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Conversion of pesticides to biologically active products on urban hard surfaces

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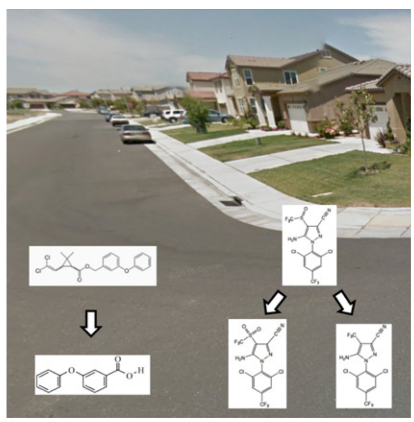
HIGHLIGHTS

- Permethrin rapidly degraded on concrete and formed 3-phenoxybenzoic acid (3-PBA).
- The main degradates of fipronil on concrete were fipronil desulfinyl and sulfone.
- Permethrin and fipronil degradates were found on concrete and in the runoff water.
- Both permethrin and fipronil degradates have toxicities to non-target organisms.
- The study revealed the active role of urban pavement in life cycling of pesticides.

GRAPHICAL ABSTRACT



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ABSTRACT

Impervious pavements such as concrete are a dominant feature of urban landscapes, but their role in the fate of environmental contaminants is largely ignored. This study considered the case of urban-use pesticides, and demonstrated for the first time that surfaces such as concrete were capable of converting pesticides to other biologically active intermediates. Rapid transformation of pesticides was observed in both bench and field scale setups. Under outdoor conditions, permethrin, a heavily used pyrethroid insecticide, quickly formed 3-phenoxybenzoic acid (3-PBA) that is a known endocrine disruptor, and the level of 3-PBA was >100 μg/L in the runoff water even 3 months after the treatment. Fipronil, a product used for termite and ant control, was quickly transformed to desulfinyl and sulfone derivatives, with the desulfinyl level exceeding that of parent in the runoff water only 1 week after treatment. Fipronil derivatives have aquatic toxicity similar or even greater than the parent fipronil. Direct sampling of deposited particles from residential exterior pavements revealed widespread presence of fipronil sulfone and desulfinyl and demonstrated their in-situ formation and accumulation on concrete. The extensive transformations were likely caused by the alkalinity and metal oxides in concrete and conducive photolytic conditions at the hard surfaces. The study findings highlight the role of urban pavements and urbanization in the geochemical cycling of anthropogenic contaminants.

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1. Introduction

Paved surfaces are a dominant component of most urban landscapes. They are used to cover streets, pedestrian sidewalks, parking lots and driveways, and are commonly connected to city drainage systems and hence the open environment (Alley and Veenhuis, 1983; Brabec et al., 2002). The percentage of pavement coverage in urban areas is site-specific and depends on land use patterns (Alley and Veenhuis, 1983; Brabec et al., 2002). For instance, the coverage of paved surfaces in residential districts in the U.S. varies from 12% for homes with large lot sizes to 65% for those with average lot sizes (USDA, 1986). In commercial and business areas, the average coverage is 85% (USDA, 1986). The impervious pavements are designed for rapid surface runoff from irrigation or rainfalls, and therefore may facilitate off-site transport of chemicals (i.e., environmental contaminants) coming into contact with them. However, despite the prevalence of pavements in urban areas and their dual function as both a sink and source of contamination, little is known about their role in the cycling and transformation of environmental contaminants (Jiang et al., 2010; Jiang et al., 2011). This is in stark contrast to the extensive studies on the environmental fate and risks of man-made chemicals in agricultural and natural systems.

Here we used pesticides as model man-made compounds to reveal that pavements such as concrete are not inert surfaces, but a catalyst of sort actively participating in the environmental cycling of chemicals, leading to the formation of biologically active intermediates. Pesticides are extensively used in urban areas for structural and landscape pest control. As replacements for organochlorine and organophosphate compounds, synthetic pyrethroids and fipronil are currently the most commonly used urban insecticides in regions such as California, United States. For instance, in 2010, 17,391 kg fipronil and 152,990 kg pyrethroids (as active ingredients) were used by licensed applicators in California alone, while unknown quantities were also applied by home owners (CDPR, 2010). To manage insects such as ants and termites, the majority of these man-made chemicals are applied on concrete surfaces such as walkways and driveways, and along the foundation of houses. Pavement surfaces may also receive pesticides via water or wind-aided transport, and atmospheric deposition. Pesticide use in residential areas has recently been linked to the ubiquitous pesticide contamination and aquatic toxicity in urban surface waters in the U.S and around the world (Jiang et al., 2010; Jiang et al., 2011; Lao et al., 2010; Jiang et al., 2012; Li et al., 2013; Hunt et al., 2016).

In this study, we investigated the transformation of two commonly used insecticides, permethrin and fipronil, on concrete surfaces. Controlled experiments, as well as sampling of particles from residential impervious surfaces and water from residential runoff, were carried out to demonstrate the conversion resulting in transformation products, i.e., 3-phenoxybenzoic acid (3-PBA) from permethrin, and fipronil desulfinyl, sulfide and sulfone from fipronil, with significant biological activity. To our knowledge, this represents the first report on such an active role of urban concrete pavements in the environmental fate and risk processes of pesticides. It is highly probable that urban hardscapes play a similar role in the cycling of other environmental contaminants.

2. Methods

2.1. Chemicals

Three commercial formulations of permethrin, i.e., a ready-to-use (RTU) liquid formulation (0.20 ± 0.02% active ingredient; Hot Shot, Spectrum, St. Louis, MO), a RTU solid formulation (0.22 ± 0.01%; Ant-B-Gone, Ortho, Marysville, OH), and a professional concentrate (35.1 ± 1.2%; Tengard, United Phosphorus, King of Prussia, PA), and a professional formulation of fipronil, Termidor® (10.1 ± 0.79%; BASF, Research Triangle Park, NC) were selected. RTU products were sold to homeowners in retail stores, and professional formulations are available only to licensed applicators.

Chemical standards of fipronil desulfinyl (97.8%), fipronil sulfide (98.8%) and fipronil sulfone (99.7%) were obtained from the U.S. Environmental Protection Agency's National Pesticide Standard Repository (Fort Meade, MD). Standards of phenoxy $^{13}C_6$-labeled *cis*-permethrin (^{13}C-permethrin, 99%, Cambridge Isotope Laboratories, Andover, MA), 3-PBA (99%, Acro Organics, Pittsburgh, PA), phenoxy $^{13}C_6$-labeled 3-PBA (^{13}C-3-PBA, 99%, Cambridge Isotope Laboratories), and decachlorobiphenyl (99.2%, Chem Service, West Chester, PA) were purchased from different sources. All solvents and other chemicals in GC/MS, LC/MS, Optima, or pesticide grade were from Fisher Scientific (Pittsburgh, PA). All glassware was baked at 400 °C for 4 h before use to prevent cross contamination.

2.2. Concrete plot experiments

Transformation of fipronil and permethrin on concrete and the occurrence of their biologically active derivatives in the runoff water were evaluated using concrete slabs (60 × 40 × 9 cm, L × W × H) that were prepared by mixing Portland cement, sand, and gravels (1:3:3, v/v/v) with water and pouring the concrete slurry into wooden frames. The concrete surface was finished with a V-shaped indention at the lower end to facilitate the collection of runoff water. All concrete slabs were allowed to cure under outdoor conditions for 6 months before use.

The concrete slabs were divided into three groups for treatments with the three formulation products. For RTU solid formulation permethrin, the product was uniformly dusted onto the surface of each concrete slab. For RTU liquid formulation permethrin, the product was directly applied using a Marson MC air-brush sprayer (Swingline, Lincolnshire, IL) at 40 psi without dilution. For the professional formulations, 2.25 mL of the fipronil concentrate and 16 mL of the permethrin concentrate was mixed with 500 mL water, and 50 mL of the mixed solution was applied onto each concrete slab using the air brush sprayer. The treatment rates were in compliance with the label instructions and the applied permethrin amounts were close for the three formulations. The application rate was 175.5, 248.3 and 233.3 μg/cm^2 of RTU solid, RTU liquid and professional formulation permethrin, and 9.12 μg/cm^2 of professional formulation fipronil.

The treated concrete slabs were subjected to simulated rainfalls (26.2 ± 2.7 mm/h for 15 min) to generate runoff water. To mimic recurring rainfall or irrigation events, the same concrete slabs received precipitations on days 1, 7, 20, 47, and 89 after pesticide treatment. Four concrete slab replicates were included for each formulation and on each precipitation day. The runoff water from each concrete slab was collected individually into an amber bottle and stored at 4 °C in the dark until extraction.

2.3. Survey of derivatives in residential areas

We sampled particles on residential outdoor hard surfaces to survey pesticide derivative levels. Details on particle collection were described elsewhere (Jiang et al., 2015a). Briefly, we randomly selected 40 single-family or duplex houses in two neighborhoods and at each house, three surfaces that directly connect to drainage pipes, i.e., curbside gutter at the bottom of driveway, sidewalk next to the lawn, and the street, were vacuumed for particles. The same surface was repeatedly sampled three times in May, July and September of the year 2011 to capture contamination levels at the beginning, middle and end of the dry summer season in California. Collected particles were kept frozen (−18 °C) and analyzed within 20 days from collection.