Bull. Environ. Contam. Toxicol. (2003) 70:644–651

DOI: 10.1007/s00128-003-0033-1

Bulletin of Environmental Contamination and Toxicology

Transferable Chlorpyrifos Residue from Turf Grass and an Empirical Transfer Coefficient for Human Exposure Assessments

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Received: 31 May 2002/Accepted: 7 December 2002

When turf grass is protected from pests, primarily weeds, insects, or fungi, there is the potential for exposure of persons that contact the treated surface. Dermal exposure is the primary route for chemicals typically used for turf grass pest control (Zartarian et al., 2000). Inhalation is also a potential route, but one of much lower magnitude due to the low volatility of most commercial products. In those cases where inhalation is important, proven monitoring methods are available (Plog and Quinlan, 2001). Increased attention has been given to the validation of procedures for determining transferable pesticide residues as a means to gauge potential human exposure from contact with treated turf.

Several techniques to measure transferable chemical residue from turf (TTR) have recently been evaluated (Klonne et al., 2001; Rosenheck et al., 2001; Fuller et al., 2001). Techniques include the California roller (Ross et al., 1991), drag sled (Lewis et al., 1993), polyurethane foam (PUF) roller (Lewis et al., 1994), shoe shuffling (Thompson et al., 1984), and foliar wash (Hurto and Prinster, 1993) analogous to procedures that are extensively used in agriculture (Iwata et al., 1977). The relationship of TTR to human contact-transfer and absorption of pesticide has not been fully studied. Evaluation of these surface sampling procedures using biological monitoring is limited to the California roller (Bernard et al., 2001). Additionally, the modified California roller has recently been evaluated as the best overall method for determining turf residues due to the sensitivity, ease of use, and low coefficient of variation (Rosenheck et al., 2001).

The objective of this work is to evaluate the effect of turf length, roller weight, number of rolls, and repeated sampling on TTR measured with the modified California roller following a chlorpyrifos application. A daily transfer coefficient (TC_{day}) was developed from previous studies of human chlorpyrifos exposure on turf (Bernard et al., 2001). The TC_{day} was applied to the TTRs measured in this work as an informal prediction of potential human exposure.

MATERIALS AND METHODS

The field experiment was conducted in January 2002 at the UC Riverside

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Agriculture Experiment Station in Riverside, CA (34.0° N, 117.3° W). Creeping bentgrass (*Agrostis palustris* var. 'Brighton') mowed at 1.6 cm and perennial ryegrass (*Lolium perenne*) mowed at 5.1 cm were used for study. Each plot was divided into 45 x 60 cm (0.27 m^2) sections that were sampled randomly. The sites included ample paths so inadvertent contact with the test plots could be easily avoided. No irrigation or precipitation occurred during data collection.

Applications of chlorpyrifos (Dursban® 2E, Prentiss Incorporated, Floral Park, NY; EPA Reg. No. 655-466) were made to plots using a fixed boom sprayer equipped with Teejet 8006 spray tips (Spraying Systems Co.®, Wheaton, IL) with dynamic pressure of 24 psi (166 kPa). The fixed boom was mounted on a tractor and adjusted to a 50.8 cm nozzle height. Applications were made at the label recommended rate of 6 oz formulation in 3 gal water applied to 1,000 ft^2.

Cloth covered foil coupons were placed in each turf site to measure spray deposition (ug chlorpyrifos/cm^2). The deposition coupons were collected and sealed in storage bags that were placed in a cooler. Deposition coupons were extracted with ethyl acetate using an Eberbach shaker for two 10-minute cycles.

Transferable turf residue was measured with the modified California Roller technique (Ross et al., 1991). The California roller (Ross et al., 1991; Bernard etal., 2001) was fitted with a short handle (ca. 60 cm) and adjusted to 25 or 30 lbs with lead shot. A 1000 cm^2 cotton cloth was placed on the treated turf. The cloth was covered with heavy rosin paper to avoid contamination (Salinas Valley Wax Paper Co., Salinas, CA). A 45 x 60 cm screen template was placed over the rosin paper. The sampling sandwich was then rolled, with one roll consisting of a complete forward and backward pass. The screen template and rosin paper were removed and the cotton cloth collected into a sealed storage bag and placed into a cooler.

The cotton cloths were extracted with ethyl acetate using the shaker for two 10-minute cycles on the high setting. Chlorpyrifos concentrations were determined by generating a standard curve with chlorpyrifos-methyl (Chemservice, West Chester, PA) as an internal standard using a Hewlett Packard 5890 gas chromatograph (Palo Alto, CA) equipped with a HP-5 column and a flame photometric detector.

Chlorpyrifos TTR was measured using the modified California roller. The effect of turf length, roller weight, number of rolls, and repeated sampling were evaluated under conditions likely to occur in pesticide exposure studies. The first study measured the effect of roller weight and number of rolls on TTRs using two turf lengths. Both the creeping bentgrass (1.6 cm) and perennial rye grass (5.1 cm) sites were treated with identical chlorpyrifos applications. Deposition coupons (3 per site) were collected 15 minutes following application, sealed in plastic storage bags and placed in a cooler. Deposition coupons were extracted with ethyl acetate within 60 minutes following collection. Both a 25- and 30-

Table 1. Deposition ($\mu g/cm^2$) of chlorpyrifos on turf grass.

	Max Label Rate[a]	Measured Deposition
Study 1:		
Creeping bentgrass	47	33.4 ± 2.76[b]
Perennial rye	47	34.2 ± 1.10[b]
Study 2:		
Perennial rye	47	25.0 ± 1.16[b]
Study 3:		
Perennial rye	47	27.0 ± 0.39[c]

[a] Three to 6 fl. ozs. Dursban® 2E (24.6% chlorpyrifos) per 1000 ft^2.
[b] Measured from deposition coupons (n = 3).
[c] Measured from deposition coupons (n = 5).

pound modified California roller were prepared for this study. 24-Hours following the chlorpyrifos application, TTR measurements in triplicate were made for each turf type using 5, 10, and 20 rolls with both 25- and 30-pound rollers.

The second study measured TTRs from previously sampled sites. A chlorpyrifos application was made to a previously untreated perennial rye grass plot for this study. Deposition coupons (n = 5) were collected 15 minutes following application, sealed in plastic storage bags and placed in a cooler. Deposition coupons were extracted with ethyl acetate within 60 minutes following collection. TTR was measured with the modified California roller method, weighing 30 pounds, with 10 rolls. TTR measurements (n = 5) were taken 24-hours following chlorpyrifos application.

At 48-hours following the chlorpyrifos application TTRs were measured on previously unsampled plots (n = 5) and plots sampled at 24-hours were resampled (n = 5). After 96-hours TTRs were measured on previously unsampled plots (n = 5), plots first sampled at 48-hours (n = 5), and sites sampled at both 24- and 48-hours (n = 5).

The third study measured TTRs using 1, 2, or 5 rolls. A chlorpyrifos application was made to a previously untreated perennial rye grass plot for this study. Deposition coupons (n = 5) were collected 15 minutes following application, sealed in plastic storage bags and placed in a cooler. Deposition coupons were extracted with ethyl acetate within 60 minutes following collection. Five TTR measurements were made with the modified California roller method, weighing 30 pounds, with 1, 2, and 5 rolls.

An analysis of variance F-test, followed by a mean separation using the Least Significant Difference (LSD) was used to determine statistically significant differences. Values presented herein are arithmetic mean values.

Table 2. Study 1: Transferable chemical residue (μg/cm^2) from short and long turf measured with 30-lb California roller method.

	Short Turf		Long Turf	
Rolls	25lb Roller	30lb Roller	25lb Roller	30lb Roller
5	0.04 ± 0.007	0.04 ± 0.004	0.11 ± 0.014	0.08 ± 0.003
10	0.05 ± 0.004	0.06 ± 0.004	0.10 ± 0.011	0.09 ± 0.004
20	0.10 ± 0.020	0.07 ± 0.002	0.15 ± 0.020	0.13 ± 0.010

Values (n = 3) are mean ± SD.

RESULTS AND DISCUSSION

In study one, the chlorpyrifos application rate measured from deposition coupons was 33.4 ± 2.76 and 34.2 ± 1.10 μg/cm^2 for the creeping bentgrass and perennial rye turf plots, respectively. The application rates were not statistically different ($p > 0.05$; Students t-test). The results of the TTR measurements are reported inTable 2. TTR measurements made on creeping bentgrass were significantly different from TTR measurements made on perennial rye ($p < 0.05$; ANOVA). The number of rolls during sampling was also significant ($p < 0.05$; ANOVA), with 5 and 10 rolls being significantly different from 20 rolls ($p < 0.05$; Least Significant Difference). The weight of the roller did not have a significant effect on TTR ($p > 0.05$; ANOVA).

In the second study, the chlorpyrifos application rate to perennial rye measured from deposition coupons was 25.0 ± 1.16 μg/cm^2 (Table 1). The result of the TTR measurements are reported in Table 3, including results from an ANOVA F test, followed by mean separation using LSD. Differences exist between sampling days and between sites resampled on day 2. No differences were detected on day 4, potentially due to the low magnitude of TTR.

Time and repeated human contacts are intuitively important determinants of potential exposure, but critical human studies of exposure and transferable (dislodgeable) spray residues are lacking. Resampling is not feasible using standard dislodgeable foliar residue procedures, but investigators usually conclude rapidly diminished exposure potential based upon analysis of serial samples.

Goh et al. (1986) used aqueous Sur-Ten solutions (ca. 0.01%) in a study of the dissipation of dislodgeable foliar residues of chlorpyrifos and diclorvos from Kentucky bluegrass. Highest levels (ug/cm^2) immediately after application declined rapidly during the following 96-hours. Pesticide residue persists in small amounts that may contribute to aggregate exposures longer than measured using DFR techniques can be measured by. Sears et al. (1987) reported that diazinon residues removed from treated turfgrass (*Poa pratensis* L) by moistened cheesecloth declined from 10% to 0.3% of the total applied in 1 day. The procedure was used to measure residues for up to 15 days when less than 0.1%

Table 3. Study 2: Transferable chemical residue (μg/cm^2) from turf grass measured with the 30-lb California roller method.

Group	Day 1	Day 2	Day 4
1	0.064 ± 0.0042*a*	0.027 ± 0.0022*b*	0.012 ± 0.0028*d*
2	-	0.038 ± 0.0050*c*	0.012 ± 0.0021*d*
3	-	-	0.015 ± 0.0021*d*

Group 1 plots sampled on day 1 and resampled on days 2 and 4. Group 2 plots sampled on day 2 and resampled on day 4. Group 3 plots sampled on day 4 only. Values with same letter are not significantly different using an ANOVA F-test, followed by mean separation using Least Significant Difference (LSD). Each value (n = 5) is the mean ± SD.

was dislodgeable (Sears et al., 1987). Residues removed from nylon carpets using the California roller are useful to estimate indoor human chlorpyrifos exposure (Krieger et al., 2001). Few exposure monitoring procedures for persons that contact treated turf have been published, e.g. Vacarro et al., 1996; Bernard et al., 2001. Limited generalizations can be made about sampling procedures to represent human exposure potential, but it is a critically important risk management issue.

In the third study, the chlorpyrifos application rate to perennial rye measured from deposition coupons was 27.0 ± 0.39 μg/cm^2 (Table 1). The results of the TTR measurements are reported in Table 4, including results from an ANOVA F test, followed by mean separation using LSD. Measured TTR following 1 and 2 rolls was significant from measured TTR following 5 rolls.

Clarification of the relationship of TTR to absorbed dose will ultimately determine the usefulness of surface residue sampling procedures for exposure assessment. In a previous paper (Bernard et al., 2001) the relationship between surface deposition and contact transfer was studied. Kentucky bluegrass (cut 2" to 3") was treated with chlorpyrifos. The surface chlorpyrifos residue was 12 ± 4 ug/cm^2 and TTR residue was 3.4 ug/cm^2 when the grass was dry to touch. following application that same day. It is assumed that the 20 minutes of structured activity (Jazzercize®) includes at least as much or body contact with treated turf than occurs normally among persons engaged in outdoor activities on turf including play or sports.

The whole body cotton dosimeters retained 1.6 mg chlorpyrifos during the 20-minute structured activity period. If this dose is considered the transferable daily dose (TDD; ug/day), and if the contact time is designated a *day*, then the following estimate of transfer coefficient (TC_{day}; cm^2/day) results:

$$\begin{aligned} TC_{day} &= TDD / TTR \times day \\ &= 1{,}600 \text{ ug/day}/(0.085 \text{ ug/cm}^2 \times 1_{day}) \\ &= 18{,}824 \approx 20{,}000 \text{ cm}^2\text{/day} \end{aligned}$$

Table 4. Study 3: Transferable chemical residue ($\mu g/cm^2$) from turf grass measured with the 30-lb California roller method.

Number of Rolls	Transferable Chemical Residue (TTR)
1	0.010 ± 0.0010*a*
2	0.013 ± 0.0012*a*
5	0.020 ± 0.0043*b*

Sampling was conducted using 1, 2, or 5 rolls. Values with the same letter are not significantly different using an ANOVA F-test (α = 0.05), followed by mean separation using Least Significant Difference (LSD). Each value (n = 5) is the mean ± SD.

Using this TC_{day} the following equation for ADD can used:

$$ADD = TTR_t \times TC_{day} \times ET \times DA$$

where,

ADD = absorbed daily dose
TTR_t = transferable turf residue on day "t" ($\mu g/cm^2$)
TC_{day} = transfer coefficient (cm^2/day)
ET = exposure time
D = dermal absorption rate (%/24 h)

Absorbed chlorpyrifos dosages calculated from TTR using the modified California roller was 0.5-2 ug/kg, remarkably similar to the estimates of 1.1 – 1.5 ug/kg based upon urine biomonitoring (5 days; Bernard et al., 2001). These levels are also similar to exposures of persons that live in chlorpyrifos-treated homes (0.7 – 8.0 ug chlorpyrifos equivalents/kg-day; Krieger et al., 2001). Background 3, 5, 6-trichloro-2-pyridinol excretion in studies conducted in this laboratory range from 0.2-0.4 ug chlorpyrifos equivalents/kg-day. The measured amounts of chlorpyrifos (attributable to chlorpyrifos and TCP) that results from contact with treated turf under extreme case conditions are up to 5-times the background level and far below Low Observed Adverse Effect Levels.

Similarly, TC_{day} can be derived from measurements of DFR. Using the DFR that corresponds to TTR_t above (Bernard et al., 2001), the resulting TC_{day} is 471 or ≈ 500 cm^2/day. The TC_{day}s differ due to the nature of the turf residue measurements. Differences are attributable to a DFR extraction performed with a Sur-ten detergent wash while TTR residue is transferred with a dry cotton cloth. Additionally, the sampling surface areas are different. A 1 m^2 turf plot has more than 1 m^2 of leaf surface area. Although the TC_{day} derived from TTR and DFR may differ, it is uncertain which will provide the more useful estimate of ADD.

Acknowledgments. Various donors supplied unrestricted grants-in-aid to the Personal Chemical Exposure Program and the California Strawberry Commission provided partial support. The senior author received partial support from The Carl Strom/Western Exterminator Company Scholarship in Urban Entomology.

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