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Wash-off potential of pyrethroids after use of total release fogger products

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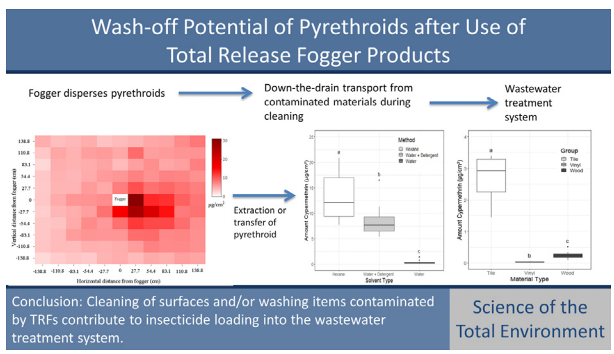
HIGHLIGHTS

- Transferability of insecticide is studied after a simulated total release fogger use
- Insecticide from the fogger is transferred from contaminated items via contact
- Detergent in water increases the extraction of insecticide from contaminated items
- Extracted insecticides can enter the wastewater system via down-the-drain transport

GRAPHICAL ABSTRACT



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ABSTRACT

Pyrethroids are frequently detected in urban wastewater. Even though treatment facilities remove most pyrethroids (> 90 %) in wastewater, residual concentrations can exceed thresholds that are acutely toxic to sensitive aquatic species. Total release foggers (also known as “bug bombs”) are widely used by the general public for insect control. It was hypothesized that these products serve as a source of pyrethroids entering the urban wastewater through the deposition of the active ingredients on various surfaces and subsequent transfer from the contaminated surfaces to the waste stream through cleaning activities. Based on experiments conducted in an enclosure, we found that substantial amounts of a pyrethroid (i.e., cypermethrin) were deposited on various surfaces after a total release fogger use. A series of experiments simulating scenarios that would be representative of common residential cleaning activities indicated that the pyrethroid could be transferred from the contaminated surfaces to other adsorptive materials via physical contact (with or without water as a solvent). The pyrethroid was readily extracted from the adsorptive materials (cotton fabric and filter paper) when water was used as a solvent. Adding a small amount of detergent to the water significantly increased the extraction efficiency compared to water alone. These results indicate that insecticides used in total release foggers can contribute to insecticide loading into the wastewater treatment system via several possible routes, such as contact with or cleaning of exposed surfaces and washing contaminated clothing after their use within a structure.

1. Introduction

Total release foggers (TRFs) (also known as “bug bombs”) are widely available for the general public's use, commonly utilizing pyrethrins or synthetic pyrethroids (with or without a synergist) as active ingredients (AIs). TRFs function by spraying an insecticide mist into the air, which falls onto exposed surfaces and objects. These products are commonly used to target indoor flying and crawling pests such as ants, bed bugs, German cockroaches, spiders, flies, and mosquitoes. Despite the widespread use of TRFs, there is a lack of available information regarding their effectiveness for controlling many of these pests under

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field conditions. Recent experiments have suggested that these products are ineffective for field populations of bed bugs and German cockroaches due to high pyrethroid resistance in field populations and a lack of penetration into the pests' harborage sites (Jones and Bryant, 2012; DeVries et al., 2019a, 2019b). These products can contribute to occupants' inhalation, ingestion, and dermal exposure to insecticidal compounds (Selim and Krieger, 2007; Keenan et al., 2009). Additionally, the misuse of TRFs can have acute impacts on human health (Centers for Disease Control and Prevention, 2008; Forrester and Diebolt-Brown, 2011; Liu et al., 2018).

Insecticides contained in TRFs are frequently detected in surface waters at amounts over toxicity threshold levels, representing a threat to aquatic ecosystems (Stehle and Schulz, 2015). Insecticides are known to enter surface waters via surface runoff from agricultural (Stehle and Schulz, 2015) and urban sources (Jiang et al., 2012). While much research has focused on the contribution of agricultural insecticides to surface water contamination, less is known about the role that indoor applications of insecticides contribute to pesticide loading in waterways. Pyrethroids have been detected in the influent and effluent of wastewater treatment plants, representing an additional source of insecticides entering surface waters (Weston and Lydy, 2010; Weston et al., 2013; Markle et al., 2014; Teerlink, 2014). While some insecticide contaminants will be removed or reduced by wastewater treatment facilities (e.g., >90 % for pyrethroids), residual insecticides that are not removed during water treatment will be discharged into surface waters, threatening aquatic ecosystems (Weston et al., 2013; Teerlink, 2014). Despite frequent detections, the sources and mechanisms of down-the-drain mass loading of pyrethroids are largely unknown (Teerlink, 2014).

As insecticides are commonly used in residential homes to control urban pests, many insecticides are found on residential floors and indoor dust (Julien et al., 2008; Stout et al., 2009). Findings by Weston et al. (2013) suggested that pyrethroid inputs from indoor activities within residential areas are a significant source of pyrethroids in wastewater. This study detected pyrethroids in wastewater influent originating from residential areas at higher concentrations than found in urban runoff, suggesting that down-the-drain transport of pyrethroids from residential homes is a significant source of pyrethroids entering treatment facilities (Weston et al., 2013). The entry mechanisms of insecticides into the waste stream are largely conceptual. Sutton et al. (2019) provides a conceptual model that discusses possible sources of pesticides entering the municipal wastewater system, with two major potential sources of down-the-drain transport being the cleaning of contaminated surfaces or washing of clothing. However, very little empirical evidence exists linking an application source as a major transport pathway into the wastestream. Teerlink et al. (2017) found that fipronil from dogs treated with spot-on products could be removed during washing. In addition, products containing permethrin used to control head lice and scabies may also contribute to the down-the-drain transport of the pyrethroid into the water treatment system during normal use (Weston et al., 2013; Sutton et al., 2019). Such sources may be of interest as permethrin has been found in higher amounts than other pyrethroids detected in wastewater treatment influent and effluent in several studies (Weston and Lydy, 2010; Weston et al., 2013; Markle et al., 2014; Teerlink, 2014).

A product survey of California retail stores found that cypermethrin was the most common active ingredient in TRFs available to the general public (Budd and Peters, 2018). In addition, Xie et al. (2021) estimated that TRFs accounted for over 40 % of all cypermethrin use by consumers. With an estimated use of 50 million TRFs annually in 2010 (Environmental Protection Agency, 2010), these products represent a significant release of pyrethroids into households. Total release foggers disperse their active ingredients across all exposed surfaces within the range of the product but primarily settle on the floor (Keenan et al., 2009, 2010). The active ingredients deposited on various surfaces can be subsequently transferred to clothing (Ross et al., 1990; Keenan et al., 2009). This provides a possible route for down-the-drain transport when the contaminated surfaces or clothing are washed, representing a potential source of pyrethroids entering the wastewater treatment system.

To understand the potential connection between the use of TRFs and pyrethroids in the wastewater systems, information on potential mechanisms by which an insecticide enters the wastewater treatment system will be helpful. To address this, we first determined the depositional pattern and quantity of a pyrethroid insecticide on various surfaces after releasing a fogger product in an enclosed space. By simulating various scenarios of transfer and extraction, the current study also investigated the potential for deposited pyrethroids to be transferred from the contaminated surfaces to other adsorptive materials (via physical contact) and subsequently into water (via extraction).

2. Materials and methods

2.1. Tent

A recreational tent (Ozark Trail 6-Person ConnecTent; 3.048 × 3.048 m; 2.49 m center height) was used as a test enclosure. Vents in the top of the tent were sealed with plastic sheets. At the bottom of the tent, interconnecting foam floor tiles (≈ 2.75× 2.75 m; Cap Barbell Inc., Houston, TX, USA) were used to provide a level floor surface. The floor was covered with butchers paper, which was replaced after each trial to prevent cross-contamination. The ambient conditions inside the tent when the fogger was activated was 24.3 ± 1.7 °C (mean ± SE; $n = 6$) and 33 ± 4.2 % RH (mean ± SE; $n = 6$).

2.2. Fogger

Product choice was based on an online search and a survey of a retail store. The product, Hot Shot® Fogger with Odor Neutralizer (0.05 % tetramethrin, 0.75 % cypermethrin (wt/wt), United Industries Corporation, St. Louis, MO, USA), was chosen as a representative TRF for this study. In all experiments, the fogger was released on a level platform (0.5 m height) placed in the center of the tent floor. The fogger was elevated above ground level per label instructions. After shaking the can, the release valve was pressed, hooking the catch while the can was stationary on the platform. The orientation of the fogger (release valve oriented towards the bottom right of Fig. 1) was consistent for all experiments. Following fogger activation, the tent was immediately sealed and left overnight to allow for the complete settling of the product.

2.3. Deposition study on horizontal surfaces - floor

To understand the deposition characteristics (e.g., quantity and spatial pattern) of the active ingredient of the fogger product, the following experiment was conducted. An 11 × 11 square grid with 27.7 cm between points was marked on the tent floor. Numbered filter paper (Whatman #1, Cytiva, Marlborough, MA, USA) squares (5 × 5 cm; $n = 120$) were placed on each point and secured to the floor of the tent with insect mounting pins. The fogger occupied the central point in the grid. The fogger was activated, and the tent was left sealed overnight.

Each piece of paper was collected approximately 18 h after product activation and placed individually into sealable plastic bags, and stored at −20 °C until extraction. All samples were extracted within 14 d of collection. From each square, a 1 × 1 cm square sample was cut out of the same corner and placed into a 2-ml glass vial (Agilent Technologies, Santa Clara, CA, USA). For each sample, 200 μl of hexane was added, and the vial was vortexed for approximately 4 s. From each sample, 40 μl hexane extract was removed and placed into a new vial containing a glass insert (250 μl, Agilent Technologies) for gas chromatography (GC) analysis (see Chemical analysis Section 2.9). This experiment was replicated three times.

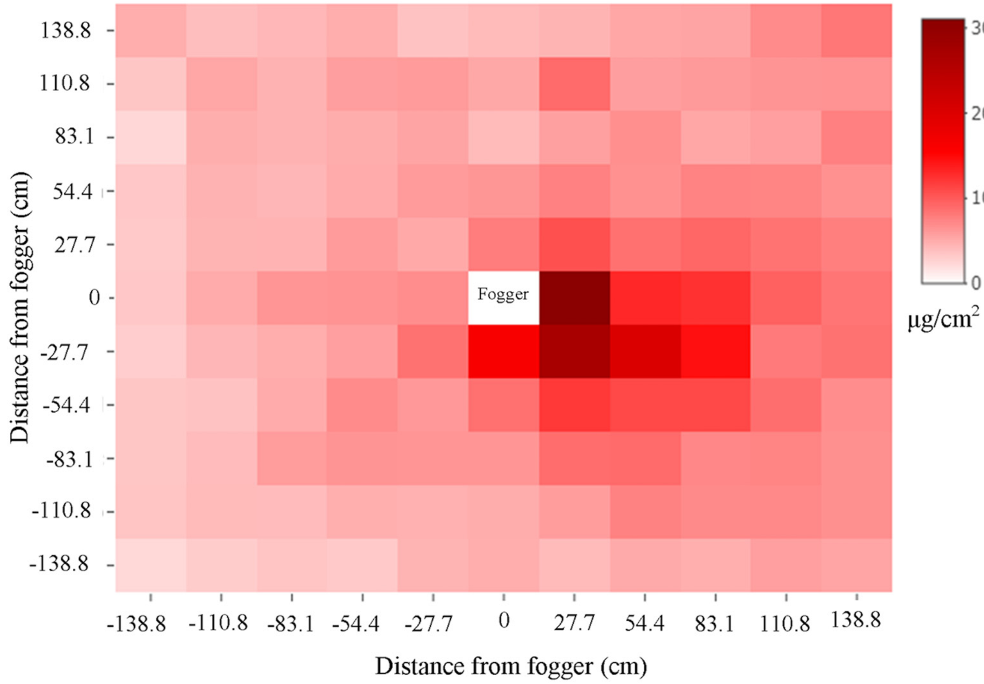

Fig. 1. Average heat map of cypermethrin deposits (μg/cm^2; $n = 3$) at various distances (cm) from an elevated (0.5 m) centrally placed fogger.

2.4. Transfer of insecticide via static or rubbing contact

To examine the transfer of insecticide from one surface to an adsorptive material (i.e., filter paper) with water as the solvent, two methods of extraction (static contact and rubbing contact) were tested. This would simulate a cleaning activity such as mopping of the contaminated surface. Six ceramic tiles (10.5 × 10.5 cm; American Olean, Dallas, TX, USA) with glazed surfaces were arranged along the perimeter of a square (1.66 × 1.66 m) surrounding the fogger at its center (this corresponds to the 83 cm distance in Fig. 1). After the activation and settling of the product, the tiles were collected and stored individually in plastic bags at −20 °C until extraction. For the static contact extraction, a 1 × 1 cm filter paper square was placed onto a corner of the tile. Twenty microliters of deionized water were added to the filter paper. After 10 s, the filter paper square was carefully removed from the tile surface by lifting it straight up. The filter paper square was placed into a 2-ml glass vial, and these vials were left uncovered in a fume hood for 24 h to dry. In each vial, 200 μl of hexane was added, and the sample was vortexed thoroughly. Finally, 40 μl of the hexane extract was pipetted out and placed into a new vial with a glass insert for GC analysis.

The second method included rubbing contact between the filter paper and the tile surface. A filter paper square (1 × 1 cm) was placed onto the upper left corner of the tile, and 20 μl deionized water was applied to the filter paper. Subsequently, with a pair of fine forceps, the filter paper was dragged 8 cm along the edge of the tile. This filter paper was then removed and extracted as described above for the static contact extraction.

2.5. Transfer of insecticide from vinyl, wood, and tile surfaces

To examine the transfer of insecticide from various surface materials to an adsorptive material (i.e., filter paper) with water as the solvent, the dragging method was repeated on various surfaces. Eight filter paper squares (5 × 5 cm) were arranged along the perimeter of a square (1.66 × 1.66 m) with the fogger located at the center, serving as the reference for pyrethroid quantification. Around each filter paper square (5 cm away), three types of materials were placed. Tiles (10.5 × 10.5 cm) were placed above, vinyl flooring (9.5 × 10 cm; Invista, Wichita, KS, USA) to the left, and acacia laminate wood flooring (10 × 10 cm; Lowe's Companies, Inc., Mooresville, NC, USA) to the right, relative to the tent entrance.

The filter paper squares were extracted as described for the floor dispersal study. The tiles, vinyl, and wood were sampled by placing a 1 × 1 cm square of filter paper on a corner and adding 20 μl deionized water before dragging the paper over 10 cm along each surface. Each paper was then placed separately into a 2-ml vial, allowed to dry overnight, and subsequently extracted with 200 μl hexane as described for the floor deposition experiment.

2.6. Transfer of insecticide from carpet surface (clean vs. dusty and contact only vs. contact with friction)

To test the transfer of insecticide from carpet to an adsorptive material without any solvent, transfer from the clean and dusty carpet was tested. This would simulate contact between the contaminated carpet surface and other materials such as socks or pants. Twenty 12 × 12 cm squares of carpet (Shaw reclaim rr textured heirloom interior carpet; polyester) were left outdoors on a rack under building eaves for approximately 4 wk. An additional twenty squares of carpet remained indoors. Twenty filter paper squares (5 × 5 cm) were spaced evenly along the perimeter of a square (1.66 × 1.66 m) with the fogger in the center, serving as the reference for pyrethroid quantification. This trial was done concurrently with a second carpet experiment (see below). The carpet squares were separated from each other by 1 cm and were placed 1 cm from the filter paper.

The carpet was sampled by placing a clean 5 × 5 cm square of filter paper on top of each square. Filter paper squares were divided by placing a large clean tile (12 × 12 cm) on top of each filter paper, completely covering the carpet. Samples were then stacked in this manner, and 9.75 kg of weight was placed on top for 24 h. This weight was chosen to simulate a person (64.3 kg) with an average total foot contact area (81.8 cm^2) standing on a carpet and transferring material to their socks (Birtane and Tuna, 2004). Samples from the clean vs. dusty groups were extracted separately. The filter paper squares were then collected and extracted as described for the floor deposition study.

To determine if the active rubbing influences the amount of insecticide transferred from the carpet surface, two additional 12 × 12 cm squares of clean carpet were placed around each filter paper square during the experiment described above. The carpet squares were placed 1 cm apart from each 5 × 5 cm square of filter paper. One group of carpet squares ($n = 20$) were extracted with the presence of friction. These carpet squares were placed on a benchtop shaker (Clinical Rotator Model 341; Fisher Scientific International, Pittsburgh, PA, USA) with a clean filter paper square (5 × 5 cm) placed in the center of each carpet square. The carpet was then covered with a glass square (12 × 12 cm), and 1 kg of sand in a flask was placed on top. Less weight was used for the friction experiment due to weight limits of the shaker. The shaker was activated and after 10 min, the filter paper square was collected. This would simulate contact between the contaminated carpet surface and other materials such as socks or other clothing with some amount of friction. The second group of carpet squares ($n = 20$) were sampled in the same manner but with weight alone (static). Each carpet square was extracted individually. The glass squares were cleaned thoroughly with acetone between trials. The filter paper was extracted as described for the floor deposition experiment.

2.7. Wash off from filter paper and fabric

To examine how much insecticide can be washed off from filter paper and fabric materials that are exposed to the fogger product, the following experiment was conducted. This experiment would simulate washing or laundering of the contaminated clothes or other fabric materials (e.g., mop). On the tent floor, 24 points were marked evenly along the perimeter of a square (1.66 × 1.66 m) with the fogger located in the center. A 5 × 5 cm piece of filter paper and cotton fabric were placed 1 cm from each side of the marked point. From each fabric and filter paper square, three 1 × 1 cm squares were cut and individually placed into 2-ml glass vials.

Three different solvent types [hexane, water, and water + detergent (1 % Liquinox®; Alconox Inc., White Plains, NY, USA)] were used for initial extraction of each type of material (filter paper and cotton fabric). To extract with hexane, 200 μl of hexane was added into the vial and vortexed. An aliquot (40 μl) of hexane extract was pipetted out and transferred to a new vial with a glass insert. For water extraction, 200 μl of deionized water was first added into the vial and vortexed. The entire water extract was pipetted out from the vial and transferred to a new vial. After adding 200 μl hexane, the vial was vortexed again before removing 40 μl of the hexane layer to a new vial with a glass insert. For the water + detergent extraction, 200 μl of a 1 % detergent solution in deionized water was used for the initial extraction. After vortexing, the extract was pipetted out and transferred to a new vial. After adding 200 μl hexane, the vial was vortexed. Since the mixture formed an emulsion, the samples were stored at −20 °C overnight to separate the mixture. From the hexane layer, 40 μl was pipetted out and placed into a new vial with a glass insert for GC analysis.

2.8. Extraction from spiked filter paper

Based on the Safety Data Sheet (SDS) of the fogger product (Hot Shot Fogger with Odor Neutralizer, 2016), light aromatic naphtha (2 % wt/wt) and petroleum distillates (3.75 %) are among the other ingredients of the product, besides the pyrethroids (0.8 %) and propellants (30 %). The remaining ingredients are either proprietary or non-hazardous and are not identified on the SDS. To determine the effect of these other ingredients on the amount of insecticide removed from a material with water as a solvent, the following experiment was conducted. Crude material from the fogger product was obtained by freezing the fogger can at −20 °C overnight and then puncturing the can to release only the propellant. The crude residue was diluted with acetone, and cypermethrin was quantified using an external standard (see chemical analysis). Based on the quantification, an aliquot (2 μl) of crude material was applied to 1 × 1 cm filter paper squares inside 2-ml glass vials, providing 25 μg of cypermethrin from the fogger crude material applied per filter paper square. For comparison, 25 μg of technical cypermethrin (> 90 %; Sigma-Aldrich, St. Louis, MO, USA) dissolved in acetone was applied to 1 × 1 cm filter paper squares inside 2-ml glass vials. The vials were allowed to dry uncapped overnight in a fume hood. These were then extracted using the three solvents (hexane, water, and water + detergent) as described in the previous section. Final hexane extracts were analyzed with a GC. Ten replications were conducted for each combination of cypermethrin source (crude or technical) and solvent (hexane, water, and water + detergent).

2.9. Chemical analysis

Between the two active ingredients present in the fogger product used, cypermethrin was chosen for chemical quantification due to its higher abundance in the product (i.e., 0.05 % tetramethrin, 0.75 % cypermethrin). The amount of tetramethrin in each sample was not determined. An automatic liquid sampler (ALS) was used to inject 2 μl of the hexane extract onto an Agilent 7890 gas chromatograph equipped with a DB-5 column (30 m × 0.25 mm inner diameter) and a flame ionization detector. Helium was used as the carrier gas, and samples were injected in splitless mode, with a temperature program of 50 °C for 1 min and then 10 °C min − 1 to 300 °C with a 10-min hold. The integration values of four peaks representing diastereomers of cypermethrin were summed (Liu and Gan, 2004). The amounts of cypermethrin in extracts and samples were determined by comparison to a calibration curve established from samples with various concentrations of technical grade cypermethrin (0.3125, 0.625, 1.25, 2.5, 5, 10, 20, 30, 40, 60, and 70 μg/ml in hexane) analyzed on the same instrument above. In experiments that involved the moving (dragging) of filter paper across a surface (Sections 2.4 and 2.5), the total amount of cypermethrin was divided by the area sampled to determine the amount of cypermethrin per square centimeter area.

2.10. Statistical analysis

Data were analyzed by conducting Shapiro-Wilk and Levene's tests to determine if there was non-normality or heteroscedasticity, respectively. When present, non-parametric tests were used to compare data. Kruskal–Wallis H test followed by Dunn's Multiple Comparisons were used to analyze the different surface types (vinyl, wood, tile), and the wash-off testing done both in the tent and with spiked filter paper. Two-sample *t*-tests were used to compare the amount of cypermethrin for the static and friction tile sampling and the extractions of samples spiked with known amounts of cypermethrin. Finally, Wilcoxon rank-sum tests were used to analyze both carpet experiments. The percent of transfer was calculated for each material based on the amount of cypermethrin recovered from filter paper in each experiment. This provides an estimate for the total amount of cypermethrin that was deposited on each surface. For the extractions using water, hexane extractions were used as an estimate for the total amount of cypermethrin. All statistical analyses were done using R version 4.0.3 (R Core Team, 2020).

3. Results

3.1. Deposition study on horizontal surfaces - floor

An average amount of 6.76 ± 2.23 μg/cm^2 (mean ± SD, $n = 3$) of cypermethrin was found on the floor of the tent (Fig. 1). On average, there was a wide range of amounts found, from a maximum of 31.05 μg/cm^2 directly adjacent to the fogger to a minimum of 2.36 μg/cm^2 in one of the tent corners (Fig. 1). There was a range of 59.04 to 0.003 μg/cm^2 cypermethrin among the total 360 samples collected. Based on the median value (5.77 μg/cm^2; $n = 360$) applied evenly across the tent floor surface area, we estimate 106 % of the product mass on the floor based on the label concentration.

3.2. Transfer of insecticide via static or rubbing contact

There was a significant effect of rubbing action on the amount of cypermethrin removed, $T = 4.623$, df = 10, $P < 0.001$, from the tile surface. Significantly more cypermethrin was removed when the filter paper was dragged (1.21 ± 0.17 μg/cm^2; Mean ± SE; n = 6) compared to the filter paper that remained static (0.35 ± 0.04 μg/cm^2; n = 6) (Fig. S1). Based on these results, actions such as wiping down a surface while cleaning would remove more cypermethrin per unit of surface area than static contact.

3.3. Transfer of insecticide from vinyl, wood, and tile surfaces

The amount of cypermethrin recovered from the reference filter paper (6.29 ± 0.57 μg/cm^2; n = 8) provides an estimate for the total amount deposited onto each surface. When a wet filter paper square was dragged along each surface, the amount of cypermethrin removed from vinyl, wood, and tiles were significantly different (H = 20.48, df = 2, P < 0.001). The amounts of cypermethrin recovered from tile (3.06 ± 0.32 μg/cm^2; n = 8), vinyl (0.03 ± 0.005 μg/cm^2; n = 8) and wood (0.26 ± 0.04 μg/cm^2; n = 8) were all significantly distinct (Dunn's Multiple Comparisons; P < 0.05) (Fig. 2). Relative to the reference filter paper, 48.6 % of the cypermethrin was recovered from the tile, compared with 0.5 % and 4.1 % from the vinyl and wood, respectively (Table 1). These results show how the amount of cypermethrin that is removed from surfaces is greatly affected by the material type.

3.4. Transfer of insecticide from carpet surface (clean vs. dusty and contact only vs. contact with friction)

The amount of cypermethrin recovered from the reference filter paper (12.79 ± 0.523 μg/cm^2; n = 20) provided an estimate for the total amount deposited onto each surface. Amounts of cypermethrin transferred by contact with static weight for 24 h from the clean (0.587 ± 0.049 μg/cm^2; n = 20) or dusty carpet (0.567 ± 0.038 μg/cm^2; n = 20) were similar (W = 210, df = 1, P = 0.787) (Fig. S2). These amounts represent a transfer rate of 4.6 and 4.4 % from the clean and dusty carpet, respectively (Table 1).

The amount of cypermethrin transferred with friction (0.174 ± 0.015 μg/cm^2; n = 20) was significantly greater than without (0.048 ± 0.004 μg/cm^2; n = 20) (W = 399, df = 1, P < 0.001) (Fig. S3). With the addition of friction, 1.4 % of cypermethrin was transferred, while 0.4 % was transferred through static contact alone (Table 1).

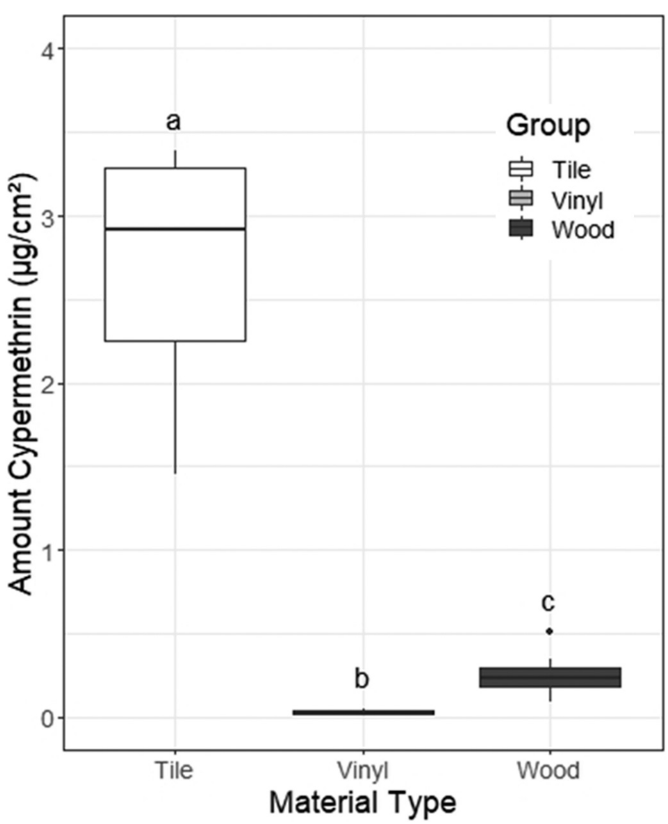

Fig. 2. Amount of cypermethrin (μg/cm^2) transferred from tile (n = 8), vinyl (n = 8) and wood (n = 8) squares following dragging of wet filter paper square across each surface. Letters indicate significant differences (Dunn's Multiple Comparisons, P < 0.05).

3.5. Wash off from filter paper and fabric

The solvent type had a significant effect on the amount of cypermethrin recovered from filter paper (H = 53.6, df = 2, P < 0.001). The amounts of cypermethrin removed from filter paper were significantly different between hexane (16.02 ± 0.94 μg/cm^2; n = 24), water (0.20 ± 0.015 μg/cm^2; n = 24), and water + detergent (11.52 ± 0.498 μg/cm^2; n = 24) as extraction solvents (Dunn's Multiple Comparisons; P < 0.05) (Fig. 3A). Using the data from hexane extraction to estimate the total amount of cypermethrin deposited, 1.2 % was removed using water alone, while 71.9 % was removed if the water contained a detergent (Table 1).

The solvent type likewise had a significant effect when tested on cotton fabric (H = 54.9, df = 2, P < 0.001). The amounts of cypermethrin removed by hexane (13.13 ± 0.872 μg/cm^2; n = 24), water (0.33 ± 0.057 μg/cm^2; Mean ± SE; n = 24), and water + detergent (8.32 ± 0.499 μg/cm^2; n = 24) were all significantly different (Dunn's Multiple Comparisons; P < 0.05) (Fig. 3B). The transfer rates of cypermethrin into water were 2.5 and 63.4 % for water only and water with a detergent, respectively (Table 1).

3.6. Extraction from spiked filter paper

When the filter paper was spiked with 25 μg cypermethrin from the fogger crude material, the solvent type had a significant effect on the amount of cypermethrin extracted (H = 25.8, df = 2, P < 0.001). The amounts of cypermethrin recovered were significantly different between hexane (25.207 ± 0.244 μg/cm^2; n = 10), water (0.015 ± 0.002 μg/cm^2; n = 10), and water + detergent (7.741 ± 0.625 μg/cm^2; n = 10) extractions (Dunn's Multiple Comparisons; P < 0.05) (Fig. 4A).

Similarly, the solvent type had a significant effect on the amount of cypermethrin recovered from filter paper spiked with 25 μg of technical cypermethrin (H = 25.8, df = 2, P < 0.001). The amounts of cypermethrin recovered were significantly different between hexane (26.038 ± 0.868 μg/cm^2; n = 10), water (0.006 ± 0.001 μg/cm^2; n = 10), and water + detergent (7.169 ± 0.452 μg/cm^2; n = 10) extractions (Dunn's Multiple Comparisons; P < 0.05) (Fig. 4B). In one sample (water extraction of technical cypermethrin), no cypermethrin was detected and was included as a zero for the analysis.

When comparing between cypermethrin sources (i.e., fogger crude material vs. technical compound) within a solvent type, there was no significant difference in the amount recovered for hexane (T = −0.328, df = 18, P = 0.747), or water + detergent (T = 0.705, df = 18, P = 0.49). However, significantly more cypermethrin was removed from the filter paper treated with crude fogger material (0.015 ± 0.005 μg/cm^2; n = 10) than the filter paper treated with technical cypermethrin (0.006 ± 0.002 μg/cm^2; n = 10) when extracted with water alone (T = 3.651, df = 18, P = 0.002).

4. Discussion

The use of TRFs is known to leave a residue on all surfaces and items that are exposed during treatment (Keenan et al., 2009). A product survey of retail stores in Northern California found that cypermethrin was the most common active ingredient in the indoor pest control products that are available to the general public (Budd and Peters, 2018). Using one of the many available TRF products containing cypermethrin as an AI as an example, we found that the active ingredient (cypermethrin) deposited onto

Table 1
Summary of average amount of cypermethrin transferred from various materials and the percent of recovery based on estimated total deposition.

Material: From	Material: To	Extraction method	Estimated total cypermethrin deposited (Mean ± SE; $\mu g/cm^2$)	Amount of cypermethrin transferred (Mean ± SE; $\mu g/cm^2$)	Transfer rate (%)
Tile	Filter paper	Physical contact (rubbing)	6.29 ± 0.57	3.06 ± 0.32	48.6
Vinyl				0.03 ± 0.005	0.5
Wood				0.26 ± 0.04	4.1
Carpet (dusty)		Physical contact (static with weight)	12.79 ± 0.523	0.567 ± 0.038	4.4
Carpet (clean)				0.587 ± 0.049	4.6
		Physical contact (static)		0.048 ± 0.004	0.4
		Physical contact (friction)		0.174 ± 0.015	1.4
Filter paper	Water	Solvent extraction (water)	16.02 ± 0.94	0.20 ± 0.015	1.2
		Solvent extraction (water and detergent)		11.52 ± 0.498	71.9
Cotton fabric		Solvent extraction (water)	13.13 ± 0.872	0.33 ± 0.057	2.5
		Solvent extraction (water and detergent)		8.32 ± 0.499	63.4

common indoor structural surfaces can be transferred to other adsorptive materials via physical contact simulating typical activity within the home by residents. The current findings suggest that cypermethrin can be subsequently extracted into the water in substantial amounts when those adsorptive materials are washed using a detergent simulating washing of indoor surfaces or laundering of contaminated clothing. Our results provide empirical evidence to support these possible routes by which common usage of TRFs by the general public can contribute to insecticide loading into wastewater treatment systems.

The deposition pattern of cypermethrin on the floor after a total release fogger use was not homogeneous throughout the test chamber. There was a distinct directionality to product deposition that remained consistent during testing. Interestingly, Selim and Krieger (2007) activated their foggers while set on a rotating surface to achieve even distribution and prevent

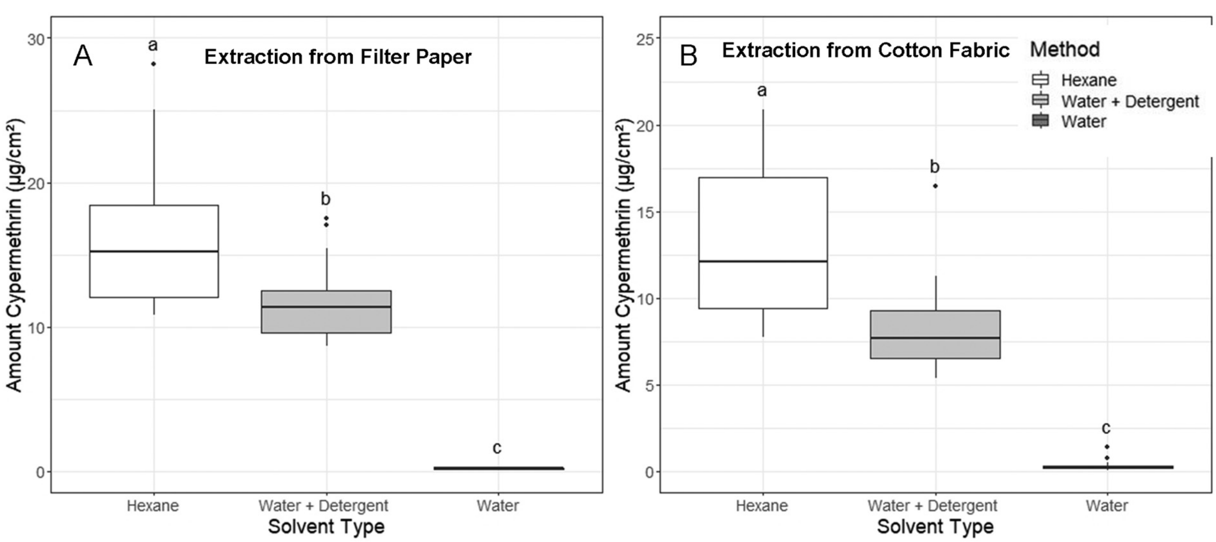

Fig. 3. Amount of cypermethrin ($\mu g/cm^2$) removed from filter paper (a) ($n = 24$) or cotton fabric (b) ($n = 24$) when extracted with hexane, water, or water with detergent following fogger activation. Letters indicate significant differences (Dunn's Multiple Comparisons, $P < 0.05$).

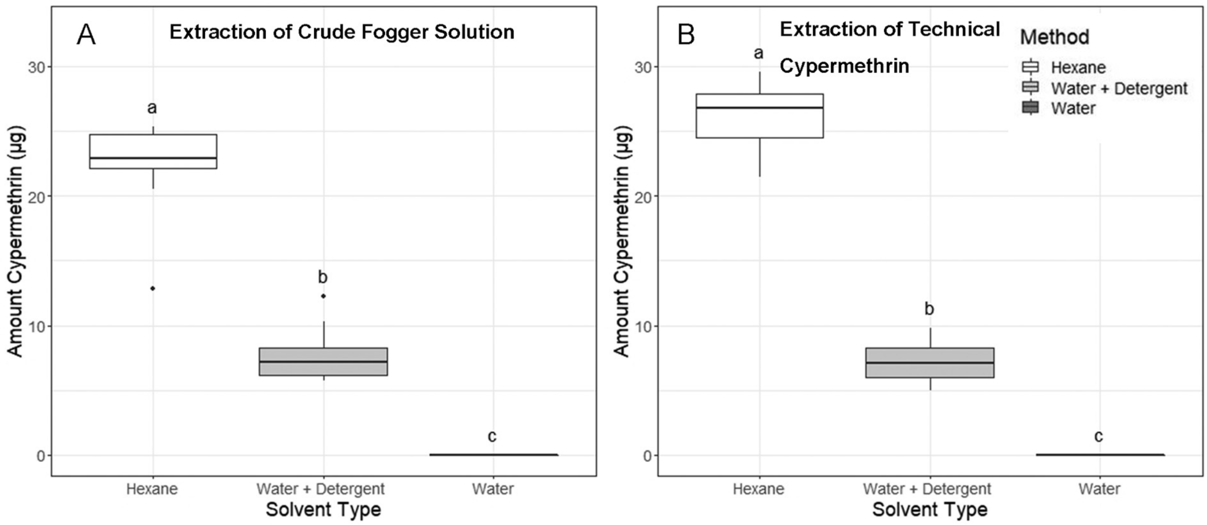

Fig. 4. Amount of cypermethrin (μg) removed from filter paper (1 cm^2) spiked with 25 μg cypermethrin from crude fogger solution (a) or technical material (b) when extracted with hexane ($n = 10$), water ($n = 10$), or water with detergent ($n = 10$). Letters indicate significant differences (Dunn's Multiple Comparisons, $P < 0.05$).

the semi-directional deposition that we observed in our floor deposition experiments. The exact reason for this directionality observed in the current study is unknown. However, it may occur as a result of the fogger nozzle being slightly bent away from the vertical axis when the release valve is depressed upon fogger activation. During all of our experiments, the release valve was oriented in the same direction (the bottom right of Fig. 1), which matches the observed directionality in the floor deposition results. The average amount of cypermethrin per unit area was highest directly adjacent to the fogger release point (max: 31.05 μg/cm^2) and decreased as distance from the fogger increased (min: 2.36 μg/cm^2). Overall, the average amount of cypermethrin deposited on the floor was 6.76 μg/cm^2. Our results follow the pattern reported by Selim and Krieger (2007), who found that increased distance from the fogger resulted in a decreased deposition of pyrethrins. The average amount of floor deposition is similar to those reported by Selim and Krieger (2007), who found average amounts of insecticides on carpet ranging from 3.66 to 10.95 μg/cm^2 after the TRF use. In contrast to our findings that increased distance from the fogger resulted in reduced insecticide deposition, Keenan et al. (2010) found consistent deposition of cypermethrin following fogger treatment. For example, in a 3.1 × 3.1 m test room, they found similar concentrations (average of 4.1 ± 1.2 μg/cm^2) of cypermethrin at various distances from a centrally placed TRF. These differences may be a result of the different methods for measuring surface deposition. For example, the current study sampled floor deposition with greater resolution due to more sample locations compared to Selim and Krieger (2007). The use of different TRFs might be an additional variable as different products likely disperse their products differently.

Keenan et al. (2009) measured the transfer rate of cypermethrin from carpeting, tile, wood, carpet, and linoleum after TRF uses. They found the transfer rate from carpeting was 5 % of total surface residue. Ross et al. (1991) found that 1–3 % of chlorpyrifos and allethrin released from TRFs could be transferred from carpeting to cotton cloth after it was rolled over the carpet surface. These results are comparable to our findings, where 4.6 and 4.4 % of cypermethrin were transferred from clean or dusty carpets to filter paper, respectively. Additionally, Keenan et al. (2009) reported a 30 and 10 % transfer rate of cypermethrin for tile and wood flooring, respectively. In the current study, we found that 48.6 % of cypermethrin was transferred from tile to filter paper, but only 4 % of cypermethrin was transferred for wood flooring. Despite the use of different extraction methods and various surface materials, these results suggest that the transferability of cypermethrin is largely dependent on the characteristics of the surface material and its interaction with the droplets of TRF formulation.

Insecticides are commonly deposited indoors following total release foggers, perimeter sprays, spot sprays, and crack-and-crevice applications (Keenan et al., 2010) and are commonly detected indoors (Julien et al., 2008; Stout et al., 2009). DeVries et al. (2019a) measured the deposition of several AIs from TRFs on various horizontal locations in residential kitchens and found an average increase of 603 times for insecticide residues 4–6 h after TRF discharge relative to the pre-activation baseline. However, the majority (66 %) of samples taken one month later were not significantly increased relative to baseline levels, while 50 % showed moderate increases. As these homes remained occupied following TRF use, this may be at least in part the result of transfer from and cleaning of these horizontal surfaces, which included the floor, counters, and the top of cabinets. This return to baseline concentrations may be a result of human activities such as cleaning or through normal contact made by residents or as a result of degradation of the insecticides over time.

Cypermethrin deposited on exposed surfaces was readily transferred to adsorptive materials with or without water as a solvent. Ross et al. (1990) found that chlorpyrifos and allethrin from a TRF could be transferred to clothing during a standardized Jazzercise routine. This study highlights the potential for such insecticide transfer by foggers, as every surface or item in the range is exposed, and insecticide application cannot be directed, such as when using methods such as baiting. The overuse of TRFs by consumers disregarding the label rate will result in higher levels of deposition on items/surfaces and likely contributes to an increase of down-the-drain transport of these insecticides. Sutton et al. (2019) proposed various potential indoor sources of insecticides entering wastewater, such as use of foggers / sprays, insecticide-treated textiles, and the washing of contaminated clothing (e.g., from occupations such as professional pesticide applicators or agricultural workers). We found that 1.2 and 72 % of cypermethrin was removed when filter paper was extracted with either water alone or water containing a small amount of detergent, respectively. Similarly, 2.5 and 63 % of cypermethrin was removed when cotton fabric was extracted with either water alone or water containing a small amount of detergent, respectively. The inclusion of a detergent greatly increased the amount of cypermethrin removed, strongly suggesting that the laundering of clothing or the cleaning of surfaces contaminated with pyrethroids contribute to down-the-drain disposal of pyrethroids.

The application of insecticides indoors appears to be a likely source of insecticides entering wastewater treatment plants, with various insecticides being detected in wastewater treatment influent and effluent (Weston and Lydy, 2010; Weston et al., 2013; Markle et al., 2014; Teerlink, 2014). For example, Markle et al. (2014) found average cypermethrin concentrations of 35 ng/l in the influent and 110 ng/l in biosolids from a sample of California wastewater treatment plants. Weston et al. (2013) measured the quantity of several common pyrethroids from wastewater samples using interceptors from residential areas and concluded that these were unlikely from stormwater runoff. Weston et al. (2013) concluded that the pyrethroid contamination they found likely occurred as a result of down-the-drain transport from indoor pesticide application due to the separation of the wastewater/stormwater systems and the lack of similarity of the detected insecticides to those previously observed from urban runoff. They further provided an example of how only 2 % of the cypermethrin in a TRF entering the drain in 1 out of 700 houses would account for the levels of cypermethrin detected (23 ng/l and 30 ng/l) in two dry-weather wastewater samples from a residential area (Weston et al., 2013). Our findings support the possibility that TRFs may be a significant source of the insecticides entering the water treatment system. For a hypothetical estimate based on the present results, consider the effects of mopping a tile floor (1 m^2) contaminated by a cypermethrin-based TFR with an average deposition of 6.76 $\mu g/cm^2$. Assuming the same transferability as found for tile to wet filter paper and the extraction of cotton fabric with water plus detergent, 20.8 mg of cypermethrin could be transferred into the wastewater system, amounting to 5 % of the original cypermethrin contents of the TRF (420 mg). A daily entry of 20.8 mg cypermethrin is similar to the 13.8–18 mg cypermethrin entering wastewater each day from 700 homes found by Weston et al. (2013). The daily transfer of only 3.3–4.3 % from a single use of the TRF tested would account for the cypermethrin found entering wastewater from the 700 homes reported by Weston et al. (2013). While this hypothetical calculation makes several assumptions, it demonstrates that a significant amount of cypermethrin may be transported to wastewater during routine cleaning and laundering after TRF application.

Some caution is warranted when interpreting our results, as we tested only one of the many TRF products available and focused only on cypermethrin transfer. The differing chemistries of other pyrethroids may impact the transferability to the wastewater stream. Additionally, experiments were conducted in semi-field conditions only. While our results strongly suggest that down-the-drain transfer of TRF products likely occurs to some extent, we did not directly quantify the down-the-drain movement of insecticides under field conditions. However, this study provides evidence that the movement of insecticides originating from TRFs contributes to the mass loading of insecticides entering water treatment plants, with subsequent potential to enter into surface waters.

CRediT authorship contribution statement

Mark Dery: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Brian Dinh:** Conceptualization, Methodology, Investigation, Data curation, Writing – review & editing. **Robert Budd:** Conceptualization, Methodology, Writing – review & editing. **Dong-Hwan Choe:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.157340.

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