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Field comparison of polyurethane foam plugs and mini-tubes containing Tenax-TA resin as trapping media for the aerodynamic gradient measurement of trifluralin vapour fluxes

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Abstract

The effectiveness of a low-volume (0.3 l min^{-1}) mini-tube (MT) sampler packed with Tenax-TA resin was compared in a field study with that of a polyurethane foam (PUF) sampler (25 l min^{-1}) for measurement of herbicide vapour concentrations in air following fall soil-incorporation of trifluralin at 690 g ha^{-1}. Based on a paired comparison, no significant difference was observed in trifluralin concentrations (ng m^{-3}) determined by gas chromatographic (GC) analysis of air samples collected using the MT and PUF samplers. As a consequence, fluxes determined using the aerodynamic gradient method of measurement for either sampler type were also similar. Because the entire air sample collected by the MT sampler was transferred onto the GC column, greater sensitivity was achieved using the MT sampler.

1. Introduction

Due to its high trapping efficiency [1,2], polyurethane foam (PUF) has been the preferred trapping medium for the determination of pesticide residues in air. As well as being inexpensive, PUF also permits relatively high air sampling flow-rates and is convenient to use both in the field and in the laboratory. One drawback to the use of PUF, however, is the time-consuming step of soxhlet extraction required both for initial cleanup and for extraction of trapped pesticides after sampling. In addition, PUF extracts generally require a concentration step to enhance sensitivity to gas chromatographic (GC) analysis.

Recently, a thermal desorption mini-tube (MT) system, in which both the MT sampler and the thermal desorption unit were automated, was evaluated for air sampling and GC analysis [3]. The MT technology offers some advantages over the use of PUF for air sampling. In addition to considerable time savings due to elimination of the soxhlet extraction and subsequent extract concentration steps, automated MT cleaning and sample desorption for GC analysis are accomplished thermally, thus eliminating the use of organic solvents. As well, the entire air sample is thermally desorbed onto the GC column (compared to the small fraction of the PUF extract

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injected) which results in increased sensitivity even though the MT air sampling flow-rate is lower (100 to 300 ml min^{-1}). Also, since conditions can be chosen to effect complete thermal desorption of trapped pesticides, no correction for pesticide recovery from the MTs is necessary. Drawbacks to the use of the MT technology are that once an air sample has been thermally desorbed, there is no possibility of re-analysis in the case of equipment malfunction, and there is no recourse when pesticide amounts trapped on the MT make quantitation impossible due to detector saturation or when air contaminants interfere with the quantitation of pesticides being monitored.

The MT system evaluated previously [3] used Tenax-TA resin as a trapping medium. This resin, which was packed into glass MTs, demonstrated trapping efficiencies (>99%) for the herbicides triallate and trifluralin [3] which were equivalent to those determined previously for PUF [1,2]. In addition, thermal desorption of these two herbicides from the resin was quantitative [3]. Recently, an attempt was made to determine whether MTs aspirated at a relatively much lower air sampling flow-rate would be as effective under field conditions in determining herbicide fluxes using the relaxed eddy-accumulation (REA) method of measurement as the PUF samplers [4]. The REA system conditionally samples air at a constant rate according to updrafts or downdrafts via PTFE inlet tubes. Unfortunately, sorption of the herbicides (triallate and trifluralin) to the inner walls of the PTFE inlet tubes of the MT sampler did not permit differentiation of the trapping/sorption effects so that air concentrations determined gas chromatographically for the two sampler types could be compared.

In the present study, the effectiveness of the MT and PUF samplers for determination of herbicide fluxes in air is again compared, this time using the aerodynamic gradient (AG) method of measurement. The AG system offers the advantage that the MT and PUF samplers become source samplers; that is, air is aspirated directly into both sampler types so that the effect of herbicide sorption on the determination of herbicide concentrations in air, as observed with the REA system [4], is circumvented. The soil-incorporated herbicide, trifluralin, was selected for study. This herbicide, applied either in the fall or pre-emergence in the spring, is used on the Canadian prairies to control grassy weeds in a wide variety of crops [5]. Significant vapour loss of this herbicide (vapour pressure = 14.80 mPa [6]) has been observed previously following spring soil-incorporation as a tank mixture with triallate [7].

2. Experimental

2.1. Study site/herbicide application

The experiment was carried out on a 300-m diameter circular plot (7 ha) of fine sandy loam soil (45.3% sand, 16.7% clay, 38.0% silt; 2.36% organic matter, pH = 6.1) located in field 20 on the Greenbelt Farm of Agriculture and Agri-Food Canada, Ottawa, ON, Canada. Wheat was grown on the site in 1993 and following harvest, the field was chisel plowed on September 22 (calendar day 265) and then cultivated on day 288. Trifluralin was then applied to the site at 690 g active ingredient (a.i.) ha^{-1} using a sprayer-equipped discer so that incorporation into the upper 10 cm of soil occurred with the application. Spraying began at 12:20 h Eastern Standard Time on day 292.

2.2. Air sampling

The sampling mast for the PUF and MT samplers was located at the centre of the treated circular plot which ensured the same fetch regardless of wind direction. PUF and MT samplers were positioned in pairs (Fig. 1) on the mast such that the inlets of both samplers were at the following heights from the soil surface: 30, 50, 75, 100, 150 and 200 cm. The samplers were positioned such that the sampler inlet centres were approximately 15 cm apart. Three manifolds, each aspirated by a single pump (GAST Mfg. Corp., Model 4VCF-10-M400X), were

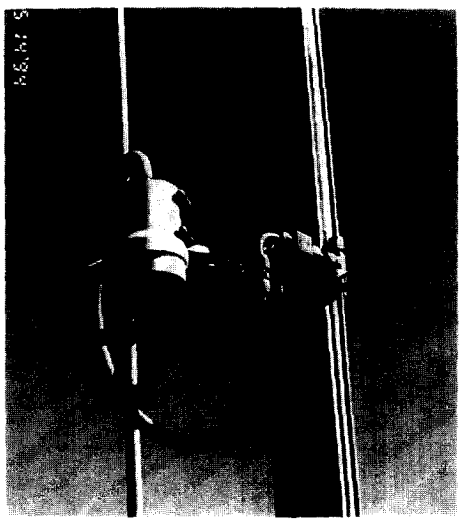

Fig. 1. Photograph showing a MT and a PUF sampler mounted at the 150-cm height on the sampling mast.

mounted on the sampling mast. One manifold, equipped with six inlets, was used for the six MT samplers. Each of the other manifolds had three inlets and was interfaced with three PUF samplers. All manifold inlets were equipped with needle valves to regulate air flow.

Each PUF sampler, which consisted of an aluminum housing and a removable glass liner into which a 45-mm diameter × 50-mm long PUF plug was inserted, was aspirated at approximately 25 l min^{-1}. The MTs (Canadian Centre for Advanced Instrumentation, Saskatoon, SK, Canada) consisted of a 2-mm I.D. × 38-mm borosilicate glass tube packed with 14 mg Tenax-TA resin centred between stainless-steel screens and were aspirated at approximately 300 ml min^{-1}. In order to avoid sampling droplet drift which occurs during application, air sampling was begun at 13:15 h when the first half of the circular plot had been sprayed and the spraying equipment was downwind of the sampling mast. Air was then sampled continuously during daylight hours over the next two days using 1- or 2-h sampling intervals as outlined in Table 1.

At the beginning of each sampling period, the air sampling flow-rate through each MT and PUF sampler was set to approximately 300 ml min^{-1} and 25 l min^{-1}, respectively, by adjustment of the needle valves and use of a flowmeter (mass airflow sensor AWM3300V, Honeywell Canada Ltd., Ottawa, ON, Canada for the MT samplers and Series 2211L mass flow transducer, TSI, St. Paul, MN, USA for the PUF samplers). At the end of each sampling period, the flow-rate through each sampler was measured again using the appropriate flowmeter. The mean of these initial and final flow-rate values for each sampler was corrected for the change in air temperature and pressure over the corresponding sampling period and the corrected flow-rate values were used for calculation of corresponding trifluralin air concentrations and fluxes.

2.3. Mini-tube analysis

The automated thermal desorption unit (ATDU; Canadian Centre for Advanced Instrumentation, Saskatoon, SK, Canada) w as mounted onto a Varian Model 3600 gas chromatograph which was equipped with a thermionic specific detector and controlled by the Varian Star chromatography workstation. The ATDU, directly interfaced to the GC system via a 30-m × 0.530-mm I.D. DB-5 fused-silica column (J and W Scientific; 1.5 μm film thickness), was operated isothermally at 240°C with a desorption cycle of 15 min. The column oven temperature program for the GC system was as follows: 70°C for 16 min, then 15°C min^{-1} to 250°C and finally hold for 2 min at 250°C. The carrier gas (helium UHP) flow-rate was 8 ml min^{-1}. Detector gas flow-rates were 4 ml min^{-1} (hydrogen UHP) and 175 ml min^{-1} (air UZ), whereas that for the detector make-up gas (helium UHP) was 22 ml min^{-1}. The detector bead current was set at 3.14 A and the detector temperature at 300°C. Under the above conditions, the desorption of trifluralin from the MTs was quantitative and the retention time for trifluralin was 25.24 min with the total run time being 30 min. The detector response was linear over the range 0.08 to 50 ng and the calibration curve passed through the origin ($r^2 = 0.99$).

Table 1
Trifluralin air concentrations and amounts analyzed as determined by mini-tube (MT) and polyurethane foam (PUF) samplers at six heights above the soil surface for each sampling period over 2 days

Sampler height (cm)	Day 292					Day 293				
	Time	MT air conc. (ng m^{-3})	Amount desorbed (ng)	PUF air conc. (ng m^{-3})	Amount injected (ng)	Time	MT air conc. (ng m^{-3})	Amount desorbed (ng)	PUF air conc. (ng m^{-3})	Amount injected (ng)
200	13:15	1441	22	1339	1.7	10:00	128	4.0	298	0.71
150	to	1662	26	1352	1.7	to	206	6.6	325	0.77
100	14:15	1920	29	1984	2.5	12:00	261	8.3	384	0.92
75		2229	34	2072	2.5		311	9.9	429	1.0
50		2607	40	2470	3.1		324	10.1	465	1.1
30		2283	36	2517	3.0		303	9.5	513	1.2
200	14:15	675	23	667	1.6	12:00	89[a]	3.3	148	0.35
150	to	846	28	805	2.0	to	104[a]	2.8	169	0.39
100	16:15	1018	35	1030	2.5	14:00	123[a]	3.9	200	0.46
75		1139	39	1140	2.8		142[a]	4.5	199	0.46
50		1308	44	1454	3.5		148[a]	4.7	205	0.47
30		1514	46	1528	3.7		143[a]	4.5	157[b]	0.35
200	16:15	395	13	409	0.95	14:00	83	2.6	93	0.23
150	to	612	19	575	1.4	to	108	3.5	115	0.28
100	18:15	939	29	864	2.1	16:00	131	4.2	138	0.34
75		1114	35	1088	2.7		135	4.3	176	0.43
50		1328	44	1336	3.2		137	4.4	145	0.36
30		1479	48	1459	3.4		149	4.7	154	0.37
200	18:15	–[c]	–	–	–	16:00	88	2.8	88	0.22
150	to	–	–	–	–	to	104	3.3	107	0.28
100	20:15	–	–	–	–	18:00	128	4.1	139	0.34
75		–	–	–	–		147	4.7	133	0.33
50		–	–	–	–		166	5.2	147	0.37
30		–	–	–	–		176	5.6	156	0.39

[a] Circuit breaker for the MT manifold pump tripped and pump did not operate for the complete sampling period.
[b] Hexane extract was inadvertently taken to dryness.
[c] No air samples were collected.

2.4. PUF extraction and analysis

PUF plugs were individually soxhlet extracted for 2 h using 300 ml of hexane [1]. The hexane extract was then concentrated to 2 ml prior to GC analysis.

A Varian Model 3400 gas chromatograph, equipped with a thermionic specific detector and on-column injector, was used with a Model 8200CX autosampler set to inject 2 μl and controlled with the Varian Star chromatography workstation. A 30-m × 0.530-mm I.D. HP-1 fused-silica column (Hewlett-Packard; 0.88 μm film thickness) was used with the following operating conditions: a column oven temperature program consisting of 60°C for 1 min, then 10°C min^{-1} to 270°C and finally hold for 3 min at 270°C; carrier gas (helium UHP) flow-rate, 7 ml min^{-1}; injector 150°C; detector gas flow-rates, 4.5 ml min^{-1} (hydrogen UHP) and 175 ml min^{-1} (air UZ); detector make-up gas (helium UHP) flow-rate, 23 ml min^{-1}; detector bead current, 3.10 A; detector temperature, 300°C. Under the above conditions, the total run time was 25 min and the retention time for trifluralin was 14.74 min. A linear detector response was observed over the range 0.4 to 50 ng, and the calibration curve passed through the origin ($r^2 = 1.00$). Amounts of trifluralin detected were corrected for recovery from the PUF plugs by soxhlet

extraction. Recovery was 83.7 ± 1.1% (mean ± standard error; $n = 12$) from PUF plugs fortified with 1 μg of trifluralin.

2.5. Vertical flux calculations

Herbicide flux was calculated for the PUF and MT samplers for each 1- and 2-h sampling period using the AG method [8]. The flux was determined as a product of the turbulent eddy diffusivity coefficient and the gradient of herbicide concentration over the six sampling heights [8,9]. The eddy diffusivity coefficient was determined from the corresponding profiles of various meteorological parameters obtained using a micrometeorological station which has been described earlier [7,9].

Micrometeorological data were collected continuously over each sampling period at 15-min intervals by a data acquisition system (Campbell Scientific datalogger) interfaced to a Digital 380 minicomputer. The eddy diffusivity coefficient was calculated for each 1- or 2-h data collection period that coincided with the air sampling periods. All profiles were corrected for the effects of atmospheric stability, as described earlier [7].

3. Results and discussion

3.1. Climatic data

Rainfall in amounts of 11.2 and 20.8 mm occurred on days 289 and 290, respectively, prior to the commencement of the study. As a consequence, the trifluralin was incorporated on day 292 into relatively moist soil. Over the air-sampling periods of the 2-day study, air temperatures showed a diurnal trend with maximum temperatures occurring in mid-afternoon (14:00 to 16:00 h; Fig. 2). Somewhat warmer temperatures were recorded on day 293. Soil surface temperatures, obtained by extrapolation of a profile of soil temperatures at 10-, 5- and 2-cm depths, also showed a diurnal trend (Fig. 2). Because of relatively cool air and soil surface temperatures and a light rain on day 293 (0.3 mm; 12:00 to 14:00 h), the soil surface tended to remain moist over the study period. Average wind speed on day 292 was 1.1 m s^{-1} whereas that for day 293 was 3.6 m s^{-1}.

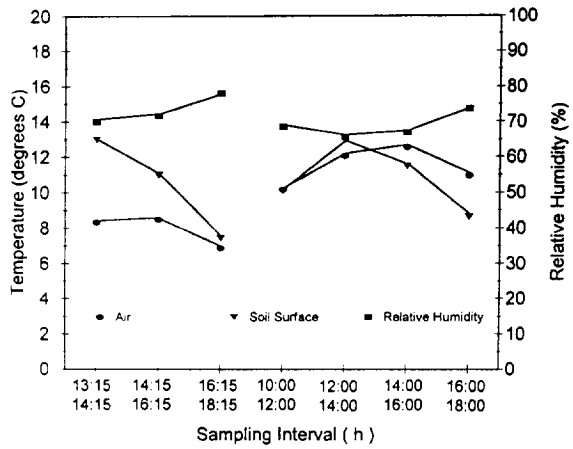

Fig. 2. Mean air temperature at the 100-cm height, mean soil surface temperature, and mean relative humidity at the 200-cm height for each sampling period over the 2-day study.

3.2. Trifluralin concentrations in air

Mean PUF air sampling flow-rates at the six heights over all sampling periods varied from 23.0–25.6 l min^{-1} and the mean volume sampled was 2.878 ± 0.014 m^3 (mean ± standard error; $n = 36$) over 2 h. The corresponding mean flow-rates (not including the 12:00 to 14:00 h sampling period when pump failed) for the MT samplers ranged from 255–286 ml min^{-1} with the mean volume sampled being 0.0321 ± 0.0002 m^3 ($n = 30$) over 2 h. Even though the volume of air aspirated through the PUF samplers was approximately 90 times that aspirated through the MT samplers, the trifluralin concentrations in air detected with the MT samplers were essentially the same as those detected with the PUF samplers (Table 1). A paired comparison of the air concentrations as determined with the MT and PUF samplers ($n = 36$ since data from the 12:00 to 14:00 sampling period on day 293 when the MT pump failed were not included) indicated no significant difference in air concentration between the two samplers. This confirms that the

relatively low air sampling flow-rate used with the MT samplers provided representative air samples for herbicide vapour analysis.

Soil surface and air temperatures (Fig. 2) were relatively cool during the sampling periods of days 292 and 293 and, because of rainfalls just prior to the start of the study, the upper 10 cm of soil and the soil surface remained relatively moist during this time. The enhancing effect of soil and soil surface moisture on volatilization of soil-incorporated pesticides [10,11], including trifluralin [7,12,13], has been well established. Thus, even though air and soil surface temperatures were relatively cool on the day of application, trifluralin concentrations in air across the six sampling heights above the soil surface were of the same magnitude as those reported earlier in studies carried out under warmer conditions [7,13]. Air concentrations at all sampling heights were greatest during the 1-h sampling period immediately after application (Table 1). Trifluralin concentrations were decreased by approximately half over the following 2-h sampling period and showed a continued decrease over the second 2-h sampling period on day 292. Twenty-four hours after spraying (12:00 to 14:00 h on day 293), air concentrations of trifluralin had decreased by a factor of 10. Such a rapid decrease in air concentrations of trifluralin following soil incorporation has been observed previously [7,13].

Amounts of trifluralin injected onto the GC column for quantitation also differed with the samples collected by the MT and PUF samples. The entire air sample was thermally desorbed from the MT onto the GC column and the amounts of trifluralin desorbed from the MTs were generally more than 10-fold greater (Table 1) than the amounts injected in 2 μl of the corresponding PUF extract (concentrated to 2 ml). Thus, for the lowest air concentration (88 ng m^{-3}) aspirated through a PUF sampler, 0.22 ng of trifluralin were injected. With the thermionic specific detector, this was equivalent to only 545 area counts and thus was close to the limit at which reliable quantitation would be obtained using this detector. In contrast, for the same air concentration aspirated through a MT sampler, 2.8 ng of trifluralin were desorbed onto the column. Assuming 0.2 ng of trifluralin to be the minimum amount that could be reliably quantitated, the MT technology would permit quantitation of trifluralin air concentrations of the order of 6 ng m^{-3}. Thus, to obtain the same order of sensitivity using a PUF sampler, the PUF plug extract would have to be concentrated to 200 μl. Alternatively, increased sensitivity using PUF samplers may effectively be achieved by transferring several microlitres of PUF extract onto a MT with subsequent GC analysis. This possibility is currently being investigated in our laboratory.

3.3. *Trifluralin fluxes*

The trifluralin fluxes calculated for both the MT and PUF samplers for the 7 sampling periods over the 2-day study are shown in Fig. 3. Flux values for each sampler type paralleled the corresponding air concentrations (Table 1). Thus, maximum fluxes were observed for the 1-h sampling period immediately after application and were of the order of 175 ng m^{-2} s^{-1} or 6.3 g ha^{-1} h^{-1}. Fluxes then decreased over subsequent 2-h sampling periods such that, 24 h after spraying, fluxes were less than 10 ng m^{-2} s^{-1} or 360 mg ha^{-1} h^{-1}. Flux values calculated for the MT and PUF samplers for each sampling period were similar reflecting the fact that the corresponding

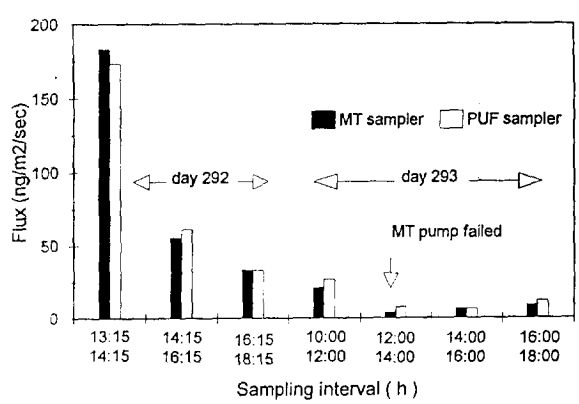

Fig. 3. Trifluralin fluxes for each sampling period over the 2-day study as calculated by the AG method using air concentration data derived from the MT and PUF samplers.

air concentrations used to derive the flux for each sampler type were not significantly different. At least part of the difference in flux between the MT and PUF samplers for the 12:00 to 14:00 h period (day 293) would have been due to failure of the pump aspirating the MT manifold.

In summary, the MT technology used in the present study provided representative air sampling for trifluralin vapour analysis following a fall soil-incorporated application. Use of the MT samplers also resulted in increased sensitivity, with respect to determination of trifluralin concentrations in air, when compared to PUF samplers. Finally, reliable trifluralin concentration gradients were obtained using the MT sampler. Potentially, trifluralin fluxes in the order of 1 ng m^{-2} s^{-1} (36 mg ha^{-1} h^{-1}) or less may be detected using the MT technology. It is concluded that the MT technology would be equally applicable for the determination of fluxes of other pesticides, provided trapping breakthrough volumes and desorption efficiencies have been determined.

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