Bull. Environ. Contam. Toxicol. (1991) 47:594–601

Bulletin of Environmental Contamination and Toxicology

Field Chamber Technique for Measuring Pendimethalin Airborne Loss from Turfgrass

J. J. Jenkins,[1] R. J. Cooper,[2] and A. S. Curtis[1]

[1]Department of Entomology and Massachusetts Pesticide Analysis Laboratory and [2]Department of Plant and Soil Sciences, University of Massachusetts, Amherst, Massachusetts 01003, USA

Airborne loss represents an important pathway for the attenuation of foliar applied pesticides. The research reported here describes the application of a field chamber technique for measuring airborne loss of the dinitroaniline herbicide pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitro-benzenamine] following application to turfgrass. Sanders et al. (1985) demonstrated the utility of this technique for measuring airborne loss of the dinitroaniline analog trifluralin (a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidene) from waste disposal sites. They compared results of field studies with laboratory studies employing a model soil and water disposal system (Sanders and Seiber, 1983). The purpose of the research reported here was to determine the applicability of this field chamber technique to the measurement of pendimethalin airborne loss from turfgrass. The validation of this technique was intended to support the development and implementation of field sampling methodology for the determination of pendimethalin airborne loss from turfgrass utilizing a replicated small plot design (Cooper et al.,1990).

In addition, to monitor foliar residues available for airborne loss a method for determining pendimethalin foliar dislodgeable residues was also developed. Foliar dislodgeable residues are thought to be those residues that are most easily dislodged from the foliar surface, as opposed to more tightly bound or penetrated residues. The measurement of foliar dislodgeable residues was originally designed to assess dermal exposure to workers reentering treated fields (Gunther et al., 1973). However, foliar dislodgeable residues may also be characterized as those residues that are most available for airborne loss, and movement to other parts of the canopy with infiltrating water or by dry deposition (Jenkins et al., 1983; Jenkins et al., 1990).

Send reprint requests to Jeffrey J. Jenkins at Dept of Agricultural Chemistry, Weniger Hall 339, Oregon State University, Corvallis, Oregon 97331-6502.

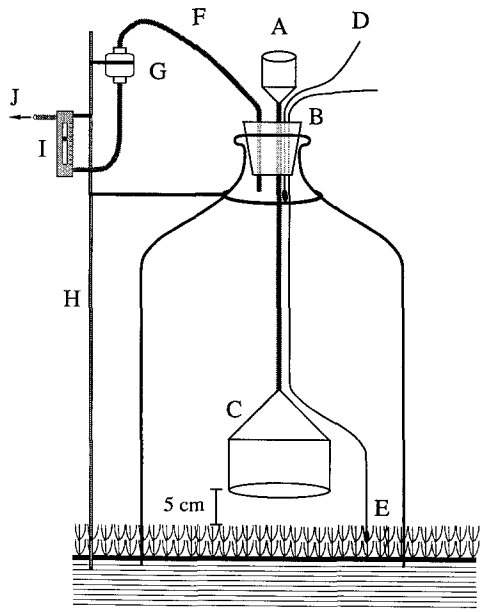

Figure 1. Diagram of field chamber: (a) intake resin trap, (b) aluminum foil covered stopper, (c) air dispersion funnel, (d) chamber ambient temperature thermistor, (e) chamber canopy temperature thermistor, (f) teflon tubing, (g) teflon resin cartridge, (h) support rod, (i) flow meter, (j) connection to vacuum pump.

MATERIALS AND METHODS

Analytical grade pendimethalin (97.5% purity) was obtained from American Cyanamid for use in laboratory experiments and for the preparation of analytical standards. Pendimethalin 60 WDG was applied at a rate of 3.4 kg a.i./1646 L H_2O/ha for field experiments. Amberlite XAD-4 polymeric resin (20/50 mesh, Rohm and Haas) was used as sampling media for pendimethalin airborne residues. In preparation for sampling, the XAD-4 resin was shaken for 1 hour in a pH 5 HCl solution, brought to pH 7 with water rinses, dried with acetone, soxhlet extracted for 7 hr with a 1:1 mixture of acetone and hexane, and air dried for 24 hr.

Field chamber design is shown in Figure 1. The chambers were constructed from 19 L Pyrex bottles with the bottoms cut off, covering a surface area of 0.06 m^2. The chambers were deactivated with Sylon-Ct (Supelco) to minimize adsorption to interior surfaces. The chamber opening was sealed with a foil-lined rubber stopper fit with two YSI model 401 thermistors (Yellow Springs Instruments) to monitor turf canopy and ambient chamber temperatures and a 47 mm Nalgene filter funnel filled with 50 ml of XAD-4 resin to remove pendimethalin from the incoming air. The Nalgene funnel was connected with teflon tubing to an inverted Buchner funnel (10 cm plate diameter) suspended

5 cm above the turf surface to disperse the incoming air. Airborne residues were collected with a Teflon in-line filter cartridge (Cole Parmer) connected via Teflon tubing to the chamber outlet. Cartridges, fitted with 100 mesh stainless steel screens (Newark Wire Cloth) were packed until full under suction with XAD-4 resin (approximately 50 ml). Air flow was maintained at 30 L/min by a pressure/vacuum pump (Gast) regulated with a factory calibrated flow meter (Cole Parmer). The teflon cartridge and flow meter were supported by an aluminum rod pushed into the ground and held in place by a 12 cm extension ring placed over the chamber neck.

Recovery of pendimethalin airborne residues from XAD-4 resin was determined in the laboratory. Four or 200 μg standard solutions of pendimethalin in 1 ml of acetone were placed in a 150 mm x 17 mm o.d. Schwarz tube (Ace Glass Inc.) and the solvent removed with a gentle stream of air. The Schwarz tube was immersed in a 65°C constant temperature oil bath and connected by teflon tubing to a cartridge packed with approximately 50 ml of XAD-4 resin. Airborne residues were collected for 2 hours by drawing air through the filter holder at 30 L/min. Pendimethalin airborne residues were extracted from the XAD-4 resin with 250 ml of 1:1 acetone-hexane on a wrist-action shaker (Burrell Inc.). The extracts and the XAD-4 resin were filtered through Whatman #1 filter paper pre-wet with 1:1 acetone-hexane and reduced to 3 ml by rotary evaporation at 45°C. The extracts were transferred to 15 ml centrifuge tubes with acetone, taken to dryness under nitrogen at 45°C, and dissolved in toluene for analysis. To determine pendimethalin residues not volatilized, the Schwarz tube was rinsed with 3 x 25 ml 1:1 acetone-hexane. The rinses were concentrated by rotary evaporation, reduced to dryness under nitrogen at 45°C, and dissolved in toluene for analysis.

To determine the trapping capacity of the XAD-4 resin cartridge the apparatus described above was modified to hold two cartridges connected in series. Recovery studies used a 1 mg standard solution of pendimethalin in 1 ml acetone. Airborne residues were collected for 2 hours by drawing air through the filter holder at 30 L/min. Pendimethalin residues remaining in the Schwarz tube and in both cartridges were determined as described above. Residues were measured in the second cartridge to determine if the trapping capacity of the first cartridge had been exceeded.

In a laboratory study Sanders and Seiber (1983) demonstrated the utility of silanization for minimizing the pesticide adsorption to the walls of their model waste disposal chamber. In the present study, distribution of pendimethalin residues between the cartridges and the silanized chamber walls was determined under field conditions. Pendimethalin airborne residues were removed from the chamber walls and air dispersion funnels with 120 ml and 50 ml of 1:1 acetone-hexane, respectively. Rinsate samples were dried with sodium sulfate, reduced by rotary evaporation, taken to dryness with nitrogen, and dissolved in toluene for analysis.

The method of Nigg et al. (1981) was used to prepare extracts of untreated Kentucky bluegrass samples for foliar dislodgeable residue recovery studies. Samples were taken with a 10.8 cm diameter golf cup cutter. The grass was separated from the thatch and soil with scissors to determine the fresh weight. The grass sample was then placed in a 1 L jar with a teflon-lined cap containing 80 ml of methanol. The sample was shaken by hand for 1 minute. The extract was decanted through a stainless steel screen, the grass was removed, and the jar rinsed with 10 ml methanol which was combined with the extract.

Foliar dislodgeable residue methanol extracts were fortified at 4 μg and 300 μg. Fortified methanol extracts were filtered through a methanol pre-wetted Whatman #1 filter paper and made 10% methanol in water with 900 ml distilled deionized water. The fortified methanol/water extracts were eluted at 20 ml/min through a 6 ml (500 mg) C18 SPE column (J. T. Baker) conditioned with two 6 ml methanol rinses followed by two 6 ml rinses of 10% methanol in water. The columns were then aspirated under vacuum to remove residual eluent. Pendimethalin residues were eluted from the column at 1-2 ml/min with 3-4 ml of 1:1 acetone-hexane, taken to dryness with nitrogen at 45°C, and dissolved in toluene for analysis.

All samples were analyzed on a Hewlett-Packard 5890A gas chromatograph with a nitrogen/phosphorus detector and 15M x 0.246 mm DB-17 capillary column (J & W Scientific). Instrument parameters were as follows: oven temperature programmed from 100°C (1 min) to 220°C (2 min) at 40°C/min; injector temperature 250°C; detector temperature 300°C; helium carrier gas flow rate 2.5 ml/min; septum purge rate 2.75 ml/min. The detection limit was 0.5 μg/sample for airborne residues, chamber interior rinses, and Schwarz tube rinses. The detection limit for foliar dislodgeable residues was 1.0 μg/sample.

RESULTS AND DISCUSSION

Recovery of pendimethalin airborne residues from the XAD-4 resin are shown in Table 1. Recovery was determined by the sum of residues extracted from the XAD-4 resin plus residues remaining in the Schwarz tube. The average recovery for the 200 μg fortification was 84% (SD=4, n=6) with less than 10% of the fortification remaining in the Schwarz tube. Average recovery for the 4 μg fortification was 77% (SD=5, n=6) with no detectable residues remaining in the Schwarz tube. No detectable residues of pendimethalin were found in any of the control samples.

Recovery of pendimethalin airborne residues for the trapping capacity experiment are shown in Table 2. Average recovery for the 1 mg fortification was 90.5% (SD=3, n=4). No detectable residues were found in the second cartridge. Pendimethalin airborne residues measured in the field were less

than 0.3 mg/cartridge (see Table 3). This value is well below the trapping capacity of the cartridge as demonstrated in the laboratory.

Table 1. Recovery of Pendimethalin Airborne Residues from XAD-4 resin cartridges.

Fortification Level (μg)	Recovery (μg) Cartridge	Schwarz Tube	Percent Total Recovery
200	166.9	8.6	87.8
200	168.3	11.0	89.7
200	152.4	12.7	82.6
200	149.5	12.3	80.9
200	147.6	18.0	82.8
200	147.9	13.0	80.5
		mean (SD)	84.1 (3.8)
4	3.2	nd	80.0
4	2.7	nd	67.5
4	3.1	nd	77.5
4	3.2	nd	80.0
4	3.0	nd	75.0
4	3.2	nd	80.0
		mean (SD)	76.7 (4.9)

Table 2. Recovery of Pendimethalin Airborne Residues from XAD-4 Resin Cartridges to Determine Trapping Capacity.

Fortification Level (mg)	Recovery (μg) Cartridge 1	Cartridge 2	Schwarz Tube	Percent Total Recovery
1.0	680.9	nd	200.3	88.1
1.0	658.8	nd	270.5	92.9
1.0	748.1	nd	176.3	92.4
1.0	830.1	nd	54.8	88.5
			mean (SD)	90.5 (2.5)

The data in Tables 1 and 2 show an apparent trend towards lower recoveries with decreasing fortification level. The trapping capacity experiment suggests that this trend is not due to loss of airborne residues from the cartridge. To determine if any residues were lost while removing the solvent from the Schwarz tube, in a separate experiment the tubes were extracted with 3 x 25 ml of acetone/hexane (1:1) immediately after removing the solvent. For the 4 μg fortification level the average recovery was 97% (SD=4, n=2), and for the 200 μg fortification level the average recovery was 101% (SD=2, n=2). A possible explanation for the observed trend is binding of a constant amount of unextractable residues to either the glass surface of the Schwarz tube or the XAD-4 resin. This would have the greatest effect at lower fortification levels.

Recoveries of pendimethalin from fortified foliar dislodgeable residue extracts are shown in Table 3. The average recovery at the 750 μg fortification level was 101.3 (SD=1, n=2). The average recovery at the 300 μg level was 95% (SD=7, n=6). The average recovery at the 4.0 μg level was 99% (SD=2, n=4), while the average recovery at the 1.5 μg fortification level was 90.2% (SD=4, n=2). The overall average recovery was 96% (SD=6, n=14).

Table 3. Recovery of Pendimethalin Foliar Dislodgeable Residues from Fortified Extracts.

Fortification Level (μg)	Percent Recovery	Fortification Level (μg)	Percent Recovery
750	100.8	4.0	101.4
750	101.7	4.0	98.7
mean (SD)	101.3 (0.6)	4.0	96.0
		4.0	98.0
300	87.7	mean (SD)	98.5 (2.2)
300	96.9		
300	107.3	1.5	93.3
300	93.7	1.5	87.0
300	93.3	mean (SD)	90.2 (4.4)
300	93.4		
mean (SD)	95.3 (6.5)		

Pendimethalin airborne residue data from the field study described in Cooper et al. (1990) were used to determine the distribution of pendimethalin airborne residues between the XAD-4 resin cartridges and the chamber surfaces under field conditions.

Table 4. Distribution of Pendimethalin Residues Between XAD-4 Resin Cartridges and Field Chamber Surfaces[1].

Diurnal Sampling Period (hr)	Chamber Surfaces μg (SD)	Cartridge μg (SD)	Total Residues μg (SD)	Percent Adsorbed
0900-1100	13 (3)	126 (16)	139 (20)	9
1100-1300	12 (8)	206 (34)	218 (42)	6
1300-1500	19 (4)	240 (27)	259 (24)	7
1500-1700	12 (4)	161 (12)	173 (16)	7
1700-1900	5 (1)	36 (3)	41 (4)	12
1900-0700[2]	3 (1)	59 (17)	64 (17)	8

[1] Average of 3 replicate field chambers.
[2] Overnight sample.

Data shown in Table 4 are average values for three replicate field chambers for each diurnal sampling period over the first 24 hrs following application.

extracted from the XAD-4 resin cartridges and field chamber interior surfaces. Percent adsorbed averaged 8% (SD=2) for the six sampling periods shown in Table 4. These data are in agreement with the work of Sanders and Seiber (1983) who reported adsorption to the walls of a silanized model waste disposal chamber of less than 10% for five of six compounds tested, including trifluralin. They also reported that adsorption varied inversely with relative humidity between 20% and 85%. In the present study, observed moisture on the chamber walls during sampling is expected to reduce adsorption.

Pendimethalin foliar dislodgeable residue data from the field study described in Jenkins et al. (1990) are shown in Table 5. Samples were taken near each of three replicate field chambers at the midpoint of the diurnal sampling periods over the first 12 hours following application. No foliar dislodgeable residue samples were taken during the first diurnal sampling periods following application to allow the residues to dry.

Table 5. Pendimethalin Foliar Dislodgeable Residues following Application at 3.4 kg a.i./ha to Kentucky Bluegrass.

Diurnal Sampling Period (hr)	Foliar Dislodgeable Residues (μg/sample)[1] Rep 1	Rep 2	Rep 3	Average (SD)
1100-1300	1239	3381	1741	2020 (1120)
1300-1500	1437	1725	1713	1625 (163)
1500-1700	1102	1435	1414	1317 (186)
1700-1900	1376	1614	2109	1700 (374)

[1] Concentration expressed as micrograms per 91.6 cm^2 turf area.

The results reported here demonstrate the utility of the field chamber technique for determining airborne residues of the dinitroaniline herbicide pendimethalin following application to turfgrass. These results also suggest that this technique may be useful in determining airborne loss of other pesticides from turfgrass. The advantages of this technique are the direct measurement of airborne residues and the ability to use a replicated design with a small plot size (<40 m^2). In assessing the applicability of this technique to the determination of pendimethalin airborne loss under natural conditions, artificial conditions inside the chamber during sampling must be considered. For example, for the data shown in Table 4 the temperature at the canopy surface inside the chambers never exceeded 36°C and ranged from 5.4 to 11.3°C higher than the canopy surface temperature outside the chamber. Increased temperature inside the chambers should result in an increase in pendimethalin vapor pressure and increased airborne loss. In addition, at higher ambient temperatures modification of the chamber may be required to reduce the temperature inside the chamber to avoid damage to the turfgrass. Another consideration is the airflow through the chamber during sampling. For the data shown in Table 4 the sampling rate was 0.03 km/hr. The fact that the flow rate is constant allows for greater control over experimental conditions as compared to open air sampling techniques, however this flow

rate is well below wind speeds that might be found under normal field conditions. To estimate airborne loss under open air conditions chamber results may have to be adjusted based on consideration of differences in temperature and wind speed (Jenkins et al., 1990). In addition, during sampling the natural environment is artificially modified. However, this sampling effect may be minimized by using short sampling periods relative to the length of the study, and by moving the chambers to a new site for each successive sampling interval.

A new method, employing C18 solid phase enrichment and clean-up, has been developed for the analysis of pendimethalin foliar dislodgeable residues on turfgrass. This method has been shown to be reproducible based upon both laboratory recovery studies and in the analysis of field samples. As foliar dislodgeable residues are thought to be those residues most available for airborne loss, their measurement in conjunction with airborne residue sampling should enhance the interpretation of airborne residue attenuation.

Acknowledgments. Primary grant support from the Golf Course Superintendents Association of America. The authors extend their appreciation to Ms. L. A. Spokas for her help with field and laboratory studies.

REFERENCES

Cooper RJ, Jenkins JJ, Curtis AS (1990) Pendimethalin volatility following application to turfgrass. J Environ Qual 19:508-513.

Gunther FA, Westlake WE, Barkley JH, Winterlin W., Langbehn L (1973) Establishing dislodgeable pesticide residues on leaf surfaces. Bull Environ Contam Toxicol 9:243-249.

Jenkins JJ, Zabik MJ, Kon R, Goodman ED (1983) A model for azinphosmethyl attenuation and movement in a Michigan orchard ecosystem: I. Development and presentation of the experimental data base. Arch Environ Contam Tox 12:99-110.

Jenkins JJ, Cooper RJ, Curtis AS (1990) Comparison of pendimethalin airborne and dislodgeable residues following application to turfgrass. In: Kurtz DA (ed) Long Range Transport of Pesticides. Lewis Publishers Inc, Chelsa, MI pp. 29-46.

Nigg HN, Albrigo LG, Nordby HE, Stamper JH (1981) Method for estimating leaf compartmentalization of pesticides in citrus. J Agric Food Chem 29:750-756.

Sanders PF, McChesney MM, Seiber JN (1985) Measuring pesticide volatilization from small surface areas in the field. Bull Environ Contam Tox 35:569-575.

Sanders PF, Seiber JN (1983) A chamber for measuring volatilization of pesticides from model soil and water disposal systems. Chemosphere 12:999-1012.

Received March 5, 1991; accepted April 4, 1991.