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Determination of a Standardized Sampling Technique for Pesticide Transferable Turf Residues

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Conducting exposure assessments for people reentering turf that has been treated with a pesticide requires some assessment of the amount of residue that can be transferred from the grass to the person. Several techniques have been proposed for assessing the amount of transferable turf residues. In 1996, the Outdoor Residential Exposure Task Force (ORETF) investigated five established turf sampling techniques for measuring transferable residues (Klonne et al. 2001). The methods investigated included the California Roller (moving a roller of specific weight over a cotton sheet placed on the turf; Ross et al. 1991), the drag sled (pulling a flat metal pan of specific weight with an attached piece of denim material across the turf; Lewis et al 1993), the PUF roller (a piece of polyurethane foam placed on a roller of specific weight that is rolled across the turf; Lewis et al. 1994), shoe shuffling (a piece of cotton cheesecloth attached to flat pans which are attached to the feet and then shuffled across the turf; Thompson et al. 1984), and the foliar wash (a section of the turf is clipped and then agitated in a solution to dislodge the residue from the turf; Hurto and Prinster, 1993). The results of this study indicated that several of the methods were equivalent and that certain modifications might improve their performance (Klonne et al. 2001). Therefore, a second study was conducted with modifications of some of the techniques, so that the best technique could be selected for use by the ORETF.

MATERIALS AND METHODS

Three techniques (described below) were evaluated in this study. The techniques were evaluated across formulation types (granular and liquid) and time (immediately following application and one day after application) for:
1) Sensitivity (amount of residue transferred to the matrix), 2) Repeatability within individuals, 3) Reproducibility among individuals, and 4) Ease-of-use.

This study was conducted using dwarf tall-fescue grown on a turf farm near Winchester, California. The turf was cut to a height of 1.75 in. [4.4 cm] just prior to testing. Two uniform plots of turf were divided into 192 subplots, each subplot measuring 2.5 by 6 ft [76 x 183 cm]. Each plot was then treated once with either a liquid or granular formulation of dithiopyr. Each plot had designated walking paths to avoid contact with test plots by study personnel.

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Each plot was treated once with either a liquid or granular formulation of dithiopyr (trade name Dimension®, manufactured by Rohm & Haas; EC: 13% active ingredient (ai), Granule: 0.25% ai) at 0.5 lb ai/acre (A). The rate of 0.5 lb ai/A was chosen from the label and is representative of other turf pesticide use rates. Dithiopyr was chosen as the surrogate test substance because of easy quantification and availability in both liquid and granular formulations.

The liquid chemical formulation was applied with a 5-ft. [152 cm] ground boom sprayer mounted 18 in. [46 cm] above the ground and pulled by a tractor. The granular formulation was applied with an 80-in. [203 cm] Gandy® (Gandy Co., Owatonna, MN) box drop spreader pulled by a tractor. The rates (0.5 lb ai/A) were verified using the calibrated sprayer or spreader output and the pass times of the tractor to calculate the total application of the active ingredient. Although the absolute application rate was not important since each transferable turf residue method was being compared to the others sampled from that block for any given application, the data indicated that the applications were at 100% and 100.4% of the target rate for the liquid and granular formulations, respectively.

The treated turf was allowed to dry 1.5 hours before sampling (dryness determined by the lack of moisture on a rubber glove when wiped through the grass). Fifteen investigators then performed two replicates of each of the three techniques, on both formulations of dithiopyr - on the day of application and then one day later. The 15 investigators were divided into three groups of five. At each sampling time, each group was assigned one of the three techniques, which were all performed simultaneously. The techniques were rotated among groups until all individuals performed all three techniques once. This entire procedure was then repeated for a second replicate.

After field sampling was complete, the investigators used an evaluation form to rank the techniques from one (best) to six (worst) with respect to the (1) time requirements for training, assembling equipment, performing each method, and clean up; and (2) simplicity of training, performance, manipulations, and clean up.

The three turf sampling techniques that were evaluated are described below.

The Modified California Roller (MCR) technique consisted of a 100% cotton percale sheet that was covered by a piece of plastic sheet and secured with clamps to a 2-ft by 3-ft [61 cm x 91 cm] rigid plastic frame. This assembly was positioned with the sheet lying on the turf. A 2-ft [61 cm] wide roller weighing 32 pounds [14.5 kg] was rolled over the plastic and cotton sheets five times, with a forward and backward motion equivalent to one roll. The percale sheet was then removed from the frame and packaged for shipment to the analytical laboratory. A more detailed description of the assembly and use of this method is presented in a companion publication (Fuller et al. 2001).

The Modified Shoe technique used one hundred percent cotton cheesecloth affixed to the bottom of platform shoes, measuring 10 in. wide by 15 in. long [25

cm x 38 cm] by 1.5 in. [3.8 cm] deep using four bar-style clamps along each of the inside and outside rims of the shoes. An open toe, roller skate-type strap-on connection was used to secure the platform shoe to the investigator's own shoes. The technique involved "shuffling" across a 6-ft [183 cm] long plot to the far end and then backward to the starting position. The shuffling was standardized by specifying the length of each shuffle and the speed of the shuffling. This provided a total sampling area of 10 ft^2 [0.93 m^2]. The cheesecloths from both shoes were combined into one sample. This method required that the subjects doing the shuffling be within the weight range of 124 to 210 lb [56.2 kg to 95.3 kg] (based on data from a previous study by Klonne et al. 2001).

The ORETF Roller technique was a hybrid of the Modified California Roller and the PUF roller (tested in the previous study, Klonne et al. 2001) techniques, where the sampling media was attached to the roller. The roller weighed 25 lb [11.3 kg] and measured 26 in. [66 cm] long and 4 in. [10 cm] in diameter. A sheet of 18 in. by 24 in. [46 cm x 61 cm] 100% white cotton cheesecloth was attached to the outside of the roller. A single layer of aluminum foil was placed between the roller and cheesecloth to prevent contamination. The ORETF Roller was pushed and pulled twice over the entire length of a 6-ft [183 cm] long plot, providing a 12 ft^2 [1.1 m^2] sampling area.

All cloth media from the modified California Roller, modified shoe, and ORETF roller techniques were immediately placed into metal cans after sample collection and then placed in insulated boxes with dry ice. The extraneous grass was carefully removed from the sampling media before it was placed in the cans. All samples were then shipped to an analytical lab where they were stored frozen until analysis. All analytical methods used for the study matrices had been validated for dithiopyr prior to use and was outlined in Standard Operating Procedures.

For this particular study, field fortification samples were prepared by spiking five samples of each (percale sheet and cheesecloth) matrix with analytical standard at 4 µg or 400 µg (4 and 400 times the limit of quantitation, or LOQ). Control samples (matrix with no chemical applied) were handled in an identical manner to the spiked samples. Field fortification samples were handled in a similar manner to the sample matrices collected for turf transferable residues as described above. For the field fortification samples, all media had mean recoveries of 73.6% to 101%, which were within the EPA-specified guidelines of 50 to 120%.

All field samples were analyzed with appropriate laboratory samples including standards that bracketed the residues found on the TTR sample matrices, solvent blanks, laboratory-spiked matrices at 1, 100, and 200 times the LOQ (LOQ = 1.0 µg), and control matrix samples. Mean recoveries from laboratory-spiked samples ranged from 74.0% to 110%, which were within the EPA-specified guidelines of 70 to 120%.

Analysis of dithiopyr was accomplished by extraction of samples with 80% iso-octane/20% ethyl acetate and analysis by gas chromatography using an electron capture detector.

To facilitate comparisons among the techniques, all residue values were normalized to μg of the ai/m^2 of area sampled/pound ai applied/Acre (μg/m^2/lb ai/A). The mean normalized values are used for comparisons of sensitivity (ability to detect the lowest amount of residues). The mean relative variance (coefficient of variability or CV), based on these individual normalized values, is used for measuring repeatability within, and reproducibility among, individuals. The most desirable technique is the one with the lowest CV values.

Since there were relatively large differences in residue levels between liquid and granular treatments, and between Day zero and Day one, a separate statistical analysis was conducted for each formulation type, day, and technique. The data were statistically analyzed using SAS software, Release 6.12 (SAS 1990). Each analysis was conducted on both arithmetic and geometric means. The conclusions using both approaches were the same. For simplicity, the data are presented as arithmetic mean values.

Sensitivity (lowest amount of detectable residue) was evaluated by comparing the amount of residue transferred to the sample media by each technique. An analysis of variance F-test, followed by a mean separation using the Least Significant Difference (LSD) was used to determine statistically significant differences.

Variability associated with repeatability when the same individual performed the same task several times was evaluated by coefficient of variability (CV) values based on the error mean square (EMS) where:

$$CV = \left(\frac{\sqrt{EMS}}{Mean} \right) \times 100$$

Variability associated with reproducibility from the same individual or different individuals performing the techniques was evaluated by CV values based on the EMS and variance among individuals where:

$$CV = \left(\frac{\sqrt{EMS + \text{variance among individuals}}}{Mean} \right) \times 100$$

RESULTS AND DISCUSSION

Sensitivity is an important criterion when determining transferable turf residues, since a lack of sensitivity will not allow for conducting proper exposure assessments (i.e., calculation of transfer coefficients following contact with treated turf). There were no statistically significant differences in sensitivity among the three techniques within each formulation (Table 1), with the exception of the modified shoe technique with the liquid formulation on Day 1.

Table 1. Sensitivity of the techniques as measured by the residue amounts ($\mu g/m^2$/lb ai) transferred to the sample matrices

Technique	Day of Application (Day 0)		1 Day after Application	
	Liquid	Granular	Liquid	Granular
Mod. California Roller	496 *a*	44 *a*	95 *a*	50 *a*
Mod. Shoes	565 *a*	54 *a*	186 *b*	167 *a*
ORETF Roller	249 *a*	31 *a*	53 *a*	82 *a*

Values with the same letter within a column and row are not significantly different at the 0.05 level of probability using an analysis of variance F-test followed by mean separation using the Least Significant Difference (LSD). Each value is the mean across 15 individuals x 2 replicates.

Table 2. Repeatability within individuals as measured by the coefficient of variability (CV)

Technique	Day of Application (Day 0)		1 Day after Application		Overall Mean CV
	Liquid	Granular	Liquid	Granular	
Mod. California Roller	16	30	24	23	23
Mod. Shoes	33	22	56	20	33
ORETF Roller	19	35	24	30	27

Each value listed for each of the days of application represents the mean CV for 15 individuals x 2 replicates. The overall mean CV is the mean CV across all days and formulation types for a specific technique.

Table 3. Reproducibility among individuals as measured by the coefficient of variability (CV)

Technique	Day of Application (Day 0)		1 Day after Application		Overall Mean CV
	Liquid	Granular	Liquid	Granular	
Mod. California Roller	17	29	29	28	26
Mod. Shoes	37	59	51	34	45
ORETF Roller	25	28	29	28	27

Each value listed for each of the days of application represents the mean CV for 15 individuals x 2 replicates. The overall mean CV is the mean CV across all days and formulation types for a specific technique.

Table 4. Ease-of-use ratings

	Mod. California Roller	Mod. Shoes	ORETF Roller
Time Required	Mean Rating[a]		
Training	1.9	2.2	3.6
Assembly	1.5	2.2	4.5
Perform	2.5	2.7	2.0
Clean-up	3.1	3.1	1.7
mean	2.3	2.6	3.0
Simplicity			
Training	1.9	2.5	3.0
Assembly	2.9	1.7	2.8
Perform	1.8	2.2	3.2
Clean-up	2.8	3.0	2.0
mean	2.4	2.4	2.8

a - Based on a rating scale of 1 to 6, with 1 "easy" and 6 "difficult". Fifteen participants rated each method.

The Modified Shoe method gave the highest mean CV for the liquid formulations, while the ORETF Roller gave the highest mean CV for the granular formulations (Table 2). The mean CVs for the Modified California Roller ranged from 16 to 30, compared to 19 to 35 for the ORETF Roller and 20 to 56 for the Modified Shoe techniques.

The Modified Shoe technique consistently produced the highest CVs for both liquid and granular formulations (Table 3). The mean CVs for the Modified California Roller ranged from 17 to 29, compared to 25 to 29 for the ORETF Roller and 34 to 59 for the Modified Shoe techniques.

The Modified California Roller was rated nearly equal to the Modified Shoe but easier than the ORETF Roller in ease-of-use (Table 4).

The Modified California Roller produced more consistent results across individuals, formulation types, and time than the Modified Shoe or ORETF Roller techniques. It also was sensitive enough to detect low levels of residues and was one of the easier techniques to use. Although no single method clearly stood out as the best method for each of the individually evaluated parameters, the Modified California Roller was deemed the best overall method for use in determining transferable residues from turf. A complete description of this method (construction of the roller and sampling frame) is presented in the companion publication by Fuller et al. 2001.

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REFERENCES

Fuller R, Klonne D, Rosenheck L, Eberhart D, Worgan J, Ross J (2001) Modified California roller for measuring transferable residues on treated turfgrass. Bull Environ Contam Toxicol (in press)

Hurto KA, Prinster MG (1993) Dissipation of turfgrass foliar dislodgeable residues of chlorpyrifos, DCPA, diazinon, isofenphos, and pendimethalin. Pesticides in Urban Environments, ACS Symposium Series 522, pp. 86-99

Klonne D, Cowell J, Mueth M, Eberhart D, Rosenheck L, Ross J, Worgan J (2001) Comparative study of five transferable turf residue methods. Bull Environ Contam Toxicol (in press)

Lewis RG, Camann DE, Harding HJ, Agrawal SR (1993) Comparison of transfer of surface chlorpyrifos residues from carpet by three dislodgeable residue methods. Measurement of Toxic and Related Air Pollutants. Air & Waste Management Association, Pittsburgh, PA

Lewis RG, Fortmann DE, Camann DE (1994) Evaluation of methods for monitoring the potential exposure of small children to pesticides in the residential environment. Arch Environ Contam Toxicol 26:37-46

Ross J, Fong HR, Thongsinthusak T, Margetich S, Kreiger R (1991) Measuring potential dermal transfer of surface pesticide residue generated from indoor fogger use: Using the CDFA roller method. Chemosphere 22: 975-984

SAS Institute, Inc (1990) SAS/STAT® User's Guide, Version 6, Fourth Ed., Vol. 1 and 2; SAS Procedures Guide®, Version 6, Third Ed., Cary, NC

Thompson DG, Stephenson GR, Sears MK (1984) Persistence, distribution and dislodgeable residues of 2,4-D following its application to turfgrass. Pestic Sci 15:353-360