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Measurement of transferable chemical residue from nylon carpet using the California roller and a new mega-California roller

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Human chemical exposures resulting from transfer of surface deposition on indoor nylon carpets may be estimated by measuring transferable residues (μg chemical/cm^2 carpet). A weighted roller developed at California Department of Food and Agriculture (CDFA) has been extensively used to sample transferable residue for estimates of human exposure in risk characterization. A modified roller has been developed to evaluate the influence of pressure on transferable chemical residue since weight and force (or pressure, kg/m^2) may vary person-to-person and activity-to-activity. A 30.5 cm diameter roller was used to apply 60 to 2100 kg/m^2 to bracket pressures exerted by humans on a flat nylon-carpeted surface. Measurements of transferable cyfluthrin residues were made after 1, 7, and 21 days. Total Soxhlet extractable cyfluthrin residues were relatively constant during the test period. Residue transferability decreased during the study period. Modest increases in the transferability of surface residues were observed over the broad range of pressures applied by the modified roller.

Keywords: Transferable residue; cyfluthrin; California Department of Food and Agriculture (CDFA) roller; California roller; exposure assessment; surface residue.

Introduction

Residential exposure to non-fumigant pesticides (those with vapor pressure $<10^{-3}$ mm Hg) following broadcast application is almost exclusively via the dermal route for adults[1] the postulated exposure of children via hand-to-mouth activities is largely believed to be a function of transfer from surfaces to hands or objects.[2] Thus, understanding the determinants of transfer from pesticide-treated surfaces to the skin is critical in estimating residential exposure. Historically, dislodgeable residues have been used as indicators of potential exposure to residents, and many different methods to measure transferability have been evaluated [vacuum sampler,[3] hand press,[4] polyurethane foam (PUF) roller,[5] California roller[6] modified California roller[7] Lioy, Wainman, Weisel (LWW) sampler[8] drag sled[9] solvent wipes[10] etc.]

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Implementation of the new US Environmental Protection Agency (USEPA) regulations on "intentional" dosing studies that may be used for regulating pesticides has virtually eliminated support for new human exposure monitoring studies with any chemical including non-pesticides, but not obviated the need for them.[11] As a result of these new regulations and the policies interpreting them, methods of estimating human exposure that do not require exposure of human volunteers have become more important. However, regardless of need, any method used to estimate human exposure must be valid.

The method most used to measure surface transferable residues in residential environments by governmental regulators and the regulated public is the California roller or some variant thereof. This method of measuring transferable residues has been quantitatively related to human dosimetry following known applications of pesticides.[1] These studies include borax,[12] cyfluthrin,[13] and chlorpyrifos[14–17] and registrant studies that have been referenced in a series of regulatory documents including propetamphos,[18] dichlorvos (DDVP),[19] and pyrethrin.[20] The modified California roller has been

adopted as an industry standard[21] and helped form the basis for regulatory default methods for estimating post-application residential exposure.[22–24]

From prior studies, it is known that several factors can influence transfer of pesticide residues from a treated surface to a person's skin. These factors include moisture,[25,26] time in contact with the surface,[27] amount of pesticide applied[15] and behavior.[28] A key component of behavior is the degree of activity and resulting intensity of contact with a source, i.e., children have been observed to engage in more vigorous activity outdoors than indoors.[29] With increased activity comes potential for increased force or pressure of skin on a treated surface.

The influence of pressure on transferable chemical residue, and ultimately human exposure, has not been extensively evaluated. Weight (kg), and ultimately force or pressure (kg/m^2), may vary substantially between individuals and activities, and may be an important determinant of chemical transfer. Weight can range from less than 10 kg for children to over 100 kg for adults.[22] Activities ranging from lying down, where up to half of the body surface area could be in contact with a treated surface, to walking, where less than 10 percent of the body surface area contacts a surface, result in different contact pressure differences that span an order of magnitude or more.

The modified California roller applies approximately 900 kg/m^2 and can be used to obtain a point estimate of chemical transfer. Using mean values, dividing the adult body weight by the surface area of half the body (1.0 m^2), feet (0.11 m^2), or hands (0.08 m^2) results in a pressure range of 100 – 1250 kg / m^2.[22] To measure transferable chemical residue at varying force, a 12-inch diameter mega-roller has been constructed that can apply 60 to 2100 kg/m^2. This range will fully bracket pressure exerted by humans on a surface. The purpose of this study was to evaluate the influence of weight on transferable chemical residue from nylon carpet 1, 7, and 21 days following application.

Materials and methods

This study was conducted at the University of California, Riverside using new 100% nylon medium pile plush carpet. The test material used to quantify transfer was cyfluthrin (Tempo® 20 WP; EPA Reg. No. 3125–380; Bayer Corporation, Kansas City, MO). The cyfluthrin concentrate was diluted and mixed with water per label instructions to yield a concentration of 0.05% (w/v) prior to application. Applications were made to carpets using a linear spray applicator equipped with a Teejet 8001E spray tip (Spraying Systems Co.®, Wheaton, IL) fixed 35-cm above a conveyer belt and pressurized to 40 psi. Percale cotton cloth-covered foil coupons were sprayed with this system to measure spray deposition (10 × 15 cm; n = 5), small carpet swatches for total chemical residue determination (10 × 15 cm; n = 15), and large carpet swatches for transferable chemical residue measurement (45 × 60 cm; n = 99) were each sprayed with cyfluthrin in random order.

The deposition coupons were collected one hour following application and sealed in Ziploc® bags that were stored frozen (−4°C) until analysis. Deposition coupons were extracted with 150 mL ethyl acetate using an Eberbach shaker for two 10-minute cycles and a 20-mL portion of the extract was retained for analysis. Total chemical residue measurement was made from small carpet swatches collected on days 1 (n = 5), 7 (n = 5), and 21 (n = 3). Carpet swatches were extracted with ethyl acetate in a Soxhlet apparatus. Following extraction a 20-mL aliquot of the 300 mL extract was retained for analysis.

Transferable chemical residue measurements were made in triplicate with the 30-pound modified California roller technique that applied twice the pressure of the 4-inch diameter by 24-inch original California roller described by Ross et al.(1991).[6] A mega-roller was constructed from 12-inch diameter pipe that was 12 inches long. It was fitted with a short handle (ca. 60 cm) that received additional weight with lead shot (0, 11, 23, 34, 46, 57, 68, 80, 91, and 103 kg) on day 1, 7, and 21 following application. For sampling, a 1000 cm^2 cotton percale cloth was placed on a treated carpet. The cloth was covered with heavy rosin paper to avoid contamination (Salinas Valley Wax Paper Co., Salinas, CA). A 45 × 60 cm screen template was placed over the rosin paper. The sampling sandwich was then rolled 10 times, with one roll consisting of a complete forward and backward pass. The screen template was removed, the rosin paper was discarded, and the cotton cloth was collected and sealed in a Ziploc® storage bag before being placed into an insulated box on dry ice. The cotton cloths were extracted with 150 mL ethyl acetate using an Eberbach shaker for two 10-minute cycles on the high setting and a 20-mL portion of the extract was retained for analysis.

Cyfluthrin concentrations were determined by generating a standard curve with chlorpyrifos-methyl as an internal standard chosen for its reproducible retention time and peak area under operating conditions. A Hewlett Packard 5890 gas chromatograph (Palo Alto, CA) equipped with a HP-5 column and an electron capture detector was used. Cyflythrin and chlorpyrifos-methyl standards were obtained from Chemservice (West Chester, PA).

Results and discussion

The cyfluthrin deposition rate, measured from cotton cloth covered foil coupons, was 3.8 ± 0.43 μg/cm^2 (Table 1). Total chemical residue in μg/cm^2, measured from Soxhlet extracted carpet swatches, was 3.9 ± 0.46, 3.5 ± 0.14, and 3.5 ± 0.60 on days 1, 7, and 21, respectively (Table 1). These observations of chemical persistence are consistent with measurements of total chemical residue previously made indoors.[30]

Table 1. Total chemical residue ($\mu g/cm^2$) as a function of time.

	Cyfluthrin deposition	*Total cyfluthrin residue*
Day 0 (application)	3.8 ± 0.43[a]	—
Day 1		3.9 ± 0.46[b]
Day 7		3.5 ± 0.14[c]
Day 21		3.5 ± 0.60[b]

[a]Measured from foil-backed cotton cloth coupons randomly placed and treated during chemical application sequence (n = 5).
[b]Measured from Soxhlet extracted carpet swatches (n = 5).
[c]Measured from Soxhlet extracted carpet swatches (n = 3).

Transferable chemical residue measured with the modified California roller and mega-roller is reported in Table 2. The 13.6 kg California roller gave a transferable residue measurement similar to the mega-roller with 80 kg of added weight. This is potentially due to the larger diameter of the mega-roller (12-inch diameter) compared with the California roller (4-inch diameter). The resulting area of the mega-roller is approximately 1.5-times greater than the California roller. And the effective area of contact of a single revolution of the larger roller on a hard surface is similarly greater than the contact area of the California roller.

The trend of transferable chemical residue measured with the mega-roller increased with weight (Fig. 1). There was a small undulation (decrease in transfer followed by increase) in transferable residue between 45 to 80 kg of added weight. This was potentially due to a breakdown of support from the carpet fibers. At lower weights, the fiber may remain erect, but the increasing weight caused the fiber to collapse. This may increase the surface area that was contacted between the cotton-cloth and the treated carpet, resulting in a lower pressure or force of contact. The trend in increasing transferability appears to resume once the carpet fiber is completely collapsed.

Table 2. Transferable chemical residue ($\mu g/cm^2$)[c] as a function of time.

Days after cyfluthrin application	*Day 1*	*Day 7*	*Day 21*
California Roller[a]	0.080 ± 0.012	0.037 ± 0.009	0.017 ± 0.003
Additional Mega-Roller Weight[b]:			
None (0)	0.043 ± 0.012	0.010 ± 0.003	0.008 ± 0.003
11	0.052 ± 0.006	0.018 ± 0.001	0.009 ± 0.002
23	0.057 ± 0.008	0.020 ± 0.005	0.013 ± 0.002
34	0.077 ± 0.007	0.031 ± 0.003	0.014 ± 0.002
45	0.076 ± 0.002	0.030 ± 0.003	0.012 ± 0.003
57	0.068 ± 0.008	0.034 ± 0.014	0.013 ± 0.004
68	0.065 ± 0.010	0.032 ± 0.007	0.018 ± 0.008
80	0.081 ± 0.020	0.038 ± 0.007	0.016 ± 0.002
91	0.083 ± 0.012	0.043 ± 0.011	0.017 ± 0.004
102	0.093 ± 0.002	0.049 ± 0.009	0.023 ± 0.003

[a]The weight of the California roller is 13.6 kg.
[b]The numbers in this column reflect the kilograms of lead shot added to the roller. The cylinder without any lead shot is referred to as zero, but the tare weight of the cylinder was approximately 2.3 kg.
[c]Mean ± standard deviation.

Chemical applications are important components of integrated pest management strategies in urban environments[31] that inevitably result in human exposure. The use of human subjects is not always feasible to evaluate the magnitude of exposure, and it has become a costly, lengthy and laborious procedure to gain approval to conduct any study involving human volunteers that might be used by USEPA to regulate pesticides. For example, since implementation of the rule in April 2006 until March 2008, only three human volunteer studies involving intentional exposure to pesticides have been approved by the USEPA, and all of those were for insect repellents.[32] However, the California roller[6,33] is a method to quickly, easily, and reproducibly measure transferable chemical residue from chemically treated surfaces that can be used to estimate potential human exposure.

It is important to recognize that any method of determining transferable residues of pesticides from a treated surface is only a surrogate for actual human exposure. The efficiency of transfer measured using varying methods (e.g., solvent wipe vs. LWW) can vary by orders of magnitude.[34] This uncertainty introduced by trying to compare measured human exposure (e.g., from biomonitoring) with source strength measured as dislodgeable residues confounds interpretation of potential exposure when estimates are based on some other method of measuring transferable residue (e.g., wipe measurements for which there are few if any corresponding human exposure monitoring data). Thus, it is important to either use a standardized method that has been used many times before with human monitoring e.g., the California roller or alternatively, be able to relate transferability from one method to that from another dissimilar method. Even within the same method, there will be experimental variability, and the set of experiments described here was designed to estimate the contribution of force to that variability.

Transferable chemical residue declined, but total residue appears to have not dissipated over a 21-day interval post application. Other studies have shown that absorbed dose in residents of treated homes does not decline in direct proportion to dislodgeable residues, typically reaching a maximum dosage within a week after application.[15] Transferability to sampling media and availability of surface residues for contact-transfer and absorption are not perfectly modeled by sampling using the California roller. Thus, although transferable residue is an indicator of exposure, and certainly more related to exposure than total residue, it is not a perfect indicator, and current interpretation of dislodgeable surface data reflects potential

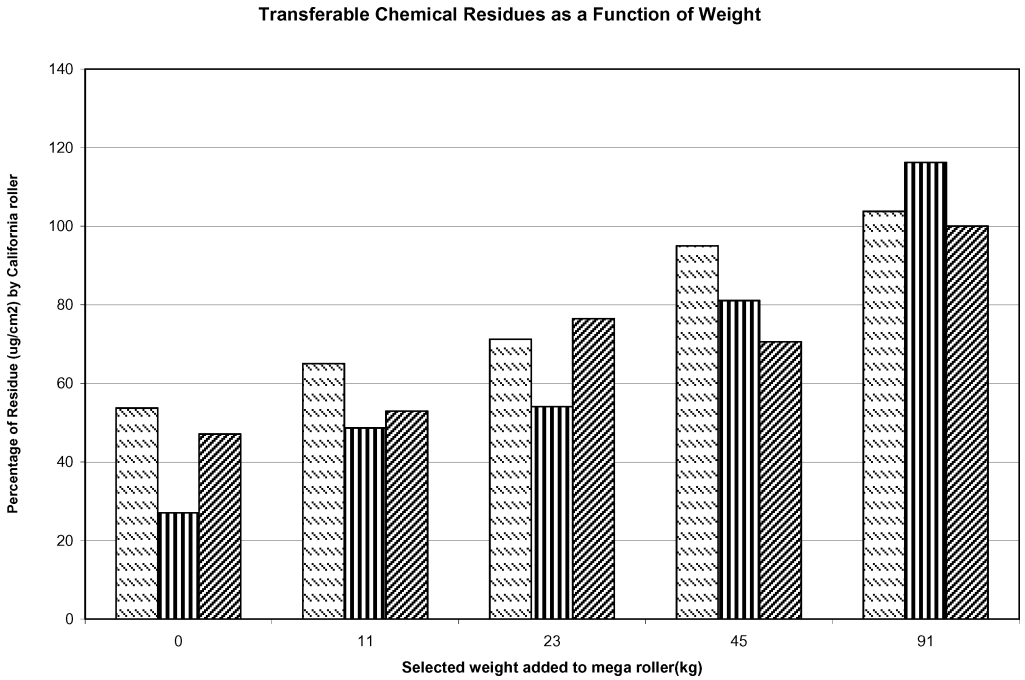

Fig. 1. Percent transferable chemical residue (μg cyfluthrin/cm^2 carpet) using the standard California roller as 100 on Day 1, Day 7, and Day 21 as detailed in Table 2.

human exposure. Although regulators have expressed concern that varying modifications of the California roller from the initial published version may produce significant differences in transferability,[35] the data presented in this paper clearly indicate that transferability will be affected less than two-fold on average due to these modifications.

Conclusion

Pesticide exposures resulting from indoor use and surface deposition on indoor nylon carpets may be estimated by measuring transferable residues (μg chemical/cm^2 carpet). A weighted roller developed at California Department of Food and Agriculture (CDFA) has been extensively used to sample transferable residue for estimates of human exposure in risk characterization. A modified roller has been developed to evaluate the influence of pressure on transferable chemical residue since weight and force (or pressure, kg/m^2) may vary from person-to-person and activity-to-activity. A 12-inch diameter roller was used to apply 60 to 2100 kg/m^2 to bracket pressures exerted by humans on a flat nylon-carpeted surface. Measurements of transferable cyfluthrin residues were made after 1, 7, and 21 days. Total Soxhlet extractable cyfluthrin residues were relatively constant during the test period. Residue transferability decreased during the study period. Modest increases in the transferability of surface residues were observed over the broad range of pressures applied by the modified roller.

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