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Fiproles in urban surface runoff: Understanding sources and causes of contamination

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Abstract

Urban-use pesticides present a unique risk to non-target organisms in surface aquatic systems because impervious pavement facilitates runoff that may lead to serious contamination and ensuing aquatic toxicity. Fipronil is an insecticide used at high rates in urban environments, especially in regions such as California. This compound and its biologically active degradation products have been detected in urban runoff drainage and downstream surface water bodies at concentrations exceeding toxicity thresholds for sensitive aquatic invertebrates, necessitating a better understanding of the runoff sources and causes of this contamination at sites of application. In this study, we evaluated sorption of fipronil, fipronil desulfinyl, fipronil sulfide, and fipronil sulfone in urban dust, soil, and concrete, matrices commonly associated with the perimeter of a residential home. Samples were also collected from five single family homes treated with fipronil in Riverside, California, for five months to determine the occurrence of fipronil and its degradates in runoff water, urban dust, soil, and on concrete surfaces. Statistical analysis was performed to determine which urban matrices contributed more significantly to the contaminant levels in runoff water. Freundlich sorption coefficients for fipronil and its degradation products in dust were 3- to 9-fold greater than their values in soil. Fipronil and its degradates were detected in 100% of runoff samples and their presence was observed in dust, soil, and concrete wipe samples for 153 d after the treatment. Linear regression analysis showed that concrete surfaces were a primary source of all four compounds to runoff, and loose dust on concrete pavement also served as an important contributor. This study represents the first comprehensive investigation of the sources and causes for surface runoff contamination by fipronil and its degradation products. Findings highlight the

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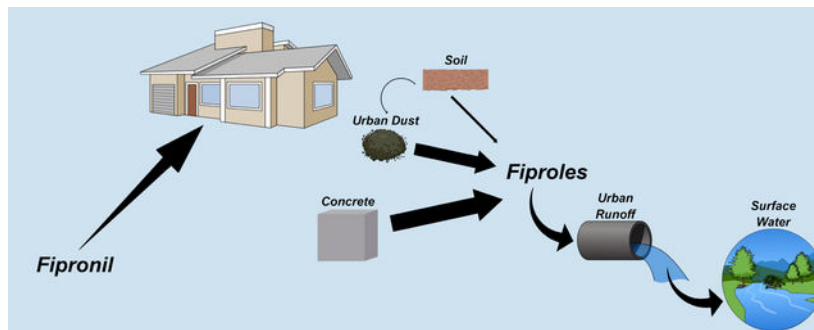
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CONFLICT OF INTEREST

The authors declare no conflict of interest.

importance to reduce fipronil residues on concrete surfaces through improved application methods and other mitigation practices.

Graphical Abstract



CAPSULE

Urban dust and concrete surfaces contribute significantly to runoff of fiproles and thus represent an important target for mitigation of their offsite transport and ensuing aquatic toxicity.

Keywords

fipronil; urban use pesticides; runoff; risk mitigation; water quality

INTRODUCTION

Urban use insecticides are primarily applied to eliminate structural pests such as ants, termites, roaches, and spiders. Extensive outdoor urban pesticide use is a cause for concern since surface runoff of these biologically active compounds into urban waterways following rainfall or irrigation has the potential to exert adverse effects in non-target aquatic organisms (Gan et al., 2012; Weston and Lydy, 2012; Weston and Lydy, 2014; Weston et al., 2013). The high incidence of impervious surfaces (i.e., concrete pavement, asphalt roads, roofs) in urban environments, which may account for 50–90% of residential and commercial surface areas, prevents infiltration of water into soil and facilitates runoff and offsite transport of pollutants such as pesticide residues to urban streams (Arnold and Gibbons, 1996). Perpetual urban expansion is projected to triple the global urban land area between the early 2000s and 2030 (Seto et al., 2012), exacerbating the issue of urban pesticide runoff and contamination to surface water.

Fipronil is a moderately hydrophobic ($\log K_{ow} = 3.9\text{--}4.1$; Demcheck and Skrobialowski, 2003) phenylpyrazole insecticide applied for a multitude of urban pest control purposes by licensed applicators. Applications include perimeter and underground injection treatments to manage ants and termites, veterinary flea and tick treatments, insect control baits, and landscape maintenance (Sadaria et al., 2017; Teerlink et al., 2017; Ensminger, 2014; USEPA, 2011). After application, fipronil degrades primarily into fipronil desulfinyl, fipronil sulfide, and fipronil sulfone following photolysis, reduction, and oxidation, respectively (Gunasekara and Truong, 2007). According to the Pesticide Use Reporting database, over

24,000 kg a.i. of fipronil were applied in 2016 in California, where use is confined to urban areas (<http://cdpr.ca.gov/docs/pur/purmain.htm>). Consequently, fipronil and its degradation products (collectively termed fiproles hereafter) are frequently detected in surface water, such as in regions like California. In a study of runoff discharge collected from residential storm drain outfalls in southern and northern California, median total fiprole concentrations were found to be 204–441 ng L⁻¹ and 13.8–20.4 ng L⁻¹, respectively, and 90th percentile total fiprole concentrations were 338–1169 ng L⁻¹ and 62.6–65.3 ng L⁻¹, respectively (Gan et al., 2012). In a recent study surveying urban creeks, rivers, and storm drain outfalls, fipronil sulfide, fipronil sulfone, fipronil desulfinyl, and fipronil were detected in 8%, 63%, 65%, and 75% of samples, respectively (California Department of Pesticide Regulation, 2016). The presence of fiproles in surface water is significant, since these compounds have been shown to exert toxic effects in a variety of non-target aquatic organisms with an LC₅₀ (fipronil) of 140–320 ng L⁻¹ for *Palaemonetes pugio*, *Neomysis americana*, and *Simulium vittutum*, and an EC₅₀ of 32.5 ng L⁻¹ (fipronil) and 7–10 ng L⁻¹ (degradation products) for *Chironomus dilutus* (Key et al., 2003; Overmyer et al., 2005; Overmyer et al., 2007; USEPA, 1996; Weston and Lydy, 2014). Therefore, in regions such as California, fiproles are ubiquitously present at toxicologically relevant levels in urban surface water ecosystems. However, little is presently known about the principal sources of fiproles in urban surface runoff, which hampers watershed-scale risk assessment as well as the development of effective strategies for mitigation. In the context of this study, runoff sources are defined as environmental matrices that contribute fiprole residues to surface runoff following known pesticide application.

Primary objectives of this study were to characterize the affinity of fiproles for common urban matrices, to investigate persistence of fiproles in urban compartments, and to identify potential sources of fiproles in urban runoff. Bench sorption experiments were conducted for fiproles in urban dust, soil, and concrete. In addition, runoff water, urban dust, soil, and concrete wipe samples were collected from multiple fipronil-treated homes in southern California from July–December 2016. This study represents the first systematic investigation of potential runoff sources of fiproles in urban residential environments. Results may be used to direct mitigation efforts of these compounds and to guide future pollution prevention initiatives for similar contaminants in urban watersheds.

MATERIALS AND METHODS

Chemicals and materials

Fipronil (98.9%), 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). Ethiprole (97.4%) was obtained from the Shanghai Pesticide Research Institute (Shanghai, China). Isotopically labeled fipronil (¹³C₄-¹⁵N₂-fipronil, 99.1%) was purchased from Cambridge Isotope Laboratories (Andover, MA). Solvents and other chemicals were of pesticide or GC-MS grade. Small concrete cubes used in the sorption isotherm experiment were made in the laboratory via a process described elsewhere (Jiang et al., 2011). The following stock solutions were prepared and stored in a

freezer before use: 100 mg L⁻¹ fiproles in acetone, 1 mg L⁻¹ ¹³C₄-¹⁵N₂-fipronil in hexane, and 5 mg L⁻¹ ethiprole in acetone.

A sandy loam soil was collected for use in the sorption isotherm experiment from the 0–30 cm depth at the South Coast Research and Extension Center in Irvine, California. Soil was air dried and sieved through a 2 mm mesh prior to use. Soil pH was 7.7, measured using a 1:2 (v/v) soil slurry (Donohue, 1992). Soil particle size composition was 66.0% sand, 16.7% silt, and 17.3% clay, as determined using the 12-h hydrometer method (Klute, 1986). Soil organic matter content was 1.1% (w/w), measured via loss-on-ignition by heating 5 g of soil at 375 °C in a muffle furnace for 24 h (Gavlak et al., 2003). Total organic carbon content (0.66%) was derived using high temperature combustion on an Elementar Vario MAX C/N Analyzer (Elementar Americas, Mt. Laurel, NJ) following the addition of HCl for carbonate removal (Schumacher, 2002).

Samples of urban dust for the sorption isotherm experiment were collected from three homes in Orange County, CA, pooled before use, and fractionated as described elsewhere (Richards et al., 2016). Dust was comprised of the following size fractions: 2 mm–425 µm (15.9% w/w), 425–250 µm (12.4%, w/w), 250–149 µm (4.22%, w/w), and 149–45 µm (67.4%, w/w). Whole dust samples were stored at 4 °C prior to use.

Sorption isotherm construction

Sorption isotherms were constructed over a period of five days by mixing concrete cube, urban dust, or the sandy loam soil (collectively: urban solids) samples in aqueous solutions simultaneously spiked with all four fiproles at 5, 20, 50, 100, 200, or 500 µg L⁻¹. NaN₃ was amended at 200 mg L⁻¹ in the solution to suppress microbial activity and CaCl₂ was added at 100 mg L⁻¹ to adjust the solution's ionic strength. Samples were prepared by adding 10 mL of the solution to a 40 mL amber glass vial containing one concrete cube, 2 g of dust (dry weight), or 2 g of soil (dry weight) and mixing on a horizontal shaker at 120 rpm for 5 d (steady state determined through preliminary experiments). No statistically significant fiprole losses occurred over the course of the incubation. Sample vials were centrifuged at 1500 rpm for 30 min to separate the aqueous and solid phases. Aqueous phases were collected and extracted with 10 mL hexane by mixing on a horizontal shaker at 200 rpm for 30 min a total of two times. Solid phase samples were mixed with 1 g NaCl and 4 g anhydrous Na₂SO₄ and then extracted with 10 mL of 8:2 acetone:hexane (v/v) by mixing at 200 rpm for 30 min a total of two times. The solvent extract of the aqueous or solid phases was evaporated to dryness under a gentle stream of nitrogen at 40 °C, and the condensed extracts from solid phase samples were subject to clean up using Florisil cartridges according to the procedure listed in the supplementary information (SI). Cleaned extracts were evaporated to dryness at 40 °C under a stream of nitrogen, and all extracts were reconstituted in 1.0 mL hexane before analysis.

Collection and analysis of runoff and solid samples from residential homes

Five homes in Riverside, CA, received standard perimeter spray treatments of a professional fipronil formulation (0.06% w/v) diluted from a suspension concentrate per the label instructions in July 2016, and the treatment was similar to the conventional treatment

described in Greenberg et al. (2010). Pre-treatment runoff concentrations of fiproles revealed low-level background contamination of all four compounds (24–134 ng L⁻¹). However, these concentrations were two to three orders of magnitude lower than 1 d runoff concentrations and were similar to 153 d runoff concentrations. Therefore, this background contamination likely did not impact the conclusions presented in this study. Fiproles in runoff, soil, urban dust, and concrete were monitored at five time points during July–December 2016. Weather during this period was very warm and dry until light rainfall occurred in December prior to the collection of the final set of samples. The results reported herein were likely not impacted by this rainfall since the final samples still contained fiproles at concentrations similar to those measured at the previous time point. Runoff samples, one from each home at each time point (n=25), were collected by building a temporary water berm approximately 6 m away from the home's garage door. Berm dimensions and composition were described in detail in Greenberg et al. (2017). Each driveway was rinsed with a hose to generate a volume of runoff sufficient for the collection of a 1 L water sample in an amber glass bottle. Sample bottles were transported to the laboratory on ice within 3 h and stored at 4 °C until extraction.

Extraction of runoff water samples was adapted from the methods in Gan et al. (2012). Briefly, water samples were combined with 30 mL NaCl and liquid-liquid extraction was performed with 60 mL dichloromethane a total of three times. Extracts were then evaporated using a Büchi RE121 Rotovapor (Flawil, Switzerland), solvent exchanged into 9:1 hexane:acetone (v/v), and cleaned up by loading into a Florisil cartridge preconditioned with hexane and eluting with 9:1 hexane:acetone (v/v). Cleaned extracts were evaporated to dryness under a gentle stream of nitrogen at 40 °C and reconstituted in 1.0 mL hexane.

At each house and sampling time point, the following urban solid samples were simultaneously collected: one soil sample from the home perimeter, two dust samples from paved surfaces, and two concrete wipe samples from concrete walkways near the driveway. Soil samples (n=25) from the 0–3 cm depth were collected into 40 mL amber glass vials. Total organic carbon content for the home soil samples was determined to be 3.80% using the aforementioned method (Schumacher, 2002). Urban dust samples (n=50) were collected using a method similar to Richards et al. (2016). Briefly, dust was sampled using a handheld vacuum fitted with a metal housing and mesh containing a Whatman GF/A glass fiber filter paper (1.6 µm pores; Maidstone, U.K.). The area to be vacuumed was marked off using a 0.5 m² frame. If additional dust was needed to obtain a sufficiently large sample, the frame was moved to an adjacent region of the concrete surface for vacuuming. Filter papers were subsequently removed from the vacuum and stored in 40 mL amber glass vials. The total organic carbon content of the urban dust samples was measured to be 6.54% utilizing the previously described method (Schumacher, 2002). Concrete wipe samples (n=50) were collected from the vacuumed areas using cotton wipes soaked in 70% (v/v) isopropanol (Jiang and Gan, 2012). A 0.04 m² frame was used to mark off the area to be wiped, and samples were then placed into 40 mL amber glass vials. All samples were transported on ice to the laboratory within 3 h and stored at 4 °C until extraction.

Soil, urban dust, and concrete wipe samples were extracted via sonication in a Fisher Scientific FS110H sonication water bath (Waltham, MA), using 20 mL aliquots of 1:1

dichloromethane:acetone (v/v) (Richards et al., 2016). Samples were placed in the sonication water bath for 15 min and centrifuged at 1500 rpm for 30 min. This extraction process was repeated a total of four times. Extracts were evaporated using a Büchi RE121 Rotovapor (Flawil, Switzerland), solvent exchanged into 9:1 hexane:acetone (v/v), and then cleaned up by loading onto a Florisil cartridge preconditioned with hexane and eluting with 9:1 hexane:acetone (v/v). Cleaned extracts were evaporated to dryness under a gentle stream of nitrogen at 40 °C and reconstituted in 1.0 mL hexane.

Chemical analysis

All samples were analyzed on an Agilent 6890N/5973B GC/MSD equipped with a 30 m x 0.25 m DB-5MS column. Helium was used as the carrier gas at 1.2 mL min⁻¹ and sample aliquots (2 µL) were injected at 200 °C. The GC oven temperature program is described in the SI. Quantification was performed using an internal standard-normalized 8-point calibration curve, with concentrations ranging from 1 to 500 µg L⁻¹. Coefficients of determination for all calibration curves fulfilled the requirement of R² > 0.99.

Quality control and data analysis

Several steps were taken to ensure the quality of results generated in this study. Instrumental controls involved running a calibration standard every 10 samples during GC/MSD analysis, adding ¹³C₄-¹⁵N₂-fipronil as an internal standard to each extract immediately before GC/MSD analysis, and determining method detection limits (MDLs) using EPA Method 40 CFR Part 136, Appendix B. The calculated MDLs for fipronil desulfinyl, fipronil sulfide, fipronil, and fipronil sulfone were 1, 2, 2, and 2 µg L⁻¹, respectively. In addition, several procedural controls were utilized. Blank samples were analyzed with every set of three (sorption isotherm experiment), seven (residential runoff), and five samples (residential urban solids). In the case of the sorption isotherm samples, which utilized field samples to determine fiprole sorption and thus were potentially contaminated with fiproles prior to spiking, low level matrix blank detections were used to correct sample concentrations as needed. Reagent blanks for the other sample types revealed no fiprole detections. Matrix spike samples were analyzed to determine extraction efficiencies, which are listed in the SI. In addition, ethiprole was added to all samples prior to extraction to assess surrogate recoveries, which were 101 ± 15% for aqueous samples from the sorption experiment, 101 ± 22% for solid phase samples from the sorption experiment, 96 ± 17% for the residential runoff water samples, and 88 ± 27% for the residential urban solid samples. Additional procedural controls are described in the SI. Statistical analyses were performed using SAS® 9.4 (SAS Institute, Cary, NC). Linear regression was performed to calculate Freundlich sorption coefficients and to assess potential correlation between pesticide concentrations in runoff water and those in various urban solids.

RESULTS AND DISCUSSION

Sorption of fiproles in different urban matrices

Chemical concentrations in the aqueous phase and on the solids at equilibrium were fit to the Freundlich equation:

$$\log C_s = \log K_f + n \log C_w \quad (1)$$

where C_s is the chemical concentration on the solids, in $\mu\text{g m}^{-2}$ for concrete or ng g^{-1} for dust and soil, C_w is the aqueous concentration in $\mu\text{g L}^{-1}$ for concrete or ng mL^{-1} for soil and dust samples, n is the non-linear factor representing the slope of the logarithmic regression line, and K_f is the Freundlich sorption coefficient.

Sorption isotherm data for concrete, dust, and soil are summarized in Table 1. It is apparent that the sorption capacities of the four fipronil compounds differed substantially within each matrix. Fiproles with larger K_f values exhibit a greater affinity for that matrix and are thus less likely to desorb than compounds with smaller K_f values. Likewise, a larger K_f value would indicate that a compound is relatively more likely to be bound to the specific solid phase as opposed to being dissolved in the aqueous phase when exposed to runoff water.

According to the K_f values generated in this study, fipronil sulfide has the greatest sorption capacity for soil (21.4 L kg^{-1}), followed by fipronil sulfone (16.6 L kg^{-1}), fipronil desulfinyl (12.9 L kg^{-1}), and the parent compound fipronil (4.75 L kg^{-1}). Freundlich sorption coefficients for the Irvine sandy loam soil used in this study were very similar to values generated in soils from Australia (Ying and Kookana, 2001). These results indicated that fipronil sulfide adsorbs to soil particles more strongly than the other fiprole compounds under the same conditions, with the parent fipronil exhibiting the weakest sorption. This implies that soil may serve as an important runoff source of fipronil compounds if they are able to desorb from soil particles or if the particles themselves are physically washed away during large volume runoff events; for the parent compound, transport in the dissolved form may be important, while for metabolites such as fipronil sulfide with higher K_f values, movement as soil particles may be more significant. It is also possible that the strong sorption of fiproles onto soil particles may preclude their offsite transport if runoff volumes are insufficient to mobilize contaminated soil particles, especially with soils containing high total organic carbon content like the residential soil collected in this study (3.80%). This is important because degradation products of fipronil are known to elicit toxicity equal to or greater than that of fipronil itself (Weston and Lydy, 2014; Schlenk et al., 2001; Chandler et al., 2004; Maul et al., 2008). In addition, surface soil may be susceptible to wind or traffic-induced erosion, and loose soil particles may be transported and deposited onto impervious surfaces to become available for offsite movement by runoff water. Alternatively, when a runoff event produces a sufficient volume of water, surface soil may be inundated and mobilized from its origin in residential environments, resulting in potential transport of fipronil compounds either in the dissolved form or attached to soil particles.

Sorption coefficients for fiproles in dust followed a trend similar to that in soil. Fipronil sulfide displayed the largest K_f value (182 L kg^{-1}), followed by fipronil sulfone (93.3 L kg^{-1}), fipronil desulfinyl (43.7 L kg^{-1}), and then fipronil (21.9 L kg^{-1}). As with soil, fipronil sulfide adsorbed to dust particles with greater affinity than the other compounds, and fipronil showed the lowest relative affinity. Since the units of the dust and soil K_f values were the same, they may be directly compared. Freundlich sorption coefficients for the dust samples

were greater than the soil for the same compounds. Therefore, fiproles were sorbed to the dust particles more strongly than the soil solid phase. A recent study showed that fiprole concentrations in dust had the tendency to increase with decreasing particle size (Richards et al., 2016). Since the dust utilized for the sorption isotherm construction in this study was composed predominantly of fine particles, it may be reasonable to assume that increased sorption to dust samples was due to larger specific surface area of dust particles. In addition, the urban dust collected in this study had a total organic carbon content of 6.54% and a previous study showed that the mean organic carbon content of dust collected in southern California was 8.3%, much higher than the organic matter content of most soils in the region (Richards et al., 2016). Since organic matter content is typically the main driver of pesticide sorption, this finding may help explain the higher sorption of fiproles in dust compared with soil. The relatively strong sorption of fiproles to dust suggested that this environmental component may serve as an important source for the offsite transport of these compounds following application, since dust particles on impervious surfaces are easily translocated during a runoff event. Past studies suggested that dust particles on impervious surfaces served as a critical source for runoff loads of pesticides and polycyclic aromatic hydrocarbons (Richards et al., 2016; Murakami et al., 2004).

Sorption coefficients for concrete surfaces cannot be directly compared to those of soil and dust due to differences in concentration units (mass/surface area for concrete and mass/mass for soil or dust particles). In contrast to the trends observed with soil and dust samples, fiprole degradation products displayed smaller sorption coefficients than the parent compound on the concrete. It is likely that the sorption trend for concrete diverges from that of soil and dust due to its alkaline nature and complex interior pore system introduced by the curing and hydration processes utilized in its formation (Jiang and Gan, 2016). Concrete's alkaline pH likely affects the ionization states of fiproles, thus altering their relative sorption affinities. Furthermore, it is possible that fiprole residues became irreversibly sorbed to the inner porous network of the concrete cubes, further differentiating sorption to this matrix from that of soil and dust. For fipronil, the K_f value was 91.2 L m^{-2} , which was considerably greater than that for fipronil desulfanyl (9.64 L m^{-2}), fipronil sulfone (2.22 L m^{-2}), or fipronil sulfide (0.908 L m^{-2}). This finding suggested that fipronil, relative to its degradates, may be sorbed strongly to concrete matrices once it is applied and will be more likely to persist within such matrices. Thus, a continuous source of fipronil and its degradation products following the transformation of fipronil on and within the concrete may emanate from concrete surfaces over extended periods of time. Concrete surfaces, in the form of abraded particles, were also suggested as a source of polycyclic aromatic hydrocarbons in urban runoff, suggesting that surfaces such as concrete may serve as a reservoir of multiple classes of contaminants in urban environments (Hoffman et al., 1984).

Distribution of fiprole residues in residential compartments

Levels and descriptive statistics of fiproles in runoff water, urban dust, soil, and concrete wipe samples collected from actual residential homes are summarized in Table 2. The variation of concentrations within each environmental compartment was high, likely due to uncontrolled differences in pesticide use history, land cover, and landscape characteristics (Gan et al., 2012; Jiang et al., 2016a). All four fiprole compounds were detected in 100% of

runoff water samples over the five month study interval. This finding was in agreement with a previous study that showed detection of fipronil in runoff water seven months after the treatment (Jiang et al., 2014). Similarly, a study surveying residential stormwater outfalls in California showed occurrence of fipronil and its metabolites year-round, with detection frequencies of 81% in northern California and 98% in southern California (Gan et al., 2012). An examination of relative concentrations of fiproles in the runoff water in this study further confirmed the persistence of these compounds in residential environments (Figure 1). Mean fiprole concentrations in runoff at 30 d after application showed an initial decrease to 10–30% of those observed after 1 d. After 30 d, mean fiprole concentrations remained at 5–60% of the 1 d values, with some fluctuations. There was an apparent increase in fiprole mean runoff concentrations from the 30 d to 79 d sampling points, which may be an artifact of the high overall variability. It is also likely that soil or dust particles containing adsorbed fiprole residues were transported from nearby treated homes onto the pavement that was sampled for runoff water during this sampling interval. This assumption was consistent with the finding that pesticide-laden fine urban dust particles were readily redistributed in residential areas, becoming uniformly present on various impervious surfaces over time (Richards et al., 2016). Together, these results indicated that mean runoff concentrations of fiproles decreased rapidly initially, but low-level emissions may continue for many months. Similar to fipronil, detectable levels of pyrethroids were observed in runoff water from concrete after repeated simulated rainfall events, suggesting that concrete surfaces may serve as a sustained reservoir of hydrophobic pesticides (Jiang et al., 2012).

The persistence of fiproles in runoff water following a single structural pesticide application highlights the importance for mitigation at the source (Table 2). Fiprole runoff loads in real-world scenarios could be substantially higher, since multiple pesticide applications may be performed to maintain pest control efficacy (Greenberg et al., 2014). The sustained presence of fiproles within dust, soil, and concrete necessitated an understanding of the relative contributions of these matrices to fiprole loads in runoff, so that the primary origin of contamination may be known and targeted in mitigation practices.

Mean concentrations of fipronil and fipronil desulfinyl in the dust showed an initial peak at 1 d after application, which was followed by a sharp decrease at 30 d and relatively low but detectable levels thereafter (Figure 2). This suggested that rapid initial degradation of fipronil took place after application, likely due to photolysis to fipronil desulfinyl and other abiotic transformations during the intense summer of southern California where temperatures often exceed 38 °C (Gunasekara and Truong, 2007). Gradual formation of fipronil sulfone was apparent beginning at the 30 d sampling point. The mean concentration of fipronil sulfide remained relatively low and constant throughout the study period. Total fiprole concentrations remained approximately the same at 79 d, 110 d, and 153 d. Fipronil sulfide was the most frequently detected degradation product in the dust (52%), but its maximum concentration (140 ng g^{-1}) was smaller than that of fipronil desulfinyl (6960 ng g^{-1}) or fipronil sulfone (311 ng g^{-1}) (Table 2). The parent compound fipronil was the most frequently detected (82%) compound and was present at mean concentrations greater than those of its degradation products throughout the entire sampling duration (Figure 2). Fipronil desulfinyl and fipronil were observed to have the highest maximum concentrations of 6960 and 4750 ng g^{-1} , respectively (Table 2). A study of the occurrence of pyrethroids and

fiproles in urban dust samples collected from the driveways, gutters, and streets of residential areas showed median fiprole concentrations of 1–2 ng g⁻¹ and maximum concentrations of 1069–6188 ng g⁻¹, with detection frequencies of 50.6–75.5% (Richards et al., 2016). These detection frequencies and maximum concentrations were similar to those observed in this study (22–82%; 140–6960 ng g⁻¹). However, degradation product concentrations and detection frequencies were lower in the present study, likely attributable to the fact that samples were collected from homes treated with a single application of fipronil. Together, results from this and other studies indicated that dust particles exposed to fipronil may retain fipronil and its degradation products for many months after application. This suggests that urban dust may serve as a source of fiproles, especially fipronil and fipronil desulfinyl, in urban runoff long after the conclusion of pest treatment activity, barring removal or offsite transport of the dust prior to the occurrence of a runoff event.

Fipronil was present in soil at similar mean concentrations throughout the sampling period (Figure 3). Fipronil sulfone levels gradually increased from 1 d to 153 d, with mean concentrations ranging from 1.43–209 ng g⁻¹. Fipronil desulfinyl and fipronil sulfide mean concentrations also generally increased over time, ranging from <DL–30.5 ng g⁻¹ and <DL–26.7 ng g⁻¹, respectively. Fipronil has an aerobic soil half-life of 188 d (Ying and Kookana, 2002), which supports the finding that mean fipronil concentrations were similar over the 153 d period considered in this study. In addition, the gradual formation and increasing soil concentrations of fipronil degradates was consistent with the relatively slow degradation rate of the parent compound. Fipronil (72%) and fipronil sulfone (64%) were detected with the greatest frequency and at the highest maximum concentrations (215 and 562 ng g⁻¹, respectively) (Table 2). Fipronil desulfinyl (32%) and fipronil sulfide (56%) were detected less frequently and at substantially lower maximum concentrations (86.7 and 42.2 ng g⁻¹, respectively). Fiproles were measured in soil samples at detection frequencies similar to those measured in dust (32–72% in soil; 22–82% in dust), but maximum soil concentrations were much lower than maximum dust concentrations (42.2–562 ng g⁻¹ for soil, and 140–6960 ng g⁻¹ for dust). It is possible that soil concentrations were low relative to dust concentrations because soil samples were collected to a depth (0–3 cm) while dust particles partially originated from wind erosion of the surficial soil (Jiang et al., 2016b). Fiproles have been shown to be enriched in fine particles characteristic of urban dust (Richards et al., 2016), suggesting that residues initially present in the surrounding soil may have contributed to contamination of loose dust particles on impervious surfaces. Results summarized herein reveal that soil treated with fipronil-based pesticide formulations remains contaminated by fiproles for a significant amount of time following the treatment and is a source of fipronil degradation products. These data collectively imply that soil has the potential to contribute fipronil and its degradation products to their loads in urban runoff. However, this contribution likely depends upon the entrance of soil particles into runoff, either by inundation of soil with a large runoff volume after a prolonged rainfall, an irrigation event, or by prior transport of soil particles onto urban impervious surfaces.

Mean concrete concentrations of fiproles were at their highest 1 d after application and decreased subsequently by 57–89% at the 30 d sampling point (Figure 4). Fipronil was rapidly transformed after application such that its degradation products were detected at high mean concentrations 1 d after application. This finding was consistent with results of a

recent study focused on the degradation of pesticides on urban hard surfaces, where it was observed that fipronil was rapidly transformed to its biologically active degradation products on concrete in bench and field experiments (Jiang and Gan, 2016). Mean concentrations then remained relatively stable for the duration of the sampling campaign, with 30 d concentrations being similar to those at 79 d, 110 d, and 153 d. Detection frequencies of fiproles in concrete ranged from 27 to 92%, with maximum concentrations of 3.19–25.4 $\mu\text{g m}^{-2}$ (Table 2). Fipronil was detected more often than its degradation products (92%). The most prevalent degradation product was fipronil sulfone (65%), while fipronil desulfinyl (27%) was detected at a higher maximum concentration (9.64 $\mu\text{g m}^{-2}$) than the other degradates, second only to the parent compound (25.4 $\mu\text{g m}^{-2}$). An investigation of the contribution of fine particles to the runoff loads of pyrethroid pesticides also revealed high concentrations of bifenthrin (approximately 100 $\mu\text{g m}^{-2}$) and permethrin (approximately 10,000 $\mu\text{g m}^{-2}$) on concrete following application of professional pesticide formulations (Jiang and Gan, 2012). Concrete data further showed that fiproles were present in the concrete at detectable concentrations for several months after initial application of fipronil for pest treatment. This suggests that concrete may act as a long-term source of these compounds in urban runoff.

Elucidation of sources for fiproles in runoff

Several linear regression analyses were performed to assess the presence of statistically significant ($p < 0.05$) linear relationships between fiprole concentrations in different urban solid matrices and concentrations in runoff water (Table 3). The goal of these analyses was to identify primary sources for fiproles in urban runoff. A statistically significant relationship would indicate that a given component may be an important source for fiproles in runoff. It was observed that statistically significant relationships existed between the runoff and concrete concentrations of fipronil desulfinyl, fipronil sulfide, fipronil, and fipronil sulfone. A previous study similarly uncovered a highly significant linear relationship between runoff concentrations of pyrethroids and their concentrations on concrete surfaces measured using a surface wipe method (Jiang and Gan, 2012). In this study, significant relationships were also found between the runoff and dust concentrations of fipronil desulfinyl and fipronil. Recent studies have also implicated dust particles in the offsite transport of hydrophobic organic contaminants, but the present study was the first to directly evaluate the connection between dust and runoff loads of fiproles (Jiang et al., 2016b; Richards et al., 2016). The significance of the concrete-runoff and dust-runoff relationships for fiproles together suggested that dust on impervious urban surfaces and residues on concrete are important sources of fiproles in runoff. Statistical analysis, however, did not show soil as a significant source for fiproles in runoff water. As discussed above, even though soil was not a direct source, it is possible that soil particles in the surface layer may be transported via wind and other mechanisms onto the impervious surfaces, indirectly contributing to the contamination of runoff water by fiproles. Soil particles likely represent a major component of urban dust; other components may include concrete fragments generated from weathering and plant debris (Jiang et al., 2016b). Taken together, the most important finding of this analysis was that the effectiveness of mitigation efforts would be improved by focusing on reduction of dust particles on impervious surfaces and prevention of pesticide contact with concrete surfaces such as driveways. Moreover, the established

regression equations may be used to predict fiprole loads in runoff using levels in urban dust and residues on impervious surfaces, before a runoff event occurs.

Contamination of surface water by fiproles poses a threat to many benthic invertebrate species (Key et al., 2003; Overmyer et al., 2005; Overmyer et al., 2007; USEPA, 1996; Weston and Lydy, 2014). Fiproles may therefore exert a significant effect on the benthic community structures of urban streams (Weston and Lydy, 2014). Mitigation efforts are essential in the prevention of such adverse ecological consequences. However, even though runoff from a given residential area enters downstream surface water as a point source, surface runoff from individual homes in a neighborhood resemble nonpoint sources and is technically challenging to control (Gan et al., 2012). Identification of concrete surfaces and urban dust as the major sources of fiprole contamination of surface runoff at the site of pesticide treatment (i.e., individual homes) highlights their importance in the effort to reduce fiprole residues around a homesite, especially on impervious surfaces.

CONCLUSIONS

The high use rate of fipronil, detection of fipronil and its biologically active degradates in surface water in urban streams, and evidence for adverse effects in non-target aquatic organisms warrant a better understanding of the distribution of these compounds among various urban compartments and their origins in runoff. Results of this study revealed that fiproles differed in their capacity to adsorb to concrete surfaces, soil, and urban dust. Therefore, these matrices likely contribute differently to contamination of runoff water by fiproles due to irrigation or rainfall events. In residential settings, fiproles were shown to persist for several months in concrete, soil, dust, and runoff water following a single pesticide treatment. Data presented in this study provided evidence that concrete and dust were likely the primary sources of fiproles for the contamination of urban runoff. Thus, mitigation efforts should focus on the reduction of fiproles in these matrices. Minimizing the occurrence of fiproles in urban dust and on concrete surfaces would serve to decrease their concentrations in runoff and their subsequent contamination of surface water following offsite transport. Modifying pesticide application practices among pest management professionals is the first step toward effective mitigation. For example, avoiding application on concrete surfaces should be enforced through regulations. In addition, removal of dust from urban surfaces (i.e., via vacuuming or sweeping) prior to pesticide application may be considered. Instituting such changes will contribute to the reduction of fiprole loading in urban runoff and a decrease in potential ecotoxicological impacts associated with their occurrence in surface water. It is important to note that the runoff concentrations reported in this study cannot be directly compared to established aquatic toxicity values since the dissolved and particulate phases were not separated via filtration and not all the fiproles present in runoff would be bioavailable. Furthermore, it is likely that substantial dilution of the surface runoff would take place in surface water, reducing the expected toxicological impact of the measurements provided here. However, the identification of runoff sources in this study was vital to prevent future toxicity to sensitive organisms. Additional research is needed to ascertain the efficacy of potential fiprole mitigation strategies at a watershed scale.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Fiproles had higher sorption affinities for dust than for soil
- Fiproles persisted for several months in urban runoff after pesticide treatment
- For the study duration, fiproles were detected in concrete, soil, and dust
- Urban dust and concrete are important sources of fiproles in runoff

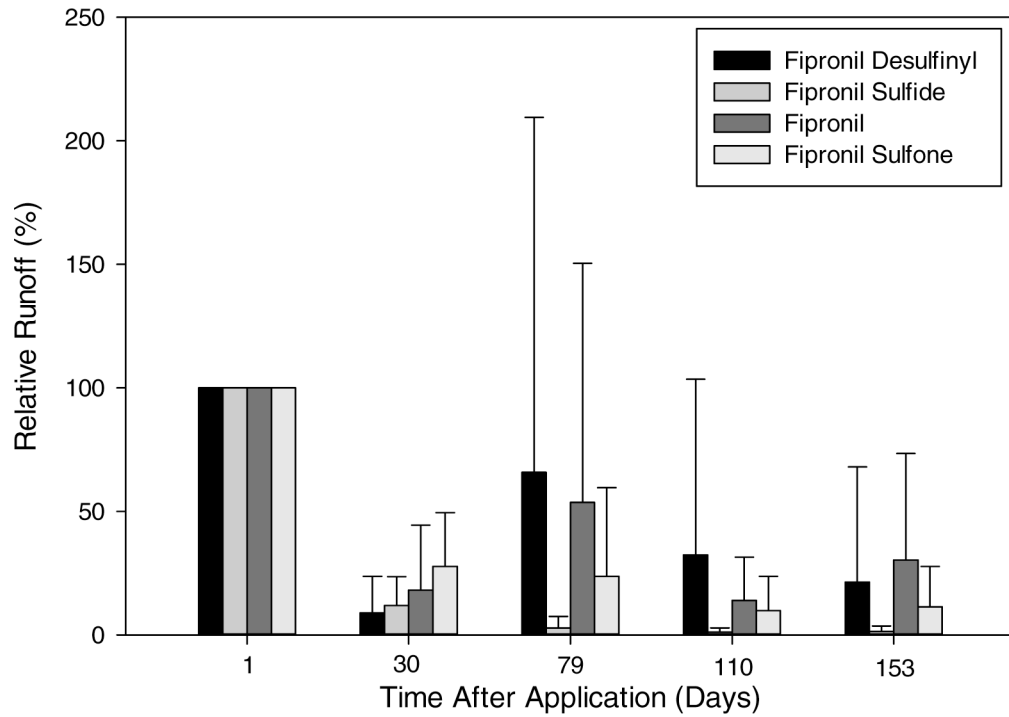


Figure 1. Relative runoff concentrations (expressed as percent of 1 d values) of fiproles in residential runoff following fipronil application. Error bars are mean \pm 1 SD.

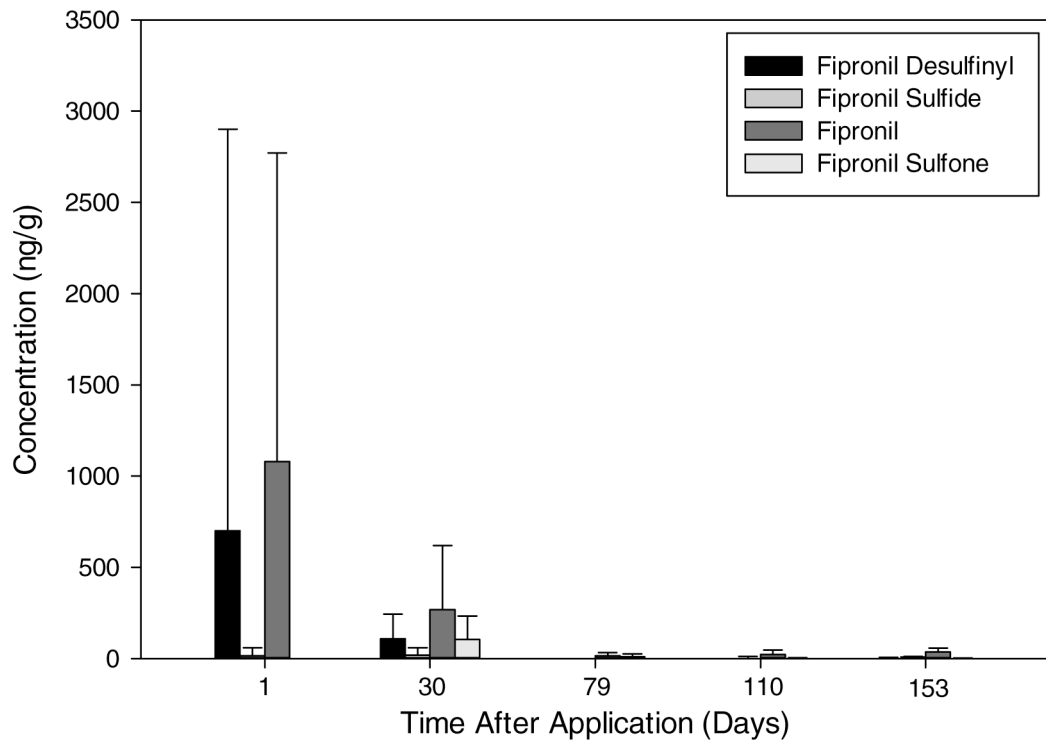


Figure 2. Concentrations of fiproles in urban dust collected from residential areas following fipronil application. Error bars are mean \pm 1 SD.

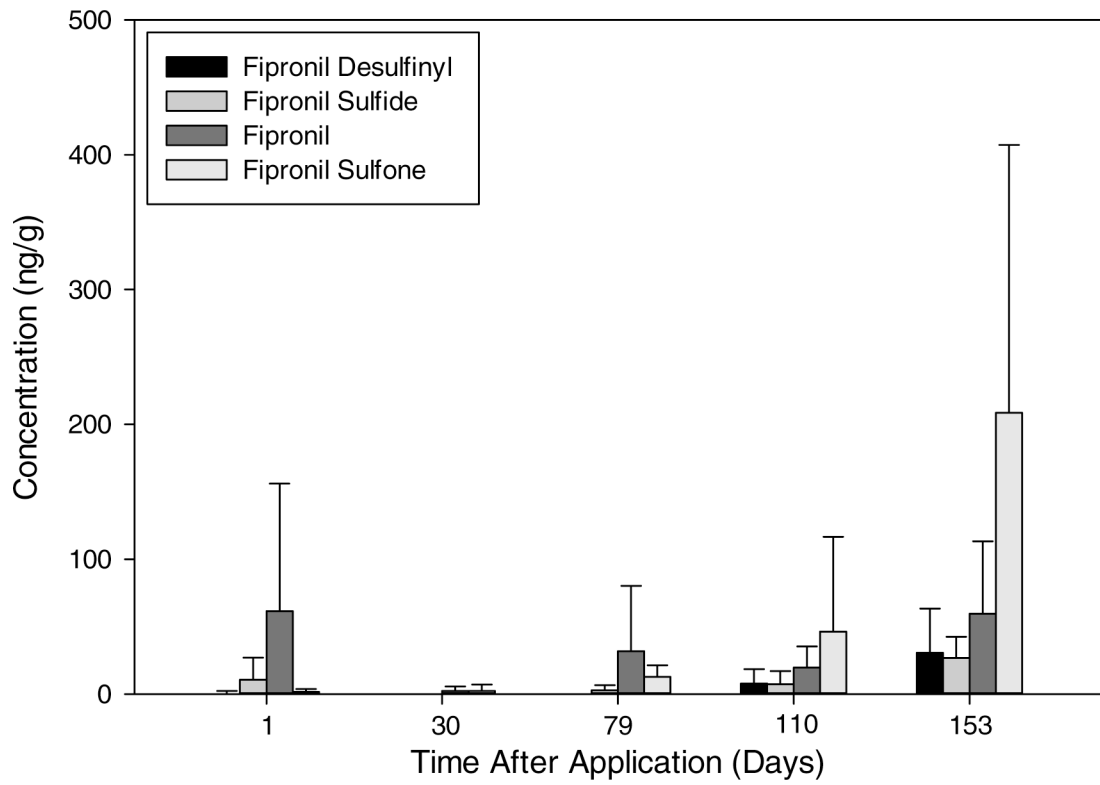


Figure 3. Concentrations of fiproles in soil collected from residential areas following fipronil application. Error bars are mean \pm 1 SD.

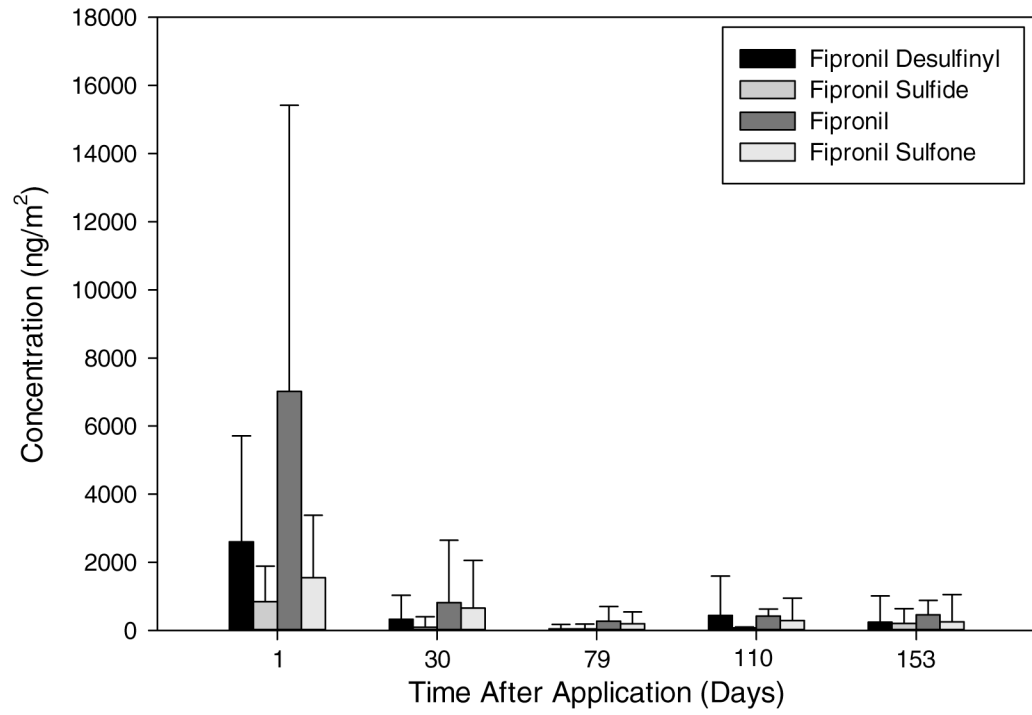


Figure 4. Concentrations of fiproles on residential concrete following fipronil application. Error bars are mean \pm 1 SD.

Table 1.

Freundlich sorption coefficients of fipronil and its degradation products in different matrices from residential homes.

Matrix	Compound	K_f	Units of K_f	R^2
	Desulfinyl	9.64		0.90
Concrete	Sulfide	0.908	$L\ m^{-2}$	0.70
	Fipronil	91.2		0.91
	Sulfone	2.22		0.82
Dust	Desulfinyl	43.7		0.82
	Sulfide	182	$L\ Kg^{-1}$	0.70
	Fipronil	21.9		0.71
	Sulfone	93.3		0.74
Soil	Desulfinyl	12.9		0.88
	Sulfide	21.4	$L\ Kg^{-1}$	0.90
	Fipronil	4.75		0.84
	Sulfone	16.6		0.90

Table 2.

Descriptive statistics for urban solid and urban runoff samples.

Matrix	Units	Compound	DF%	Median	75 th Percentile	90 th Percentile	Min	Max
Water ^a	ng L ⁻¹	Desulfinyl	100	82.1	293	4850	15.2	380000
		Sulfide	100	27.6	216	3450	5.78	163000
		Fipronil	100	161	517	2420	11.5	166000
		Sulfone	100	104	247	939	10.5	161000
Dust ^b	ng g ⁻¹	Desulfinyl	22	<DL ^e	<DL	45.4	<DL	6960
		Sulfide	52	1.39	6.57	20.4	<DL	140
		Fipronil	82	32.8	88.5	734	<DL	4750
		Sulfone	40	<DL	7.76	50.5	<DL	311
Soil ^c	ng g ⁻¹	Desulfinyl	32	<DL	9.63	25.1	<DL	86.7
		Sulfide	56	1.97	12.6	39.3	<DL	42.2
		Fipronil	72	11.0	53.2	128	<DL	215
		Sulfone	64	5.23	73.4	157	<DL	562
Concrete ^d	ng m ⁻²	Desulfinyl	27	<DL	395	2490	<DL	9640
		Sulfide	58	59.6	80.0	781	<DL	3190
		Fipronil	92	320	504	4070	<DL	25400
		Sulfone	65	40.5	444	2150	<DL	4960

^a
n=25^b
n=50^c
n=25^d
n=50^eBelow detection limit

Table 3.

Linear regression analysis of mean runoff concentrations versus mean urban solid concentrations. Statistically significant regressions are indicated by *.

Matrix	Compound	Regression Equation	R ²	p-value
Dust	Desulfinyl	$C_{\text{runoff}}^a = -2680 + (114) (C_{\text{dust}}^b)$	0.98	0.0015*
	Sulfide	$C_{\text{runoff}} = -1460 + (896) (C_{\text{dust}})$	0.20	0.454
	Fipronil	$C_{\text{runoff}} = -2170 + (32.6) (C_{\text{dust}})$	0.95	0.0054*
	Sulfone	$C_{\text{runoff}} = 8830 - (93.1) (C_{\text{dust}})$	0.083	0.639
Soil	Desulfinyl	$C_{\text{runoff}} = 22200 - (815) (C_{\text{soil}}^c)$	0.092	0.619
	Sulfide	$C_{\text{runoff}} = 6140 + (81.3) (C_{\text{soil}})$	0.0031	0.929
	Fipronil	$C_{\text{runoff}} = -5130 + (349) (C_{\text{soil}})$	0.34	0.304
	Sulfone	$C_{\text{runoff}} = 9670 - (55.7) (C_{\text{soil}})$	0.11	0.579
Concrete	Desulfinyl	$C_{\text{runoff}} = -8340 + (33.0) (C_{\text{concrete}}^d)$	0.98	0.0012*
	Sulfide	$C_{\text{runoff}} = -4400 + (44.8) (C_{\text{concrete}})$	0.97	0.0025*
	Fipronil	$C_{\text{runoff}} = -2320 + (5.23) (C_{\text{concrete}})$	0.99	0.0001*
	Sulfone	$C_{\text{runoff}} = -7860 + (24.5) (C_{\text{concrete}})$	0.90	0.0138*

^aRunoff concentrations expressed in units of ng L⁻¹

^{b, c}Dust and soil concentrations expressed in units of ng g⁻¹

^dConcrete concentrations expressed in units of ng m⁻²