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Pavement Dust as a Source for Pesticide Runoff Contamination in Urban Environments

Problem Statement

Pesticides used around homes may transport off-site as attachment to loose soil and dust particles to urban streams. Understanding the pathways through which soil/dust particles are contaminated by pesticides will provide information useful for developing effective mitigation strategies to protect urban surface water from pesticide contamination.

Background and Goals

Pesticides such as pyrethroids and fipronil are frequently found in urban runoff as a result of insecticide use for preventive and eradicative structural pest control. Recent studies have linked pavement surfaces such as driveway, sidewalks and street pavement to the sustained occurrence of pyrethroids and fipronil in residential runoff. Loose particles on the impervious surfaces have been found to contain significant levels of pyrethroids and fipronil (and metabolites). Given that these particles are easily dislodged and moved in a surface runoff event, the loose solids on pavement are considered a primary source for pesticides contaminating surface runoff and urban streams draining residential areas. While these studies have established the linkage between impervious surfaces and runoff contamination, it is unknown where the pesticide-laden dust particles come from, or how they are moved between the various compartments in a residential environment at the individual home scale. These knowledge gaps hinder the development of more holistic management strategies.

The objectives of this project were to understand the potential causes for pesticide contamination of pavement dust and interactions of micro-compartments surrounding a home in dust movement.

Project Completion Assessment and the COVID Impact

The project had a start date of July 1, 2018. Due to the COVID-19 pandemic, research activities were mostly suspended from the beginning of 2020. We subsequently requested a one-year no-cost extension till June 30, 2021. Even with the extension, many restrictions were

in place, essentially preventing sample collection at individual homes. To a great degree, physical presence in laboratories was also limited because of the needed compliance with social distancing and capacity limitations. This unprecedented event has certainly impacted the overall output of this research project. Here we report a comprehensive evaluation on fipronil with a focus on exploring the sources of contamination of pavement dust.

Fiproles in Urban Surface Runoff: Understanding Sources and Causes of Contamination

Primary objectives of this study were to characterize the affinity of fipronil and its biologically active metabolites (referred as "fiproles" here forth) for matrices commonly found around a private home site, to investigate persistence of fiproles in urban residential compartments, and to identify potential sources of fiproles in urban runoff. Bench sorption experiments were conducted for fiproles in urban dust, soil, and concrete to gain mechanistic insights. In addition, runoff water, urban dust, soil, and concrete wipe samples were collected from multiple fipronil-treated homes in southern California. This study represents the first systematic investigation of potential runoff sources of fiproles in urban residential environments.

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. Fiproles in runoff, soil, pavement dust, and concrete were monitored at five time points over about five months. Runoff samples, one from each home at each time point, were collected by building a temporary water berm approximately 6 m away from the home's garage door. 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. Water samples were extracted and analyzed for fiproles.

At each house and sampling time point, the following urban solid samples were simultaneously collected: one soil sample from the home perimeter (0-3 cm depth, at the same distance within the band of application), two dust samples from paved surfaces, and two concrete wipe samples from concrete walkways near the driveway. Dust was sampled from 0.5 m^2 using a handheld vacuum fitted with a metal housing and mesh containing a glass fiber filter paper. Concrete wipe samples were collected from 400 cm^2 of the vacuumed areas using cotton wipes soaked in 70% (v/v) isopropanol. Soil, urban dust, and concrete wipe samples were extracted and analyzed for fiproles.

Sorption of Fiproles in Different Urban Residence Matrices

Batch sorption experiments were conducted to determine phase partition coefficients by fitting the data to the Freundlich equation:

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

where C_S is the chemical concentration on the solids, in $\mu g \ m^{-2}$ for concrete or $ng \ g^{-1}$ for dust and soil, C_w is the aqueous concentration in $\mu g \ L^{-1}$ 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. Aqueous solutions (10 mL) spiked with fiproles at 5-500 $\mu g \ L^{-1}$ were equilibrated with 2 g of soil or dust solids by mixing on a horizontal shaker at 120 rpm for 5 d. Sample vials were centrifuged at 1500 rpm for 30 min to achieve phase separation, and the aqueous and solid phases were separately extracted with solvents and analyzed for chemical concentrations to derive C_s and C_w.

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.

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
	Desulfinyl	43.7		0.82
Dust	Sulfide	182	$L\ kg^{-1}$	0.70
	Fipronil	21.9		0.71
	Sulfone	93.3		0.74
	Desulfinyl	12.9		0.88
Soil	Sulfide	21.4	$L\ kg^{-1}$	0.90
	Fipronil	4.75		0.84
	Sulfone	16.6		0.90

According to the K_f values generated in this study, fipronil sulfide has the greatest sorption capacity for soil (21.4), followed by fipronil sulfone (16.6), fipronil desulfinyl (12.9), and the parent compound fipronil (4.75). 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 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%). 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), followed by fipronil sulfone (93.3), fipronil desulfinyl (43.7), and then fipronil (21.9). 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 particles. 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 used 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%, much higher than the organic carbon content of most soils in the region. Since organic carbon content is the main driver of pesticide sorption, this finding helps 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.

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 or dust due to its alkalinity and complex interior pore system introduced by the curing and hydration processes (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 desulfinyl (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.

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 compartment was high, likely due to uncontrolled differences in pesticide use history, land cover, and landscape characteristics. 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). An examination of relative concentrations of fiproles in the runoff water 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. 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. 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.

Table 2. Descriptive statistics for urban solid and urban runoff samples.

Matrix	Units	Compound	DF%	Median	75th Percentile	90th 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, [e] Below detection limit
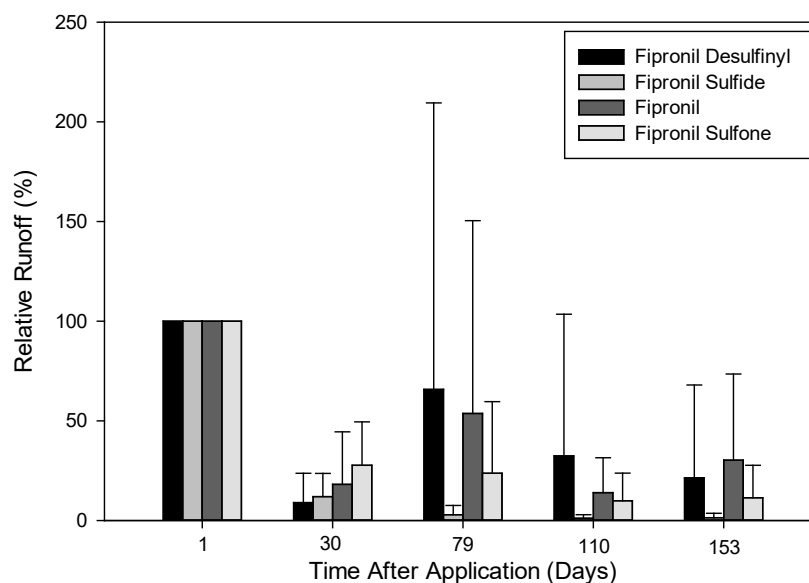
Figure 1. Relative runoff concentrations (expressed as percent of 1 d values) of fiproles in residential runoff following fipronil application. Error bars are mean ± 1 SD.
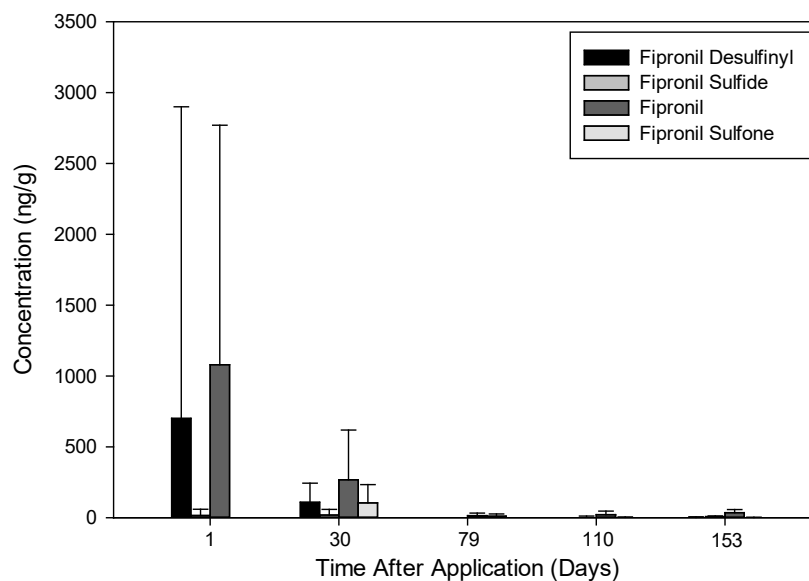

Figure 2. Concentrations of fiproles in urban dust collected from residential areas following fipronil application. Error bars are mean ± 1 SD.

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. Gradual formation of fipronil sulfone was apparent beginning at the 30 d sampling point. The mean concentration of fipronil sulfide remained relatively low 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.
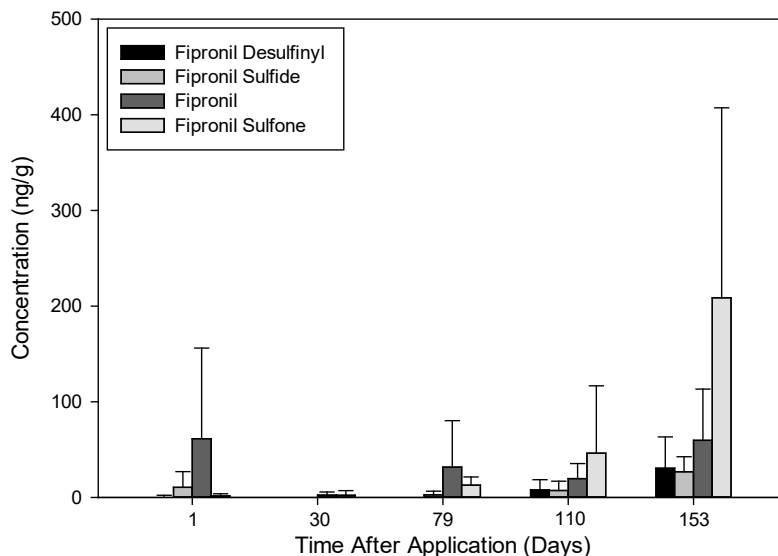

Figure 3. Concentrations of fiproles in soil collected from residential areas following fipronil application. Error bars are mean ± 1 SD.

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. 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 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). Soil concentrations were low relative to dust concentrations likely 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., 2016). 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.
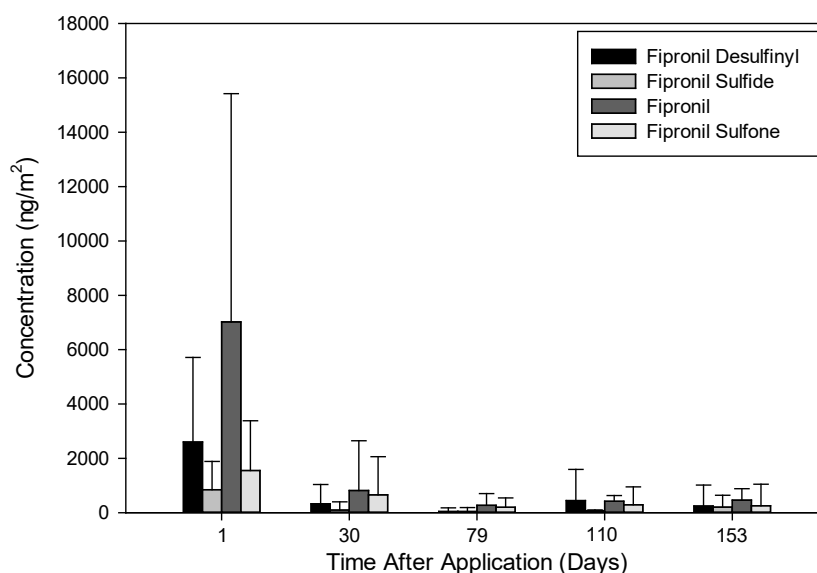

Figure 4. Concentrations of fiproles on residential concrete following fipronil application. Error bars are mean ± 1 SD.

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 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 µg 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 µg m^{-2}) than the other degradates, second only to the parent compound (25.4 µg m^{-2}).

Understanding 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 levels in runoff water (Table 3). The goal of these analyses was to identify primary sources for fiproles in urban runoff. Statistically significant relationships existed between the runoff and concrete concentrations of fipronil desulfinyl, fipronil sulfide, fipronil, and fipronil sulfone. Significant relationships were also found between the runoff and dust concentrations of fipronil desulfinyl and fipronil. Previous studies also implicated dust particles in the offsite transport of hydrophobic organic contaminants (Jiang et al., 2016; Richards et al., 2016), but the present study was the first to directly evaluate the connection between dust and runoff loads of fiproles. 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 at the surface 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., 2016).

Table 3. Linear regression analysis of mean runoff concentrations versus mean urban solid concentrations. Statistically significant regressions (P < 0.05) are indicated by *.

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

[a] Runoff concentrations expressed in units of ng L^{-1}

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

[d] Concrete concentrations expressed in units of ng m^{-2}

Summary and Implications

Data presented in this study provided evidence that dust on paved surfaces was likely the primary source of fiproles for the contamination of urban runoff. The contamination of dust particles on the pavement could include two probable causes: 1) contamination of pre-existing dust during pesticide spray treatments, and 2) redistribution of fine surface soil particles from nearby environments onto the paved surfaces due to wind-, traffic- and water-facilitated movement. The fact that dust collected from paved surfaces have much higher organic matter content than a bulk soil and that dust particles also have larger surface areas underpin the significant role of dust and fine soil particles in trapping contaminants such as pesticides and subsequently contributing to urban runoff contamination.

Fipronil is a moderately hydrophobic compound (log K_{ow} = 3.9-4.1) and its metabolites fipronil sulfone, fipronil desulfinyl, and fipronil sulfide have comparable hydrophobicity. Therefore, behaviors of fipronil after outdoor applications should have close relevance for

insecticides such as pyrethroids that are hydrophobic. Therefore, fine soil and dust particles should play an even greater role in contamination of runoff water by pyrethroid insecticides. On the other hand, the phase distribution and movement of polar and water-soluble insecticides such as neonicotinoids may differ greatly, and the role of movement in the dissolved form may be predominant. In addition, chemicals in dissolved form are capable of travel over longer distance and are present in water column. These differences must be considered in assessing and mitigating risks of hydrophobic and polar pesticides in urban environments.

For hydrophobic pesticides such as fipronil and pyrethroids, mitigation efforts should start with minimizing the contamination of soil and concrete surfaces. Modifying pesticide application practices among pest management professionals is the first step toward effective mitigation. For example, avoiding application on dusty concrete surfaces or spraying onto bare soil surfaces may be promoted as strategies to reduce runoff contamination. For polar pesticides such as imidacloprid, as they may quickly migrate into subsurface soil layers due to weak sorption, a time interval between application and the onset of irrigation events or rain events should be strongly recommended to minimize the potential of runoff water contamination.

References

Cryder, Z., L. Greenberg, J. Richards, D. Wolf, Y.Z. Lou, and J. Gan. 2019. Fiproles in urban surface runoff: Understanding sources and causes of contamination. *Environmental Pollution* 250: 754-761.

Greenberg, L., Rust, M.K., Richards, J., Wu, X., Kabashima, J., Wilen, C., Gan, J., and D.H. Choe. 2014. Practical pest management strategies to reduce pesticide runoff for Argentine ant (Hymenoptera: Formicidae) control. *Journal of Economic Entomology* 107: 2147-2153.

Jiang, W. and J. Gan. 2012. Importance of fine particles in pesticide runoff from concrete surfaces and its prediction. *Environmental Science & Technology* 46: 6028-6034.

Jiang, W., and J. Gan. 2016. Conversion of pesticides to biologically active products on urban hard surfaces. *Science of the Total Environment* 556: 63-69.

Jiang, W., Luo, Y., Conkle, J.L., Li, J., and J. Gan. 2016. Pesticides on residential outdoor surfaces: Environmental impacts and aquatic toxicity. *Pest Management Science* 72: 1411-1420.

Richards, J., Reif, R., Luo, Y., and J. Gan. 2016. Distribution of pesticides in dust particles in urban environments. *Environmental Pollution* 214: 290-298.