chronic toxicity effects is needed using environmentally relevant concentrations.

4.3.3 Persistence in Water

Given that 3-PBA is relatively polar, water may be expected to be the primary environmental compartment in an aquatic system. Many different processes may affect the dissipation of 3-PBA in water, such as volatilization, hydrolysis, photolysis, and biotic degradation. In order to understand the relative contribution of some of these processes, degradation of 3-PBA was examined with or without natural irradiation as well as under sterile or non-sterile conditions.

Persistence of 3-PBA in surface water appeared to be significantly influenced by exposure to sunlight as well as by sterilization. As an example, the half-lives of the dark sterilized treatment were 2.3 to 6.0 times longer than those of the irradiated, non-sterilized treatments (Table 4.3). The irradiated unsterilized treatment exhibited the most rapid 3-PBA dissipation for all three types of surface water examined in this study, with the concentration of 3-PBA decreasing from 10.0 μg ml^{-1} to 1.0 ± 0.1, 3.6 ± 0.3, and 3.6

± 0.7 μg ml^{-1} for the Wood Creek, Salt Creek, and San Diego Creek water after 283 total h, respectively (168 light h) (Figure 4.3). Half-lives were estimated to be 4.0 ± 0.6, 9.6 ± 1.0, and 10.3 ±1.8 d for the Wood Creek, Salt Creek, and San Diego Creek surface water, respectively, under non-sterilized irradiation conditions (Table 4.3). These half-lives were similar to those in Katagi (1992) that reported half-lives of 3.0 to 3.6 d, depending upon the addition of additives such as hydrogen peroxide and humic acid. In contrast, the dark sterilized treatments gave the longest half-lives, and the half-lives were about 24.1 d for all three surface water types under dark, sterilized conditions, suggesting that 3-PBA stability was not appreciably influenced by water chemistry.

The Wood Creek water had a significantly shorter 3-PBA half-life than water from the Salt Creek and San Diego Creek ($p < 0.05$) under non-sterilized irradiation conditions. The Wood Creek sediment also showed shorter 3-PBA persistence than sediments from the other two sites. This may be attributed to the fact that the Wood Creek site is a constructed wetland that receives runoff water likely containing 3-PBA from nearby residential areas. Furthermore, the retention time of the runoff water would be longer at the Wood Creek site, so it is possible that microbial communities have developed that can more efficiently degrade 3-PBA. In the Wood Creek water under dark non-sterile conditions, 3-PBA was also significantly less persistent than in the other two water sources ($p < 0.05$). Under dark non-sterile conditions, the degradation processes should be limited to hydrolysis and volatilization ($k_{hydrolysis+volatilization}$) as well as biotic degradation (k_{biotic}). However, hydrolysis and volatilization processes should be the only ones affecting the dark sterile treatment. Therefore, any differences between the dark sterile and dark non-sterile half-lives should be attributed to biotic degradation. In order to discern the relative importance of these processes, first order rate constants were calculated for the hydrolysis and volatilization, biotic degradation, and photolysis using the above equations. It is apparent that k_{biotic} was larger for the Wood Creek sample than the other two water samples, validating a more active role by microorganisms (Table 4.4). Moreover, photolysis of 3-PBA also appeared to be more significant in the Wood Creek water than in either Salt Creek or San Diego Creek water (Table 4.4). Previous research has shown that pH can influence the degradation of 3-PBA, with increased photolysis occurring at lower pH values (Katagi, 1992). Therefore, the increased photolysis could be due to the lower pH of the Wood Creek water (Table 4.2). Additionally, the Wood Creek water had lower DOC than the other two water samples, but Katagi (1992) did not see a difference in 3-PBA photolysis between DI water and water amended with 1 mg L^{-1} of humic acid. However, the water samples in this study contained DOC levels ranging from 25.7 to 38.2 mg L^{-1}, and therefore the effect that DOC at high concentrations on photolysis of 3-PBA should not be discounted.

From the first order rate constants derived for the individual 3-PBA dissipation processes, photolysis appeared to the dominant process contributing to 3-PBA dissipation in surface water (Table 4.4). This was in agreement with the short half-lives of 3-PBA under irradiated conditions, whether with or without sterilization. Katagi (1992) previously studied the photolysis of 3-PBA and found that indirect photolysis was more important with ether cleavage of 3-PBA happening due to hydroxyl radicals. Biotic degradation was the second most important process for Wood Creek water, but was less important than hydrolysis and volatilization for Salt Creek and San Diego Creek water. The lack of biotic degradation in water from the latter two sites may be due to their higher DOC, which likely acted as an alternative and possibly easier carbon source for the microbes.

The results of 3-PBA degradation in urban stream samples under natural sunlight suggested that 3-PBA was not very persistent in surface aquatic systems. With the longest half-life of 24 d under dark sterilized conditions, which are unlikely to occur in natural systems, the risk of acute effects from 3-PBA exposure to organisms dwelling in the water column may be low. However, as mentioned previously, residential areas may inject a constant source of 3-PBA to urban streams, and therefore the ecotoxicological risk due to chronic exposure merit further research.

4.4 Conclusions

The persistence of 3-PBA varied widely amongst the different environmental media examined in this study. For instance, 3-PBA was quite stable in soil, but only persisted for 4 to 10 d in surface water or sediment. However, even though short persistence was seen in water and sediment, it is likely that 3-PBA is pseudo-persistent in the urban environment due to continuous input from the frequent application and transformation of pyrethroids in residential areas. The findings of this study should help guide future risk assessment by government environmental agencies by providing some of the first-hand data on 3-PBA persistence in natural systems. Additionally, this study highlights the importance of examining the toxicological effects of long-term, low dose exposure to 3-PBA by aquatic organisms. Similarly, future environmental monitoring should consider groundwater underlying areas where pyrethroids are used, due to the persistence of 3-PBA in soil and its lower affinity for sorption which may make its transport to groundwater likely.

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Table 4.1. Properties of the soil and sediment examined in this study.

Matrix	pH	OC (%)	Sand (%)	Silt (%)	Clay (%)
Clay	8.2	2.4	6.2	23.8	70.0
Sandy Loam	8.6	0.6	66.0	16.7	17.3
Wood Creek Sediment	7.1	2.7	64.9	30.3	4.8
Salt Creek Sediment	7.4	8.9	51.3	22.5	26.2
San Diego Creek Sediment	7.6	0.4	73.0	25.5	1.5

Table 4.2. . Properties of the surface water examined in this study.

Water Source	**pH**	**DOC (mg L^{-1})**
Wood Creek	7.3	25.7
Salt Creek	7.8	30.3
San Diego Creek	8.5	38.2

Table 4.3. Half-lives of 3-phenoxybenzoic acid in soil, sediment, and surface water.

Matrix	**Conditions**	**Half-life (d)**	**Statistics**
Soil			
Clay	Aerobic 90% Water Holding Capacity	>35	NS
Sandy Loam	Aerobic 90% Water Holding Capacity	>35	NS
Sediment			
Wood Creek	Aerobic	4.6 ± 1.0	$R^2 = 0.84^{***}$
Wood Creek	Anaerobic	36.3 ± 11.8	$R^2 = 0.47^{**}$
Salt Creek	Aerobic	9.1 ± 3.9	$R^2 = 0.57^{*}$
Salt Creek	Anaerobic	18.7 ± 6.2	$R^2 = 0.51^{**}$
San Diego Creek	Aerobic	6.1 ± 1.7	$R^2 = 0.75^{**}$
San Diego Creek	Anaerobic	51.7 ± 26.2	$R^2 = 0.22^{NS}$
Surface Water			
Wood Creek	Sunlight Irradiation	4.0 ± 0.6	$R^2 = 0.91^{***}$
Wood Creek	Sterilized and Sunlight Irradiation	15.2 ± 3.2	$R^2 = 0.89^{**}$
Wood Creek	Dark	10.7 ± 2.0	$R^2 = 0.75^{***}$
Wood Creek	Sterilized Dark	24.1 ± 8.0	$R^2 = 0.57^{**}$
Salt Creek	Sunlight Irradiation	9.6 ± 1.0	$R^2 = 0.91^{***}$
Salt Creek	Sterilized and Sunlight Irradiation	13.8 ± 2.6	$R^2 = 0.89^{**}$
Salt Creek	Dark	15.2 ± 3.2	$R^2 = 0.71^{***}$
Salt Creek	Sterilized Dark	24.1 ± 6.0	$R^2 = 0.86^{**}$
San Diego Creek	Sunlight Irradiation	10.3 ±1.8	$R^2 = 0.78^{***}$
San Diego Creek	Sterilized and Sunlight Irradiation	15.2 ± 5.6	$R^2 = 0.74^{*}$
San Diego Creek	Dark	24.1 ± 6.0	$R^2 = 0.54^{**}$
San Diego Creek	Sterilized Dark	24.1 ± 8.0	$R^2 = 0.60^{**}$

NS Denotes no statistical significance.

* Denotes significance at the $p < 0.05$ level.

** Denotes significance at the $p < 0.01$ level.

*** Denotes significance at the $p < 0.001$ level

Table 4.4. Degradation kinetics of 3-PBA in three different sources of surface water from urban areas in southern California.

	Wood Creek	**Salt Creek**	**San Diego Creek**
	---------------------------h^{-1}-----------------------		
$k_{hydrolysis+volatilization}$	0.0012 ± 0.0004	0.0012 ± 0.0003	0.0012 ± 0.004
k_{biotic}	0.0015 ± 0.005	0.0007 ± 0.0004	NS
$k_{photolysis}$	0.0042 ± 0.0005	0.0017 ± 0.0002	0.0024 ± 0.0006

NS Denotes no statistical significance.

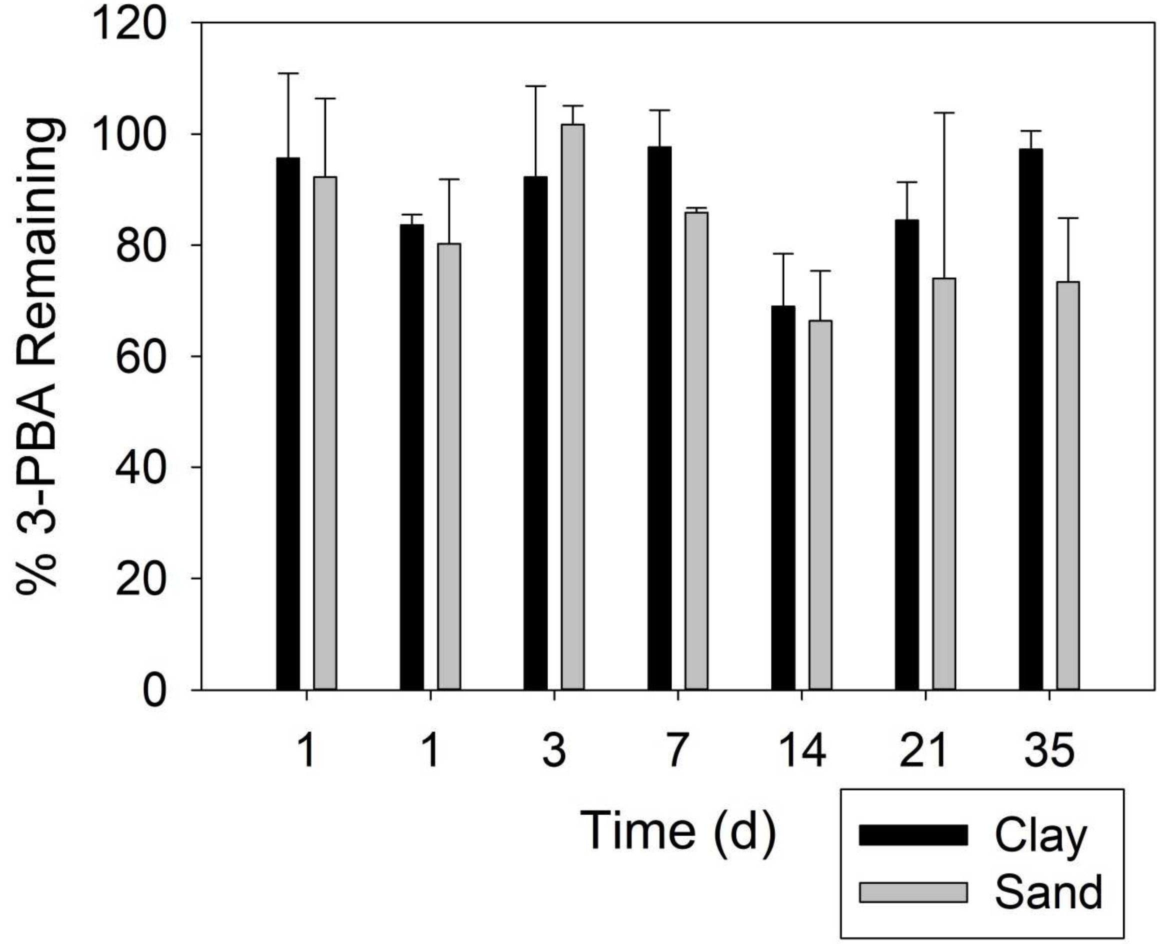

Figure 4.1. Persistence of 3-PBA in clay and sandy loam soils.

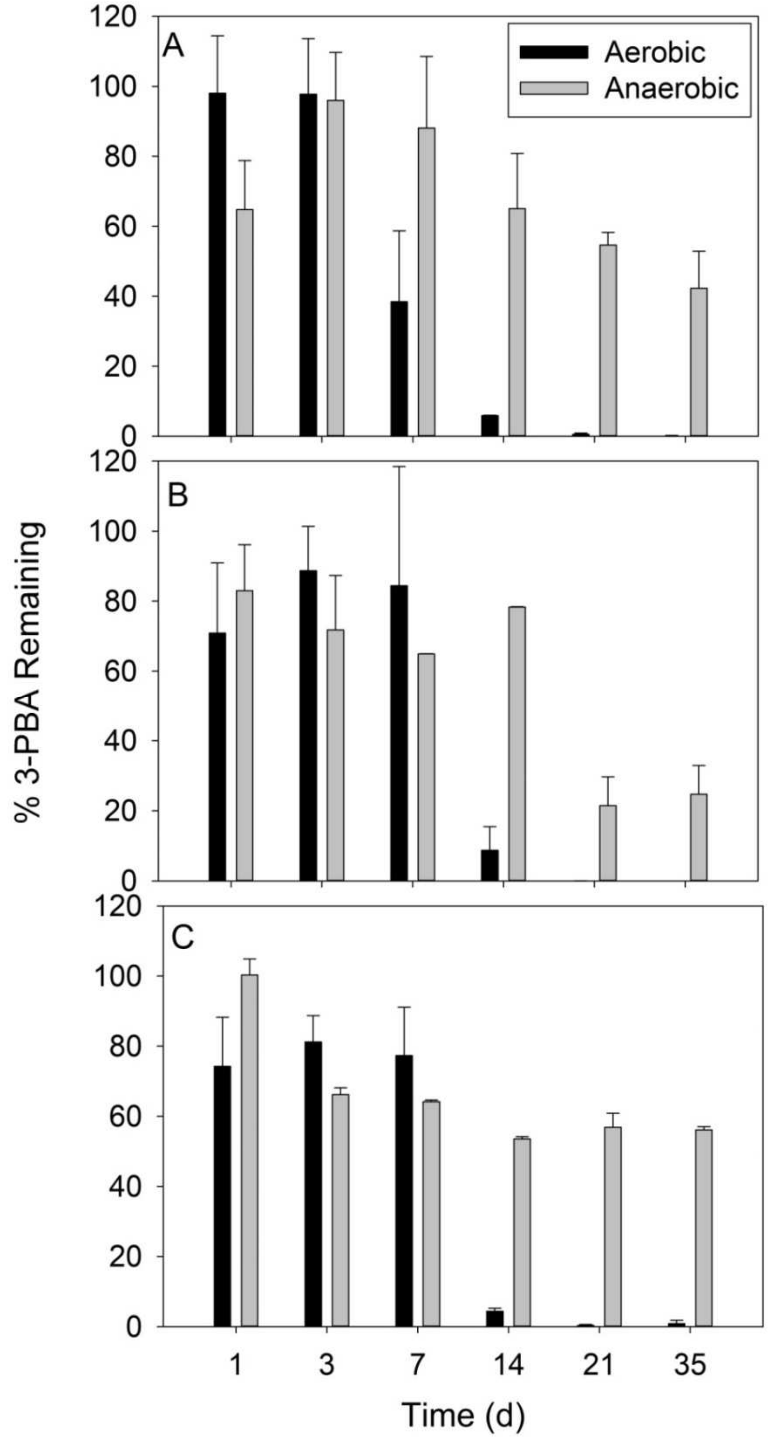

Figure 4.2. Persistence of 3-PBA in sediments from (A) Wood Creek, (B) Salt Creek, and (C) San Diego Creek under aerobic and anaerobic conditions.

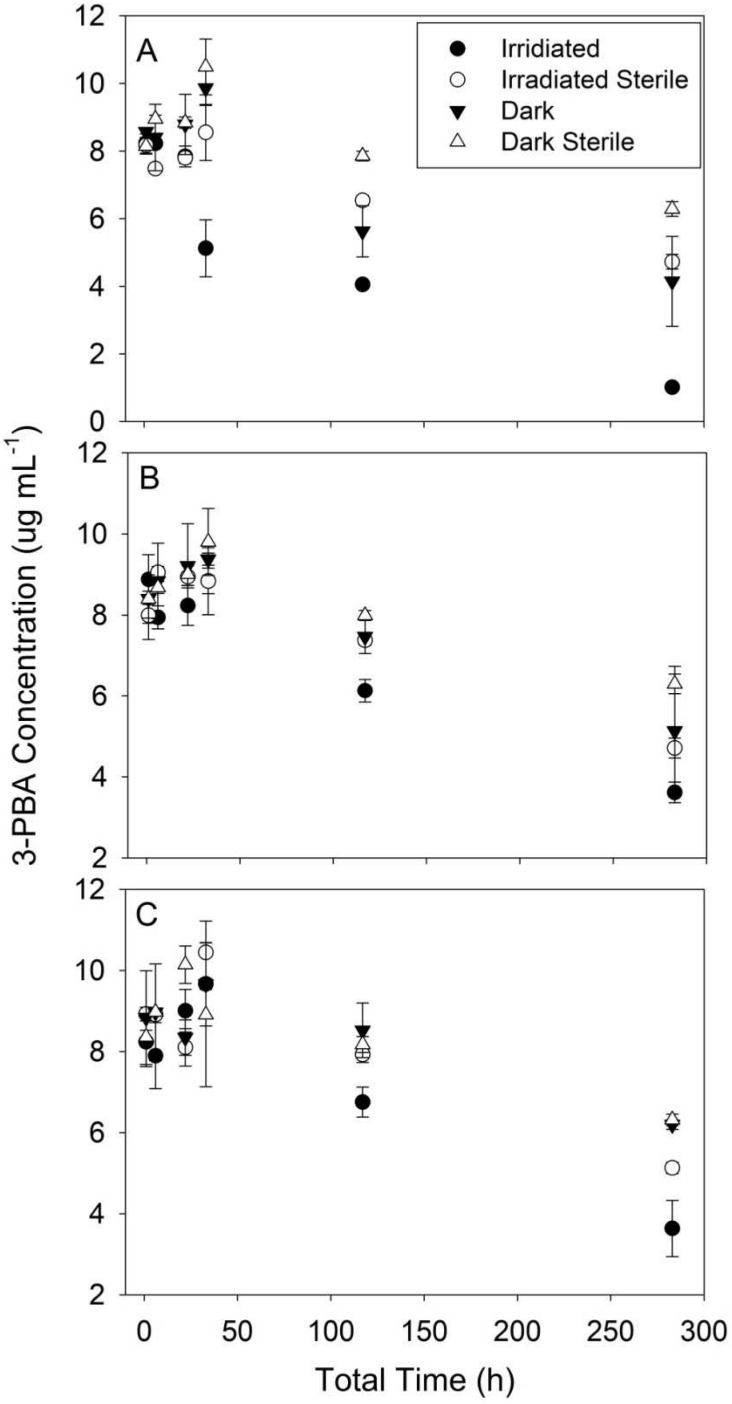

Figure 4.3. Concentrations of 3-PBA over 283 total h (168 h light) in surface water taken from (A) Wood Creek, (B) Salt Creek, and (C) San Diego Creek.

Chapter 5 General Conclusions and Future Work

5.1 Distribution of pesticides in dust particles in urban environments

In regions with a mild climate, pesticides are often used around homes for pest control. Recent monitoring studies have linked pesticide use in residential areas to aquatic toxicity in urban surface water ecosystems, and suggested dust particles on paved surfaces as an important source of pesticides. To test the hypothesis that dust on hard surfaces is a significant source of pesticides, we evaluated spatial and temporal patterns of current-use insecticides in Southern California, and further explored their distribution as a function of particle sizes. Pyrethroid insecticides were detected in dust from the driveway, curb gutter and street at 53.5-94.8%, with median concentrations of 1-46 ng g-1. Pyrethroid residues were uniformly distributed in areas adjacent to a house, suggesting significant redistribution. The total levels of pyrethroids in dust significantly ($p<0.01$) decreased from October to February, suggesting rainfalls as a major mechanism to move pesticide residues offsite. Fipronil as well as its degradation products, were detected at 50.6-75.5%, and spatial and temporal patterns of fipronil residues suggested rapid transformations of fipronil to its biologically active intermediates. Moreover, pyrethroids were found to be enriched in fine particles that have a higher mobility in runoff than coarse particles. Results from this study highlight the widespread occurrence of pesticides in outdoor dust around homes and the potential contribution to downstream surface water contamination via rain-induced runoff.

5.2 Degradation of Pyrethroids and Formation of 3-Phenoxybenzoic Acid on Urban Impervious Surfaces

Urban insecticide use including structural pest control and landscape maintenance accounts for a large fraction of the total insecticide use. For instance, in California, reported urban insecticide use in 2014 amounted to 1.8 million kg (as active ingredients), of which 1.77×10^5 kg was synthetic pyrethroids. Pyrethroid use has been associated with acute toxicity to water column and benthic invertebrates in urban streams. Many pyrethroids may be transformed to a common intermediate, 3-phenoxybenzoic acid (3-PBA), an endocrine disrupting compound. However, little is known about the formation of 3-PBA from pyrethroids in urban settings. In this study, we examined the stability of five common pyrethroids, permethrin, lambda-cyhalothrin, deltamethrin, fenpropathrin, and esfenvalerate, on concrete surfaces and the derivation of 3-PBA under sunlight. Irreversible binding, hydrolysis, photolysis and volatilization led to rapid dissipation of pyrethroids on irradiated 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 formation of 3-PBA on concrete further varied among the different compounds, and was transient, with an average half-life of 4.2-6.7 h. Trace levels of 3-PBA were consistently found in two streams draining urban neighborhoods, suggesting that urban use of pyrethroids resulted in 3-PBA contamination of urban surface waters. Findings from this study suggested that urban hardscapes such as concrete pavement are reactive surfaces, highlighting the need to consider formation of biologically active intermediates such as 3-PBA from urban-use pesticides.

5.3 Persistence of 3-Phenoxybenzoic Acid in Soil, Sediment, and Water

The use of pyrethroids has led to their presence in urban and agricultural runoff at levels toxic to arthropods and fish. However, when pyrethroids enter the environment they can undergo transformation by hydrolysis, photolysis, and either chemical or biological oxidation to form different products. A common pyrethroid transformation product is 3-phenoxybenzoic acid (3-PBA), which has been shown to have endocrine disrupting activity. While the degradation of pyrethroids in environmental media has been well studied, very little research has been conducted on their biologically active degradation product 3-PBA. In order to help fill the knowledge gap, this study consisted of examining the persistence of 3-PBA in soil, sediment, and water was examined and half-lives were calculated from the first-order degradation rates. Half-lives of 3-PBA varied widely depending on the environmental matrix examined, with half-lives being greater than 35 d in soil, 4.6 to 9.1 d in aerobic sediment, 18.7 to 51.7 d in anaerobic sediment, 4.0 to 10.3 d in water under irradiation from sunlight, and 10.7 to 24.1 d in water under dark conditions. These results suggest that soil may be a significant source of 3-PBA to surface or ground water, due to the long persistence of 3-PBA. Additionally, 3-PBA persistence was low in sediment and water taken from urban streams, but near continuous additions of 3-PBA from nearby residential areas may make 3-PBA pseudo-persistent in these systems. Therefore, further monitoring of 3-PBA in surface and groundwater should take place, as well as toxicological studies on the impact of long-term low dose exposure to 3-PBA by aquatic organisms.

5.4 Future Work

Based upon previous research and the research contained in this dissertation, pyrethroids have a widespread distribution throughout urban areas with impervious surfaces and dust particles being major sources and off-site transport pathways for pyrethroids, as well as being sites for pyrethroid transformation. Pyrethroids are commonly detected in urban streams, and now their biologically active transformation product, 3-PBA, has also been detected in surface water. However, in order to have a more complete understanding of the risk 3-PBA poses; more research needs to be done regarding the occurrence of 3-PBA in urban streams, soil, and groundwater, as well as some basic research on its chemical properties such as K_{ow} and K_{oc} in order to help model its fate in different systems. Additionally, more toxicological data is necessary to accurately define the risk of 3-PBA, as most previous research has focused mainly on the biological targets that 3-PBA interacts with under acute exposure. From the research conducted in this dissertation, future toxicological studies should focus on the effects of long-term low dose exposure of organisms to 3-PBA, as well as the effects this may have on different life stages i.e. growth and development.