Bull. Environ. Contam. Toxicol. (2001) 67:771–779

DOI: 10.1007/s00128-001-0189-5

Bulletin of Environmental Contamination and Toxicology

Comparative Study of Five Transferable Turf Residue Methods

D. Klonne,[1] J. Cowell,[2] M. Mueth,[2] D. Eberhart,[3] L. Rosenheck,[4] J. Ross,[5] J. Worgan[6]

[1] Toxicology and Exposure Assessment Services, Inc., 2901 Patrie Place, Raleigh, NC 27613, USA
[2] Monsanto Company, 800 North Lindbergh Avenue, Building U, St. Louis, MO, USA
[3] Bayer Corporation, 8400 Hawthorn Rd., P.O. Box 4913, Kansas City, MO 64120, USA
[4] Syngenta Crop Protection, 410 Swing Road, Greensboro, NC 27419, USA
[5] infoscientific.com, Inc., 5233 Marimoore Way, Carmichael, CA 96508, USA
[6] Pest Management Regulatory Agency, Health Canada, AL6605E1, 2250 Riverdale Drive, Ottawa, Ontario K1A 0K9, Canada

Received: 19 December 2000/Accepted: 13 September 2001

The Outdoor Residential Exposure Task Force (ORETF) was formed in 1994 to develop a database of dermal and inhalation exposure to homeowners and professional lawn care operators who mix, load, and apply pesticides to turf, and for people who reenter turf following pesticide treatment. The ORETF is a consortium of 33 agricultural chemical producers, formulators, and distributors and encompasses the vast majority of basic agricultural chemical registrants in the U.S. One of the priorities of the ORETF was to evaluate several available transferable turf residue (TTR) techniques and recommend a single technique for use by member companies.

Various methods have been used to determine the transferability of pesticide residues from grass and other surfaces (Cowell et al. 1993, USEPA 1997). The ORETF evaluated five different methods to conduct a direct comparison of their performance on turf: California roller (Ross et al. 1991), drag sled (Lewis et al. 1993), PUF roller (Lewis et al. 1994), shoe shuffling (Thompson et al. 1984), and the foliar wash (Hurto & Prinster 1993).

The purpose of this study was to select the best overall transferable turf residue method based on such criteria as sensitivity (lowest amount of residue detectable), repeatability within an individual, reproducibility across individuals, independence from physical-chemical properties and formulation types, and ease of use.

MATERIALS AND METHODS

A bluegrass turf farm near St. Louis was selected as the test site. The turf was cut to a height of 3 in. [7.6 cm] just prior to testing. Each of the pesticide formulations was applied to a different block of turf. Each block was then divided into enough 6-ft x 2-ft [183 cm x 61 cm] plots so that each test plot was sampled only once. Each block of experimental plots had designated walking paths to avoid contact with test plots by study personnel.

Two different active ingredients (ai) were used for the study. Dithiopyr (Dimension®, 0.25% granule and 12.7% liquid, Rohm & Haas) was selected as a lipophilic compound while 2,4-D (2,4-dichlorophenoxyacetic acid, 29.6%

Correspondence to: D. R. Johnson, Stewart Agricultural Research Services, Inc., Post Office Box 509, Macon, MO 63552, USA

granule, 47.8 % emulsifiable concentrate, 25.5% wettable powder, and 96.7% aqueous solution, Riverdale Chemical Company) was selected as a hydrophilic compound. Two different formulations of dithiopyr were used: a liquid emulsifiable concentrate (EC) and a solid granule (G). Four different formulations of 2,4-D were used: an EC, a wettable powder (WP), an aqueous solution (AS), and a granule.

The liquid chemical formulations were applied with a 5-ft. [152 cm] ground boom sprayer mounted 17 in. [43 cm] above the ground and pulled by an all-terrain vehicle. Granular formulations were applied with a 42-in. [107 cm] Gandy drop spreader (Gandy Co., Owatonna, MN) that was pulled while walking backwards (to avoid walking through the treated area after the granules were applied) at a timed rate. The application rates were 0.5 lb ai/A for dithiopyr and 3 lb ai/A for 2,4-D.

The liquid application rates were verified using the calibrated sprayer output and the pass times of the tractor to calculate the total application of the active ingredient. The calculated application rates for the two different active ingredients and the various formulations described above ranged from 79 to 101% of target (overall mean for all liquid applications = 94.1% of target). The granular application rates were verified by weighing the granules collected in pans placed in the spreader path. The calculated mean application rate was 127.9% of target. However, it should be noted that the actual application rate is not critical since each transferable turf residue method was being compared to the other methods sampled from that block for any given application.

The sensitivity (lowest amount of detectable residue) and intra-individual and inter-individual variability were evaluated by having five individuals perform each of the five techniques a total of four times in different blocks following an application of the dithiopyr EC formulation. No block was sampled more than once. All individuals performed the same technique simultaneously and all the techniques were performed sequentially on the same day.

The sensitivity and applicability of the five techniques to different active ingredients, formulations, and sampling times were determined in a separate evaluation by having four individuals simultaneously perform each technique on each of the eight ai and formulation combinations on the day of application (Day 0) and again one or two days after application.

The sampling regimen was not initiated on Day 0 until 1 to 2 hours after the liquid sprays had dried, as determined by the lack of moisture on a rubber glove when wiped through the grass. Participants also filled out a questionnaire to rate each of the techniques for ease-of-use after completing the sampling regimen.

Five different TTR techniques were evaluated as described below.

The California Roller (CR) technique (referred to as the Roller over Media technique in Ross et al. 1991) consisted of a 2-ft [61 cm] wide roller constructed with a 4-in. [10 cm] diameter plastic pipe, filled with 25 lb [11.3 kg] of lead shot, and attached to a 4-ft. [122 cm] long handle. The roller was covered with ¼ in. [0.64 cm] polyurethane foam to prevent skidding and to better cover uneven ground. A 20 in. x 6 ft [51 cm x 183 cm] cotton percale sheet was covered by a slightly larger sheet of plastic and metal frame which were also fixed to the ground with nails. The roller was pushed over the length of the sheet, then pulled back to the starting position 5 times (i.e., the roller went the length of the sheet 10 times).

The Drag Sled (DS) technique (Lewis et al. 1993) consisted of a 6 in. x 6 in. [15 cm x 15 cm] metal pan with 32 lb [14.5 kg] of metal on top. An 8 in. x 8 in. [20 cm x 20 cm] piece of white denim was attached to the bottom of the sled. The sled was pulled one time down the length of the 6 ft [183 cm] test plot by a 5-ft [152 cm] cable attached to the sled.

The PUF Roller technique (referred to as the Media Roller technique in Lewis et al. 1994) consisted of an 8 in. x 2 in. [20 cm x 5.1 cm] diameter solid stainless steel cylinder that was covered with a 7 in. x 4 in. [18 cm x 10 cm] piece of polyurethane foam (PUF). The cylinder had 2 wheels and a handle attached to it so that it could be pushed or pulled the length of the test plot. Within the test plot, the roller was pushed the length of the 6 ft [183 cm] plot and then pulled back to its starting position. It was then picked up and moved to another unsampled section within the plot and pushed and pulled the length of the plot. This was repeated one more time, for a total of 3 samplings within the test plot.

The Shoe Shuffling (SH) technique (referred to as the Media Wipe technique in Thompson et al. 1984) consisted of a 10 in. x 8 in. [25 cm x 20 cm] metal pan to which a 6-ply 18 in. x 24 in. [46 cm x 61 cm] sheet of cotton cheesecloth was attached to the bottom. The pans were then attached to the investigator's shoes and they were shuffled the length of the plot and then shuffled backwards to the starting position. The cheesecloths from both shoes were combined for analysis.

The Foliar Wash (FW) technique (referred to as the Turfgrass Wash technique in Hurto and Prinster 1993) consisted of cutting the top inch [2.5 cm] of a 16-in. [41 cm] wide swath of grass with a reel mower and collecting the grass clippings into a catch bag. The mower was pushed once down the length of the 6 ft [183 cm] test plot. The grass clippings were mixed well within the bag from which approximately 25-grams were collected. The sample was weighed and then extracted for 20 minutes with 250 mL of a 0.01% Aerosol OT® solution while on a reciprocal mechanical shaker. The solution was decanted and another 250 mL Aerosol OT® added to repeat the extraction procedure. This solution was also decanted and added to the first sample to make up a 500 mL extraction sample. Leaf surface area and density measurements are also required for this technique and were determined by collecting four 4-in. [10 cm] diameter turf plugs for leaf area measurements with a leaf area meter after being placed on transparent tape. Leaf weight was determined by cutting four 1 ft^2 [929 cm^2] samples down to the thatch level with shears and immediately weighing the samples.

All cloth media from the CR, DS and SH techniques, and the foam media from the PUF technique were immediately placed into metal cans after sample collection and then placed onto dry ice. Before placing into sample cans the extraneous grass was carefully removed from the sampling media. The extraction solution from the FW technique was put into a sample jar that was also immediately placed on dry ice. All samples were then shipped to an analytical lab where they were stored frozen until analysis. The stability of the compounds under these conditions was previously verified. Similarly, all analytical methods used for the study matrices had been validated for each ai prior to use and was outlined in Standard Operating Procedures.

For this particular study, field fortification samples were prepared by spiking five replicates of each matrix with analytical standard at 4, 40, and 400 x the limit of quantitation (LOQ) for both substances (LOQ for dithiopyr = 1 μg; LOQ for 2,4-D = 15 μg). 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 transferable turf residues as described above. For the field fortification samples, all media had mean recoveries of 61.1% to 113.4% across all spike levels for all matrices for both chemicals. These recoveries 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, and control matrix samples. Laboratory-spiked matrices (1 to 25 times the LOQ) had mean recoveries of 82.1 to 101.4% across all spike levels for all matrices for both chemicals. These recoveries were within the EPA-specified guidelines of 70 to 120%.

Analysis of dithiopyr was accomplished by extraction of samples with iso-octane and analysis with gas chromatography using an electron capture detector. Analysis of 2,4-D was accomplished by changing the ethylhexyl ester and amine salt moieties to the acid form by extraction with an aqueous solvent containing NaOH. The samples were then partitioned into ethyl acetate and esterified with BF_3/methanol for quantification by gas chromatography with 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 0 and Day 1, a separate statistical analysis was conducted for each formulation type, day, and technique. The data were analyzed using SAS Release 6.12 software (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 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 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 the 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 for selecting a transferable turf residue method since a lack of sensitivity would negate the ability to conduct proper exposure assessments (i.e., to calculate transfer coefficients – see the following equation) following contact with treated turf. However, one only needs a good match between the sensitivity of the transferable turf residue (TTR) technique and the simultaneous exposure assessment technique (e.g., whole-body dosimetry) being used. That is, the most sensitive technique is neither required nor desired if it is much more sensitive than the concurrent whole body-dosimetry and it has a high measure of variability. This is because each transfer coefficient (TC) is a function of the specific method used in its determination:

$$TC\ (cm^2/hr) = \frac{Exposure\ (\mu g/hr)}{TTR\ (\mu g/cm^2)}$$

Thus, high sensitivity of the transferable turf residue method results in low transfer coefficient values relative to the residues found on the transferable turf residue media (assuming that the exposure component of the equation is held constant), and vice-versa for transferable turf residue methods with lower sensitivity.

In this study, the foliar wash technique was much more sensitive to the hydrophilic residues of the 2,4-D liquid and granular formulations but was no more sensitive to the lipophilic dithiopyr than the other techniques on the day of application (Table 1). This was also generally true on Day 1, although the

Table 1. Sensitivity (ug/m^2/lb ai/A) of the techniques for eight separate formulations as measured by the residue detected on the sample matrices

Technique	Dithiopyr EC	2,4-D EC	2,4-D WP	2,4-D AS	Dithiopyr G	2,4-D G
	Day of Application (Day 0)					
CR	389 ***a***	706 ***a***	933 ***a***	554 ***a***	439 ***b***	7 ***a***
SH	382 ***a***	664 ***a***	918 ***a***	652 ***a***	742 ***c***	12 ***a***
PUF	80 ***a***	224 ***a***	325 ***a***	197 ***a***	144 ***a***	3 ***a***
DS	76 ***a***	520 ***a***	979 ***a***	391 ***a***	1021 ***d***	20 ***a***
FW	668 ***a***	4611 ***b***	4220 ***b***	5071 ***b***	380 ***b***	73 ***a***
	1 Day After Application					
CR	5.0 ***ab***	1.5 ***a***	1.5 ***a***	2.0 ***a***	14.1 ***a***	6.3 ***a***
SH	4.7 ***ab***	5.2 ***a***	4.0 ***a***	3.6 ***a***	11.9 ***a***	106 ***b***
PUF	0.0 ***a***	3.2 ***a***	7.8 ***a***	4.5 ***a***	1.4 ***a***	4.6 ***a***
DS	0.2 ***a***	3.3 ***a***	2.6 ***a***	3.4 ***a***	13.4 ***a***	7.5 ***a***
FW	7.9 ***b***	29.7 ***b***	28.5 ***b***	39.3 ***b***	9.8 ***a***	12.1 ***a***

Values with the same letter within a day of application and column are not significantly different ($p<0.05$) using an analysis of variance F test, followed by mean separation using the Least Significant Difference (LSD). Each value is the mean across 4 individuals.

differences between the foliar wash and other techniques were smaller. Although the differences did not achieve statistical significance, the PUF roller technique generally had the lowest sensitivity of all the techniques across all the formulations on Day 0. The California Roller, drag sled, and shoe shuffling techniques generally had similar sensitivity across the formulations on Day 0. All the techniques collected much lower residues from the liquid applications on Day 1 than on Day 0. This was also true for the dithiopyr granular formulation, while residues for the 2,4-D granular formulation were similar on both days, probably because the absolute residues collected were low on both days.

The repeatability within individuals is an important parameter because it sets a lower-end estimate of the inherent variability of the method. That is, the technique has precision associated with it that is related to the materials used, how well the sampling regimen is defined, etc. For the 5 techniques evaluated in this study, all the techniques had lower CVs on Day 0 than Day 1, with the exception of the foliar wash with both formulations (Table 2). This is probably related to the lower absolute residue values that occur on Day 1 and the fact that a small difference in residue levels generally produces a larger CV. The foliar wash had the largest CV on Day 0 and the California Roller the lowest. The other three techniques were similar and intermediate between the California Roller and foliar wash values on Day 0. On Day 1 all the techniques (except the foliar wash) had greater variability, as just discussed. However, the PUF roller technique became notably worse on Day 1 compared to Day 0. Overall, the PUF roller technique

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 - ***a***	Granular - ***b***	Liquid - ***a***	Granular - ***b***	
CR	13	10	35	51	27
SH	19	33	69	48	42
PUF	20	20	169	68	69
DS	27	21	63	41	38
FW	32	96	21	54	51

a - Liquid values calculated across 4 liquid treatments (dithiopyr EC, 2,4-D EC, 2,4-D WP, and 2,4-D AS). Each value is based on 20 replicates: 5 people repeating the technique 4 times.
b - Granular values calculated across 4 granular treatments (dithiopyr & 2,4-D granule & watered-in granule). Each value is based on 20 replicates: 5 people repeating the technique 4 times.
The overall mean CV = 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 - ***a***	Granular - ***b***	Liquid - ***a***	Granular - ***b***	
CR	13	10	34	47	26
SH	21	36	73	45	44
PUF	22	21	168	67	70
DS	27	21	63	39	38
FW	42	91	22	55	52

a - Liquid values calculated across 4 liquid treatments (dithiopyr EC, 2,4-D EC, 2,4-D WP, and 2,4-D AS). Each value is based on 20 replicates: 5 people repeating the technique 4 times.
b - Granular values calculated across 4 granular treatments (dithiopyr & 2,4-D granule & watered-in granule). Each value is based on 20 replicates: 5 people repeating the technique 4 times.
The overall mean CV = mean CV across all days and formulation types for a specific technique

had the greatest CV, with the California Roller having the lowest CV. The other three techniques were intermediate and similar to one another.

The repeatability among individuals is an important parameter because it takes into account both the ability of one person to perform the task with precision and also the consistency across multiple individuals. The CV was quite similar to that observed for the repeatability within individuals for each of the techniques, indicating that the variability was inherent in the method and not due to other factors such as difficulty in understanding how to properly use the technique (Table 3).

With regard to ease of use, the study participants rated the foliar wash as the most labor and time intensive. The California Roller was the most difficult to use and the drag sled was the easiest to use.

The results of this study indicated that several of the techniques performed well but no one method stood out as the single best transferable turf residue method. Based on the lack of clear-cut results of this study for deciding on a single overall best transferable turf residue method, another follow-up study was conducted (see the companion paper by Rosenheck et al. 2001). The polyurethane foam roller technique was not pursued in the second study because of the high CV and lack of sensitivity for the dithiopyr EC on Day 1. The foliar wash technique was dropped because of the disparity of sensitivity for hydrophilic versus lipophilic compounds, and because it was difficult and both labor and equipment-intensive. The drag sled was dropped because of its lack of sensitivity to the dithiopyr EC and because it was not easily amenable to engineering changes to increase its surface sampling area. The California Roller was pursued in the next study because it performed well with regard to both sensitivity and variability, but modifications were made to improve it's ease-of-use. The shoe shuffling technique was pursued because it performed well in this study, but again modifications were made to improve consistency across individuals. In addition, a third technique was developed as an alternative to the PUF roller and the California Roller techniques. This technique consisted of cheesecloth attached to a large roller, as a type of hybrid technique of the PUF roller and California Roller. The description and comparative results of these three modified techniques are reported in Rosenheck et al. 2001.

Acknowledgments. We gratefully acknowledge the contributions of J. Evans and J. Dawson of the Environmental Protection Agency. Also, the ORETF is indebted to the many members of the Technical Committee who devoted months of their time to these projects but could not be named as authors of this publication.

REFERENCES

Cowell JE, Adams SA, Kunstman JL, Mueth MG (1993) Comparison of foliar dissipation and turf dislodgeable residue sampling techniques. Pesticides in Urban Environments, ACS Symposium Series 522, pp. 100-112

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

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

Rosenheck L, Cowell, J, Mueth M, Eberhart D, Klonne D, Norman C, Ross J (2001) Determination of a standardized sampling technique for pesticide transferable turf residues. Bull Environ Contam Toxicol (in press)

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

U.S. Environmental Protection Agency (1997) *Draft* Series 875 - Occupational and residential exposure test guidelines, Group B - Postapplication exposure monitoring test guidelines, Version 5.3, July 24, USEPA, Office of Prevention, Pesticides, and Toxic Substances.